

In-Situ Control of DNAPL Density Using Polyaphrons

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Once spilled into soils, dense nonaqueous phase liquids (DNAPLs) such as chlorinated solvents migrate deep into the subsurface because of their high density. Their downward migration typically continues until capillary forces balance gravitational forces or until essentially impermeable strata are reached. Efforts to mobilize the DNAPL for remediation purposes risks driving the contaminants deeper, which has spurred research for modifying buoyancy forces in situ. In this paper, a novel means of controlling the density of a DNAPL phase using polyaphrons is presented. Polyaphrons are a class of high internal phase ratio emulsions (HIPREs) that have unusual properties such as indefinite stability and flow properties through porous media. They provide a means of selectively delivering a light organic phase liquid to the vicinity of the DNAPL phase. Upon destabilization of the polyaphron by a polyvalent cation, the light internal phase mixes with the DNAPL to produce a nonaqueous phase of lower density than the original contaminant. The negative buoyancy of the DNAPL can thus be reversed. This approach holds great promise for manipulating DNAPL densities prior to or during remediation treatments.

Introduction

Dense organic liquids are widespread environmental contaminants, especially at Department of Defense sites where chlorinated solvents are the most prevalent contaminants found in the subsurface (1). These contaminants are termed dense nonaqueous phase liquids (DNAPLs) to differentiate their behavior in the subsurface as compared to lighter organics. Specifically, DNAPLs migrate below the water table where they tend to pool on top of fine-grained strata or become trapped by interfacial forces in the form of disconnected ganglia. Further downward migration of the contaminant can occur due to an increase in the hydraulic potential, lateral spreading of a pool to a vertical fracture, or a reduction in interfacial tension due to changes in subsurface chemistry.

Despite the extent of DNAPL contamination problems, consistently successful remediation techniques have not yet been developed. The low volatility of these fluids makes stripping techniques relatively ineffective, while their low solubility reduces the efficiency of dissolved-plume treatments such as reactive barriers. Consequently, the most pressing research needs for DNAPL problems are in the areas of source-zone identification and remediation.

The major drawback to performing aggressive source-zone treatments using current technology is the risk of unintended downward mobilization into previously uncontaminated strata (2). This issue is especially of concern with surfactant-enhanced remediation treatments, which can be used to promote solubilization and/or mobilization of a DNAPL. The use of upward hydraulic gradients to offset downward DNAPL motion has been proposed (3) but is difficult to implement in practice. Alternatively, the treatment design can impose limits on the amount that the interfacial tension is reduced, limiting mobilization but allowing accelerated DNAPL removal via solubilization (4). However, mobilization is considerably more efficient than solubilization (5) and therefore is preferable if the risk can be mitigated.

Clearly, techniques to improve DNAPL buoyancy offer important benefits (especially when coupled with surfactant flooding), and they have received significant attention recently. Most studies have focused on cosolvent flooding using three- and four-carbon alcohols. These cosolvents are soluble in water, yet they partition with varying strengths into the DNAPL phase, which can reduce its density. The drawback to cosolvent approaches is their reliance on equilibrium phase behavior, which leads to a number of practical problems that are detailed in the next section.

This paper describes a fundamentally new approach for in-situ density reduction in which light, inert, hydrocarbon species are delivered to a contaminant source zone using polyaphrons (which are highly stable colloidal droplets that contain an organic phase; see below for additional details). The polyaphrons are destabilized in the vicinity of the DNAPL by delivering a specific chemical at the desired location, which allows for mixing of their internal hydrocarbon phase with the denser contaminant. The result is a controlled reduction of the contaminant density that offers significant benefits over other methods. These benefits include the long-term stability of the density conversion (i.e., the process is essentially irreversible), the ability to reduce contaminant density well below groundwater density, and the potential to achieve density reversal using relatively small volumes of injected chemicals.

Background

Density Modification Treatments. The aim of density modification treatments is to increase DNAPL buoyancy either by decreasing the density of the DNAPL phase or by increasing the density of the surrounding groundwater. Miller et al. (6) have proposed using the latter approach by injecting high-density brines into the contaminated strata, and a few integrated approaches have been developed in which the density of both phases are modified (7, 8). However, the most prevalent strategy is to reduce DNAPL density by cosolvent flooding with alcohol solutions, a process that causes swelling of the DNAPL phase due to equilibrium partitioning of the alcohol and a corresponding reduction of its density.

Although earlier studies examined cosolvents for improving solubility, Brandes and Farley first recognized their importance in the context of density modification (9). They generated ternary phase diagrams for four sets of contaminant–alcohol mixtures: trichloroethylene (TCE) and tetrachloroethylene (PCE), each mixed with 2-propanol (IPA) and *tert*-butyl alcohol (TBA). Additionally, they performed upward-directed column experiments and documented differences in displacement efficiency resulting from differences in the phase behavior of the mixtures. Early on, the issue of density modification was also discussed by Imhoff et al. (4), but in a different context: they focused on the use of methanol,

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precisely to avoid phase partitioning. The rationale for this approach was that under certain circumstances (primarily cases where upward mobilization cannot be assured), it may be beneficial to avoid DNAPL swelling, while at the same time taking advantage of the increased DNAPL solubility afforded by the alcohol.

Roeder et al. (10) [citing earlier work by Milazzo (11)] recognized the importance of using a strongly partitioning alcohol if density modification is to be undertaken and performed numerical simulations for a 1-butanol flood to displace TCE. In cases where no pooling of the TCE occurred, the simulations showed horizontal and/or slight upward movement of the contaminant, along with significant free-phase recovery as an LNAPL.

Lunn and Kueper (3) compared partitioning (1-propanol) versus nonpartitioning (ethanol) alcohols when used with upward-directed flooding to remove PCE from a two-dimensional cell. They observed mechanistic differences in the recovery mechanisms, though both alcohols provided for very efficient PCE displacement under the conditions used. To improve recovery efficiency, they modified the upward-directed injection to a three-step process (7): (i) injection of 1-propanol for density reduction; (ii) injection of ethylene glycol + 1-propanol to provide a miscible, neutral-buoyancy displacement; (iii) injection of a polymer solution to prevent viscous fingering. The same authors subsequently studied the use of 2-butanol, which, though less miscible with water than propanol, provides stronger partitioning into the DNAPL and, under ideal conditions on the phase diagram, can reduce the organic phase (PCE) density below the aqueous phase density (12). They rank the effectiveness of the various alcohols using a criterion called the downward mobilization potential, which quantifies the balance between capillary forces at the base of a pool and the hydrostatic head of contaminant. Roeder et al. used *tert*-butyl alcohol in horizontal column and sandbox experiments (8). Because (unlike the unbranched butanols) *tert*-butyl alcohol alone cannot reverse the density difference, their cosolvent flood included additives (sucrose and glycerin) to increase aqueous phase density.

More recently, extensive tests have been performed using 1-butanol as the cosolvent with chlorobenzene (CB), TCE, and PCE (13–15). Kibbey et al. (13) point out that density reversal (for the higher-density DNAPLs) requires the concentration of 1-butanol in the aqueous phase to be close to its saturated value, which can present practical problems for cosolvent delivery because of the tendency for dispersive dilution to occur in the subsurface. Ramsburg and Pennell (15) performed displacement studies in two-dimensional heterogeneous flow cells using CB and TCE as contaminants. In each case, the DNAPL was recovered by horizontal injection of a 1-butanol preflood solution (for density modification), followed by a surfactant flood that contained 20% (wt) 1-butanol (to prevent stripping of the alcohol from the DNAPL).

While the use of cosolvents remains promising for DNAPL recovery, it has disadvantages in the context of density modification. The most significant issues are the following, which ultimately stem from the equilibrium thermodynamic behavior.

(i) The NAPL will maintain its low density only as long as it is in equilibrium with alcohol in the groundwater. As noted by Kibbey et al. (13), for heavier DNAPLs such as TCE and PCE, maintaining the lower-density condition in the contaminant phase requires the groundwater to be nearly saturated with 1-butanol. If surfactant flooding is employed, this requirement becomes especially demanding because most surfactants increase alcohol solubility in the aqueous phase. From a remediation standpoint, maintaining alcohol-saturated conditions in the groundwater may be impractical

because of engineering (i.e., dilution problems), cost, and/or ecology, especially for sites requiring long-term remediation for complete cleanup.

(ii) The volume of injected solvent required by the process may be prohibitively large for two reasons. The first is simply the need to maintain near-saturation in the groundwater, as described above. A second reason is associated with the phase behavior, which dictates that most of the injected alcohol remains in the aqueous phase. For example, in the TCE flow experiments from ref 15, the 1-butanol concentration dropped from 60 to 55 g/L as the alcohol solution passed over the DNAPL source zone, meaning that only 8% of the injected solvent partitions into the organic phase during the preflood. During the subsequent surfactant flood, no alcohol partitioning occurred (the 20% 1-butanol in solution served only to maintain the lower DNAPL density). In total, the injected volume of 1-butanol was 26 times the initial DNAPL volume, yet only 4.7% of the total cosolvent contributed to density modification. This behavior will be exacerbated in three-dimensional heterogeneous reservoirs.

(iii) The lowest achievable contaminant density is limited by the equilibrium thermodynamics, which for DNAPLs of interest is slightly below 1.0 g/mL [attainable when the DNAPL is in equilibrium with high aqueous phase concentrations of 1-butanol or 2-butanol (12, 13, 15)].

As noted below, these problems can be largely overcome through use of polyaphrons to control DNAPL density.

Polyaphrons. Polyaphrons are a class of biliquid foams consisting of small droplets of a dispersed organic phase, encapsulated in an aqueous surfactant shell (16). They form a class of the so-called HIPREs that typically have very large ratios of dispersed phase to continuous phase volume. They are used in numerous applications, some of which are described in a recent review (17). Upon dilution of the polyaphron solutions with water, the foam-like structure is transformed into a stable dispersion of colloidal droplets, whose sizes are usually in the 1–10- μ m range. They possess unusual attributes critical to the density modification application described here. First, they maintain their essential structure during transport through granular porous media (17, 18). This trait depends, of course, on the morphology and pore size of the media. It should be noted that the polyaphron sizes listed above are for the conditions used in this work. Sizes can be reduced (to the submicron range) or increased (up to 100 μ m) by tailoring the surfactants and concentrations. Second, they maintain indefinite stability, meaning that if the solutions are left undisturbed, coalescence will not occur, even over extended periods. At the same time, the polyaphron solutions exhibit a switch-like response to externally controlled destabilizing conditions. For instance, the anionic surfactant-stabilized polyaphrons used in this work can be destabilized by introducing certain polyvalent cations such as Al^{3+} . (The mechanism for this process and the physical/chemical state of the destabilized solution are not yet fully understood.) Destabilization of the polyaphron at the location of the DNAPL allows intermixing and, potentially, the desired density modification of the DNAPL. For more information on the properties and applications of polyaphrons, see refs 16 and 17.

Experimental Methods

Flow System and Porous Media. The potential for polyaphrons to control density of a DNAPL was studied in experiments in a 2-in. i.d. vertical glass column packed with 300–425- μ m silica sand (Quickrette Co.) to a height of 30 cm. The sand was rinsed with deionized water and then soaked in 1 M hydrochloric acid overnight to remove fine materials prior to use. The size range of the sand particles was selected specifically to provide a balance between capillary and gravitational forces. It was fine enough so that the DNAPL

TABLE 1. Summary of Experimental Conditions

expt	polyaphron			Al(NO ₃) ₃			HTAB solution			vol ratio (hexane/ DCB)	DCB recovery (%)
	vol injected (PV)	Darcy velocity (cm/s)	injection direction	vol injected (PV)	Darcy velocity (cm/s)	injection direction	vol injected (PV)	Darcy velocity (cm/s)	injection direction		
1							2.00	0.93	upward		
2	0.70	1.25	upward	0.70	1.25	upward	1.00	0.84	upward	8	97
3	0.67	1.41	upward	0.44	1.56	upward	1.25	1.27	upward	8	81
4	0.67	1.36	upward	0.44	0.42	upward	1.00	1.23	upward	8	70
5	0.70	1.36	downward	0.61	1.13	downward	1.05	1.13	downward	8	
6	0.45	1.41	upward	0.43	1.45	upward	1.50	a	downward	4	

^a 0.82 for the first 0.5 PV; 1.64 for the rest.

was easily trapped by capillary forces during injection of freshwater but sufficiently coarse so that reduction of the interfacial tension (IFT) by a surfactant induced significant mobilization by gravitational/buoyant forces.

Fluids were injected into the bottom or top of the column using a fluid metering pump. During displacement experiments, flow rates were kept low so that the viscous drag forces on the trapped globules were small as compared to capillary and gravitational forces. Fluids were collected at the effluent of the column for compositional analysis.

Chemicals. 1,2-Dichlorobenzene (DCB) was selected as a representative chlorinated solvent. HPLC-grade DCB was obtained from Sigma Chemical. DCB has a density of 1.306 g/mL and a viscosity of 0.01308 g/cm·s. The interfacial tension between DCB and water is 40 dyn/cm.

Hexane (Sigma Chemical) (density = 0.66 g/mL) was used as the density-modifying agent; other light organics could be used equally well. Tergitol 15-s-5 (Sigma Chemical) was the organic phase surfactant used in the polyaphrons. Sodium dodecyl benzene sulfonate (SDBS) (Aldrich) was used as the aqueous phase surfactant in the polyaphrons.

Aluminum nitrate nonahydrate (Aldrich) was dissolved to 50 mM concentration and used for in-situ destabilization of the polyaphrons. Surfactant flooding of the column was performed using a 4 g/L solution of hexadecyl trimethylammonium bromide (HTAB) (Sigma).

Preparation of Polyaphron. Polyaphrons were made using the method described by Sebba (16): 5 mL of deionized water containing 4 g/L SDBS was placed in a beaker and stirred until a stable foam was formed. Then, 95 mL of hexane containing 0.5% (by volume) Tergitol 15-s-5 was gradually added to the foam to form a concentrated polyaphron solution (95% organic phase). This solution was diluted to the desired concentration prior to use in the flow experiments.

Sand Column Experiments. The proposed density modification process consists of two key steps:

(i) delivery of the polyaphron solution to the vicinity of the DNAPL source;

(ii) in-situ destabilization of the polyaphron to allow mixing of its light internal phase with the DNAPL.

The column experiments were designed to test of the feasibility of this process and to allow a preliminary sensitivity analysis of various parameters in the process.

In each experiment, sand was placed into the column using a wet packing procedure similar to that used by Roeder et al. (8). First, the column was filled with water to about 40% of the total 30 cm height. Dry silica sand was then added into the column until the total height was reached. The column was shaken several times after each 2-cm layer of sand was added. The pore volume was estimated to be 240 mL by comparing masses of the dry versus wet columns. In each experiment, a 10-mL sample of DCB was placed by syringe into the column to act as a simulated source zone. Eight pore volumes of deionized water were injected in the upward direction to promote trapping of the DCB by capillary forces.

This process caused only slight movement of the original source, and no bulk phase DCB was lost from the column. These 10-mL source zones were, of course, not exactly reproducible; their structures prior to the flow experiments were affected by packing densities, syringe placement, etc. Because we focus on gross differences in behavior in the current work, no effort was made to further characterize each source beyond its volume and general placement in the column.

For visualization, the DCB was dyed using organic soluble Oil-Red-O at a concentration of 0.27 g/L. During the density modification experiments, the column was photographed to provide qualitative information about the DCB movement. These photographs were transformed into binary images using MATLAB's image processing toolbox, which allowed computation of the center of mass of the imaged DCB. (The computed center of mass is not intended to represent the true center of mass of the three-dimensional source because analysis is performed on a projected two-dimensional image and because the column is opaque beyond a few grain layers. However, this technique provides a qualitative measure of the contaminant motion.) In some experiments the column effluent was collected in 20-mL glass vials, and in selected experiments, it was analyzed using NMR to quantify the composition of the displaced organic fluid.

During the displacement experiments, water, the polyaphron solutions, aluminum solutions, and/or surfactant solutions were injected from either the top or the bottom of the column at constant flow rate. The fluid volumes, flow rates, and injection direction are summarized in Table 1 and discussed below. All velocities reported below are superficial velocities.

Results and Discussion

Results of Column Experiments. A baseline experiment (expt 1) was performed without density modification by injecting 4 g/L HTAB surfactant in the upward direction at 0.93×10^{-3} cm/s. Under these conditions, hydrodynamic drag was not large enough to counteract gravitational forces. Hence, as the surfactant reduced the interfacial tension, the bulk DCB phase was mobilized in the downward direction as shown in Figure 1, despite the upward flow direction. This experiment demonstrates the balance between interfacial and gravitational forces that was described above and provides a comparative baseline for the density modification experiments. It is also a good illustration of the fundamental danger posed by surfactant flooding in the field.

Figure 2 contains images from a density modification experiment (expt 2) conducted with upward-directed flow for all fluids. In the experiment, 0.7 pore volume (PV) polyaphron solution (containing 50 vol % hexane as the discontinuous phase) was injected, followed by 0.7 PV of 50 mM Al(NO₃)₃ to promote destabilization of the polyaphron. Both fluids were injected at a superficial velocity of $1.25 \times$

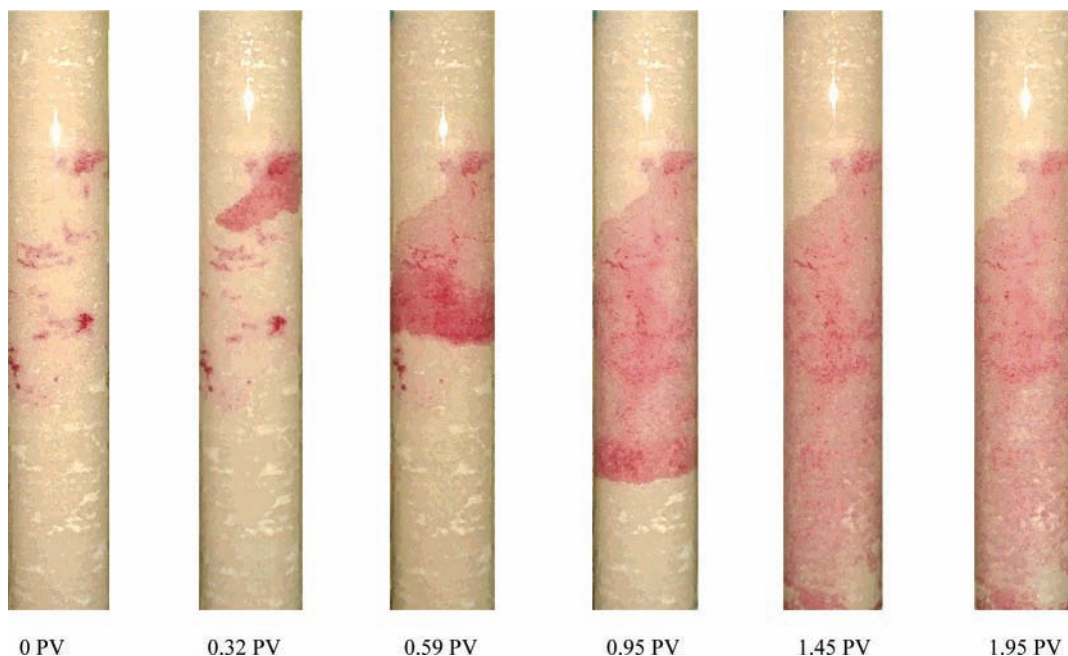


FIGURE 1. Experiment 1: DCB movement due to upward-directed injection of HTAB surfactant.

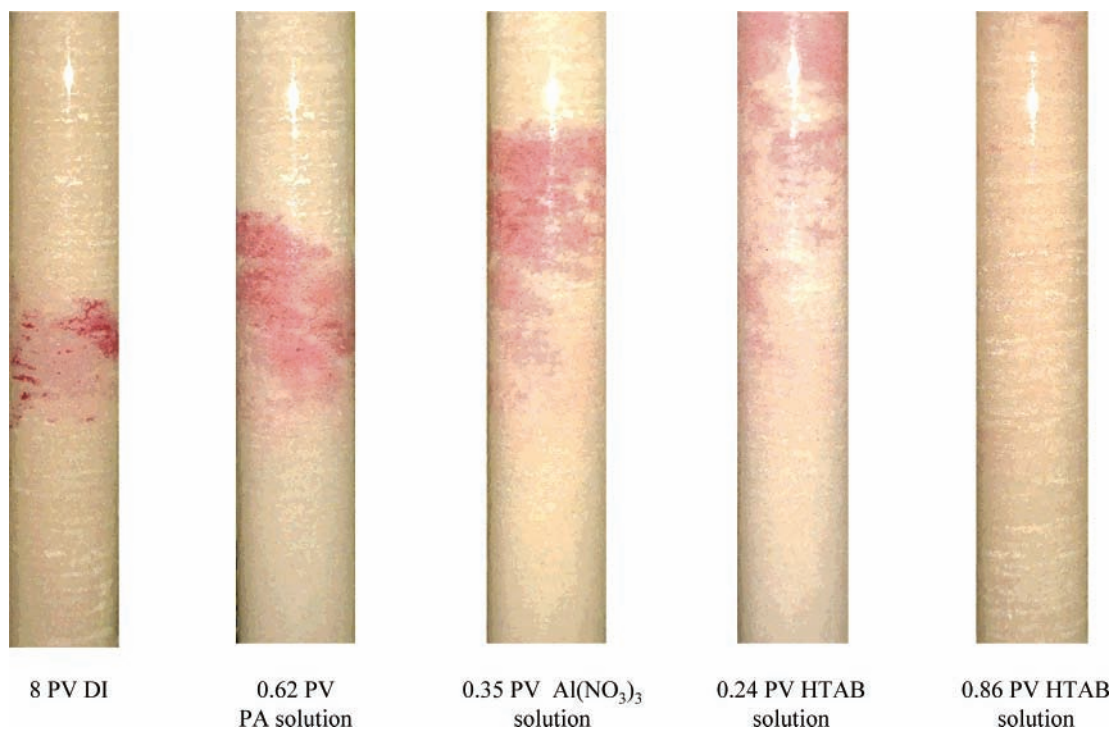


FIGURE 2. Experiment 2: DCB movement due to an upward-directed polyaphron treatment for density modification, followed by surfactant injection.

10^{-3} cm/s. Subsequent injection of 1.0 PV of HTAB surfactant at 0.84×10^{-3} cm/s caused displacement of the contaminant as a light, organic phase mixture of DCB and hexane. In this and similar experiments (expts 3 and 4), DCB recoveries of the bulk organic phase effluent ranged from 70% to 97%, depending on details of the treatment procedure and also on uncontrollable factors such as the exact initial distribution of contaminant in the column. Effluent compositions from two of the experiments (expts 3 and 4) are plotted in Figure 3, showing that most of the NAPL leaves the column as a light organic phase. [One data point has a high DCB content, indicating that a small amount of dense organic was collected at the effluent. This data point contradicts the expt 1 results:

that viscous forces were not strong enough to carry the DNAPL upward. A number of possible explanations exist for the anomalous data point; likely explanations include higher local velocities due to channeling, that the bulk polyaphron solution acted as a high-viscosity fluid, or simply that the small density change was enough to change the balance of drag versus gravitational forces.] A couple of notes should be made. First, due to the low solubility of DCB and the short time frame of the experiments, the mass displaced from the column by dissolution is small (estimated to be less than 2% of the total DCB mass). Also, because DCB and hexane exhibit essentially ideal mixing behavior, so the density of effluent fluid composed of 30% DCB is approximately 0.85 g/mL.

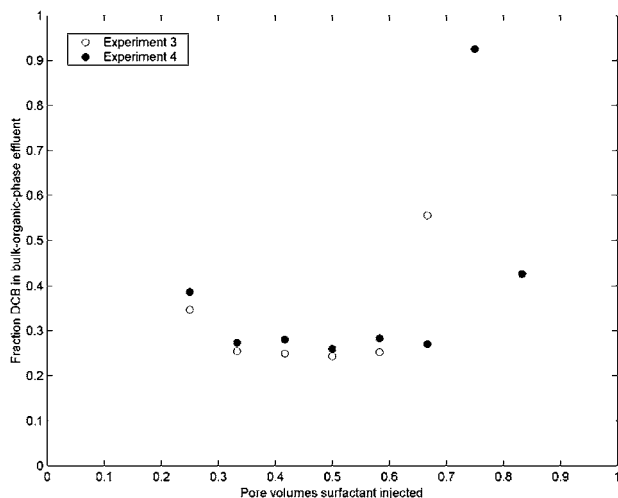


FIGURE 3. Effluent organic phase compositions from two different density modification treatments.

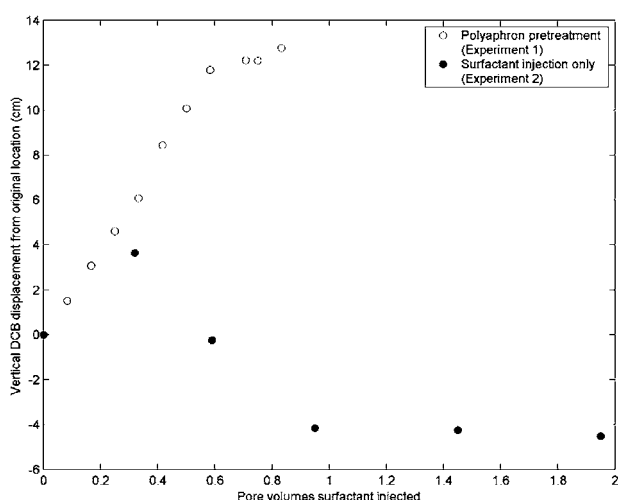


FIGURE 4. Vertical DCB location in the column during surfactant injection: comparison with and without density modification.

More significant than the effluent composition is the behavior of the bulk contaminant as compared to the untreated behavior. This contrast is illustrated in Figure 4, which is a plot of contaminant-source location versus PV surfactant solution injected. (The data were obtained from center-of-mass measurements made on the digitized images.)

The final experiment described in this section is identical to expt 2 except that injection of the polyaphron, the Al^{3+} solution, and the surfactant solution was performed in the downward direction. This change in procedure eliminated the possibility of upward DNAPL motion occurring because of viscous forces acting in the direction of flow. Figure 5 contains images of the experiment. No bulk organic phase was detected in the effluent, and a moderate upward movement of the DCB was observed despite the downward directed flow. This behavior provides additional confirmation (independent of the NMR analysis) that in-situ density reversal occurred.

Parameters in the Process. In practice, the volume of the light organic phase as compared to the contaminant volume (e.g., the hexane/DCB ratio in the current experiments) will be the major factor to gauge the treatment efficiency. The experiments described above were performed using an 8:1 hexane/DCB ratio, and ideally this value should be lower. While more realistic situations (i.e., large, heterogeneous, three-dimensional systems) would suggest that a low efficiency might be necessary, a significant amount of process

optimization remains to be done, including the identification of crucial design and treatment parameters. Although much new research will be required (because of the complex microscale behavior), certain observations and conclusions can be made from the macroscopic column experiments.

In the upflow experiments, a large fraction of hexane flowed out of the column in the form of stable polyaphron particles. This observation indicates inefficient in-situ contacting between the polyaphron and the injected cation, most likely due to plug-flow displacement of the polyaphron solution by the cation solution. This behavior is caused in large part by the experimental setup: the homogeneous medium and the one-dimensional flow geometry tend to encourage a plug-flow type displacement. Additionally, the significantly larger bulk density of the cation solution than the polyaphron solution promotes a gravitationally stable displacement. (It should be noted that this latter effect should compete with a viscous instability brought on by the higher bulk viscosity of the polyaphron solution, though it is not known which effect is dominant under the current conditions.)

A number of possible solutions exist for this problem. If the flow has a strong vertical component (upward or downward), then the injection sequence (polyaphron vs cation) can be designed with the heavier solution above the lighter solution. Likewise, viscous fingering can aid in mixing the two bulk fluids. Under some conditions, taking advantage of these flow instabilities would require reversal of the injection sequence (i.e., injecting the destabilizing cation ahead of the polyaphron). An experiment was performed to test this scenario using upward-directed flow, in which the Al^{3+} solution was injected prior to the polyaphron solution. The results were qualitatively similar to the Figure 2 results, suggesting that reversal of the injection sequence is a viable design strategy.

A second (and probably better) solution to the contacting problem is based on the hypothesis that the bulk polyaphron may exhibit yield stress behavior in a porous material, meaning that a certain critical stress (e.g., pressure gradient) must be applied before motion of the bulk solution occurs. Assuming this were true, flow through the continuous aqueous phase would occur even at pressure gradients below the critical value, thus allowing a destabilizing cation solution to be injected slowly into the bulk polyaphron solution without mobilizing it significantly. This possibility appears feasible based on two column tests that were performed without DNAPL present. In the first case, 0.625 PV of polyaphron solution was injected into the bottom of the column, followed by 0.83 PV of Al^{3+} . The flow rates of both fluids were 1.64×10^{-3} cm/s. During injection of Al^{3+} , a large fraction of the polyaphron solution was recovered in the effluent. In the second experiment, the injection rates were reduced to 0.41×10^{-3} cm/s. In this case, virtually no polyaphron nor bulk organic was observed in the effluent. These results have important implications because this method can be applied to horizontal injections as well as vertical, the former being more likely in a field situation.

We consider finally the location of the DNAPL relative to the polyaphron solution prior to destabilization and the surfactant flood. If the light phase organic (from the polyaphron solution) is located above the DNAPL at the onset of surfactant flooding, gravity-induced motion of the two fluids will move them apart from one another. If the reverse is true—the lighter phase beginning below the DNAPL—the natural motion in response to IFT reduction will move the fluids toward one another, promoting mixing.

Considering all of these factors together suggests a preliminary strategy for effective remediation:

(i) inject the polyaphron solution to a location where it is intermixed with or below the trapped DNAPL;



FIGURE 5. Experiment 5: DCB movement due to a downward-directed polyaphron treatment followed by downward-directed surfactant injection.

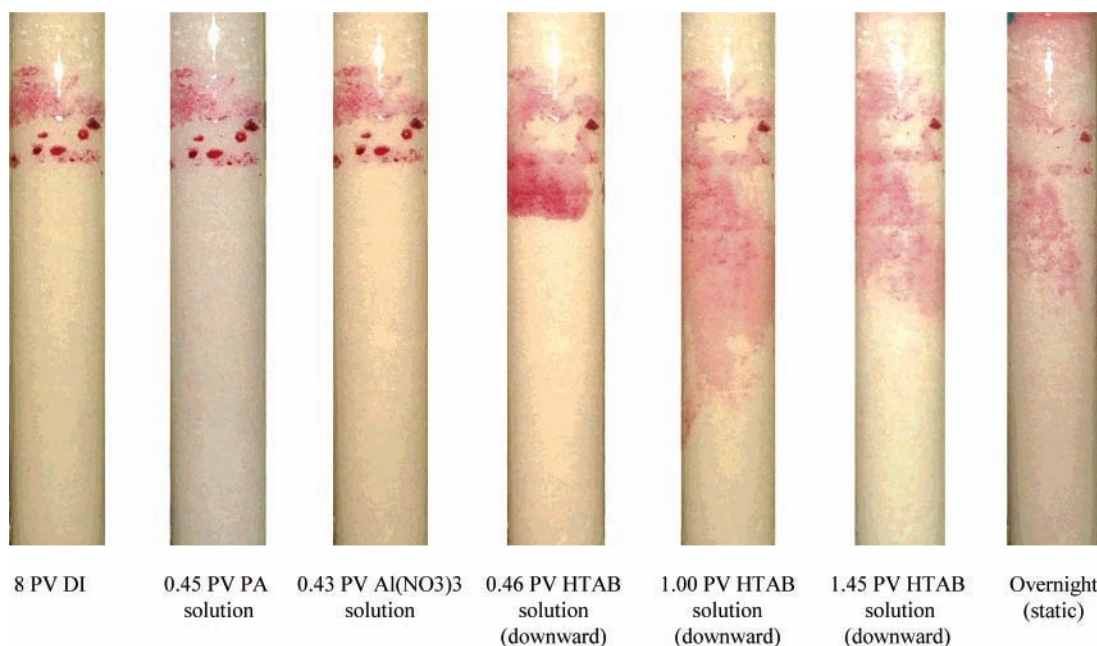


FIGURE 6. Experiment 6: 4:1 hexane/DCB ratio experiment. Downward mobilization of the DCB (during downward surfactant injection) is stopped by the lower bank of destabilized polyaphrons.

(ii) inject an appropriate cationic solution so as to destabilize the polyaphron solution;

(iii) inject surfactant solution to induce mixing and mobilization of the organic phase fluids.

A final column experiment (expt 6) was run using a more efficient 4:1 hexane/DCB ratio and incorporating some of these ideas. The standard procedure for DCB placement was employed but at a higher position in the column. Upward injection of 0.45 PV of polyaphron solution (40% hexane by volume) followed by 0.43 PV of Al^{3+} solution was then

performed. The higher positioning of the DCB in this experiment allowed a significant fraction of the polyaphron bank to remain below the DCB in the column. Subsequently, HTAB was injected in the downward direction: 0.5 PV at 0.82×10^{-3} cm/s followed by 1.0 PV at 1.64×10^{-3} cm/s. As shown in Figure 6, initial DNAPL migration was downward. However, the contaminant was caught by the destabilized polyaphron bank and its motion reversed, despite downward flow of surfactant. The final image from Figure 6 was taken after a static shut-in overnight. In this experiment, the

movement of the DCB *against* the viscous drag force shows that the contaminant density was made significantly lower than 1.0 g/mL, even with the more efficient 4:1 hexane/DCB ratio.

Advantages of the Procedure. The proposed approach exhibits a number of important attributes:

(i) The volume of injected chemicals (not including water) is small in comparison to other techniques for density modification. In principle, the relative injected volume could be reduced to approximately a 1:1 ratio of light organic to DNAPL, although this possibility requires further research.

(ii) The final contaminant density is dictated by the volume of material injected and the mixing efficiency rather than thermodynamic considerations. Thus, the final contaminant density is easily controlled and can be made significantly lower than the groundwater density if necessary.

(iii) Because the light organic phase is immiscible with groundwater (encapsulated in the form of a polyaphron solution during injection), it cannot be diluted by dispersive mixing. (The polyaphron bank can indeed be spread by dispersion but without chemical dilution.) This is a significant advantage in heterogeneous strata, where the efficiency of chemical treatments can be severely degraded by dispersion.

(iv) Through the use of a nearly insoluble (in water) light organic species, the density modification process is essentially irreversible, which allows the procedure to be undertaken as a true pretreatment for any number of remediation strategies. As such, problems such as subsequent delays or the possibility of a long remediation treatment are of little consequence.

The most important fundamental question that must be addressed is the mechanism of microscale mixing between the two organic phase fluids. Neither column experiments nor preliminary micromodel visualization experiments show evidence of direct coalescence between polyaphron particles and the bulk DNAPL phase during the flow of polyaphrons through the porous medium, which suggests that destabilization is a crucial step in the mixing process. It remains unclear whether mixing occurs during destabilization or whether the mobilization of the bulk DNAPL by IFT reduction is a crucial step in the mechanism.

Important technical issues include heterogeneity and chemistry in the field, which can produce dramatically different behavior than is observed in column studies. The effective delivery of polyaphrons to the source depends on identification of the source zone, which is a challenging problem in and of itself. Tracers are a common tool for source-zone identification, and because the small polyaphron particles respond mainly to hydrodynamic rather than gravitational forces, we believe that their flow patterns are similar to dissolved solutes (i.e., tracers). Hence, the use of tracers to create templates for polyaphron injection will be studied.

Finally, an important environmental issue is the identification of more environmentally friendly light phase organics

than hexane or kerosene, which will allow the development of truly benign chemical formulations. Research is underway to examine the performance of naturally occurring organics such as vegetable oils for this purpose.

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Note Added after ASAP Posting

This paper was released ASAP on 08/21/2003 with nomenclature errors in the 5th, 7th, 8th, and 9th paragraphs of the Background section. The correct version was posted on 08/28/2003.

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