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Soil Clean-Up by Surfactant Washing. V. Supplementary Laboratory Testing

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ABSTRACT

A number of problems bearing on the surfactant flushing/washing of soils contaminated with hydrophobic organic compounds were investigated. These included the following:

1. Development of a simple ultraviolet (UV) spectrophotometric method for the analysis of PCBs in sodium dodecylsulfate (SDS) solution
2. Study of the settling of clay fines from SDS solutions
3. Evaluation of laboratory-scale columns versus stirred flasks for use in preliminary feasibility studies
4. Determination of the extent to which SDS is lost during the processes of soil treatment and reclamation

INTRODUCTION

In the earlier papers in this series, bench-scale work on soil surfactant washing and some aspects of mathematical modeling were discussed (1) and the design and evaluation of a small pilot-scale soil surfactant washing system were described and explored (2–4). Related work on the recovery of surfactant solution for recycle has been done by Underwood et al. (5,

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6). Soil surfactant washing is a technology which is under development for the removal of hydrophobic organic contaminants from soils when these compounds are of sufficiently low volatility that soil vapor extraction cannot be used and when the compounds are not sufficiently biodegradable to permit bioremediation techniques to be used. It competes with steam stripping and low temperature thermal treatment.

There were a number of secondary objectives in this study which were necessary to support its prime purpose. These included the following:

1. Development of a simple ultraviolet (UV) spectrophotometric method for the analysis of PCBs in sodium dodecylsulfate (SDS) solution
2. Study of the setting of clay fines from SDS solutions
3. Evaluation of laboratory-scale columns versus stirred flasks for use in preliminary feasibility studies
4. Determination of the extent to which SDS is lost during the processes of soil treatment and reclamation

In the present paper we address these problems.

ULTRAVIOLET SPECTROPHOTOMETRIC ANALYSIS OF PCBs IN SDS SOLUTION

In these surfactant washing studies a large number of analyses for aromatic organics was anticipated. If done by gas chromatography, these analyses are time-consuming and expensive, since considerable sample preparation is required. Given the aromaticity of the target compounds (biphenyl and PCBs), the high concentrations of these compounds expected, and the absence of aromatic chromophores in the SDS, UV spectrophotometry appeared to be a viable choice.

Since clay fines and other suspended solids would interfere with spectrophotometric determinations, the aqueous samples containing SDS, biphenyl (or PCBs), and suspended solids were first extracted with spectrograde hexane. Ten milliliters of sample was placed in a 40-mL vial. Twenty milliliters of hexane was added, and the vial closed and shaken until an emulsion was formed. The vial was allowed to stand for a few minutes and then shaken again to insure adequate extraction. The vial was opened and about 2 g of solid sodium chloride was added to the mixture. This caused the emulsion to break up. A disposable pipet was then used to siphon off the top layer, consisting of hexane and aromatic(s). A second hexane extraction was carried out if the concentration of PCBs was expected to be large. The combined hexane extracts were then volumetrically diluted with hexane as necessary to permit the UV spectra to be run.

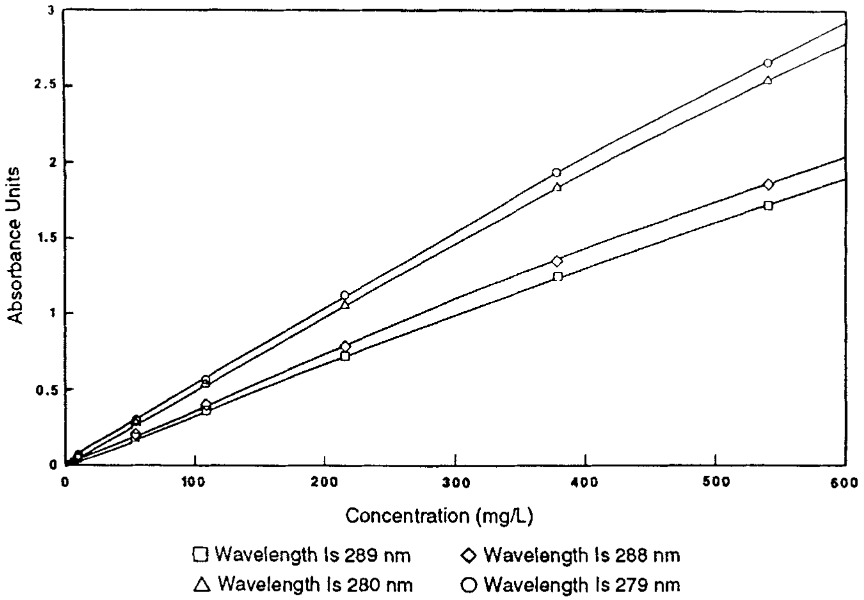

FIG. 1 PCB standards calibration curves.

Calibration curves were made at four different wavelengths with hexane solutions of Inerteen, a PCB mixture marketed some years ago by Monsanto. The results are shown in Fig. 1, and the least-square slopes, intercepts, and r^2 values are given in Table 1. The analytical reproducibility of the procedure is indicated in Tables 2 and 3, in which data on three aliquots of each of four samples are reported.

Percent recoveries of PCBs were determined for two surfactant solutions which were spiked with known quantities of Inerteen. These solutions were prepared, mixed for 24 hours (magnetic stirrer), then sampled,

TABLE 1
PCB Calibration Curves—Linear Regression Output[a]

Wavelength (nm)	Slope	Y-Intercept	r^2
289	3.16×10^{-3}	2.49×10^{-2}	0.999
288	3.41×10^{-3}	2.56×10^{-2}	0.999
280	4.70×10^{-3}	3.29×10^{-2}	0.999
279	4.90×10^{-3}	3.38×10^{-2}	0.999

[a] Number of observations = 6. Degrees of freedom = 4.

TABLE 2
Analytical Reproducibility for UV Spectrophotometric Analyses of PCBs, mg/L; Four Samples (3 Aliquots of each) at Four Wavelengths

Sample ID	PCB concentration in hexane extract (mg/L): Wavelength (nm)					Final PCB concentration in SDS solution[a] (mg/L)
	289	288	280	279	Mean ± SD	
S-1 E-1[b]	52.6	54.4	57.4	58.0	55.6 ± 2.6	111 ± 5
S-1 E-2	53.2	55.0	57.9	58.4	56.2 ± 2.4	112 ± 5
S-1 E-3	54.1	55.8	58.8	59.3	57.0 ± 2.5	114 ± 5
S-2 E-1	139	148	147	150	146 ± 5	292 ± 10
S-2 E-2	143	152	151	154	150 ± 5	300 ± 10
S-2 E-3	153	161	161	164	160 ± 5	320 ± 10
S-3 E-1	494	503	505	505	502 ± 5	1004 ± 10
S-3 E-2	478	480	491	492	488 ± 6	976 ± 12
S-3 E-3	500	510	514	514	510 ± 7	1020 ± 14
S-4 E-1	344	335	349	344	343 ± 6	686 ± 12
S-4 E-2	350	340	355	349	349 ± 6	697 ± 12
S-4 E-3	360	350	365	359	358 ± 6	717 ± 12

[a] The standard deviation (SD) shown in this table is the deviation associated with the analytical technique. Final concentration includes dilution factor.

[b] Where S is the sample number and E is the aliquot number.

TABLE 3
PCB Concentrations, mg/L, with Combined Analytical and Procedural Standard Deviations

	Sample			
	S-1[a]	S-2	S-3	S-4
PCB concentration	112 ± 7	304 ± 24	999 ± 34	700 ± 28

[a] Where S is the sample number. Each sample has three aliquots included in the deviation calculation.

TABLE 4
Evaluation of Percent Recovery of PCBs Using Hexane Extraction Technique

Sample no.	Actual concentration (mg/L)	Analysis (mg/L)	Percent recovery
1	280	318 ± 12	113
2	56	53 ± 1	95

extracted, and analyzed. The results are given in Table 4. By way of comparison, the USEPA Method 8080 (GC, packed column) accepts a range of percent recoveries from 8 to 127% for Aroclor 1260 and 38 to 158% Aroclor 1254.

SETTLING OF CLAY FINES FROM SDS SOLUTIONS

From preliminary studies it was evident that the settling of clay fines from SDS solutions preparatory to further treatment would be necessary under some circumstances if these contaminant-laden surfactant solutions were to be recovered for recycle. In this section we describe qualitative and quantitative studies of various techniques for facilitating the settling of the clay sediments in these solutions. The effects of pH, the addition of ferric or aluminum ion, and the addition of coagulants and flocculants were explored. Experiments were also carried out on soil contaminated with biphenyl to assess the effects of a contaminant on the settling of clay fines from these surfactant solutions.

The process of settling clay particles from aqueous systems has been studied extensively in the fields of water and wastewater treatment. Metcalf and Eddy (7) provide a comprehensive review of the subject and give examples of its application. While the results of these studies were utilized in this work, there was a major difference, in that these solutions contained relatively high concentrations of SDS micelles in addition to the clay colloids. Any settling techniques employed must leave the SDS unaffected.

Particle aggregation is generally accomplished by reducing or eliminating the repulsive effects of the electric double layers of the particles. This is commonly done by 1) adding potential-determining ions or electrolytes which reduce the thickness of the diffuse double layer, thereby reducing the zeta potential of the particles; 2) by adding polyelectrolytes that neutralize particle charge and also cause bridging; and 3) by adding chemicals that form hydrolyzed polynuclear metal ions. All three techniques were explored.

The effects of potential-determining ions (H^+ and OH^-) were studied by investigating the effects of sulfuric acid and sodium hydroxide. Other electrolytes could not be used because they tended to salt out the SDS or formed insoluble salts with it.

Several coagulants and flocculants were studied. The coagulants were positively charged, had a relatively low molecular weight, and had a high charge-to-mass ratio. The flocculants used had a high molecular weight and a lower charge-to-mass ratio than did the coagulants. A cationic, an anionic, and a neutral flocculant were screened.

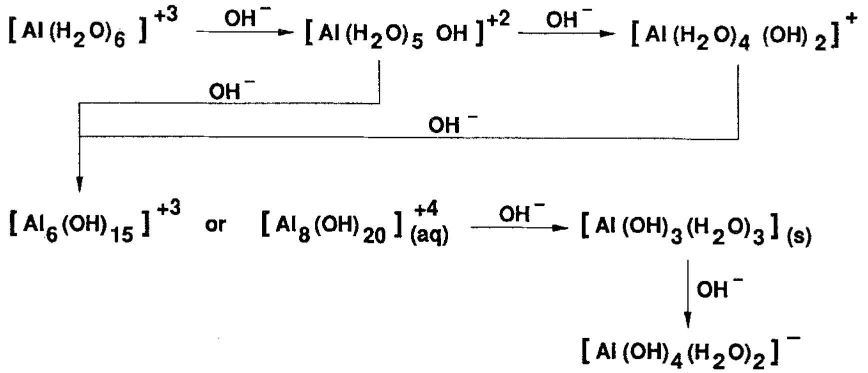

FIG. 2 Alkaline hydrolysis products.

Aluminum sulfate and ferric chloride were also tested. These cations react with water to form polynuclear hydrolyzed metal ions. Aggregation brought about by the addition of aluminum sulfate or ferric chloride is a complex process. The complex hydrolysis products of these metals are responsible for the aggregation, rather than free Al^{3+} or Fe^{3+}. The distribution of hydrolysis products present depends upon how the solution has been prepared and how long it has been standing. Thus a freshly prepared solution may behave differently from a solution that has been prepared and stored. A diagram illustrating schematically some of the possible hydrolysis products of aluminum is shown in Fig. 2.

Experimental

The SDS used was obtained from Fluka Chemical Co. in powder form and was 99% pure. The 50 mM SDS solutions used were freshly prepared using 14.4 g SDS dissolved in 1 L deionized water. The aluminum sulfate, sulfuric acid, hydrochloric acid, and sodium hydroxide were A.C.S. certified grade chemicals from Fisher Scientific. The ferric chloride was Baker Analyzed grade from J. T. Baker. Two coagulants and three flocculants were obtained from Nalco Chemical Company. The coagulants were designated as 8105 and 8108 and were both cationic. The three flocculants were as follows: 7192 was cationic, 7181 was nonionic, and 7763 was an anionic flocculant.

Two types of clays were used in the study. Both were obtained from the Nashville, Tennessee, area. One was a red ferruginous clay and is designated "red clay." The other clay was lighter in color, an orange-tan; it is designated "orange clay." Both clays were air dried, ground, and sieved before use. The sieving removed rocks and larger hard clay aggregates.

All settling experiments were performed in 100 mL glass graduated cylinders. A Spectronic 21 spectrophotometer (Milton Roy Co.) was used for determining the optical density at 600 nm of the solutions to assess turbidity. A Fisher Accumet pH meter was used for all pH determinations.

A qualitative visual study was first performed with the red clay. Control columns were filled with 50 mM SDS solution and 2.00 g clay to a total volume of 100 mL. Test columns were prepared similarly, followed by addition of the treatment chemical. The cylinder was covered with parafilm and gently inverted five times; time zero was taken from the last inversion of the cylinder. Differences in settling were assessed qualitatively by backlighting and examining visually.

One molar (1 M) stock solutions of ferric and aluminum ion were prepared. The treatment concentrations are reported in terms of these ions, although there was in fact very little free Al^{3+} or Fe^{3+} present in the systems under treatment. A 1-mL portion of stock solution was added to the 100-mL portion of SDS/clay solution being treated, so the final solution concentration was nominally 0.01 M in Fe^{3+} or Al^{3+}. Initially both the ferric and the aluminum solutions formed precipitates with the SDS. The aluminum formed a fluffy white precipitate which disappeared after the solution was mixed. The ferric ion formed an insoluble yellow precipitate which did not redissolve on mixing, for which reason further testing of Fe^{3+} was not carried out.

A significant difference in the settling rates of the control columns and the columns treated with aluminum was easily visible after 30 minutes. The solution treated with aluminum was much clearer after 30 minutes; after 24 hours it was completely clear to the eye, while the untreated column was still markedly turbid.

On the basis of these results a more quantitative technique was developed. The top portion of the solution in the column under study is withdrawn with a pipet and its optical density measured at 600 nm, at which wavelength Al^{3+} and SDS do not absorb.

The first experiments compared the settling efficiencies of columns containing SDS solution, clay, and aluminum sulfate to columns containing only SDS solution and clay. The columns were prepared as previously described. Each column contained 2 g clay and 99 mL of 50 mM SDS solution. Three columns contained 0.5 mL of 1.00 M Al^{3+} solution; three contained 1.0 mL of the Al^{3+} solution, and three contained only SDS and clay. One of each type of column was sampled at time intervals of 30 minutes, 1 hour, and 2 hours. The columns were sampled by drawing the top 50 mL solution off with a pipet. Care was taken to avoid mixing up the solution in the column. The sample was placed in a beaker and the pH of the solution was measured. The solution was then gently stirred to make sure that any sediments were thoroughly mixed but that no foaming occurred. A portion of the solution was then placed in a cuvette and the absorbance was measured.

On the basis of the data from these experiments, all subsequent experiments were carried out for time periods of 2 hours, measured from the last inversion of the column. To test reproducibility, two additional columns containing 1 mL Al^{3+} solution were run. Columns containing only clay and SDS solution were run with each set of runs for comparison.

The effect of pH was investigated next. Columns containing clay, SDS, and varying amounts of sulfuric acid were run, as were columns containing clay, SDS, and combinations of sulfuric acid and aluminum sulfate. Columns containing clay, SDS, and combinations of sodium hydroxide and aluminum sulfate were run at pHs in the range 4 to 10. A precipitate formed when the pH of these samples was above 4. The pHs of the samples were reduced to 3.5 before the absorbance readings were taken. The procedures for sampling the columns were the same as described above.

Coagulants and flocculants were also tested for their effectiveness. These experiments were performed in the same manner as was described above for experiments with added aluminum sulfate.

Several experiments were conducted to see what, if any, effect the presence of a hydrophobic contaminant would have on the settling rates of the clay fines. As biphenyl was to be used in the pilot-scale surfactant washing studies, it was used as the contaminant in this work, serving as a surrogate for PCBs. The soil was spiked at levels of 1 and 10% by weight. The biphenyl was weighed out and dissolved in hexane. The hexane solution was then transferred quantitatively to a beaker containing the clay. The hexane solution and clay were mixed thoroughly, and the hexane was allowed to evaporate at room temperature. The spiked clay was then used in settling experiments as described above.

Results

The results of the settling experiments were as follows.

As mentioned above, the preliminary experiments which were followed visually indicated that settling was greatly improved by the addition of Al^{3+}. The first set of quantitative experiments were performed to study the effects of varying amounts of Al^{3+} on the settling rate of the clay fines. It was found that if more than 1.2 mL of the 1 M Al^{3+} was added to a 100-mL portion of 50 mM SDS solution, a permanent precipitate was formed, so 1.0 and 0.5 mL portions of Al^{3+} (0.01 and 0.005 M in the test solutions) were used in the studies. A total of nine column experiments were performed in this initial test. The red clay was used in all of these experiments. Three columns contained 0.01 M Al^{3+}, three contained 0.005 M Al^{3+}, and three contained only surfactant solution and soil. One of each type of column was sampled at settling times of 0.5, 1, and 2 hours. The results are given in Table 5. The columns treated with 0.01 M aluminum yielded the lowest absorbances, and these were very substantially lower than those for columns run without added aluminum ion. Two more columns were run with 0.01 M Al^{3+} for 2 hours; the results from these runs are included in Table 6 and give some idea of the reproducibility of the experiments.

For purposes of assessing the effectiveness of the various treatments the percent settling enhancement (PSE) was defined as follows:

$$\text{PSE} = \frac{\text{(absorbance of PS column)} - \text{(absorbance of sample column)}}{\text{(absorbance of PS column)}} \times 100$$

where:

Absorbance of PS column = absorbance at 600 nm of supernatant from a column with plain soil and SDS solution (no additive) after 2 hours

Absorbance of sample column = absorbance at 600 nm of supernatant from the column containing the treatment chemical in addition to soil and SDS solution after 2 hours

PSE values for the studies with Al^{3+} treatment are given in Table 6. An idea of the reproducibility of the absorbances obtained from the experiments with untreated solutions is obtained from Table 7.

TABLE 5

Settling of Red Clay in the Presence of Aluminum Ions

	0.005 M Al^{3+}		0.01 M Al^{3+}		0 M Al^{3+} (plain soil)	
Time (h)	Absorbance[a]	pH	Absorbance[a]	pH	Absorbance[a]	pH
0.5	0.265	4.40	0.246	3.98	1.493	7.13
1.0	0.259	4.39	0.181	3.90	0.628	6.99
2.0	0.215	4.26	0.160	3.97	0.611	7.00

[a] At 600 nanometers.

TABLE 6
Reproducibility of the Settling of Red Clay at 2 Hours Using 0.01 M Al^{3+}

Sample no.	Absorbance[a]	pH	Percent settling enhancement
1[b]	0.160	3.97	69
2	0.146	4.03	71
3	0.153	4.04	70
Average	—	—	70

[a] At 600 nanometers.
[b] Taken from Table 5.

TABLE 7
Reproducibility of Settling of Clay Fines in Plain Soil Columns at 2 Hours (No enhancement)

	Red clay		Orange clay	
Sample no.	Absorbance[a]	pH	Absorbance[a]	pH
1	0.611	7.00	1.630	9.50
2	0.590	6.97	1.700	9.51
3	0.540	7.01	1.660	9.28
4	0.480	6.96	1.510	9.51
5	0.408	7.08	—[b]	—
6	0.453	7.02	—	—
Average absorbance	0.514 ± 0.080	NA	1.625 ± 0.082	NA[c]

[a] At 600 nanometers.
[b] "—" indicates not tested.
[c] "NA" indicates not applicable.

TABLE 8
Behavior of Red Clay with Addition of Sulfuric Acid

Molarity of H_2SO_4	Absorbance[a]	pH	PSE
1.2×10^{-4}	0.482	5.40	5.0
1.2×10^{-3}	0.302	3.44	41
1.0×10^{-2}	0.303	2.19	41
6.0×10^{-2}	0.225	1.91	56

[a] At 600 nanometers.

TABLE 9
Behavior of Red Clay Using a Combination of Sulfuric Acid and Aluminum Ions

Sample	Absorbance[a]	pH	PSE
0.01 M H_2SO_4/0.005 M Al^{3+}	0.177	2.29	66
0.01 M H_2SO_4/0.01 M Al^{3+}	0.124	2.20	76

[a] At 600 nanometers.

The effects of pH adjustment with sulfuric acid were explored next. The run parameters and the resulting PSE values are given in Table 8. The PSE values ranged from 5 to 56%, increasing with decreasing pH, which ranged from 5.4 to 1.9. The PSE values obtained were not as good as the values obtained with the aluminum sulfate treatment.

We next used two combinations of sulfuric acid with aluminum sulfate. One milliliter of 1 M sulfuric acid with either 0.5 or 1.0 mL of 1 M Al^{3+} solution was used. The results are given in Table 9. The slight enhancements in settling efficiencies which result would not appear to justify the cost of the acid, the additional handling equipment, and the corrosion problems which would be involved.

The next set of experiments involved the use of 1 mL aluminum solution and pH adjustment to values between 4 and 10 with sodium hydroxide. When the pH of the solution in the column was adjusted to values of 4 or above, a very light precipitate was formed which remained suspended in the SDS solution. As seen from the data in Table 10, the PSE values at pHs of 6 and 8 were much lower than the PSE at pH 4. One speculates that the hydroxide ion is causing the zeta potential of the clay particles to become large and negative, hindering the settling of the clay fines. At pH 10, the aluminum hydroxide precipitate redissolves. The PSE of the

TABLE 10
Effect of pH Variation on the Settling of Red Clay Fines in the Presence of 0.01 M Al^{3+}

Sample no.	Absorbance[a]	pH	PSE
1	0.130	4	75
2	0.270	6	48
3	0.310	8	40
4	0.124	10	76

[a] At 600 nanometers.

column at pH 10 is about equal to that at pH 4. The slight improvements in PSE values seen at pH 4 and pH 10 over those resulting from simple aluminum sulfate treatment would not appear to justify such pH modification in the field.

Two positively charged coagulants were screened. These were low molecular weight compounds with a relatively high charge-to-mass ratio. Since the clay fines have a net negative charge, it was thought that neutralization of this charge could facilitate their settling. The results of the settling experiments with coagulants are given in Table 11. The coagulants were first used on the red clay at concentrations of 1 and 40 mg/L. The coagulant designated 8105c appeared to hinder the settling process, since the absorbance values were actually higher than those for the plain soil columns, hence the negative value reported for the PSE. The coagulant designated 8108c did not perform much better, as seen from the very small PSE obtained for this experiment.

Three flocculants were screened: a cationic (7192f), an anionic (7763f), and a nonionic (7181f). Flocculants have high molecular weights and a lower charge-to-mass ratio than coagulants. Flocculants work through adsorption and the bridging of clay fines, causing the fines to come together and form large particles. The flocculants were screened at concentrations of 0.5 and 5 mg/L. The results for the flocculation experiments are given in Table 12.

The flocculants were first used on the red clay at a concentration of 0.5 mg/L. The largest PSE obtained with any of them was about 20%, which was not considered sufficient to warrant screening them on the orange clay. At 5 mg/L flocculant concentrations, all of the flocculants tested caused a discernible decrease in suspended red clay fines. The 7192f and 7763f flocculants both had PSEs of about 60%. That of the 7181f flocculant was 78%.

TABLE 11
Results of Coagulant Testing

Coagulant	Coagulant concentration	PSE	
		Orange clay	Red clay
8105c	1	—[a]	−10.5
8108c	1	—[a]	1.0
8105c	40	8.2	−6.4
8108c	40	4.7	6.9

[a] Not tested based upon results from red clay.

TABLE 12
Results of Flocculant Testing Including a Comparison of Duplicates for Each Type of Clay

Flocculant	Flocculant concentration (ppm)	PSE Orange (1)	PSE Orange (2) (clay type)	PSE Red (1)	PSE Red (2)
7192f	0.5	—[a]	—	18	—
7181f	0.5	—	—	10	—
7763f	0.5	—	—	20	—
7192f	5.0	12	21	60	58
7181f	5.0	27	27	78	81
7763f	5.0	86	87	61	62

[a] "—" indicates not tested.

For the orange clay at the 5 mg/L flocculant level, the PSE for the anionic flocculant (7763f) was about 87% while the other two flocculants yielded PSEs below 30%. To evaluate reproducibility, the three flocculants were tested again at 5 mg/L with the orange and red clays. These results are also given in Table 12, and they indicate that reproducibility is satisfactory.

The data from the flocculation experiments seem to indicate that the selection of the "better" flocculant depends upon the specific clay. Whereas all of the flocculants work to some degree on the red clay, only the anionic flocculant seemed to work on the orange clay. This is in contrast to the behavior of Al^{3+}, which worked equally well on both types of clays, yielding with the orange clay a PSE of 66% and with the red clay a PSE of 61%.

We next tested what we felt to be the two best settling treatments on clay contaminated with biphenyl to see if the presence of this hydrophobic organic interfered. The orange clay was used and was spiked with biphenyl at concentrations of 1 and 10% by weight (10,000 and 100,000 ppm). For the orange clay, the anionic flocculant and the aluminum sulfate solution had resulted in the highest PSEs, so these two treatments were tested. In addition, a soil column containing only SDS solution and the biphenyl spiked clay was also run, as was a column containing only SDS solution and spiked clay.

The results of these experiments on biphenyl spiked clay are given in Table 13. For the anionic flocculant treatment, the presence of biphenyl in the soil caused a decrease in the PSE of 5 to 10% for the soil spiked at 1%, and of 20 to 25% for the soil spiked at 10%. For the experiments

TABLE 13
Settling of Fines from Orange Clay in the Presence of Biphenyl

Additive	Additive concentration	PSE		
		No Biphenyl	1% Biphenyl	10% Biphenyl
7763f	5.0 ppm	86	77	67
7763f	5.0 ppm	87	82	64
Al^{3+}	0.01 M	66	71	75
Al^{3+}	0.01 M	—	71	73
Plain soil	—	—	−7.3	Out of range

in which aluminum sulfate was used, the opposite trend was seen. Biphenyl at the 1% level appeared to cause about a 5% increase in PSE, while at the 10% level it resulted in a roughly 10% increase in PSE. The PSEs for the columns containing only SDS and biphenyl contaminated soil were worse than those for the noncontaminated plain soil columns. The column containing clay spiked with 1% biphenyl had a PSE of −7.3%, while the column containing clay contaminated with 10% biphenyl resulted in readings outside of the range of the instrument.

We conclude that ferric ion is unsuitable for use because of its reaction with SDS, and that the coagulants tested were relatively ineffective. Results with the flocculants were somewhat better, but appeared to be dependent on the type of clay. Aluminum sulfate at approximately 0.01 M concentration appeared to be most effective, and the refinement of pH adjustment did not seem to result in major improvements in settling.

USE OF COLUMNS VERSUS STIRRED FLASKS IN PRELIMINARY FEASIBILITY STUDIES

The purpose of this phase of the investigation was to evaluate two procedures which could serve as preliminary feasibility tests for the removal of hydrophobic organic contaminants from soil. In the past we had performed laboratory-scale treatability studies using columns. This approach was limited by the reproducibility with which one could pack the columns and the relatively long times required to perform a study. It was hoped that the use of stirred flasks would provide a more rapid means of carrying out treatability studies.

Experimental

Two techniques for extracting PCBs from soil with surfactant solution were tested. The first employed stirred flasks in a batch extraction technique in which the contaminated soil is stirred with SDS solution in an Erlenmeyer flask for a predetermined period. The second is a soil column extraction technique in which the contaminated soil is packed into a glass column with a frit at the bottom to allow flow of SDS solution through the column.

The stirred flask experiments were carried out in 1 L Erlenmeyer flasks which were stirred on magnetic stirrers for 24 hours. The Tennessee orange clay mentioned previously was used in both the stirred flask experiments and the soil column experiments to be described shortly. The PCB mixture used was Inerteen, an Askarel which was produced some years ago by Monsanto. A run was carried out as follows. The soil was spiked by dissolving 0.50 g of the PCB mixture in hexane and mixing this with 50 g of soil to give a concentration of 10,000 mg/kg. The hexane was then allowed to evaporate at room temperature. The spiked soil was then transferred to a 1-L Erlenmeyer flask and 500 mL of 50 mM aqueous SDS solution (Fluka, >97% purity) was added to the soil mixture. A stirring bar was dropped in, and the flask was tightly capped with aluminum foil. The flask was then placed on a magnetic stirrer which was operated at a speed sufficient to keep the bulk of the soil suspended but slow enough to prevent foaming of the SDS solution.

It was necessary to separate the soil from the SDS solution prior to sampling so that several successive washings of the soil with fresh SDS solution could be made. To facilitate this, 5 mL of 1 M Al^{3+} (as aluminum sulfate solution) was added to the flask 5 minutes before turning the magnetic stirrer off. The SDS and contaminated soil mixture were then transferred to glass centrifuge carriers and centrifuged for 30 minutes. After centrifuging, the SDS solution was decanted and stored in a clean Erlenmeyer flask until the sample could be processed. The soil was transferred back into the original Erlenmeyer flask, and a fresh 500 mL portion of SDS solution was added. The flask was then placed on the magnetic stirrer. This process was repeated until the required number of washings had been carried out.

In the soil column experiments, 50 g of the Tennessee orange clay were used in each column. The clay was spiked with PCBs by the procedure described above. The spiked clay was then mixed with 300 g washed sea sand to increase its porosity to permit a reasonable flow rate of SDS solution through the column. Pure clay soil would not be a suitable candidate for in-situ flushing technology and could present rather severe problems for ex-situ washing as well.

Cylindrical Pyrex columns were used for the soil column experiments. These were 48 mm o.d. by 122 cm in length. The inner diameter was 44 mm. Each column was slightly tapered at one end to accept a glass funnel

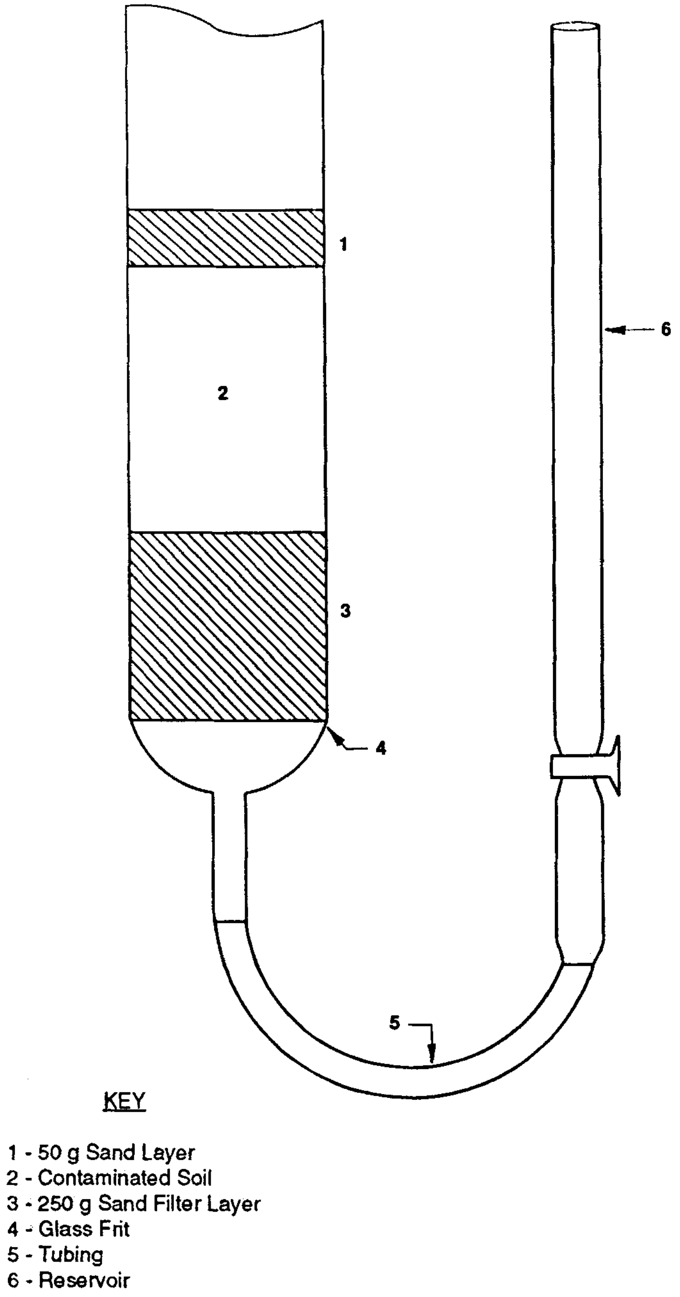

FIG. 3 Experimental configuration for determining pore volume of the soil-packed column.

that contained a coarse glass frit. The glass funnel was attached to the column by means of an aluminum fitting (43 mm o.d. by 5 cm) that was fitted with two rubber O-rings to prevent the column from leaking. Once the column was assembled, parafilm was wrapped tightly around the outside of the joint as an extra precaution against leakage. The glass funnel was fitted with a piece of rubber tubing on the stem, and a pinch clamp was placed on the rubber tubing for control of the solution flow out of the column.

The columns were packed as follows. First, 250 g washed sea sand was poured into the bottom of the column to act as a filter and to keep clay fines from washing out of the column. This was followed by the spiked clay/sand mixture.

The pore volume of the column was determined as follows. A reservoir was set up beside the column as shown in Fig. 3. The reservoir had a stem and stopcock at the bottom, by which it was attached to the bottom of the column by means of a rubber tube. The reservoir was filled with 50 mM SDS solution, SDS solution was allowed to fill up the column to the level of the glass frit, and the level of the solution was then marked on the container. The SDS solution was allowed to flow slowly into the column until the SDS solution reached the top of the clay/sand mixture. The volume of SDS solution required then gives the pore volume of the clay/sand mixture and the underlying sand layer. A similar experiment gives the pore volume of the underlying sand layer alone.

Once the soil in the column was saturated with SDS solution, 50 g sea sand was poured onto the top of the sample to act as a cap to prevent disturbance of the sample when SDS solution is added through the top of the column.

The SDS solution was allowed to sit in the column for a period of 24 hours, after which a pore volume was collected from the tubing at the bottom of the column. The clamp on the tube was then closed again and the column allowed to stand for another 24-hour period. This procedure was repeated until the required number of samples had been taken. The SDS solution samples were extracted with hexane and analyzed spectrophotometrically by the procedure described above.

We now turn to the results of these experiments. Table 14 gives the results of the stirred flask experiments. Each wash number represents a 24-hour contact time with 500 mL of 50 mM SDS. The results are quite varied, and they show that the stirred flask technique is not very reproducible. The initial washing frequently failed to produce any appreciable quantity of solubilized PCBs; this is presumed to be due to extensive adsorption of surfactant onto the clay, probably to the point where the SDS concentration actually in the aqueous phase is below the critical micelle concentration (cmc) of the surfactant.

TABLE 14
Results from the Stirred Flask Experiments

Sample no.	PCB concentration in SDS solution[a] (mg/L): Wash[b] No. 1	2	3	4	5	6	7
1	BMDL[c]	203 ± 8	190 ± 6				
2	142 ± 8	240 ± 10	119 ± 6				
3	BMDL	336 ± 10	147 ± 8	65 ± 8			
4	BMDL	BMDL	234 ± 10	169 ± 6			
5	BMDL	113 ± 16	215 ± 26	94 ± 14	44 ± 8		
6	BMDL	114 ± 16	179 ± 22	90 ± 10	58 ± 6		
7	129 ± 18	213 ± 26	130 ± 16	54 ± 8	25 ± 10	25 ± 6	
8	59 ± 20	234 ± 18	84 ± 20	28 ± 20	BMDL	BMDL	
9	BMDL	97 ± 12	177 ± 12	109 ± 10	46 ± 10	84 ± 12	25 ± 8
10	76 ± 10	232 ± 10	127 ± 10	24 ± 8	52 ± 10	17 ± 8	63 ± 8
Mean and SD at each wash no.	41 ± 57	178 ± 96	160 ± 47	79 ± 47	38 ± 21	32 ± 36	44 ± 27

[a] The reported concentration reflects an average using four wavelengths around the two incompletely resolved UV peaks.

[b] Each wash represents a 24-hour contact time.

[c] Below Method Detection Limit of 5 mg/L.

Centrifugation alone was not adequate to settle the clay particles from solution, so aluminum sulfate was used. Even with this, the SDS solutions were not always completely clear after centrifuging. Table 15 shows the relative quantities of clay fines in each sample and the concentration of PCBs in the sample. Fines were estimated by allowing them to settle and then measuring the height of the fines layer at the bottom of the cylinder.

As could be anticipated by the propensity of PCBs to sorb to fines, there was a rather good correlation between the amount of clay fines in the SDS solution and the concentration of PCBs. A paired flask experiment was performed in which two flasks contained the same amounts of soil, PCBs, and SDS. Both were stirred for 24 hours. One was then sampled directly, without settling out the clay fines; fines were removed from the other sample by the procedure described above. The sample from which the fines had not been removed contained 840 mg/L of PCBs; that from which the fines had been removed contained only 340 mg/L.

The data in Tables 14 and 15 indicate that the PCBs are not being desorbed very efficiently from the clay particles in the flask experiments. This could reflect poor contact between the contaminated soil and the SDS solution. A substantial portion of the soil remained on the bottom of the flask at the maximum stirring speeds at which excessive foaming did not occur. This, the lack of reproducibility, and the very labor-intensive nature of the procedure are serious problems with this technique.

TABLE 15
Height of Clay Fines and Corresponding PCB Concentration on a Per Wash Basis

Stirred flask no.	Wash no.	Height of settled clay fines (mm)	PCB concentration (mg/L)
1	1	None	BMDL[a]
	2	4	203
	3	4	190
2	1	3	142
	2	7	240
	3	2	119
3	1	None	BMDL
	2	6	336
	3	7	147
	4	7.5	65
4	1	None	BMDL
	2	2	BMDL
	3	12	234
	4	10	169
5	1	None	BMDL
	2	9	113
	3	8	215
	4	9	94
	5	8	44
6	1	None	BMDL
	2	9	114
	3	9.5	179
	4	7.5	90
	5	5.5	58
7	1	5	129
	2	8	213
	3	3.5	130
	4	2	54
	5	3	25
	6	None	25
8	1	4	59
	2	8	234
	3	7	84
	4	4.5	28
	5	5.5	BMDL
	6	None	BMDL
9	1	None	BMDL
	2	5	97
	3	8	177
	4	6	109
	5	6	46
	6	None	84
	7	None	25

(continued)

TABLE 15. Continued

Stirred flask no.	Wash no.	Height of settled clay fines (mm)	PCB concentration (mg/L)
10	1	4.5	76
	2	4	232
	3	4.5	127
	4	4	24
	5	3.5	52
	6	None	17
	7	None	63

[a] Below Method Detection Limit of 5 mg/L.

We next examine the results of the soil column experiments. Table 16 presents PCB concentrations in the first four washes (pore volumes) for the first five column experiments. Each wash was in contact with the contaminated soil for 24 hours. A pore volume was approximately 150 mL for each column. The flow through the columns, even with added sand, was often extremely slow; in some instances up to 6 hours was required to obtain a single sample. Flow rates for the soil columns during sampling are given in Table 17.

Formation of a white crystalline solid was noted in almost all of the samples taken from the columns; it was suspected that this could be SDS salts with calcium, magnesium, or iron, and that this might be the cause of the clogging of the columns. Therefore a 10-g sample of the soil was extracted with 0.2 M HCl, and the extract was tested for Fe(III) [formation of $Fe(OH)_3$], Ca(II) (precipitation of calcium oxalate), and Mg(II) (magne-

TABLE 16
Results from Soil Column Experiments

Column no.	PCB concentrations (mg/L): Wash no. 1	2	3	4
1	112 ± 7	304 ± 24	999 ± 35	700 ± 28
2	40 ± 6	550 ± 16	821 ± 20	—[a]
3	136 ± 6	523 ± 32	1066 ± 24	571 ± 22
4	162 ± 6	240 ± 16	959 ± 24	668 ± 16
5	154 ± 6	35 ± 6	702 ± 14	—

[a] "—" indicates no sample taken.

TABLE 17
Soil Column Flow Rates

Column no.	Flow rates (mL/min): Wash no. 1	2	3	4
1	2.30	0.81	0.73	0.52
2	1.25	0.60	0.51	—[a]
3	3.75	1.30	0.64	0.43
4	3.75	1.00	0.70	0.37
5	2.14	0.45	0.10	—

[a] "—" indicates no sample taken.

sium reagent). Tests for calcium and iron(III) were positive; that for magnesium was negative.

Several reagents for the suppression of the interferences caused by Fe(III) and Ca were investigated; EDTA, sodium and potassium carbonates, and sodium orthosilicate were used as pretreatments. Table 18 presents the effects these treatments had on the SDS solution flow rates.

Approximately 1500 mL of 0.01 M disodium EDTA was run through a column, after which it was observed that the flow rate of SDS solution through the column was about twice as large as that through similar columns which had not been treated. Use of EDTA in a field-scale operation, however, presents serious problems of environmental impact and expense.

Sodium and potassium carbonate solutions (0.1 M) were studied next. As seen from Table 18, neither performed satisfactorily. The flow rate of the sodium carbonate-treated column was virtually zero. The last treatment studied, 0.1 M sodium orthosilicate, however, gave quite satisfac-

TABLE 18
Flow Rates from Pretreated Soil Columns

Treatment solution/ concentration	Flow rates (mL/min): Wash no. 1	2	3	4	5	6
EDTA/0.01 M	3.75	2.14	1.61	1.25	0.73	—[a]
Na_2CO_3/0.1 M[b]	—	—	—	—	—	—
K_2CO_3/0.1 M	1.20	0.90	—	—	—	—
Na_2SiO_3/0.1 M	7.80	7.43	6.50	7.43	6.24	6.50

[a] "—" indicates no sample taken.

[b] Flow was unacceptably low, therefore no flow rate measurements were taken.

tory results, yielding good flow rates for all six of the washes taken. One pore volume of solution was discharged from the column in about 20 minutes.

In conclusion, we first note that our stirred flask technique for screening surfactant washing/flushing was not very reproducible (presumably due to inadequate mixing of the soil with the surfactant solution) and was extremely laborious. The column tests were substantially easier to carry out and yielded reasonably reproducible results. Soils which contain calcium and iron may require pretreatment to prevent blinding of the soil by the formation of insoluble salts of SDS; pretreatment with sodium silicate appears to be satisfactory as a means of tying up these metals. Passage of four pore volumes of 50 mM SDS solution resulted in the removal of 63, 69, and 61% of the 500 mg PCB spike from soil/sand samples which had not been pretreated. Passage of six pore volumes of SDS resulted in the removal of 78% of the PCB spike from a soil/sand sample which had been pretreated with sodium silicate.

ANALYSIS OF RECLAIMED SOLUTION FOR SDS CONCENTRATION

In the development of surfactant flushing/washing, it was necessary to demonstrate the efficacy of recycled surfactant solution in solubilizing hydrophobic contaminants, which has been discussed in an earlier paper in this series. It was also necessary to demonstrate that the SDS concentration in the recycled solution has not been excessively depleted. The initial SDS concentration in the surfactant solution used in the pilot-scale facility was 2.5% by weight. Samples were taken from two different pore volumes of reclaimed effluent from the pilot-scale apparatus described elsewhere (3). The first sample (I) had, after flowing through the test soil bed, been treated in the pilot-scale air-stripping column (for removal of VOCs) and in the solvent-extraction column (for removal of semivolatiles) and had been passed through the soil bed a second time prior to analysis for SDS. The second sample (II) had been passed through the soil bed and treated in the air-stripping and solvent-extraction columns once prior to analysis.

The Methylene Blue method for anionic surfactants as described in *Standard Methods for the Examination of Water and Wastewater* (8) was used for the analyses. The results, shown for triplicate analyses, are given in Table 19. These are somewhat high, and they appear to reflect a positive interference from the humic materials present in the samples, both of which had a brown, tea-like coloration. Humic acids contain organic carboxylate groups which are mentioned in *Standard Methods* as causing

TABLE 19
Results of Analyses of Recycled Surfactant Solution for SDS Concentration

Test method	Sample	Average SDS concentration (% w/w)	Range (% w/w)	Standard deviation[a] (%)
Methylene Blue	KCP-PV3F-1325	2.7	2.4–3.0	±0.31
	KCP-PV4F-1325	2.8	2.5–3.1	±0.28
Gravimetric	KCP-PV3F-1325[b]	2.56	—	—
	KCP-PV4F-1325[c]	2.49	—	—

[a] Based upon triplicate analyses.

[b] SDS concentration = total residual percent solids (2.58) less percent dissolved solids in tapwater (0.013) less percent solids in filtered SDS solution from soil test bed (0.011) = 2.56%.

[c] SDS concentration = 2.51 − (0.013) − (0.011) = 2.49%.

positive interferences in the Methylene Blue method for anionic surfactants.

A second method, involving gravimetric total solids determination, was therefore employed. One vial of each sample solution was weighed. The solutions were then evaporated to dryness at 110°C, cooled, and reweighed. At this point they contained a waxy, slightly dirty white solid. The vials were then rinsed free of the residue, dried, and reweighed. The gravimetric data, also reported in Table 19, have been adjusted for the average total dissolved solids concentration in Nashville, Tennessee, tap water. (The SDS solution used in the pilot-scale facility had been prepared with tap water.) The average total dissolved solids concentration in this tap water was reported as 130 mg/L. The suspended solids concentration measured in the recycled surfactant solutions was 110 mg/L. Both these contributions were subtracted from the calculated total solids concentrations; the resultant concentrations attributed to SDS are 24.9 (I) and 25.6 (II) g/L, very near the initial SDS concentration of 25 g/L.

The values determined by both methods indicate that losses due to sorption or other mechanisms do not appear to be significant with the soil matrix used in the pilot-scale apparatus. The ability of the reclaimed surfactant solution to remove hydrophobic organics from the soil lends further support to this conclusion (3).

CONCLUSIONS

Several problems related to the development of the surfactant flushing/washing of soils contaminated with hydrophobic organics were addressed.

These include the following:

1. A simple UV spectrophotometric method for the analysis of PCBs in sodium dodecylsulfate (SDS) solution was developed.
2. The use of aluminum sulfate as a coagulant for the settling of clay fines from spent surfactant solutions was found to give better and more consistent results than several other treatments.
3. A comparison of laboratory-scale columns versus stirred flasks for use in preliminary feasibility studies led to the conclusion that laboratory-scale column studies are both more reproducible and less labor intensive than stirred flasks.
4. A determination of the extent to which SDS is lost during the processes of soil treatment and reclamation indicated very little losses after the first pore volume or so had been passed through the soil.

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