The use of surfactants for *in situ* extraction of organic pollutants from a contaminated aquifer

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Abstract

Many common organic pollutants are characterized by low solubilities and high interfacial tensions; these characteristics combine to render pump-and-treat processes ineffective. Surfactants can dramatically increase the solubility of organic compounds in groundwater and lower their interfacial tensions; both effects theoretically can greatly increase the extraction efficiency of pump-and-treat systems. Lowering of interfacial tensions can result in movement of dense contaminants downward in an aquifer, potentially contaminating underlying layers. Increasing a pollutant's solubility increases the fraction of pollutant present as dissolved phase, increasing the efficiency of extraction using a modified pump-and-treat technique. Thus we propose that a surfactant solution intended for extraction of dense organic liquids should be optimized for solubilization, with a minimal reduction of interfacial tensions. The results of porous media experiments comparing the extraction efficiency of over 100 surfactants indicate that solubilization ability is the most important factor; although both the extent of reduction of interfacial tension and the tendency to form spontaneous emulsions must also be considered. Using a suitable surfactant mixture, a pool of tetrachloroethylene can be extracted from a lab-scale saturated porous media model in 7 to 14 pore volumes, depending upon the geometry of the contamination. Mass balance calculations indicate complete removal of the contaminant and analysis of sand samples at the conclusion of the experiment indicates less than 1 milligram of contaminant remains. In contrast, concentrations of the effluent average only 6 ppm when distilled water is used for flushing, producing no measurable reduction in the volume of the pool in 14 pore volumes. These experiments suggest that utilizing surfactants to increase the solubility of dense organic pollutants can be an effective and relatively inexpensive way of *in situ* remediation of contaminated aquifers.

Introduction

Many organic liquids that are common groundwater pollutants cannot be efficiently extracted by pump-and-treat methods due to their low solubilities in water and high interfacial tensions with water [1–3]. Their low solubilities result in only a small fraction of the contaminant entering the groundwater as a dissolved phase, the remainder persists as a separate non-aqueous phase liq-

uid (NAPL). Pump-and-treat systems recover only dissolved phase contaminant and thus cannot efficiently remove contaminants with low solubilities. A non-aqueous phase can, in principle, be directly recovered from an extraction well if the traction of the groundwater flow is sufficient to overcome capillary forces that retain the non-aqueous phase [4]. However, the high interfacial tensions between groundwater and NAPL result in large capillary forces that retain the NAPL [3,5]. Thus conventional pump-and-treat operations cannot remove the majority of NAPL at a given site [2].

Surfactants have the ability both to increase the solubility of organic liquids in water and to decrease the interfacial tension between NAPL and water; thus, potentially increasing the ability of pump and treat operations to extract contaminants either through solubilization or through mobilization of NAPL.

Surfactants have been used extensively in enhanced oil recovery to increase the mobility of crude oil. Surfactants and cosolvents are blended to reduce interfacial tension between oil and water to less than 0.001 dynes/cm (10^{-6} N/m), a reduction of over four orders of magnitude [6–8]. Not surprisingly, in view of the similarity between the problem of recovery of crude oil (a non-aqueous phase liquid) and that of extraction of an organic liquid from a contaminated aquifer, various workers have proposed the use of surfactants for *in situ* remediation (e.g. [9,10]).

Laboratory studies have shown that surfactants can aid in the washing of soils contaminated with various hydrocarbons [11–13], and PCBs [11], although a rudimentary field test was unsuccessful [13]. A recent evaluation of the importance of various parameters in predicting the performance of surfactants noted the significance of adsorption losses of surfactant in laboratory tests and reviewed published surfactant research [10]. A field test of the use of surfactants to extract wood-treating oils from a contaminated aquifer achieved mixed results [14]. This surfactant flooding process apparently utilized interfacial tension reduction to enhance the mobility of the non-aqueous phase liquids.

In light of the well-developed theoretical basis for the utilization of surfactants, and the number of promising laboratory studies, it may seem surprising that none of the field tests that have been reported has been highly successful. However, based on our own research, we believe their are several good reasons for difficulties in application of surfactants to field sites, including:

(1) Attainment of ultra-low interfacial tensions is not only unnecessary, but, if the contaminant is denser than water, may be undesirable.

(2) Although surfactants do have the capability to aid in the extraction of organic contaminants from contaminated soils or aquifers, the systems involved are sufficiently complex that an empirical approach (i.e.: trying a few surfactants to see which works best) is unlikely to be successful.

(3) The required data for formulation of an optimum surfactant mixture,

including data on interfacial tensions, solubilization, emulsion stability, toxicity, and biodegradability, is not available.

In this paper we argue that a surfactant mixture should be optimized for solubilization, without excessive reduction of interfacial tensions. We believe that the experiments cited below demonstrate that such a mixture can be used in a modified pump-and-treat process, to efficiently extract a wide range of common organic pollutants. We also report the initial results on a large-scale comparative study of commercial surfactants that we have undertaken to provide a data base for formulation of surfactant mixtures.

In our process, an array of injection and extraction wells is utilized to circulate an aqueous surfactant solution through a contaminated aquifer. The surfactants we use are non-toxic and biodegradable, and thus do not pose an additional load on the environment. On the surface, volatile organic compounds are separated from the surfactant solution by air stripping, and the surfactant solution is reinjected. Non-volatile compounds can also be separated from the surfactants, although the process must be tailored for each compound, and requires more sophisticated separation techniques. At the conclusion of treatment, clean water is pumped through the aquifer to remove the surfactants. The surfactants are readily biodegradable and should be disposable as normal waste water at the conclusion of the process.

Relevant aspects of NAPL behaviour

Non-aqueous phase liquids (NAPLs) will sink rapidly through the unsaturated zone under the force of gravity. Capillary forces will retain a small fraction of NAPL in every pore through which it passes. If the NAPL density is greater than that of water, then the dense non-aqueous phase liquid (DNAPL) will tend to drop through the saturated zone, again leaving behind a fraction of its volume in each pore through which it passes due to capillary forces [1,5]. The proportion of the pores that remains filled with DNAPL is the residual saturation; the magnitude of residual saturation depends upon pore geometry [1,5,15,16].

Capillary forces also resist the entry of DNAPL into water-filled pores, sufficient pressure must be developed by the NAPL to overcome these capillary forces before it can invade a saturated layer. This required pressure, the displacement entry pressure [17], is produced by accumulation of DNAPL to a sufficient height to produce the required hydraulic head.

The displacement entry pressure increases with decreasing grain size. As a result, DNAPL tends to stop its vertical movement and spread laterally when a finer-grained layer is encountered. Downward motion will continue if a coarser grained channel is encountered, or if a sufficient thickness of DNAPL accumulates to generate the required displacement entry pressure. Downward flow

will continue until the entire volume has been immobilized as residual saturation or when an impermeable layer is encountered [3,15,16].

The high interfacial tensions between DNAPL and groundwater results in large capillary forces and large displacement entry pressures, as a result DNAPL is generally unable to enter small pores or fractures in a water-wet matrix [16]. If the interfacial tension between DNAPL and groundwater is greatly reduced, the DNAPL will be able to enter smaller pores, possibly enabling it to penetrate low-permeability layers that it could not previously enter, thus promoting downward migration in the aquifer. In many cases, the risk of the DNAPL moving downward into previously uncontaminated zones may be unacceptable. The ultra-low interfacial tensions utilized in enhanced oil recovery are four orders of magnitude below those of a NAPL/water system; such low interfacial tensions would allow DNAPL to move rapidly downward through previously impenetrable layers.

Experiments in our laboratory have found that reduction of interfacial tensions to less than 1 dyne/cm (10^{-3} N/m) causes very rapid downward migration of the DNAPL through course, medium or fine sands. The downward flow is much faster than the horizontal migration induced by pumping of the groundwater [3,15]; thus the initial result of the introduction of surfactant solutions that greatly reduce interfacial tension into a saturated reservoir is a rapid downward migration of DNAPL to an impermeable (clay) layer. Once the vertical migration is stopped by an impermeable layer, horizontal flow of the DNAPL may become significant. If lowered interfacial tensions allow DNAPL to move horizontally along the top of an aquitard towards an extraction well, the DNAPL may penetrate any fractures or zones of higher permeability it encounters. Thus in any aquifer that is not floored by a completely impermeable layer, DNAPL may penetrate the floor of the aquifer and contaminate underlying layers. Since it is seldom possible to demonstrate that no high permeability pathways (fractures, sand lenses, root holes etc.) exist in an aquitard, we believe that designing a system with very low interfacial tensions may generally be undesirable when dealing with dense contaminants.

A further argument against reliance on ultra-low interfacial tensions, that also applies to contaminants with lower density than groundwater (LNAPL) is that attainment of ultra-low IFTs generally requires precise control of a multi-component system, something that is difficult to maintain in the subsurface due to dilution from groundwater, adsorption on solid phases of the reservoir and chromatographic separation of the components during porous media flow [4]. In light of the results of reported field tests of surfactant use for enhanced oil recovery (EOR, see e.g. [6,8]), it seems unlikely that 100% removal of contaminants could ever be obtained by direct recovery of non-aqueous phase.

Increasing the solubility of the contaminants is an alternative to mobilizing the non-aqueous phase (the two processes are not mutually exclusive, all sur-

factants that increase solubility also lower interfacial tensions). If the contaminants can be dissolved into the groundwater, they can be extracted by conventional pump and treat techniques.

Relevant aspects of surfactant chemistry

Surfactant molecules are characterized by having one polar end and one non-polar end [18–21]. When water, a polar solvent, is in contact with a NAPL, (NAPLS are generally non-polar), the surfactant molecules will concentrate along the interface between the two phases with their polar ends in the water and their non-polar ends in the NAPL. The presence of the surfactant lowers the interfacial tensions; even in very low concentrations, surfactants may reduce interfacial tensions by more than an order of magnitude.

When present in sufficient concentrations, surfactant molecules from aggregates, called micelles [19–22]. Micelles may be envisioned as spheres of surfactant molecules arranged with their non-polar ends together in the interior of the sphere. Micelles are capable of incorporating molecules of a non-polar phase, increasing the solubility of the non-polar phase. The mechanism of dissolving in a micellar solution is termed solubilization [21].

The solubility of most organic liquids can be greatly increased by surfactants. For example solubilization of 3.5 grams of tetrachloroethylene (synonyms perchloroethylene or PCE) per gram of surfactant has been reported [19]. This would correspond to a solubility of 175,000 parts per million in a 5% (by weight) aqueous solution of the surfactant, an increase of nearly three orders of magnitude from its solubility in water (200 ppm). By increasing the solubility, the amount of contaminant entering the dissolved phase increases and hence the amount of contaminant recovered per unit volume in pump-and-treat operations also increases.

The increase in solubility is dependent upon the organic compound and the surfactant. There is no method of accurately predicting which surfactant will be the best solubilizer of a given compound. There are, however, some guidelines that can be used to aid in the search; studies have related surfactant type [20], hydrophile/lipophile balance (HLB) [19,20] and structure [17,23] to solubilization potential.

A review of the chemistry of surfactants is beyond the scope of this paper; however, of the three major types of surfactants, anionic, cationic and nonionic (e.g. [24]) nonionics are known to be particularly good solubilizers as are some mixtures of nonionics and anionics. The selection of nonionic surfactants can be guided by determination of the HLB number of each compound. The HLB number is a measure of the relative strength of the polar end to the non-polar end of a surfactant molecule; solubilization of any compound is maximized at a specific HLB number for a given system at a given temperature [20]. The optimum HLB for a given compound may be determined by comparing the

solubilization ability of surfactants from the same chemical family that have different number of moles of ethylene oxide, and hence different HLBs. Determinations of HLB number are shown in Fig. 1 for PCE and TCE (trichloroethylene) in water at 18°C. Once the appropriate HLB is determined, surfactants from different chemical families may be compared at this HLB to determine the chemical type which is the most effective solubilizer.

The HLB number can be calculated from the formula for nonionic surfactants, and is provided by many manufacturers. Assignment of HLB for anionic surfactants is more problematical, and a value is seldom provided. Many types of surfactants, particularly anionic surfactants, cannot be obtained in the correct HLB range but may be effective solubilizers. The solubilization of such surfactants must thus be individually determined. Structure of the surfactants has also been linked to solubilization ability [20,23]; however, no general relation that allows selection of optimum solubilizers has been reported. Thus to obtain optimum solubilization, an exhaustive comparison of available types, mixtures and surfactant/cosolvent mixtures must be undertaken. We are in the process of conducting such a study for common groundwater pollutants.

Another property of surfactants that is relevant to remediation techniques is the tendency of surfactants to form and stabilize emulsions. Of particular importance is the formation of spontaneous emulsions [25–27] along the interface between DNAPL pools and surfactant mixtures. These emulsions can affect extraction of the contaminants in several ways. They can inhibit solubilization by forming a thick emulsion layer that isolates the DNAPL from the
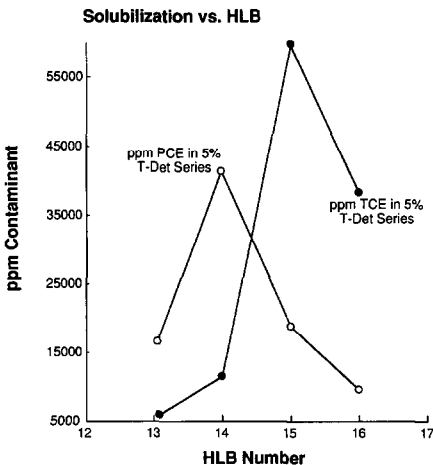

Fig. 1. Solubilization versus hydrophobic/lipophilic balance number (HLB) for PCE and TCE. Changing the number of ethoxylate units in each molecule of surfactant (T-Det is a nonylphenol ethoxylate) changes the hydrophilic/lipophilic balance, and hence the solubilization ability of the surfactant. The data shows that different families of surfactants must be compared at the same HLB to provide a meaningful measure of solubilization ability.

surfactant solution. They can block pores in the aquifer and thus isolate the contaminant from further cleaning. They can enhance solubilization by increasing the surface area for reaction or they can aid in extraction if they are transported with the groundwater. Since the character of emulsions depends not only upon the system, but upon the type of mixing that occurs, we have found the only reliable way of determining the effects of spontaneous emulsion formation on the extraction ability of a surfactant is to compare their performance in porous media.

Typically, spontaneous emulsification occurs in our experiments along the interface between PCE pools and the aqueous surfactant solutions, where the surfactant solution encounters concentrations of PCE in excess of the amount that can be solubilized. Some surfactants formed such dense persistent emulsions in porous media experiments that they could clearly be eliminated from consideration. However, we found no correlation between the formation of emulsions and the efficiency of extraction of contaminants for those surfactants that formed very thin emulsion layers or formed no visable emulsions.

Evaluation of surfactants for extraction of tetrachloroethylene

Based on the performance of various surfactants in simple porous media tests, we decided that selection of the optimum surfactant could not be determined from existing data, nor could any single parameter (surfactant type, HLB, critical micellar concentration, interfacial tensions, solubilization abil-

TABLE 1

Solubilization ability of the best solubilizers for PCE, of 120 tested. Standamox LAO-30 is included in the table as it was among the most efficient extractors (see Table 2) although it was not among the best solubilizers. Solubilization is reported in grams of PCE solubilized per gram of surfactant. Data from [32]

Trade name	Chemical type	Solubilization (g/g)
Siponic 25-9	Linear alcohol ethoxylate	2.75
Tergitol Min-Foam 1X	Ethylene oxide/propylene oxide (EO/PR) alkoxylate of secondary alcohol	1.21
Tergitol XL-80N	EO/PO alkoxylate of primary alcohol	1.022
Tergitol N-10	Trimethyl nonanol ethoxylate	0.964
Rexophos 25/97	Phosphated nonylphenol ethoxylate	0.951
Tergitol 15-S-12	Secondary alcohol ethoxylate	0.91
DeSophos 14DNP	Alkyl ether phosphate ester	0.847
Siponic 218	Ethoxylated thioether	0.814
Emcol CNP-110	Alkylaryl polyoxycarboxylate	0.807
Witconal H-31A	Polyethyleneglycol monooleate	0.659
Emphos CS-341	Polyoxyalkylated alkylaryl phosphate ester	0.656
T-Det N 9.5	Nonylphenol ethoxylate	0.609
Witconal TD-100	Oxyalkylated alkyl alcohol	0.583
Standamox LAO-30	Lauryl dimethyl amide oxide	0.44

ity or emulsion stabilization) be used to predict performance. We thus undertook a systematic study of a large number of surfactants to determine if a combination of parameters could be used, and to provide the data to evaluate the influence of each parameter. In this study tetrachloroethylene (PCE) was used as the contaminant.

Surfactants were selected for screening from recommendations of application chemists from several surfactant manufacturers. We also compared surfactants mentioned as being effective solubilizers of chlorinated solvents in the literature, surfactants listed as solubilizers in manufacturers brochures and examples of most available chemical families in the appropriate HLB range. We have evaluated approximately 120 surfactants at this time. This work is still in progress; however, data on the best surfactants found to date is given in Table 1.

Solubilization

Solubilization was determined by mixing an excess amount of PCE with 25 ml of a 1% (w.w) aqueous solution of the surfactant in a 25 ml vial. The vials were rotated on their long axes slowly for a minimum of 24 hours and then analyzed. The vials were then placed back on the rotator for a minimum of another 24 hours. This process was continued until no increase in concentration was obtained for 3 consecutive analyses. The surfactants that yielded the highest solubilization values for PCE are listed in Table 1.

If emulsions formed during mixing, the solutions were allowed to stand until the emulsions settled out before analysis. In some cases the emulsions did not settle out even after several weeks making determination of solubilization impossible. Centrifugation of these emulsions yielded near zero concentrations of PCE, indicating the micelles were being separated as well as the emulsions. The solubilization limit for these surfactants was determined by incremental addition of PCE. Perchloroethylene was added to a surfactant solution in 50 μl aliquots, and the solutions mixed until all PCE was solubilized. An additional 50 μl was then added and the process repeated until emulsification occurred. In most cases, emulsion formation occurs when the solubilization limit is exceeded, thus the solubilization limit was estimated from the amount of contaminant required to induce emulsification.

Interfacial tensions

Interfacial tensions between aqueous surfactant solutions and PCE were measured with a Du Nuoy ring tensiometer. No correlation was found between interfacial tensions and performance of the surfactants in extraction tests. however, there is a direct correlation between interfacial tension and vertical mobility. Hence it is possible to select good solubilizers that do not produce

TABLE 2

Interfacial tensions (IFT) of various aqueous surfactant solutions with PCE. This list illustrates the range of interfacial tensions that can be obtained with common surfactants. All measurements were in 1% (w/w) aqueous solution at 18°C. Data from [31]

Trade name	Chemical type	IFT (dynes/cm)
Liposorb O-5	Polyoxyethylene (5) sorbitan monooleate	16.8
Ameroxol LE-4	Ethoxylated fatty alcohol	16.2
Cyclomide DO280	Oleic diethanolamide (1:1)	12.8
Ethomid O/17	Ethoxylated amide	10.0
Witconal H-31A	Polyethyleneglycol monooleate	8.9
DeSophos 14DNP	Alkyl ether phosphate ester	6.6
Siponic 218	Ethoxylated thioether	6.1
Tergitol 15-S-12	Secondary alcohol ethoxylate	4.5
Renex 30	Polyoxyethylene (12) tridecyl ether	3.8
Rexophos 25/97	Phosphated alkyl phenol ethoxylate	3.2
Sandoxylate SX-418	Ethoxylated alcohol	2.6
T-Det N 9.5	Nonylphenol ethoxylate	2.4
Ethal DA-6	Polyoxyethylene decyl ether	2.4
Emcol CNP-110	Alkylaryl polyoxycarboxylate	1.3
Agrimul S-300	Aromatic sulfonate-oxide condensate blend	1.2
Cyclomide DL 207/S	Oleic diethanolamide (2:1)	0.9
Tergitol XH	Polyalkylene glycol ether	<1
Tergitol XD	Polyalkylene glycol ether	<1

extreme decreases in interfacial tension. Interfacial tensions for the best performing surfactants are shown in Table 2. It has been shown that maximum lowering of interfacial tensions will be obtained when solubilization is at a maximum [28,29] and thus solubilization is often used to screen surfactant mixtures for ultra-low interfacial tensions [8,28,29]. It is not necessary however, to utilize such optimized mixtures to get adequate solubilization; we have found that solubilization in excess of 1 gram of PCE per gram of surfactant may readily be obtained without reducing interfacial tensions by more than one order of magnitude.

Emulsification

Nearly all surfactants that are good solubilizers also form spontaneous emulsions when the surfactant mixtures encounter pools of PCE in the porous media experiments. The thickness of the emulsion layer and the persistence of the emulsions varied highly between surfactants. Emulsion stability is dependent upon the technique used to prepare emulsions (stability generally increases with shear rate during mixing) as well as on the surfactant. Conventional tests for emulsification use very high shear rates to prepare stable

emulsions, conditions that are not relevant to the subsurface. The character of emulsions which form does affect the performance of the surfactants in porous media experiments, as described below, thus it is an important parameter in surfactant selection.

Porous media experiments

Initial experiments to determine the effectiveness of various surfactants at extracting PCE from a saturated aquifer were performed using a simple horizontal column apparatus. The experiments utilized 1.25-cm diameter glass tubes. The center section, approximately 30 cm long, was horizontal, the two ends were vertical, forming a flat-bottomed U. One end of the tube was capped, the tube was partially filled with water and then homogeneous coarse sand was added until one half of the tube was filled. With the long section of the tube held nearly vertical, one half milliliter of PCE was added and allowed to settle as a single pool on the bottom of the tube; then additional sand was added to fill the remainder of the tube. The PCE remained as a discrete pool on the bottom of the sand-filled, saturated tube. A detailed description of these experiments can be found in [30].

A 5% (w/w) aqueous surfactant solution was then circulated with a peristaltic pump at a rate of about 3 ml per hour. Total volume of the apparatus was about 40 ml with a pore volume of 12 ml. The contaminant was dyed red with Sudan IV to enhance visibility. The effluent was sampled periodically and analyzed by gas chromatography. The amount of PCE remaining was also estimated visually. Results of a successful experiment are shown in Fig. 2. An illustration of the increased extraction efficiency due to surfactants can be seen by comparing Fig. 2(a), that shows the results of a surfactant flooding experiment, to Fig. 2(b), that show the results using water only.

At the conclusion of the test the sand was removed from the column and the amount of PCE remaining in the sand was determined with an ether extraction. The results of these experiments indicated that solubilization was the most important factor in determining extraction efficiency. In general, the higher the solubilization ability, the faster the PCE was removed. The results of the best performing surfactants are listed in Table 3.

The correlation was not perfect, however, several of the best solubilizers, including Ethal DA-6 and Mazawett 77, were not highly effective in the porous media experiments, while Rexophos 25/97, not one of the best solubilizers, was highly effective. These differences were attributed largely to the character of the spontaneous emulsions formed along the interface between the PCE pool and the surfactant solution. In some cases surfactants that are good solubilizers formed thick, immobile emulsions. Such emulsions slow the cleaning process. Other surfactants, such as Rexophos, formed thin emulsion layers that spread-out over a large area, increasing the surface area and hence the
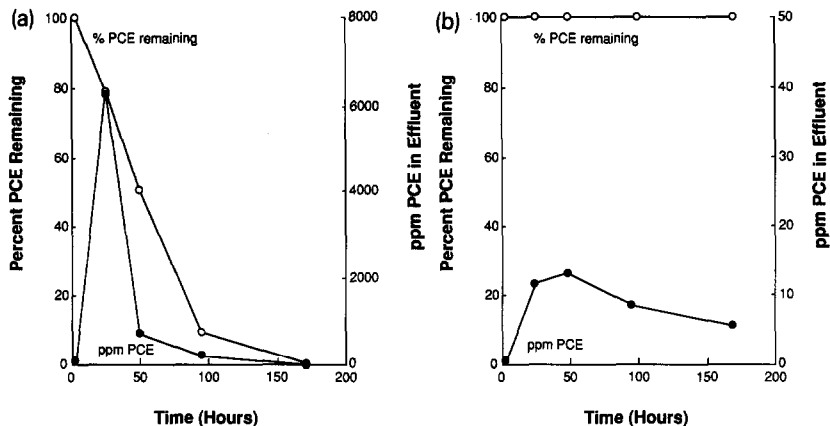
Fig. 2. (a) Results of a porous media experiment simulating the extraction of DNAPL (PCE) from the saturated zone. Concentrations of PCE in the effluent exceeded 6000 ppm, compared to its aqueous solubility of 200 ppm. At the conclusion of the experiment, no visible PCE remained. Compare these results to those shown in Fig. 2(b), which shows the results of using only water in the same experiment. (b) Results of attempting to remove a pool of DNAPL (PCE) by water flooding. The average concentration of PCE in the effluent was less than 10 ppm, reflecting its low aqueous solubility. No visible change in the amount of contaminant occurred within 170 hours (compare to Fig. 2a).

solubilization rate. The only reliable way we have found to evaluate the effect of the emulsions formed by various surfactants is with porous media experiments.

Several surfactants formed spontaneous emulsions that were stable over several weeks (longer than the duration of the experiment). These surfactants were tested to see if the emulsions could be transported in porous media. None of the emulsions were visibly mobilized, nor were any of the emulsifiers tested as effective at extraction as the good solubilizers.

We also investigated various mixtures of surfactants. No mixtures have been found that yield significantly higher solubilization values than the best pure surfactants; however, a mixture of Rexophos and T-Det has yielded the highest performance in the porous media experiments (Table 3). The increase in performance of this mixture over its individual components (that are also very good performers) is attributed to the different emulsion characteristics of the mixture. Nonylphenol ethoxylate (T-Det), one of the end members, is a very effective solubilizer, but also tends to form dense, persistent, emulsions. The addition of Rexophos dramatically reduced the emulsion formation and emulsion stability, improving the solubilization rate of the mixture.

Cosolvents also can change the emulsion character and solubilization ability of surfactant solutions. We have evaluated butyl alcohol, methanol and two propylene glycol ethers as cosolvents. Although some increase in solubilization

TABLE 3

Relative extraction efficiency of the most effective surfactants rested. The time listed in the right-hand column is the time required to completely clean a 1.0 ml PCE pool from the base of a glass U-tube column. All experiments utilized 5% (w/w) surfactant solutions and all experiments were run at the same flow rate. The mixture of Rexophos and T-Det yielded the fastest clean-up of all mixtures tested. The cleaning time for the distilled water control experiment is extrapolated from a 50-day experiment. Data from [30]

Surfactant name	Chemical type	Time (days)
Rexophos 25/97 and T-Det N-9.5	1:1 mixture	3
DeSophos 14-DNP	Phosphate ester	3
Witconal H-31A	Polyethyleneglycol monooleate	4
Witconal TD-100	Oxyalkylated alkyl alcohol	6
Cyclomide DO 280	Oleic diethanolamide (2:1)	6
Rexophos 25/97	Phosphated nonyl phenol ethoxylate	7
Standamox LAO-30	Lauryl dimethyl amine oxide	7
T-Det N 9.5	Nonylphenol ethoxylate	8
Distilled water	Control	5000

can be obtained with the cosolvents, none of the blends tested provided a significant improvement upon the extraction efficiency of the pure surfactant. The cosolvents do change the character of the emulsions which form, generally making the individual particles smaller and increasing their stability. None of the emulsions has proved to be mobile under normal subsurface conditions.

The results of the horizontal column experiments indicated that there was no correlation between interfacial tensions and extraction efficiency. The best performers had intermediate interfacial tension values (no surfactant blends were used that yielded the ultra-low interfacial tensions required for mobilization of the DNAPL). Nor was any correlation found between emulsion persistence and performance. Both T-Det and Rexophos form persistent emulsions, although one is thick and the other thin, while many other emulsifiers were ineffective. The mixture of T-Det and Rexophos has minimal emulsion formation and outperformed the pure components. The only good correlation was between solubilization ability and extraction efficiency.

More quantitative experiments have been run on those surfactants that performed well in the horizontal columns. These experiments use rectangular pyrex glass boxes, approximately 20 cm × 10 cm × 7 cm deep. A thin layer (about 1 cm) of saturated sand was put in the boxes, then 1 ml of PCE was added in the center, forming a small pool on the base of the box. The box was then filled with saturated sand and covered with an aluminum top that was sealed with silicone sealant. Teflon tubing was used for injection and extraction wells. Te-

flon-faced septa provided access for the stainless steel needle of a one-microliter syringe for sampling the pore fluids during the experiment.

Initially distilled water was circulated for 24 hours, then a 5% (w/w) aqueous surfactant solution was pumped into the injection well at a constant rate of about 300 ml per day (one pore volume is approximately 500 ml). When the surfactant solution is injected, the interfacial tension between PCE and the treatment solution is reduced, resulting in lateral spreading of the PCE pool. The extent of the spreading was dependent upon the extent of lowering of the interfacial tension. White emulsions almost immediately formed on the surface of the PCE pool, the amount of emulsion depended upon the type of surfactant used. The PCE and emulsion tended to move slowly toward the extraction well, although in our experiments they never reached the well. The amount of movement also depended upon the surfactant. The volume of PCE was monitored by visual examination through the bottom of the apparatus; the progress of the extraction was monitored by analyzing the effluent.

The effluent was collected periodically and analyzed by direct injection on a gas chromatograph. Mass balance calculations, based on effluent concentration and volume, were used to determine extraction efficiency. Samples were also taken from three depths from each sample port to monitor movement of the contaminants. These experiments found that the same surfactants that were effective in the horizontal column experiments were effective in the glass boxes, supporting the data from the simple horizontal column experiments [31].

Extraction efficiency was determined both by mass balance calculations and by analysis of the sand from the boxes at the conclusion of the experiments. The boxes were opened and excavated carefully to remove all but the bottom half inch of sand. A sample of sand was then taken from the center of the location where the DNAPL pool had been. The sand was placed in a separatory funnel and shaken with 50 ml of ether. Analysis of the ether extract was then done by gas chromatography. The sensitivity of this extraction depended upon the individual surfactants; however, in general 1 mg of residual PCE can readily be detected.

The number of pore volumes required to remove the contaminant, which is a critical factor in evaluating the effectiveness of the method, is a function of the geometry and volume of contamination as well as pump rate and surfactant mixture. Pools take longer to solubilize than isolated ganglia in zones of residual saturation. The increase in cleaning efficiency of areas of residual saturation compared to that of pools is probably due to the much larger surface area and hence more rapid solubilization provided by isolated ganglia. In the most effective runs, the boxes were completely cleaned of PCE pools in about 7 pore volumes while residual saturation require much smaller volumes.

If pools of DNAPL are not present, not only is extraction much more rapid, but lower concentration of surfactants can be used. We have found that 1%

(w/w) surfactant solutions are highly effective at removing DNAPL present at residual saturation. A higher concentration may be used to speed extraction of large DNAPL pools.

Vertical migration due to the addition of surfactants has been investigated in a glass cell 25 cm wide, 25 cm high and 7 cm deep. The bottom 4 cm of the cell is filled with saturated coarse sand, above this is a 2-cm thick clay layer, that acts as an aquitard. The clay layer dips gently toward the front of the cell, keeping any DNAPL pools against the front face. The cell is packed with saturated sand above the clay layer. PCE is introduced through a stainless steel well that penetrates the sand to a depth of about 7 cm. The PCE moves rapidly downward through the sand, spreading slightly on finer-grained layers. A sufficient volume of PCE is added to generate a pool of about 5 ml volume on the clay layer.

An extraction well, formed of 2 inch PVC tubing screened over its entire length, is located at one end of the box. An identical injection well is located at the other end. Initially distilled water is circulated for a minimum of 24 hours, then a surfactant solution is introduced. The surfactant solution lowers the interfacial tensions between PCE and water. In experiments using coarse and medium sand this results in immediate downward flow of the PCE suspended as residual saturation within the sand. Within one pore volume, all visible suspended PCE has been removed through a combination of solubilization and downward flow. When fine-grained sand is used, no visible vertical mobilization of the PCE occurs (the surfactants used have interfacial tension with PCE of 2.5–5 dynes/cm) and the PCE is removed soley by solubilization.

An emulsion layer often forms immediately on the top of the PCE pool. The PCE in the pool is then removed slowly by solubilization. Even in depressions with narrow throats (1 mm throat, 5 mm deep depression in the clay) the PCE is readily removed. When topography of the clay layer forms a valley, and deep pools result, the pool remains covered with emulsion, but declines regularly in volume. Neither the emulsion layer nor the PCE pool is mobilized by the surfactant solutions, removal is by solubilization.

Field test

A field test of our surfactant flushing process is now in progress at Canadian Forces Base Borden in Ontario, Canada. The test is being conducted in collaboration with the Solvents-In-Groundwater Program of the University of Waterloo's Centre for Groundwater Research. Preliminary data show rapid removal of PCE from the aquifer (individual multi-level monitoring points have recorded over 11,000 ppm PCE), with no discernable vertical mobilization. Results of this test should be presented for publication in late 1991.

Summary and conclusions

We have identified several surfactants that are capable of solubilizing large volumes of chlorinated solvents while not lowering interfacial tensions more than one order of magnitude. We believe that such surfactant mixtures provide a method of rapid extraction of organic contaminants, at a relatively low cost. Use of surfactants increases the efficiency of pump-and-treat operations by several orders of magnitude.

Although most of our work to date has been on PCE and TCE, we have also studied the use of surfactants for the extraction of benzene, carbon tetrachloride, dichloroethane, methylene chloride and vinyl chloride. Although the screening for these compound is still in progress, mixtures have been identified that effectively solubilize and extract each of these compounds.

Our experiments indicate that lowering interfacial tensions to 5 dynes/cm or less results in rapid downward migration of PCE. Similar behavior would be expected of all DNAPLs. Thus, in many cases, introduction of surfactants that dramatically lower the interfacial tensions may introduce an unacceptable risk of spreading of the contamination into underlying uncontaminated zones.

Acknowledgements

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