Risk Reduction during Chemical Flooding: Preconditioning DNAPL Density In Situ Prior to Recovery by Miscible Displacement

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Dense, nonaqueous phase liquids (DNAPLs) are separate phase compounds that commonly contaminate groundwater supplies. Miscible displacement methods using surfactants and alcohols to recover the DNAPLs have been proposed, but concerns have been raised about mobilizing the DNAPLs deeper into previously uncontaminated media. In this paper, the concerns are addressed by reducing DNAPL density prior to elimination of interfacial tension. Laboratory-measured equilibrium phase behavior demonstrates the ability of 2-butanol to reverse the density contrast between tetrachloroethene (PCE) and water prior to miscibility, resulting in a DNAPL phase less dense than the aqueous phase. Laboratory experiments using an upward gradient flow cell demonstrate that 2-butanol, introduced as an aqueous solution to a PCE pool suspended within a water-saturated sandpack, partitions strongly into the PCE. Pools of PCE exposed to 1 pore volume of water saturated with 2-butanol and subsequently recovered by miscible displacements with 1-propanol showed that between 56.6% and 97.6% of the DNAPL mass was recovered for total alcohol complements of between 0.24 and 1.0 pore volume. In all two-phase samples produced, the NAPL phase was less dense than the aqueous phase. Analysis of a static DNAPL pool shows that the use of a 2-butanol preflood may prevent the downward mobilization predicted to occur for more conventional alcohol floods.

Introduction

Nonaqueous phase liquids (NAPLs) released into the subsurface represent a significant threat to groundwater supplies (*1, 2*). This class of water-immiscible organic compounds may be denser (DNAPLs) or less dense (LNAPLs) than water. Below the water table, DNAPLs become distributed as residual blobs and ganglia trapped in individual pore spaces and as pools suspended by capillary barriers (*3*). Because they are only sparingly soluble in water, DNAPLs dissolve relatively slowly and have the potential to create large plumes of contaminated groundwater. Pump-and-treat systems designed to hydraulically contain such plumes and accelerate DNAPL dissolution can be successful in preventing contaminant migration but have been ineffective at returning sites to precontamination levels. To potentially shorten the

time frame necessary to remediate sites contaminated with DNAPL, it may be necessary to directly recover residual and pooled DNAPL.

Chemical flooding has been shown in laboratory experiments and field trials to be capable of removing a large percentage of the NAPL mass from porous media (*4–8*). Two groups of chemical flooding techniques include enhanced dissolution and physical mobilization. Enhanced dissolution using cosolvents (*6, 9*) or solubilizing surfactants (*5, 10*) are designed to increase the solubility of the NAPL in the aqueous phase to accelerate NAPL recovery. These techniques may not induce downward mobilization of residual DNAPL because they do not eliminate interfacial tension (IFT). For pooled DNAPL, however, even modest IFT reduction may result in downward mobilization. Furthermore, because of solubility and potential mass transfer limitations, enhanced dissolution techniques may require many pore volumes of flooding solution for large percentage mass removal (*5, 6, 11*). Techniques using mobilizing surfactants or miscible alcohol floods, on the other hand, can be much more efficient. However, because of the extreme reduction and or elimination of IFT between the DNAPL and aqueous phases, these methods may carry the unacceptable risk of downward mobilization for both pooled and residual DNAPL (*5, 7, 8, 12*).

Researchers have suggested using upward flow to arrest downward DNAPL mobilization during chemical flooding (*4, 5, 7*). The alcohols *tert*-butyl alcohol (*4*) and 1-propanol (*7*) were found to reduce the density of the DNAPL phase concurrent with mobilization using upward flow. However, prior to miscibility, the density of the DNAPL phase remained higher than the aqueous phase, and without adequate hydraulic control, the risk of downward mobilization persisted. Roeder et al. (*13*) present results from batch experiments for the methanol/water/1-butanol/trichloroethene (TCE) system demonstrating that the NAPL phase may become less dense than the aqueous phase if sufficient 1-butanol partitions into the NAPL. Results from two-dimensional numerical simulations were presented that suggest that TCE contamination, predominantly distributed as residual, may be recovered as an LNAPL. Additionally, Falta et al. (*14*) describe the importance of density manipulation of pooled DNAPL to prevent downward mobilization during its recovery by alcohol flooding.

The objective of this study is to execute a series of laboratory experiments to demonstrate that the risk of downward mobilization of pooled DNAPL during chemical flooding can be reduced by using aqueous solutions of 2-butanol, which reduce DNAPL density prior to miscible displacement. Tetrachloroethene (PCE), which is significantly more dense than water, was used as the DNAPL contaminant. Equilibrium phase behavior, fluid properties, batch experiments, and density predictions are used to design 2-butanol prefloods capable of reducing the density of pooled PCE in situ without eliminating IFT. Subsequently, two-stage alcohol floods are conducted using a partitioning preflood of 2-butanol followed by a miscible 1-propanol mainflood to recover the PCE as an LNAPL. A theoretical analysis is then presented to assess the effects of preflooding on a NAPL pool in the absence of upward gradients.

Methods

Experimental Phase Behavior. Equilibrium phase behavior was determined for the ternary system PCE/water/2-butanol by mixing the three fluids together in varying ratios and analyzing the resulting two-phase mixtures for composition,

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TABLE 1. Fluid Properties (at 20 °C unless Noted Otherwise)

fluid	density (mg/L)	dynamic viscosity (cP)	manufacturer	solubility (mg/L)
PCE	1.63[b] (25 °C)	0.87[b] (25 °C)	Fisher Scientific	150[a]−200[b]
100% 2-butanol	0.802[c]	3.91[e] (25 °C)	Fisher Scientific	84000[d] (23 °C)
10% vol 2-butanol	0.985[d] (23 °C)	1.31[d] (23 °C)		
100% 1-propanol	0.803[c]	2.26[c]	BDH	∞
90% vol 1-propanol	0.831[c]	2.86[d] (22 °C)		∞
water	0.998[c]	1.002[c]		

[a] Ref 15. [b] Ref 2. [c] Ref 16. [d] Laboratory measured. [e] Ref 17.

TABLE 2. Summary of Experimental Conditions and Results

expt	2-butanol flood size (PV)	concn 2-butanol (% vol)	1-propanol flood size (PV)	total alcohol (PV)	PCE mass recovery (%)	mass balance (%)
1	1.5	10.0	0	NA[a]	NA	NA
2	2.0	10.5	0	NA	NA	NA
3	1.0	10.4	0	0.10	1.2	98.2
4	1.0	10.5	0.125	0.22	58.3	86.6
5	1.0	10.4	0.125	0.22	56.6	94.7
6	1.0	10.0	0.25	0.33	80.4	93.4
7	1.0	7.9	0.375	0.42	90.7	94.3
8	1.0	9.7	0.5	0.55	92.7	96.6
9	1.0	9.4	1.0	1.00	97.6	99.2

[a] NA, not applicable.

density, viscosity, and IFT. The properties and manufacturers of the fluids used are presented in Table 1. The PCE was dyed red with Sudan IV (Fisher Scientific certified grade) to a concentration of 100 mg/L. Phase compositions were analyzed using an HP 5890-II gas chromatograph equipped with an autoanalyzer, a 6 ft stainless steel Porapak S packed column from Chromatographic Specialties Inc., and flame ionization (FID) and thermal conductivity (TCD) detectors. 2-Butanol (detection limit = 100 mg/L), 1-propanol (detection limit = 10 mg/L), and PCE (detection limit = 2 mg/L) concentrations were measured using the FID, while the TCD was used for quantifying water content. Densities were determined using 5 mL pycnometers, viscosities were measured using capillary viscometers, and IFT was measured using a DeNouy ring tensiometer (ASTM D971). All experiments and measurements were conducted at 23 ± 2 °C.

Density Reduction Calculations. Ternary phase behavior data were used in a computational procedure to estimate the density reduction of a PCE pool exposed to a solution of water saturated with 2-butanol. The method uses two functional fits and the principles of ternary phase equilibria to determine phase compositions for a specified overall composition. The miscibility envelope (binodal curve) is represented by a third-order polynomial fit to the NAPL phase compositions of the ternary phase data. To simulate the tie-lines, the method of Bachman as described by Bergelin et al. (18) was used. From the phase compositions, the densities of the phases are calculated assuming volume conservation. Using this calculation procedure, simulations to assess the ability of aqueous 2-butanol solutions to modify PCE density were conducted. Details of the calculation routine are presented in Lunn (19).

Laboratory Column Experiments. Two types of column experiments were conducted as summarized in Table 2. First, two experiments were conducted to assess the effect of preconditioning a PCE pool with aqueous 2-butanol. Following this, a series of seven miscible displacement experiments were conducted using 1-propanol to determine the effect of 2-butanol preflooding on displacement efficiency.

All experiments employed an upward flow parallel plate flow cell (Figure 1) described by Lunn and Kueper (7). The column dimensions were designed to allow the initiation
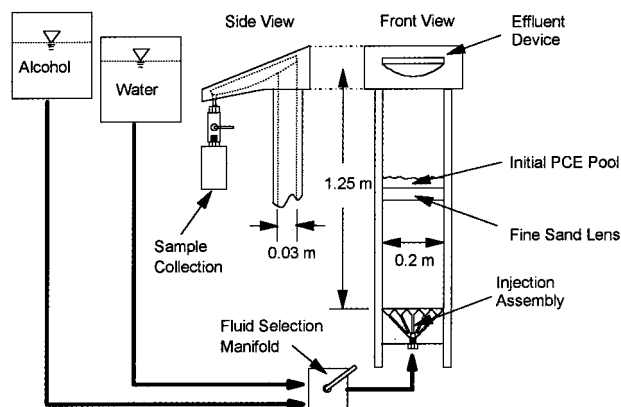

FIGURE 1. Experimental apparatus (after Lunn and Kueper (7)).

and propagation of hydrodynamic instabilities in two dimensions, while suppressing them in the third dimension. For each experiment, a 50 mL PCE pool was suspended on a fine sand lens at the center of a sandpack composed of a coarse sand medium. The coarse sand has a hydraulic conductivity of 4.0×10^{-3} m/s, a porosity of 0.38, and an entry pressure for dyed PCE (IFT with water = 38 mN/m) of 590 Pa. The fine sand had a hydraulic conductivity of 2.8×10^{-4} m/s, a porosity of 0.40, and an entry pressure to the dyed PCE of 1470 Pa. Influent reservoirs provided constant pressure (12870 ± 100 Pa) injection at the base of the sandpack that resulted in an upward hydraulic gradient of 0.05 ± 0.01. Fluids were recovered from an effluent assembly at the top of the apparatus for subsequent analysis by gas chromatography. Further details of the apparatus, packing techniques, and PCE emplacement technique can be found in Lunn and Kueper (7) and Lunn (19).

For the first two tests, the PCE pools were exposed to 1.5 PV and 2.0 PV (1 PV = 3050 mL) of water saturated with 2-butanol. The 2-butanol solution was driven with a water flood of several pore volumes. In situ fluid samples were taken by syringe in these first two experiments by means of small diameter (approximately 2 mm o.d.) Teflon tubes with perforated ends placed in the sandpack above the pooled PCE. Two-phase samples were taken after the PCE had been

exposed to 1.0 and 1.5 pore vol of the 2-butanol solution and were analyzed for composition and density.

In addition to the above tests, miscible displacement experiments were conducted to assess the effect of pre-flooding with 2-butanol on alcohol flooding. Seven experiments were conducted as summarized in Table 2. Each experiment involved a 1.0 pore volume injection of a 10 vol % 2-butanol preflood solution followed by a 90 ± 2 vol % mainflood of 1-propanol. Some variation in the 2-butanol concentration is noted in Table 2 because of difficulty of dissolving 2-butanol in water. The mainflood size varied from 0 to 1 PV and was driven by several pore volumes of water. All effluent was collected in 125, 250, and 500 mL bottles and was analyzed for composition. All two-phase samples and selected single-phase samples were analyzed for density and viscosity. Two-phase samples were subsequently diluted with ethanol or 2-propanol until miscibility was achieved to obtain an accurate measurement of the overall sample composition.

A final alcohol flood using in excess of 1 PV of 90 vol % 2-propanol was used at the termination of each experiment to determine how much PCE remained in the apparatus and to conduct a mass balance. All experiments achieved a mass balance of greater than 90% except experiment 4, which was repeated as experiment 5. Losses are attributed to PCE evaporation from the vented effluent assembly and fluid losses during two-phase sample handling.

Downward Mobilization Potential. For hydrostatic conditions, if the capillary pressure at the base of a DNAPL pool exceeds the displacement pressure of the capillary barrier it is perched on, the DNAPL will migrate downward. To calculate the capillary pressure, it is necessary to determine pool height. To accomplish this, the effects of IFT, NAPL volume, and phase density contrast must be considered in conjunction with porous media properties. Longino and Kueper (5) developed an expression for the volume of a NAPL pool in terms of pool height by adopting the Brooks and Corey (20) capillary pressure function and integrating NAPL saturation over the depth of the pool, resulting in the following:

$$V_{NW} = A\phi \left[H - S_r H - \left(\frac{(1 - S_r)P_D^\lambda}{(-\lambda + 1)\Delta\rho g} \right) \times \right.$$
$$\left. ((P_D + \Delta\rho gH)^{-\lambda+1} - P_D^{-\lambda+1}) \right] \quad (1)$$

where V_{NW} is the volume of NAPL in the pool, A is the pool area, ϕ is the porosity of the medium, H is the pool height, S_r is the dimensionless Brooks−Corey fitting parameter representing the residual wetting saturation of the porous medium, P_D is the entry pressure of the porous medium occupied by the pool, λ is the dimensionless Brooks−Corey fitting parameter characterizing the pore size distribution, $\Delta\rho$ is the density difference between the NAPL and aqueous phases, and g is the gravitational constant. The fitting parameters λ and S_r were obtained by fitting the Brooks−Corey capillary pressure saturation relationship to laboratory-measured data. Equation 1 is used in conjunction with phase behavior properties to determine the height of a DNAPL pool given porous media and fluid properties. After pool height is calculated, if the capillary pressure (P_C) at the base of the pool, determined from

$$P_C = (P_D + \Delta\rho gH) \quad (2)$$

is greater than the entry pressure of the capillary barrier (P_D'), then mobilization will occur. IFT is incorporated into the procedure because P_D and P_D' are proportional to IFT (21). To evaluate the risk of downward mobilization of a static
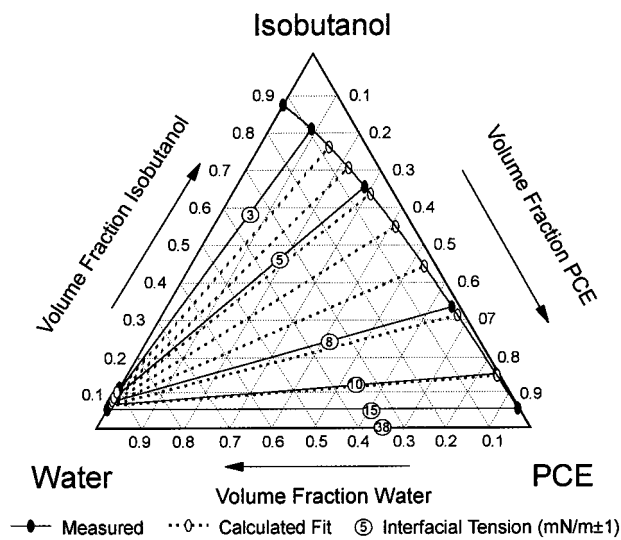

FIGURE 2. Ternary phase diagram for the PCE/water/2-butanol system.

pool exposed to alcohol, the mobilization potential (M_p) is defined:

$$M_p = \left(\frac{P_D' - P_C}{\Delta\rho g} \right) \quad (3)$$

The mobilization potential is evaluated here for a static 50 mL PCE pool suspended on a fine sand capillary barrier. The dimensions and properties of the pool and porous media are chosen to match the conditions of this study. The Brooks−Corey parameters for the coarse sand were determined to be $\lambda = 5$ and $S_r = 0.11$ (19). Calculations compare the effects of ethanol, 1-propanol, and 2-butanol exposure to the PCE pool. Phase behavior properties presented in this study are used for the 2-butanol calculations. Ethanol and 1-propanol data required for the calculations are taken from Lunn (19).

Results and Discussion

Experimental Phase Behavior. The laboratory-measured ternary phase diagram for the system PCE/water/2-butanol is presented in Figure 2 (figures use the term isobutanol for 2-butanol). Also plotted in Figure 2 are the measured IFT values for each tie-line and the numerical fit to the phase diagram. The phase diagram displays type II behavior (22) with two immiscible pairs: 2-butanol and water or PCE and water. The slopes of the tie-lines indicate the partitioning of 2-butanol between the aqueous and NAPL phases, with the aqueous phase compositions plotting at the left end points and the NAPL phases plotting at the right end points. As the 2-butanol content increases, the tie-lines slope down increasingly to the left, indicating that a larger percentage of it partitions into the NAPL phase. The IFT drops from an initial PCE/water value of 38 to 3 mN/m at high 2-butanol content. This potentially increases the risk of downward mobilization. However, the NAPL density is also changing as presented in Figure 3 in which the NAPL phase density declines almost linearly until the NAPL phase becomes less dense than the aqueous phase. Also shown in Figure 3 are the phase viscosities, which demonstrate that the NAPL phase becomes much more viscous than the aqueous phase as 2-butanol content increases.

Density Reduction Calculations. The phase diagram clearly shows that 2-butanol is not completely miscible in water. It could be very difficult to deliver a nonaqueous 2-butanol solution to a DNAPL pool given the influence of porous media heterogeneity on immiscible phase migration pathways. Without solubility enhancements such as surfac-
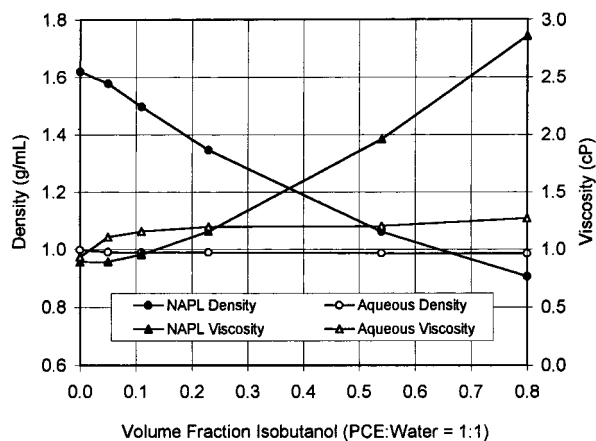
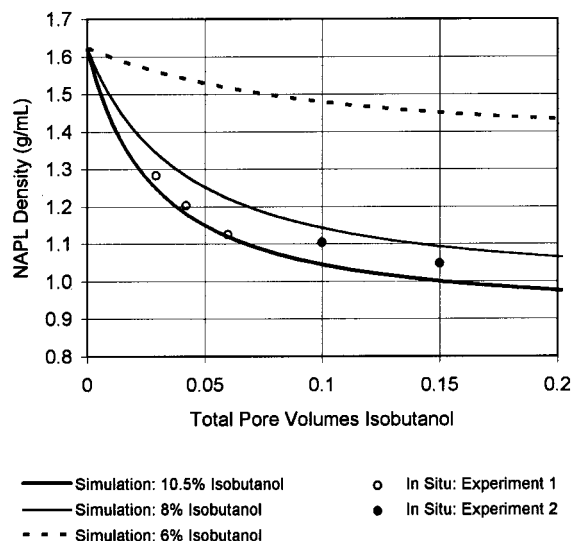FIGURE 3. Phase densities and viscosities for the PCE/water/2-butanol system.

FIGURE 4. NAPL density reduction calculations and results from in situ samples for a PCE pool exposed to aqueous solutions of 2-butanol.

FIGURE 5. Effluent histories for the 0.125 PV 1-propanol flood (experiment 5) with a 2-butanol partitioning preflood.

FIGURE 6. Effluent histories for the 1.0 PV 1-propanol flood (experiment 9) with a 2-butanol partitioning preflood.

tants and miscible alcohols, approximately 10 vol % represents the limit of 2-butanol concentration that can be injected as an aqueous phase.

Figure 4 presents results from density reduction calculations for a 50 mL PCE pool exposed to aqueous 2-butanol along with density measurements taken in situ from PCE pools during experiments 1 and 2. The density reduction curves demonstrate that higher 2-butanol concentrations are more effective at reducing NAPL density because a higher proportion of the injected 2-butanol partitions into the DNAPL phase. The curves also demonstrate that the rate of density reduction decreases with 2-butanol volume, and thus, for flood optimization, the tradeoff between additional 2-butanol volume and density reduction must be considered.

The laboratory-measured density values plotted in Figure 4 match well with the calculated curves, although the measured density reductions were lower than the predicted values. This is attributed to dilution of the 2-butanol slug by connate water as well as incomplete equilibration between phases during the experiments. A 0.1 PV partitioning preflood of 2-butanol (delivered as a 1.0 PV slug of 10 vol % 2-butanol) was chosen for miscible displacement experiments.

Laboratory Column Experiments. Summary results for the sequential 2-butanol/1-propanol miscible floods are presented in Table 2. Recoveries ranged from 1.2% to 97.6% of the total PCE mass. PCE recovery for the base case
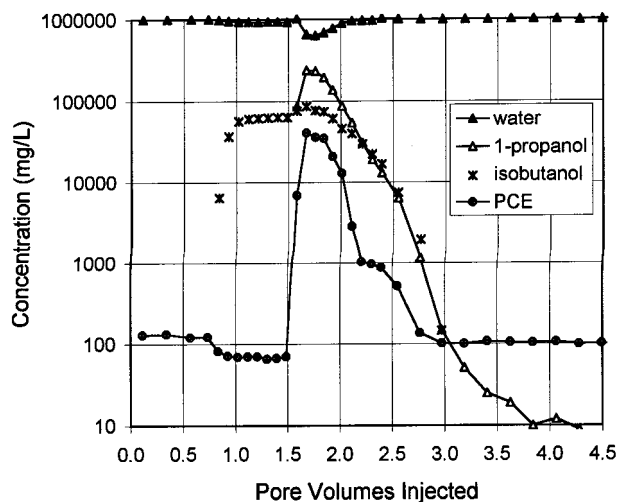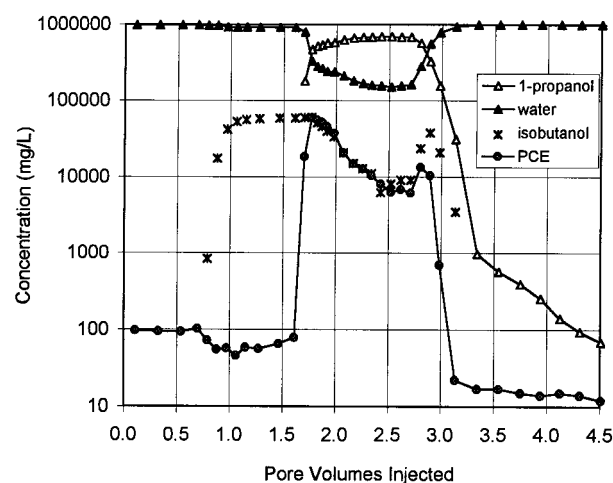
(experiment 3) of a 2-butanol preflood alone was 1.2% and represented recovery by dissolution only. This experiment demonstrates that, for a 1.0 PV slug of 10 vol % 2-butanol without the benefit of a following miscible mainflood, very little PCE is recovered and the alcohol is not efficiently utilized. If a continuous 2-butanol flood was employed, it is likely, given the DNAPL density reduction illustrated in Figure 3, that NAPL mobilization by immiscible displacement would eventually occur. This is not anticipated to be very efficient, however, and would leave behind residual DNAPL since the IFT would not be completely eliminated. In contrast, the subsequent use of even a small 1-propanol flood recovers significant mass because miscible displacement is achieved. The 0.125 PV flood of 1-propanol, (experiment 5) for example, recovered 56.6% of the PCE mass. Experiments using larger 1-propanol floods recovered incrementally more mass with near complete recovery (97.6%) for the 1.0 PV flood of 90 vol % 1-propanol (experiment 9).

Two example effluent histories are presented in Figures 5 and 6 for the 0.125 PV and 1.0 PV 1-propanol floods (experiments 5 and 9). Each plot includes the overall effluent concentrations of the four components water, PCE, 2-butanol, and 1-propanol. Both experiments show background PCE concentrations of between 100 and 120 mg/L. 2-Butanol breakthrough occurs at approximately 0.8 PV, and concentrations quickly build to approximately 60 000 mg/L. An injected concentration of 10 vol % 2-butanol corresponds to
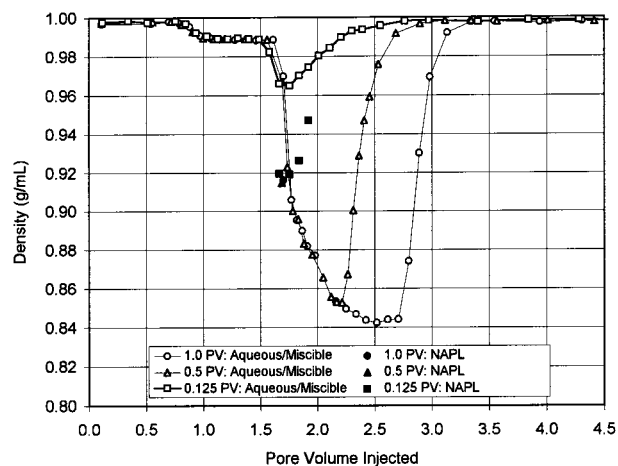
FIGURE 7. Effluent density histories for experiments 5, 8, and 9.

FIGURE 8. Effluent viscosity histories for experiments 5, 8, and 9.

approximately 84 000 mg/L. Some dilution occurs due to dispersion and fingering and some of the 2-butanol partitions into the PCE pool. PCE recovery first occurs at approximately 1.6 PV of injected fluid, concurrent with 1-propanol breakthrough. Experiments with smaller 1-propanol floods recovered more NAPL mass as a separate phase than experiments with larger 1-propanol floods, which recovered most of the PCE mass as a miscible phase. This is consistent with loss of miscibility for smaller alcohol floods due to dispersion and hydrodynamic instabilities.

The 0.125 PV slug (experiment 5) shows PCE concentrations falling back to near background values after reaching a peak concentration. The larger flood (experiment 9) shows a sharp rise in PCE and 2-butanol concentration at the tail end of the 1-propanol flood. This is the result of increased hydrodynamic displacement efficiency at the distal end of larger alcohol floods as discussed by Lunn and Kueper (7). Note that the 2-butanol concentrations decrease later than the PCE values because as the 1-propanol concentrations decrease and the flood resorts to a waterflood, the 2-butanol in any remaining NAPL phase partitions back into the aqueous phase, leaving PCE behind as residual blobs spread throughout the sandpack. The 2-butanol detection limit (100 mg/L) was higher than for PCE, and it is likely that 2-butanol continues to tail to some extent. The final PCE concentration after the alcohol was flushed from the sandpack is related to the amount of PCE left in the apparatus, with concentrations of 100 and 15 mg/L for the two effluent histories described.

For all two-phase samples in experiments 3−9, the NAPL phase was recovered as an LNAPL. Furthermore, all miscible samples with elevated PCE concentrations were less dense than water. This combination greatly reduces the probability of introducing the original DNAPL deeper into uncontaminated porous media. Figure 7 provides the effluent phase density histories for the 0.125, 0.5, and 1.0 PV 1-propanol floods (experiments 5, 8, and 9). Errors bars for measured density are approximately the same size as the data points (±0.002 mg/L). The NAPL samples have solid symbols to distinguish them from aqueous and miscible samples. All three experiments were initially characterized by a two-phase bank driven by the 1-propanol flood. The initial NAPL sample recovered from the bank had approximately the same density (0.916 ± 0.005 g/mL) in all three experiments and was less dense than the corresponding aqueous phase (0.966 ± 0.005 g/mL). After the initial two-phase samples, the effluent from the two larger experiments became miscible because of the 1-propanol content. The 0.125 PV flood did not reach sufficient 1-propanol concentration for complete miscibility and continued to recover two-phase effluents until the supply
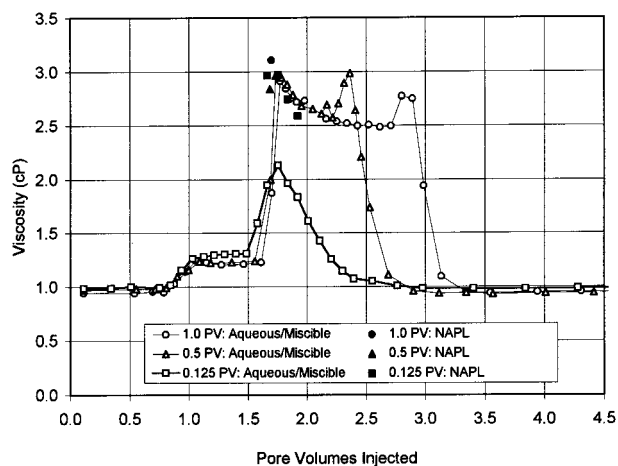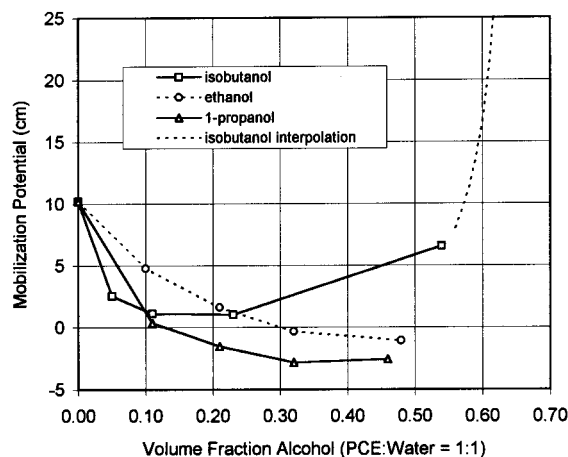

FIGURE 9. Downward mobilization analysis of a static DNAPL pool exposed to various alcohols.

of 1-propanol was exhausted. The solid squares in Figure 7 demonstrate that, even without a sustained miscible zone, all NAPL is recovered as an LNAPL.

Phase viscosities (±5%) are presented in Figure 8 and show that the recovered NAPL phase is always more viscous than the aqueous phase. This contributes to the inability of the 1-propanol to recover the 2-butanol/PCE NAPL in an efficient miscible displacement because the combination of a less viscous and less dense driving flood (1-propanol) results in an unconditionally unstable process (23). Viscous fingering of the relatively low viscosity 1-propanol (2.6 cP) into the NAPL ($\approx$ 3 cP) is consistent with NAPL viscosity measurements shown in Figure 3.

Downward Mobilization Potential. While calculations and experiments have demonstrated that in situ density reduction of a PCE pool can be accomplished and the pool subsequently recovered as an LNAPL, the present study exclusively uses upward gradients. However, it may not always be possible to sustain upward gradients across a contaminated site. Therefore, analysis of downward mobilization potential for a DNAPL pool exposed to different alcohols is presented for a situation without upward flow.

Figure 9 presents the results of mobilization potential calculations utilizing eq 3. Positive values indicate the additional pool height that would be required to initiate downward mobilization. Negative values indicate that downward mobilization would occur. As can be seen, in a static case, exposure to ethanol and 1-propanol would cause downward mobilization into the fine sand lens. 2-Butanol, in contrast, induces enough density reduction to offset the

effects of IFT reduction and therefore prevents downward mobilization. The additional DNAPL pool height necessary for downward mobilization is initially reduced but then increases and asymptotically tends to infinity as the density contrast approaches zero at an 2-butanol fraction of approximately 0.67. In fact, the downward mobilization risk is eliminated when the density contrast is reversed. The significance of these data is that preconditioning of a DNAPL pool using a partitioning preflood of 2-butanol need not be conducted in an upflow mode. Once the density of the DNAPL is reduced to that of water, the requirement for a vertical flood to offset downward mobilization may prove unnecessary.

Acknowledgments

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