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SURFACTANT FLOODING OF DIESEL-FUEL-CONTAMINATED SOIL*

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Abstract

The use of surfactants to mobilize oil in water solutions has been developed in the oil industry to enhance oil recovery from reservoirs. Not as well researched is the use of surfactants as a soil-remediation technique. This study used surfactant solutions to leach undisturbed soil cores taken from a site that had been contaminated with No. 2 diesel fuel after a puncture of a transfer line. Preliminary screening of 22 surfactants was performed prior to this study to choose the surfactants to be used in the flooding of the columns. Surfactants chosen resulted in 87% to 97% removal of the diesel fuel during batch extraction. Prior to flooding the columns with surfactants, the columns were leached with deionized water to compare with leaching by the surfactant. Water flooding resulted in removal of <1% of the diesel fuel. Surfactant solutions removed generally <1%. The poor removal efficiencies from the surfactant flooding, especially when compared to results from the surfactant screening extractions, were attributed to channeling

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of the solutions through the columns. The column floodings, therefore, were essentially nonequilibrium extractions whereas the batch-screening extractions reached an equilibrium.

Introduction

As our society becomes increasingly aware of the hazards associated with pollutants in our soil and water supplies, it also becomes aware of the need for improved remediation techniques. Remediation techniques such as pump and treat, excavate and treat, or excavate and landfill are being implemented today with varying degrees of success. The choice of technique depends on many factors, especially the location of the contaminated area, hydrogeology of the site, characteristics of the soil, and nature of the contaminant. This paper examines one experimental technique, in situ surfactant flooding, at the bench-scale treatability level, using undisturbed soil cores contaminated with No. 2 diesel fuel. This technique is being considered, along with air stripping and in situ bioremediation, for a site in which approximately 60,000 gal of diesel fuel has spread to depths of up to 32 m (105 ft). The soil cores used in the bench scale studies were taken from the contaminated site. Results from this study on surfactant flooding are presented and discussed.

Background

Surfactants. The use of surfactants in mobilizing petroleum oils from the ground is a well-known technique developed by the oil industry. Much research has been conducted on enhancing oil recovery from oil reservoirs by studying the interactions between surfactant solution, soil, and oil [1]. The use of a surfactant as a valuable candidate for oil recovery involves its ability to solubilize oils in water. The fundamental properties of a surfactant responsible for this phenomenon are its amphipathic structure, monolayer orientation at interfaces, and adsorption at interfaces [2]. Basically, the surfactant is made up of two functional groups, a hydrophilic head group and a lipophilic carbon chain. The two groups line up between the oil and water phases with their opposing ends dissolved in the respective phases. This creates a third layer at the interface, decreasing the interfacial tension (IT) between the oil and water. The balance of the head group and carbon tail determines which phase the surfactant molecule will dissolve into more readily. That is, if the head group is more heavily balanced, the surfactant as a whole will be more water soluble. In this case, it will tend to pull oil into solution as droplets encased in surfactant molecules. This balance is called the hydrophilic-lipophilic balance (HLB) [3].

The extent to which the IT is decreased depends largely on the concentration of surfactant in a particular solvent or liquid. Previous studies have shown that the point at which the IT is at its minimum is at the surfactant concentration where the most surfactant is found at the interface and the partition coefficient equals 1.0 [4]. This point is called the critical micelle concentration (CMC), the concentration at which aggregates or micelles begin to form from the excess surfactant in solution. Therefore, it is of interest to determine the CMC of a surfactant in a particular solution prior to its use.

Surfactants are categorized into four general groups depending on the electrostatic charge of the head group. These groups are anionic, nonionic, cationic, and amphipathic. Anionic surfactants are widely used in oil recovery because they are highly water soluble and because their negative charge tends to be repulsed by a typical soil of a negative net surface charge. Head groups of important commercial anionic surfactants include sulfonates, sulfates, and phosphates. Nonionic surfactants are uncharged and are soluble through hydrogen bonding at oxygen or hydrolyzed groups. Typical nonionic surfactants contain a polyoxyethylene group as the soluble group. Nonionics and blends of anionics/ nonionics have also been successful in their use as oil recovery enhancers. Cationic surfactants contain a positive functional head group, typically an amino or quaternary nitrogen group. Their use has been more as softeners and coating agents, and they do not usually perform well in soil of negative net surface charge [5].

Surfactants in Remediation. Although surfactant use in enhanced oil recovery has been explored in some detail, its use as a remedial flooding technique is still in the preliminary experimental stages, and few studies are available in the literature to date. Examples of some studies are discussed here.

Abdul et al. [6] looked at the performance of commercially available anionic and nonionic surfactants to clean a sandy soil contaminated with automatic transmission fluid (ATF). Using a batch shaker method, they mixed 5 g of contaminated soil with 100 mL of 0.5% by volume surfactant solution for 30 min. After the soil settled, the decant and several rinses of the soil were analyzed for ATF. The soil was also analyzed for remaining ATF. Results showed that the surfactant removed between 56% and 84% of the contaminant but that washing the soil with water alone removed only 23%. Two of the better performers, removing 81% and 82%, were further screened at several different concentrations (0.1%, 0.25%, and 1.0%). For both of these surfactants, a concentration of 0.5% from the initial screening gave the best removal while various other concentrations removed between 37% and 76%.

Ellis et al. [7] also tested several commercially available surfactants at the bench-scale level. They looked at treating both PCB(polychlorinated biphenyl)-contaminated soil and soil contaminated with hydrocarbons. They chose several surfactants and combinations of surfactants, including Richonate YLA (anionic) and Hyonic NP-90 (nonionic) which had been previously tested by the Texas Research Institute (TRI) to flush gasoline from sand. These surfactants were chosen based on the following criteria: adequate water solubility, low clay-particle dispersion to avoid pore-space clogging, good oil dispersion, and adequate biodegradability to limit the environmental impact of the surfactant.

Ellis et al. then performed shaker tests similar to Abdul to screen the various solutions. They used 100 g of soil mixed with 200 mL of surfactant solution; the mixture was agitated for 1 hour. Again both soil and decanted leachate were analyzed. A 1:1 blend of the nonionic surfactants Adsee 799 (Witco Chemical Co.) and Hyonic NP-90 (Diamond Shamrock) performed best, removing 93% of the hydrocarbons and 98% of the PCBs. These results were 1 to 2 orders of magnitude better than removal with water alone. Optimum concentrations of these surfactants were determined to be 0.75% by volume in further tests.

Following the screening process, Ellis et al. used the surfactant combination to perform flooding experiments on packed columns of Freehold soil spiked with PCBs and chlorinated phenols. Initially, columns were flooded with water. This was followed by several pore volumes of the surfactant solution and then a final wash of water. Results showed the initial and final water rinses to be ineffective in reducing contamination. However, after 3 pore volumes of surfactant solution, 74.5% of the pollutant was removed. After 10 pore volumes, 85.9% removal resulted. Further studies on column flooding using various concentrations of the surfactant combination verified the optimum of 0.75% by volume obtained in the screening process.

Several studies are taking bench-scale results into the field at the pilot-scale level. Following screening and column studies performed in the laboratory, Nash [8] tested some of the more successful surfactants on a site contaminated with waste solvents, waste lubricating oil, and JP-4 fuel. In 10 holes dug 1 foot deep, Nash applied solutions at 3 inches per day for 4 to 6 days. Conclusive results were not obtained due to inherent difficulties in working in the field. Nash encountered two major problems: (1) difficulty in obtaining accurate contamination levels from sampling because of the nonuniform distribution of the contaminant on the soil, and (2) dilution of the flooding solution because of rainy weather during the surfactant application period.

Surfactant flooding as a technique still has far to go before it will be considered a demonstrated and proven technology. Due to the uniqueness of each site and the interaction between surfactant, soil, and contaminant, even pilot-scale studies must be fine-tuned before conclusive results can become available for the development and application of this technique. This paper contributes to the development of this technique by presenting results of column-flooding tests on undisturbed soil cores.

Methods

The soil used in this study was taken from a site in California that had been contaminated with No. 2 diesel fuel. Undisturbed soil cores were obtained using a split spoon auger from one boring reaching to a depth of 32 m (105 ft) and cut into 38 cm (15 in) columns with a diameter of 18 cm. Ten of these columns were cut into halves of 19 cm (7.5 in). The top halves were used for the leaching and flooding experiments.

Characterization of the soil was performed on soil samples taken approximately 2 inches from the surface of each column separately. Tests and methods employed are listed in Table 1.

The columns were first leached with three effective pore volumes (EPV) of deionized water and then drained. EPVs were estimated by noting the time it took for initial flooding of the entire soil core at a constant flow rate. Calculated pore volumes for the columns were approximately three times greater than the estimated effective pore volumes measured. Flooding the columns for 3 to 4 EPVs with a 1.5% surfactant solution followed leaching them with water. Leaching and flooding of the columns were performed using a constant head, up-flow method through aluminum bases and tops. The original core polybutyrate casings served as column walls so as not to disturb the soil samples.

Table 1. Soil Characterization Tests Performed on Grab Samples Taken from Surface of Each Soil Core

Tests	Methods[a]
Hydraulic Conductivity[b]	EPA 9100
pH	EPA 9045
Cation Exchange Capacity	EPA 9081
Porosity	MSA
Soil Dry Weight	MSA
Particle Size, Dry Sieve	ASTM
Particle Size, Hydrometer	MSA

[a] Reference Sources: EPA-"Test Methods of Evaluating Solid Waste" [9], MSA-"Methods of Soil Analysis, Part 1" [10], and ASTM [11].

[b] Determined on 2-inch diameter, 2-inch long cores taken from the top of the soil column.

Preliminary screening of several commercially available surfactants was performed on site of the soil using a batch-shaker test. Three of the better performers from this screening were chosen for the subsequent flooding experiments. The initial plan was to flood at least nine columns, thus allowing triplicates of each of the three chosen surfactants. However, due to these constraints and to disturbances of the columns (especially the clogging of column chamber inlets while draining the columns after leaching), only four columns were flooded. The columns chosen and the surfactants used for each column are listed in Table 2. Characteristics of the soil in each column are summarized in Table 3. Results of soils collected at other depths are also presented in Table 3 for comparison.

Each EPV of surfactant eluate and drained leachate was collected separately. Each collection was subjected to liquid-liquid extraction using a carbon disulfide solvent at a 0.025:1.0 solvent/solution ratio and analyzed for total petroleum hydrocarbons (TPH) by gas chromatography (GC). Soil grab samples taken from the top of each column before and after flooding were subjected to a slurry extraction at a 1.0:1.0 solvent/solution ratio also using carbon disulfide. Then they were analyzed by GC for TPH. The extraction method was modified from the "California Leaking Underground Fuel Tank Manual" [12] and Wilson [13]. After all treatments were completed, the columns were destroyed, the soils from each column were mixed, and duplicate grab samples from each of the mixed soils were analyzed for TPH. Alkanes between C12 and C19, key components of the diesel fuel, were identified and their concentrations were determined by GC to indicate the presence of selective mobilization by the surfactant solution.

Table 2. Soil Columns and Surfactants Used in Bench-Scale Surfactant Flooding Tests

Column Depth (m)	Surfactant/ Code Number	Surfactant Type	Chemical Name
6.3	PSVS/18	Anionic	Polysodium Vinyl Sulfonate
17.1	Cyanamer P-35(L)/15	Anionic	Sodium Polyacrylate
23.2	Cyanamer P-35(L)/15	Anionic	Sodium Polyacrylate
26.2	Surfynol 485/13	Nonionic	Exthoxylated Tetramethyl-decynediol

Table 3. Results of Soil Characterization Tests Performed on Samples Taken from Soil Cores Employed for Leaching and Flooding Experiments

Depth (m)	Hydraulic Conductivity (cm/s)	Porosity (%)	pH	CEC[a] (meq/100-g)	Dry Soil (%)	Texture Class
6.3	7.03×10^{-4}	45.34	8.3		88.98	Sandy Loam
8.4	4.23×10^{-4}	42.84	8.1	23.98	86.9	Loam
14.8	2.39×10^{-3}		7.7	19.58		
17.1	1.64×10^{-3}	28.95	7.5	19.67	87.92	Sandy Loam
23.2	5.43×10^{-5}	26.2	7.9	14.51	87.6	Clay Loam
26.2	1.15×10^{-4}	45.81	7.7	8.88	89.05	Sandy Loam
32.0	6.79×10^{-3}	42.64	7.8	19.39	86.99	Loam

[a] Cation Exchange Capacity.

Results

Surfactant Screening. Partial results from the surfactant screening tests are presented in Table 4. (For complete results see Peters et al. [14]) Surfactants 13 (nonionic), 15, and 18 (both anionic) were chosen to use for column-flooding studies based on their high level of performance in removing TPH from soil during the screening process.

Column Flooding. Table 5 lists results of the TPH analysis taken from soil grab samples from both before and after flooding as well as the percent removal as indicated by these values. A wide range of percent removal, between -42% and 68%, resulted. A minus percent removal indicates more TPH was measured on the treated soil compared to that measured before treatment.

Table 6 compares TPH values from the soil grab samples taken from the tops of the columns at different times during the water leaching and surfactant flooding experiments to samples taken from the well-mixed column soil after columns were broken up following water leaching and surfactant flooding. No apparent decrease was observed in the mixed soil following treatment and, in some cases, the TPH values were higher. Duplicates taken on soil grab samples varied, in some cases, by orders of magnitude. Duplicates from the well-mixed soil generally differed by 15%.

Table 7 compares the TPH concentration (in mg/kg soil) measured in the total leachate collected from the floodings to TPH on the soil before flooding. The percent removal for the flooding was very low (<1%) with the exception of one core, the 17.1 m-column, which showed a removal of slightly >9%.

Table 4. Partial Results from Batch Extraction Surfactant Screening Tests[a]

Surfactant (Code No.)	% Removed	% Enhanced	Surfactant Type
Surfynol 485 (13)	97.90	45.09	Nonionic
Surfynol 468 (14)	95.84	42.03	Nonionic
Cyanamer P-35(L) (15)	93.00	37.84	Anionic
PSVS (18)	87.28	29.35	Anionic
Cyanamer P--70 (17)	80.00	18.56	Anionic
Emcol CC-42 (1)	65.68	negli.	Cationic
Witconol 2648 (6)	9.55	negli.	Nonionic
Control - plain water	67.48	---	---

[a] Ratio of Soil to Surfactant was 10 mg soil to 50 mL of 2% surfactant solution. Shaking time was 1 h.

Table 5. Total Petroleum Hydrocarbons, TPH, in Soil Before and After Flooding Measured by Grab Sampling on Intact Columns

Depth (m)	Total Petroleum Hydrocarbons, (mg/kg)		Removal (%)
	Before Flooding	After Flooding	
6.3	1236	1024	17.15
17.1	33	46.9	-42.09
23.2	328	225	31.4
26.2	18132	5823	67.89

Table 6. Total Petroleum Hydrocarbons, TPH, on Soil Taken from Column Tops at Various Stages of Leaching and Flooding and from Mixed Column Soil after Flooding

Column Depth (m)	Total Petroleum Hydrocarbons, (mg/kg				TPH from Mixed Column Soil (mg/kg)
	Before Leaching	After H_2O Leaching	Before Surfactant Flooding	After Surfactant Flooding	
6.3-a	890	1060	930	1020	1460
6.3-b			1540		1280
8.4-a	3650	7210	7520		3590
8.4-b					8360
17.1-a	4180	1140			2780
17.1-b	4570	33		46.9	3590
23.2-a	2960				777
23.2-b	74.5	328		225	874
26.2-a					10800
26.2-b	795	4660	18100	5820	11100

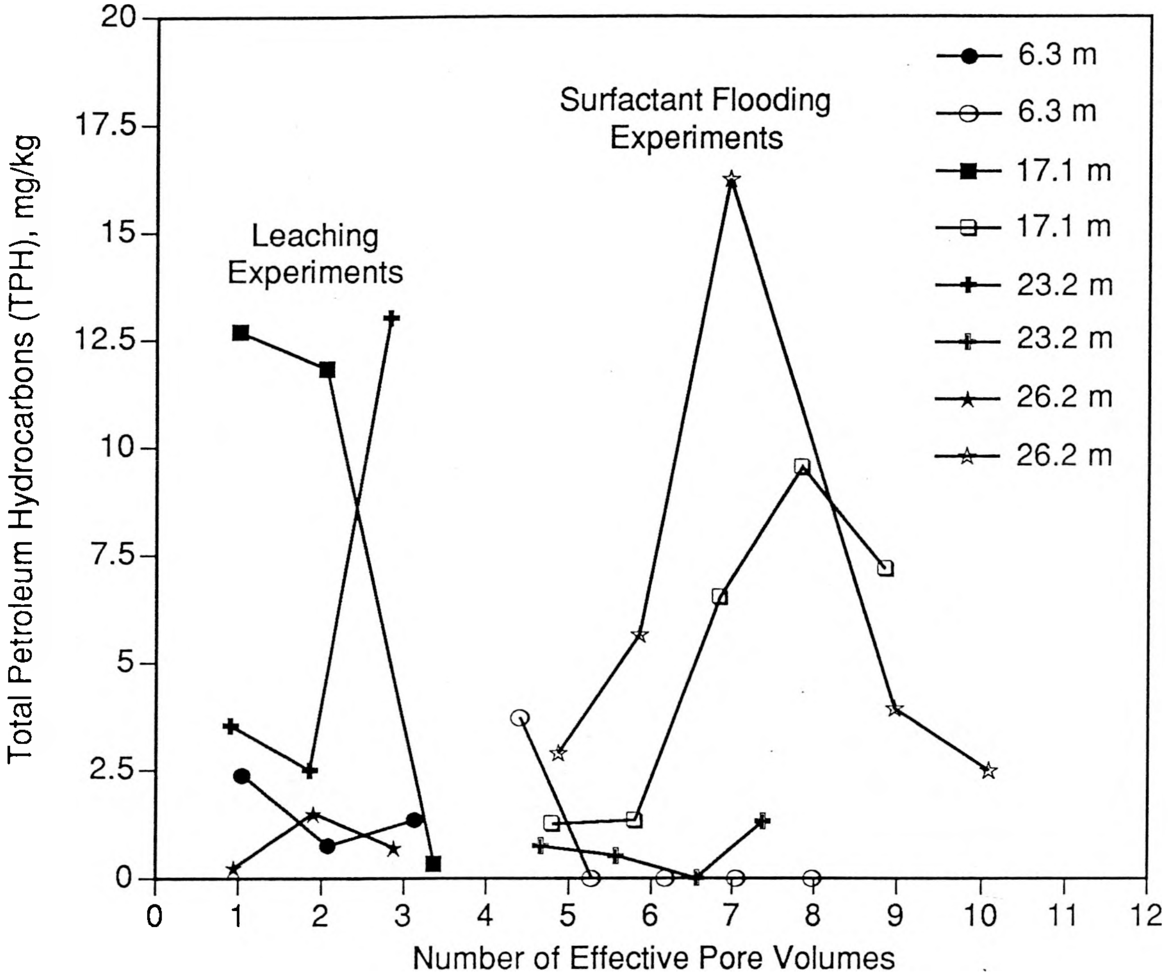
Table 7. Total Petroleum Hydrocarbons, TPH, Measured on Soil Before Flooding and in Leachate from Surfactant Flooding

Column Depth (m)	Total Petroleum Hydrocarbons, (mg/kg)		% Removal
	Before Flooding	In Leachate from Surfactant Flooding	
6.3	1240	0.68	0.055
17.1	33	3.05	9.242
23.2	328	0.33	0.101
26.2	18100	3.79	0.021

Figure 1 represents the TPH measurements in mg/L for each EPV collected by leaching the columns with deionized water and subsequently flooding them with surfactant solution. The dotted line in the middle of each curve indicates points between the final water leachate collection and the first surfactant flooding collection. Generally, a downward trend is seen with each successive collection of the water leachate with the exception of the 23.2-m column. For the surfactant flooding, the 17.1-m and 26.2-m columns showed an increase in TPH removal as more EPV of solution was passed through the column. The 6.3-m column showed an improvement in TPH removal for the first surfactant collection over that of the water leachate. However, no more TPH was removed with further EPV addition. The 23.2-m column also showed a general drop in TPH removal with surfactant flooding except for the last collection. A break in the curve between the 7th and 9th EPV for the 26.2-m column indicates where the column had been drained and stored for 1 month before being resaturated and flushed with 2 additional pore volumes. The columns were also drained between leaching and flooding.

Table 8 compares the amounts (mg) of TPH removed in approximately 3 EPVs of leachate with water with approximately 4 EPVs after flooding with surfactant. The 6.3-m column using surfactant 18 (S-18) showed similar amounts removed with and without surfactant. The 17.1-m column using S-15 also resulted in similar removals between the two leachates with a slight improvement for the case of surfactant application. The 23.2-m column using S-15 showed a drastic decrease whereas the 26.2-m column using S-13 indicated a substantial increase.

Figure 2 shows removal of individual alkanes in the flooding eluate. No removal of alkanes occurred for the 6.3-m column using S-18. The 17.1-m column showed increased removal of alkanes (as it did for TPH) with each successive flooding, peaking with the 4th EPV. The concentrations of C14 and C15 were as high as they were initially on the soil. The 23.2-m column had little removal of alkanes (as with TPH), C14 and C15 generally having the greatest



Total Petroleum Hydrocarbons (TPH), mg/kg
Number of Effective Pore Volumes
0
2.5
5
7.5
10
12.5
15
17.5
20
0
1
2
3
4
5
6
7
8
9
10
11
12
Leaching Experiments
Surfactant Flooding Experiments
6.3 m
6.3 m
17.1 m
17.1 m
23.2 m
23.2 m
26.2 m
26.2 m

1
2
3
4
5
6
7
8
9
10
11
12
13
14
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16
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32
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36
37
38
39
40
41
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43
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45
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47
48
49
50

Figure 1. Total Petroleum Hydrocarbon (TPH) Concentrations Measured in Each Leachate Collected for Leaching and Surfactant Flooding Experiments.

Table 8. Total Amounts of Total Petroleum Hydrocarbons in Water and Surfactant Leachates Successively

Column Depth (m)	Total Petroleum Hydrocarbons, (mg)	
	Deionized Water (~ 3 Pore Volumes)	Surfactant Leachate (~ 4 Pore Volumes)
6.3	6.68	4.46
17.1	21.83	24.09
23.2	16.63	2.35
26.2	1.85	26.66

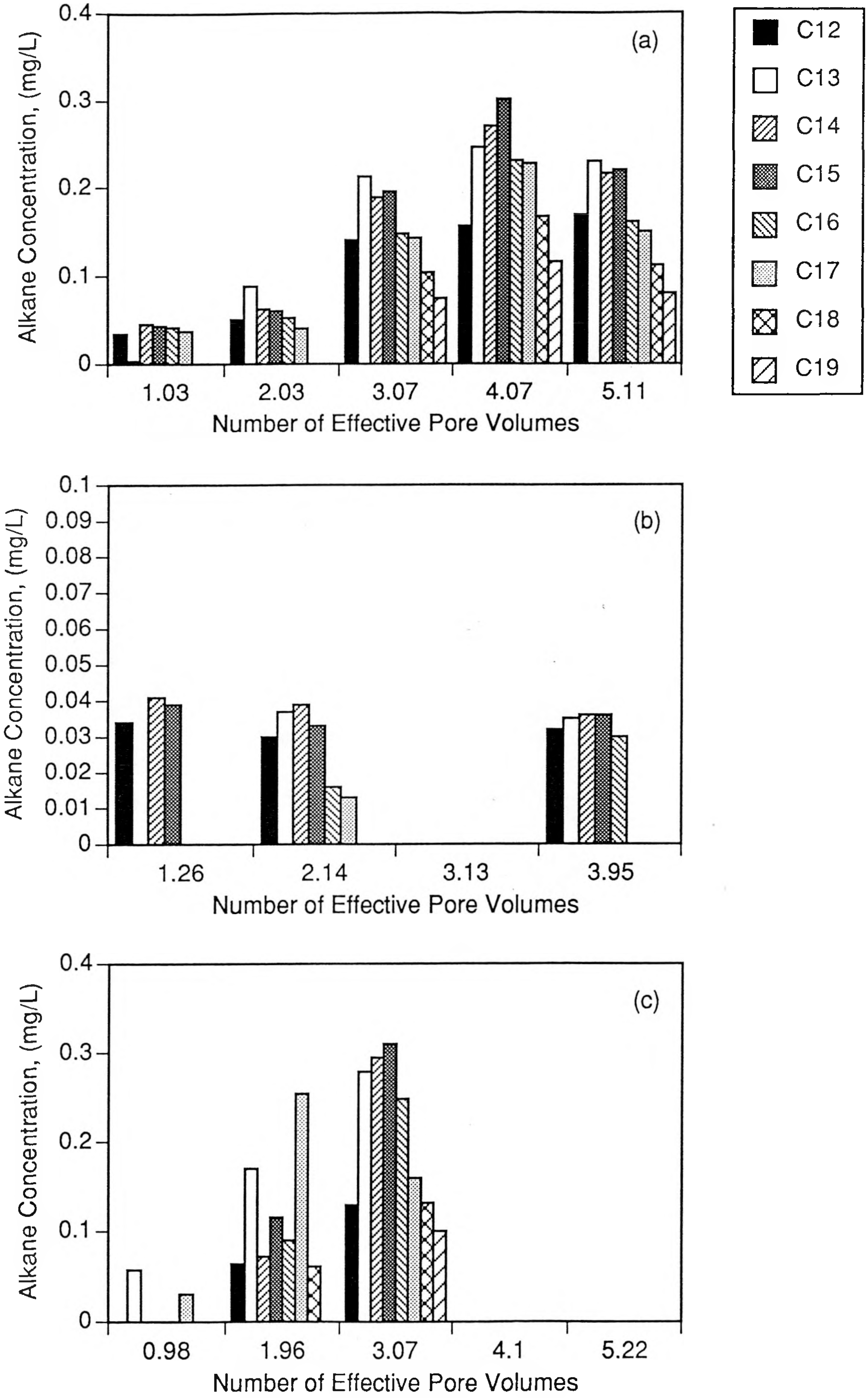
(a)
Alkane Concentration, (mg/L)
0.4
0.3
0.2
0.1
0
1.03
2.03
3.07
4.07
5.11
Number of Effective Pore Volumes
C12
C13
C14
C15
C16
C17
C18
C19
(b)
Alkane Concentration, (mg/L)
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1.26
2.14
3.13
3.95
Number of Effective Pore Volumes
(c)
Alkane Concentration, (mg/L)
0.4
0.3
0.2
0.1
0
0.98
1.96
3.07
4.1
5.22
Number of Effective Pore Volumes

Figure 2. Individual Alkane Concentrations Measured in Each Effective Pore Volume Collected During Surfactant Flooding for Columns (a) 17.1-m, (b) 23.2-m, and (c) 26.2-m.

concentration of the alkanes again. The 26.2-m column, however, seemed to favor C13 and C17 for the first two collections. No alkanes were found in the collections of the 4th and 5th EPV or for the second drain of the 26.2-m column. These were collected after the column had been drained and in contact with the surfactant for more than a month.

Discussion

The percentage of TPH leached from the floodings varied over a wide range of values. These final percentages were based on initial concentrations measured on the soil (Table 5). These initial values were obtained by extracting TPH from samples taken off the top surface of the column (i.e. grab samples) and were assumed to represent the entire column. However, due to the presumed nonuniform distribution of the contaminant on the soil and nonuniform migration of the contaminant upward through the column while flushing, it was not possible to obtain a good representative value. Variation in TPH values of the grab samples was apparent when comparing these values to those obtained from the well mixed soil after the columns were destroyed (see Table 6). The differences in the values before and after flooding (see Table 5) were generally within one order of magnitude. Statistically, these differences may not be significant. (Multiple sampling for statistical evaluation was not done in order to prevent core disturbance.) If these values are not significantly different, then Table 5 indicates that no measurable decrease in contamination levels resulted from the surfactant floodings.

A better representation of TPH removed from the core is obtained by comparing TPH values of the total leachate to initial TPH values on soil (Table 7). In this case, extraction was performed on the total volume of leachate rather than a grab sample involving the soil. Also, the problem of nonuniform distribution which is inherent with soils is not a major consideration in liquids. Additionally, the values obtained with this method were more consistent than those obtained with soil grab samples (compare Tables 5 and 7).

A comparison of TPH removal values obtained by leaching columns with water alone and with surfactant solution (Table 8) shows that the only substantial increase in amounts of TPH removed was observed in the 26.2-m column (S-13); a dramatic decrease was observed in the 23.2-m column and slight differences in columns 6.3-m and 17.1-m. These results indicate that using surfactants 15 and 18 resulted in no improvement over using water alone but that surfactant 13 was quite successful in enhancing the diesel fuel mobilization. The generally poor performance of these surfactants is in contrast to the screening results (Table 4) and the results of other studies [5-8].

An alternative explanation for the low removals in the column tests when compared to the screening test [14] involves laboratory observations. Extensive channeling was observed in the columns after they were handled and dried before the leaching and flooding studies were performed. The leachate, therefore, likely passed through the columns with relatively little contact with the soil. Residual oil in the soil bulk matrix was most likely unaffected by these floodings. Some TPH concentrations in the water leaching were relatively higher than those for the surfactant floodings due possibly to water initially displacing diesel fuel from large pores in a plug-flow manner.

Because of the artifact introduced by channeling, leachate volumes are expressed as effective pore volumes, defined as the volume of water necessary to initially flood the soil columns. Figure 1 shows the concentration of TPH measured in each effective pore volume collected for both water leaching and surfactant flooding. Initially the following trends (assuming uniform soil/solution contact) were predicted for most of the columns: (1) an initially high contaminant concentration in the first leaching which would have represented the oil front due to piston flow and (2) with the addition of the surfactant solution, an increase in TPH removed with each successive flushing until an equilibrium plateau would be reached. The trend for the four columns in the water leaching portion of the collections did show a general decrease with subsequent pore volumes except for the 17.1-m column. This most likely indicated that the initial passes of water through the column displaced the oil in the larger pores. However, what was observed for the surfactant flooding collections turned out to be different for each column. The 6.3-m column using S-18 indicated the presence of TPH only during the first surfactant collection. The 23.2-m column (S-15) also showed very low concentrations, even lower than that seen in the water leachates, and decreased with each collection. The 17.1-m columns using S-15 and the 26.2-m column using S-13, however, both showed increasing TPH concentrations during the first few collections. For the 26.2-m column, a plateau may have been reached if the flooding had not been interrupted. The 17.1-m column shows a peak concentration in leachate for the 4th pore volume. This peak may have been due to the surfactant causing dispersion of colloidal-sized particles into solution. Possibly surfactant 15 caused eventual clogging of soil pores by surfactant/soil or surfactant/oil aggregates, resulting in a decrease of contaminant in the leachate. Surfactant 18 may also have reacted with the soil in this way. The potential needs to be examined for these surfactants to cause soil dispersion and clogging of pores.

Since each column was unique, other variables in addition to channeling likely played key roles in the results obtained. These variables include differences in solution/soil contact, initial concentration of TPH in the core, nonuniform distribution of TPH, variation in soil texture, and dispersion of soil aggregates by the particular surfactant.

Alkanes C12-C19 were shown by GC to be the main constituents of the diesel fuel found in the soil cores. The concentrations of each compound in the successive effective pore volumes were compared to determine if preferential mobilization was occurring. Before leaching, C14-C16 in the soil were at their highest concentration; C13, C17, and C18 were substantially lower; and

C12 and C19 had the lowest concentrations. This pattern was generally found in the leachates for the 17.1-m column using S-15 and the 23.2 m column using S-15, indicating no preferential mobilization of these alkanes (Figure 2). However, the first two pore volumes collected from the 26.2-m column using S-13 showed possible preferential mobilization of C13 and C17. This pattern is not repeated in subsequent collections, suggesting that the three surfactants caused no preferential mobilization of any one of these alkanes.

Although these results may be due to unavoidable experimental disturbances for the undisturbed cores, they are a good indication of what may happen in the field when implementing this technique in a saturated soil, especially in soils that have low hydraulic conductivity of the bulk matrix, lenses of clay or sand, and fractures. The flooding fluids will take the highest-pressure-gradient path through sand lenses or fractures and fail to contact the bulk of the soil matrix where much of the contaminant may be contained if the spill occurred prior to fracturing. After the initial spill, however, the diesel fuel can be expected to redistribute, especially after a number of years, in such a way that subsequent transport of the contaminant will occur primarily in the bulk matrix of finer pores rather than in the fractures. Travis and Doty [15] have discussed problems with pump and treat methods for remediating contaminated aquifers. They point out that none of the numerous superfund sites which have implemented a pump and treat remediation technique have seen a substantial lowering of contaminant levels even after 10 years of continuous treatment. They indicate reasons for this behavior include sorption of water insoluble contaminants to organic matter in soils as well as the preferential flow of water through high permeability channels at the site. Although the use of a surfactant solution will aid in mobilizing insoluble contaminants, as seen by the success of the equilibrium-extraction batch-screening process performed prior to this study, the problem of preferential flow in cracks seems to dominate success of contaminant removal by flooding. The use of surfactants to decontaminate soil may be better employed using an on-site soil-washing technique following excavation.

Summary and Conclusions

Use of surfactants may prove to be a good technique for separating diesel fuel from a soil as indicated in results obtained in preliminary screening tests and from results of other studies performed on laboratory-packed soil columns, assuming flow through the bulk matrix. Removal efficiencies for these cases were as high as 97%. However, results presented here using undisturbed, diesel-fuel-contaminated soil cores taken from a site indicate that removal of diesel fuel from the soil flooded with surfactant solution was generally less than 1%. Low removal efficiencies in these soil cores are attributed to experimental artifacts such as channeling of the surfactant solution through cracks developed unavoidably in the cores during shipping, handling, and leaching.

As an applied technique, these results suggest that in situ surfactant flooding, especially for sites that contain fractures or are prone to channeling, is not an effective method of removing diesel fuel from the soil. However, the use of a surfactant solution for washing the soil on-site after excavation could be an effective soil-remediation technique given the right surfactant or combination of surfactants for the site and contaminant.

Nomenclature

ASTM	American Society of Testing and Materials
ATF	automatic transmission fluid
CEC	cation exchange capacity, meq/100-g

CMC	critical micelle concentration
EPA	U.S. Environmental Protection Agency
EPV	effective pore volume
GC	gas chromatograph
HLB	hydrophilic-lipophilic balance
IT	interfacial tension
MSA	Methods of Soil Analysis
pH	$- \log [H^+]$
PCB	polychlorinated biphenyl
PSVS	polysodium vinyl sulfonate
TPH	total petroleum hydrocarbons
TRI	Texas Research Institute

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