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Soil Clean-Up by Surfactant Washing. II. Design and Evaluation of the Components of the Pilot-Scale Surfactant Recycle System

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ABSTRACT

The components of a pilot-scale system to recycle and reuse a surfactant solution containing contaminants from remediated soil were designed, fabricated and successfully tested. Use of surfactants in soil washing or flushing can expedite remediation manyfold as the aqueous solubility of hydrophobic compounds is increased. The process is of even greater utility when the contaminants are also nonvolatile and nonbiodegradable. Biphenyl was used to represent nonvolatile contaminants. Not only was 99% biphenyl removal (initial concentration 1000 mg/kg) from soil achieved in 7 pore volumes of 2.5 wt% sodium dodecyl sulfate (SDS) solution, but there was no decrease in the effectiveness of the recycled solution in removing the biphenyl compared to the virgin solution. Approximately 1 ppm biphenyl remained in the SDS solution after recycle. Toluene was used to represent volatile contaminants. Toluene removal from the soil test bed was 98% when using the same SDS solution. There was approximately 3 ppm toluene in the recycled surfactant solution. Again, the effectiveness of recycled surfactant solution in removing toluene from soil was the same as the virgin material.

INTRODUCTION

The presence of over 1400 Superfund sites on the promulgated National Priorities List (NPL) throughout the United States is well known and documented. There are over 30,000 sites on CERCLIS, the Comprehensive Environmental Response Compensation and Liability Information System List. There are also many unlisted sites (residential, industrial, undeveloped, Department of Defense, Department of Energy, etc.) which contain hazardous chemicals. Any of these sites could contain chemicals which would be difficult to treat. ''Difficult'' chemicals are those that are hydrophobic and refractory (essentially insoluble in water and not easily amenable to biodegradation, respectively), and that lack adequate vapor pressure to make vapor stripping feasible. The prime example of this type of chemical is polychlorinated biphenyls (PCBs).

While flushing appears in many Records of Decisions (RODs) (1), a detailed review of the RODs (2, 3) indicates that these are frequently water flushes which would not adequately address the difficult chemicals (4). Organic chemicals which are difficult to treat may, however, be addressed by surfactant-supplemented processes. Surfactant-supplemented processes will also remove less-difficult-to-treat organic constituents such as volatile organic compounds (VOCs), polyaromatic hydrocarbons (PAHs), chlorinated and nonchlorinated aliphatic solvents, aromatic solvents, etc. There are several washing technologies currently available. Some appear to be easily adaptable to include a surfactant-based washing process.

The research performed by Eckenfelder Inc. addresses a major problem identified by the United States Environmental Protection Agency (USEPA) which limits the successful implementation of surfactant in-situ surfactant flushing or ex-situ washing (SF/W). This is the separation of surfactant from the soil (especially clay soils) and regeneration of the

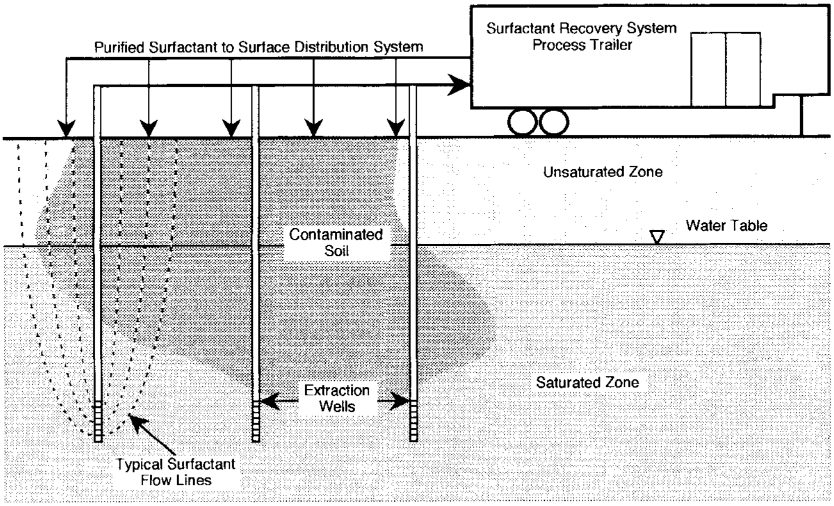


FIG. 1 In-situ surfactant flushing system concept.

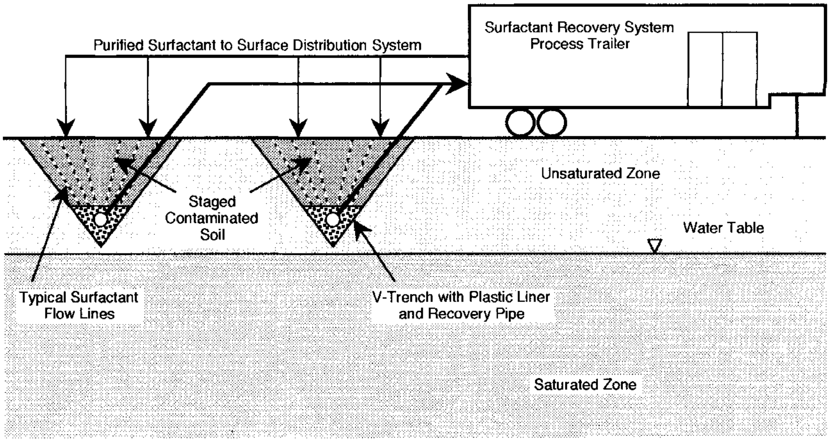


FIG. 2 Ex-situ surfactant washing system concept.

surfactant for reuse. The value to site remediation lies in the fact that the presence of a surfactant greatly increases the solubility of hydrophobic organic compounds within the aqueous phase, thus often increasing the cleanup rate above that achievable by simple water flushing, which is controlled by the compounds' low aqueous solubilities.

Figures 1 and 2 illustrate in-situ surfactant flushing and ex-situ surfactant washing (respectively), and show how they might be implemented at a typical site. For the ex-situ washing approach, the contaminated soil is excavated and placed in lined V-trenches above the water table prior to treatment. (Treated soil could remain on site consistent with federal and state regulations on consolidation and landfilling.) The mobile surfactant recovery system shown in both figures is the same for both flushing and washing. Its design and testing form the basis of the research in this and the following papers in the series.

BACKGROUND

The effectiveness of surfactant flushing/washing (SF/W) is related to the ability of surfactants to solubilize "water-insoluble" compounds. Surfactant molecules or ions consist of a hydrophobic portion (often a long hydrocarbon chain) and a hydrophilic portion (an ionic or polar head, or a polyethoxyethylene chain). These surfactants therefore tend to concentrate at polar–nonpolar interfaces (such as air–water), and, at sufficiently high concentrations, form aggregates (micelles). In the micelles formed

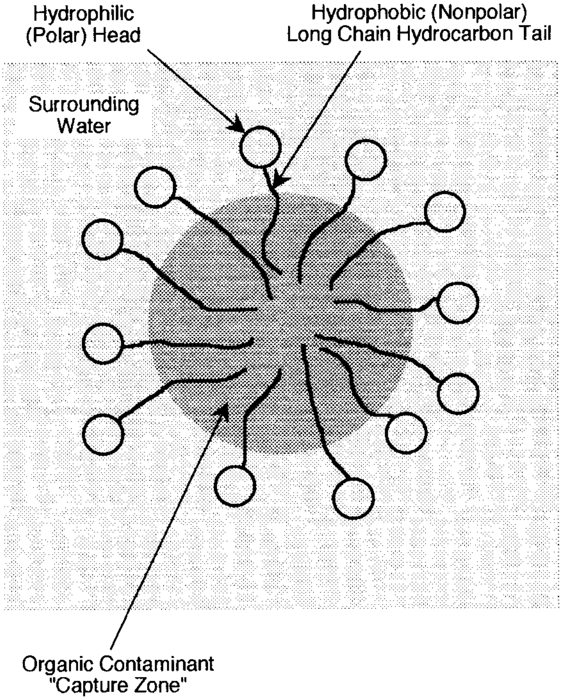


FIG. 3 Cross-sectional view of a typical ionic surfactant micelle.

in aqueous solutions, the polar or ionic portions of the surfactant molecules are presented to the aqueous phase, while the nonpolar, hydrophobic hydrocarbon tails of the molecules are clustered together away from contact with the water molecules (see Fig. 3). Hydrophobic chemicals are solubilized as an approximately linear function of the concentrations of the surfactant, provided that the solution is above the critical micelle concentration (cmc, the surfactant concentration at which micelles first start to form).

The surfactant selected by Eckenfelder Inc. for previous laboratory-scale testing (5) and the present pilot-scale testing, is sodium dodecyl sulfate (SDS). It is also known as sodium lauryl sulfate (NLS). SDS is a 12 carbon, straight chain, anionic surfactant that is commercially available and relatively inexpensive. In addition, SDS is biodegradable and relatively nontoxic (6). The anionic character of SDS permits its recovery and reuse by solvent extraction and also reduces its tendency to sorb to relatively negatively charged soil particles (e.g., clays). The cmc for SDS is 0.231 wt% or 2.31 g/L.

Research by Eckenfelder Inc. targeted the collection of pilot-scale data on the implementation of SF/W technologies for the remediation of soils containing nonvolatile/semivolatile, hydrophobic, refractory organic compounds. The initial data were collected for biphenyl, which is a relatively nonhazardous hydrophobic compound, and toluene, which represents a class of VOCs frequently found at hazardous waste sites. The laboratory-spiked soil served as a precursor to the testing of field-contaminated soil containing PCBs. This research built upon the favorable results from a completed study at the laboratory scale in 1990 under a USEPA SBIR Phase I research grant. This pilot-scale effort included the removal of the nonvolatile organic compounds and VOCs from soil, the recovery and reuse of the surfactant solution, and the production of a small volume of concentrated waste.

Supplementing these efforts was the development of an analytical protocol for rapidly measuring biphenyl and toluene concentrations. The analytical procedure employed ultraviolet (UV) spectrophotometry.

There were secondary objectives which supplemented the pilot-scale testing. These included the effects (through a laboratory-scale study) of the desorption/diffusion kinetics of SF/W, development of a UV spectrophotometric analysis method for PCBs in SDS solution to monitor progress within a rapid turnaround time, and the development of an improved method for settling fines in supernatant SDS solutions. Other secondary objectives include the development and comparison of column studies versus stirred container studies as preliminary feasibility tests. The results of this research will be presented in Paper V of this series.

The primary objectives are divided into two phases. Phase I included the design and/or assembly of the pilot-scale unit and the testing of the individual components. Phase II research involved the testing of the integrated pilot-scale unit on the simultaneous removal of volatile and nonvolatile components in a 152-pound (68.9 kg) soil test bed and the continued treatment of the soil with the recycled surfactant solution. The results of the Phase I testing are given in this paper. The next paper in the series will cover the Phase II results.

SYSTEM DESIGN

An SF/W pilot-scale system was designed and fabricated to evaluate the scale-up feasibility of the technology and ultimately to demonstrate the integrated process on larger volumes of soils contaminated with difficult to treat organic compounds, among others.

The pilot-scale system was designed to simulate in-situ surfactant flushing of up to 1 ton of contaminated soil with recovery, regeneration, and reuse of the surfactant. A process schematic of the pilot-scale surfactant flushing and recovery system is illustrated in Fig. 4.

The recovery and recycle process is an integration of several unit operations: 1) an air stripping column and activated carbon adsorber for removal of VOCs from the surfactant, 2) a countercurrent solvent extractor for removal of semivolatile and nonvolatile organics, 3) a solvent-recovery system for removal and concentration of semivolatile and nonvolatile organics from the extractor solvent, and 4) a hyperfiltration unit for concentrating the surfactant solution since overpumping of surfactant flushing recovery wells is required to insure that the surfactant and mobilized contaminants are completely recovered during in-situ treatment. The process for the recovery and recycle of surfactant employed for ex-situ washing is the same as for in-situ flushing with the exception of the elimination of the hyperfiltration unit.

Soil Flushing Operations

During operation, fresh surfactant solution is prepared in batches in a makeup tank and is then transferred to the surfactant solution feed tank. From the feed tank, the surfactant solution is transferred to a soil test

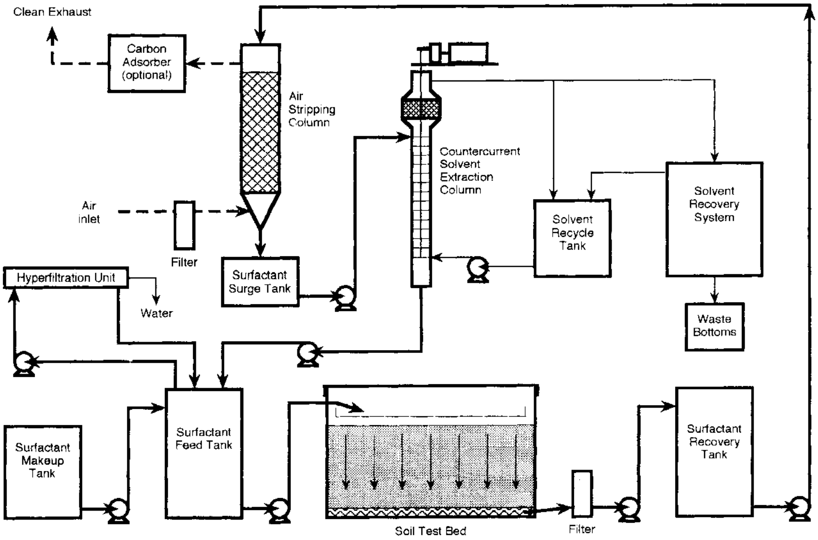


FIG. 4 Pilot-scale surfactant recycle process schematic.

bed which has a soil capacity of 670 L (175 gal or 1 ton of soil). After flowing through the contaminated soil and solubilizing the organic contaminants, the surfactant solution is recovered from below the soil test bed and is pumped through a 5-μm particulate filter and into the surfactant recovery tank. Both the feed tank and recovery tank have capacities of 246 L (65 gal).

Air-Stripping Column Operations

The recovered surfactant solution, which now contains solubilized organic compound(s), is pumped from the surfactant recovery tank into the top of the air stripping column where it trickles down through a 183-cm (6 ft) tall by 15.4 cm inside diameter (6 in. schedule 40 pipe) packed bed of 1.6 cm (⅝ in.) NOR-PAC (a trademark of N.S.W. Corp.) polypropylene packing (Jaeger Products, Inc.).

NOR-PAC is a cylindrical shaped packing with a high active surface area for gas/liquid contacting, a low packing factor, and geometric symmetry. The packing has a surface area of 101 ft^2/ft^3 and a void space of 88%. It also has the lowest pressure drop of all comparable packings, which permits maximum throughput in a given column.

The surfactant solution flows by gravity out of the bottom of the air-stripping column and is collected in the surfactant surge tank. Air is simultaneously introduced to the bottom of the air-stripping column and flows upward, countercurrent to the surfactant solution, to strip any VOCs that may be present in the contaminated surfactant solution. The air exits the top of the air-stripping column and, if VOC concentrations are high enough to require treatment, the air is passed through an activated carbon unit prior to exhaust to a laboratory fume hood. Removal of VOCs from the surfactant solution before it is introduced to the solvent extraction column is necessary to avoid accumulation of VOCs in the solvent. If VOCs are present in the solvent, the subsequent solvent regeneration step (distillation) becomes much more complex than it is if only nonvolatile/semivolatile compounds are present in the solvent which is to be regenerated.

Solvent Extraction Column Operations

The recovered surfactant solution, still laden with nonvolatile and/or semivolatile organics, is pumped from the surfactant surge tank to the top of a Karr (a trademark of Otto H. York Co., Inc.) reciprocating plate extraction column. The surfactant solution comprises the heavy continuous phase in the solvent extraction column and flows downward countercurrent to a lighter heptane solvent phase which is introduced from the bottom and passes upward as the dispersed phase while extracting the organics from the aqueous surfactant phase. The purified surfactant solution (i.e., with the volatile, semivolatile, and nonvolatile organic compounds removed) is discharged from the bottom of the solvent extraction column back into the surfactant feed tank. The solvent exits the top of the unit through a de-entrainment section and is then split; part passes to the solvent recovery system and part to a solvent recycle tank which serves as a solvent feed tank for the extraction column. The partition coefficients for the hydrophobic organic compounds between the solvent and surfactant solution are large (typically in excess of 50) so that a substantial residual concentration of organic compounds in the solvent will not interfere significantly with the rate of removal of the organic contaminants.

The Karr reciprocating plate extraction column contains multiple open-type stainless steel perforated plates mounted on a central shaft which can be reciprocated by means of a variable speed drive mechanism located above the column. Figure 5 shows the plate design and arrangement within the column. The main portion of the column is a high borosilicate glass pipe that is 5.1 cm (2 in.) diameter by 183 cm (6 ft) tall. The top of the column contains a 10.2-cm (4 in.) diameter expanded section that contains a Teflon (a trademark of E. I. du Pont de Nemours and Co., Inc.) mesh de-entrainment pad. The top and bottom heads and feed rings are made of glass-filled Teflon.

The amplitude of the plate reciprocation can be varied between 0 and 4.4 cm (0 and 1¾ in.), and the speed of reciprocation can be varied from 0 to over 400 strokes per minute. The wide range of reciprocation rate and amplitude allow for optimum column agitation adjustments.

The Karr extraction column technology was chosen for the pilot-scale system application because its design minimizes potential emulsification problems with the surfactant and solvent that were identified during smaller scale laboratory tests. The reciprocating plates do not impart significant angular momentum to fluids. Shear between dispersed and continuous phases is consequently uniform, and droplet size distribution is narrow (7).

Heptane was chosen as the solvent for pilot-scale testing to facilitate a rapid turnaround chemical analysis for organic contaminants without introducing analytical interferences. Other less volatile, less expensive, commercially available in bulk solvents, such as mineral spirits, would be used for field application of the technology.

Solvent Recovery System Operations

The solvent recovery is achieved by a commercially available solvent still which has been modified for continuous feed and a visual assessment

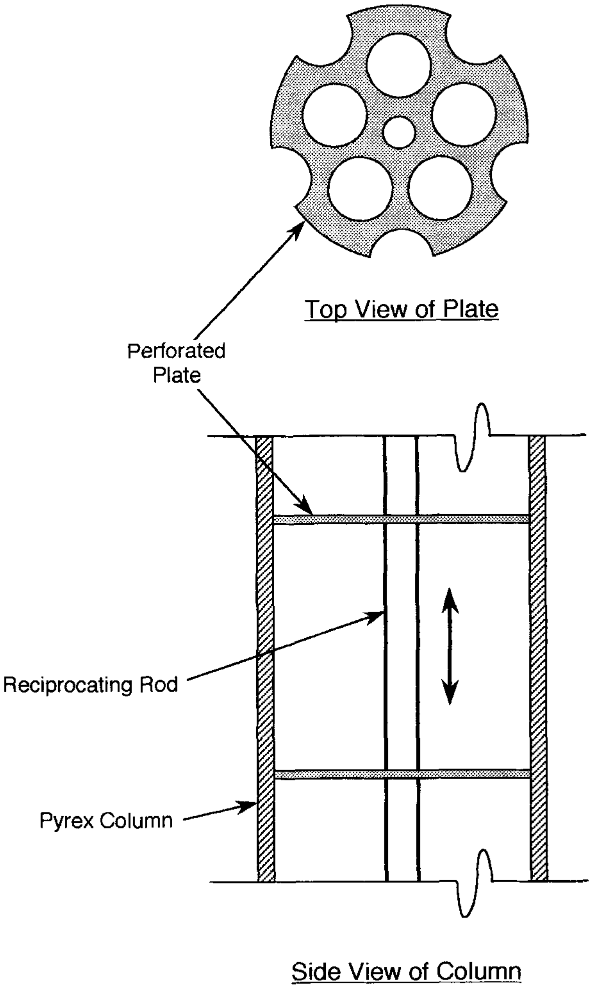


FIG. 5 Karr column perforated plate arrangement.

of the volume of "bottoms" during operations. The solvent recovery system has a 19 L (5 gal) capacity, stainless steel boiling chamber. The chamber is surrounded by an oil bath that is heated with a 1.5-kW oil immersion heater with a built-in thermostat.

The heptane solvent vapors generated within the boiling chamber are recondensed in a tube-and-shell condenser which is cooled by water on the shell side. The recovered and purified solvent is then returned to the solvent recycle tank for reintroduction into the bottom of the solvent extraction column. The nonvolatile and/or semivolatile contaminants present in the solvent from the solvent extraction column are concentrated in the bottom of the boiling chamber and can be periodically tapped off.

Hyperfiltration System Operations

Hyperfiltration membrane technology is being demonstrated as part of the pilot-scale system for removal of excess water from the recovered surfactant. For other applications, the membrane system has been proven to be a low cost alternative to evaporation. Field application of in-situ surfactant flushing would require overpumping of the extraction well(s) to assure complete recovery of the surfactant solution. Since a greater volume of aqueous surfactant is recovered than is injected, it will be necessary to reduce the volume of the recovered surfactant so that it can be used in the system at the appropriate concentration.

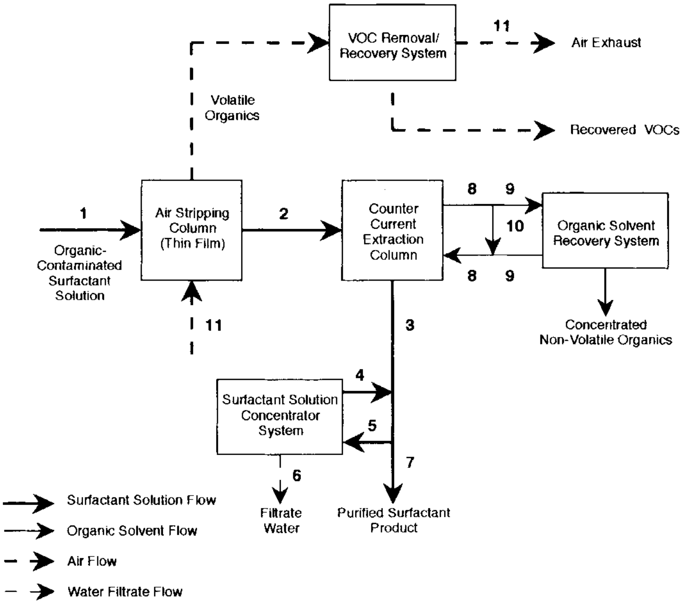
The pilot-scale hyperfiltration system consists of a high-pressure vane pump, a membrane housing, a membrane filtration element, and related control valves, flowmeters, and pressure gauges. During operation, the recovered surfactant solution is pumped from the surfactant feed tank and is pressurized by the vane pump to 150 to 200 psig. The surfactant solution then enters one end of the membrane housing which contains a 5.1-cm (2 in.) diameter by 61-cm (24 in.) spiral-wound crossflow filter element. The element membrane is selected to allow permeation by water but not by the larger surfactant molecules. A portion of the water is forced through the semipermeable membrane and exits the unit as "permeate." The surfactant is retained by the membrane and exits the unit as "concentrate" which is then returned to the surfactant feed tank.

Process Capacity Measurements

The process components have undergone preliminary tests without contaminants present to provide information on flow capacities and operating parameters. The pilot system design flow-sheet capacities are presented in Fig. 6.

The air-stripping column was not subjected to capacity tests because it was substantially overdesigned compared to the other process units. The air-stripping column diameter was dictated by the minimum size of the NOR-PAC packing that was available, thus, the column diameter is two or three times larger than is actually required.

The Karr reciprocating plate extraction column was tested with both water and a 25 g/L SDS solution as aqueous phases and with heptane as the organic phase or solvent. With the water and heptane system, the



Stream No. / Component	Stream Flows, ml/min										
	1	2	3	4	5	6	7	8	9	10	11
Surfactant Solution	280	280	280	112	56		224				
Organic Solvent								280	56	224	
Air											14,000
Water Filtrate						56					
Total ml/min	280	280	280	112	56	56	224	280	56	224	14,000

FIG. 6 Surfactant recycle system flow sheet.

column's capacity was not reached even while both phases were fed at 500 mL/min and with the plate reciprocation rate maximized at 400 cycles per minute (CPM). The 25 g/L SDS and heptane system was tested at 500 mL/min for each phase. The SDS product stream was slightly turbid due to entrainment of small heptane droplets, even with the plate reciprocation rate at zero CPM. An emulsion that was 5 to 10 cm thick formed at the SDS/heptane interface at the top of the column; however, the de-entrainment pad successfully separated the phases. The testing operation was repeated at 400 and at 300 mL/min per phase. Based on the reduced SDS product turbidity, it is projected that the column can be effectively operated at 300 mL/min per phase with a moderate plate reciprocation rate of 25 to 50 CPM.

The solvent recovery system distillation rate was tested with water. Based on the differences in latent heat of vaporization, the heptane distillation rate is calculated to be at least 80 mL/min. This exceeds the design rate of 56 mL/min as shown in Fig. 6.

The hyperfiltration unit was tested with water at a pressure of 180 psig. The permeate rate was 390 mL/min, which substantially exceeds the design rate of 56 mL/min.

EXPERIMENTAL WORK

The first phase of addressing the primary objectives included the design, construction, and testing of the individual process components which would be integrated into the continuous surfactant recycle system in Phase II of the primary objectives work. The individual components of the recycle system were initially tested for leaks, stability, and performance (i.e., meeting design criteria). This was done using water and/or surfactant solution. No compounds simulating contaminants were used in this preliminary testing.

The goals of this phase of the project were to identify any unanticipated problems and to see if the pilot-scale processes worked on this scale. There was no effort to maximize removal efficiency, minimize treatment time, etc. Based upon the knowledge obtained during Phase I of the primary objectives study, Phase II was able to address several aspects of the process which resulted in overall performance improvement.

The soil used in the testing was a mixture of topsoil from a farm in east-central Mississippi and sand from Camden, Tennessee. The topsoil was sandy clay or clayey sand with brown clay, and the sand was white with very little clay. The mixture was a 3:2 ratio of topsoil to sand based on weight. Table 1 summarizes the characteristics of this mix.

The primary research performed under the primary objectives of Phase I consists of two parts, one of which addresses the surfactant-based removal of nonvolatile compounds (as represented by biphenyl) and the second of which addresses the surfactant-based removal of volatile compounds (as represented by toluene). Biphenyl was selected as representative of hydrophobic compounds of low volatility. The compound could be considered a surrogate for testing with PCBs. The aromaticity of biphenyl permits its relatively rapid determination by UV spectrophotometry. The selection of toluene reflects its solubility (significant on an environmental scale), volatility, and aromaticity, again permitting a UV analysis. Both biphenyl and toluene exhibit degrees of aerobic biodegradability higher

TABLE 1
Blended Soil Characteristics

	Soil/sand blend[a]
pH	5.9
Organic content, %	3.5
Specific gravity	2.568
Moisture content, %	11.8
Sieve analysis:	
Less than 2.38 mm, %	99.3
Less than 0.075 mm, %	18.9

[a] Blend made up of 60% topsoil from a farm in east-central Mississippi and 40% high purity sand from a sand mine outside of Camden, Tennessee.

than their chlorinated counterparts. Table 2 is a summary of physical and chemical parameters for biphenyl and toluene.

Included in Table 2 are the chemical and physical data on heptane, the solvent used in the solvent extraction column to separate the semivolatile and nonvolatile, hydrophobic materials from the SDS solution. Heptane

TABLE 2
Summary of Physical and Chemical Parameters for Biphenyl, Toluene, and Heptane[a]

Parameter	Biphenyl	Toluene	Heptane
Molecular formula	$C_{12}H_{10}$	C_7H_8	C_7H_{16}
Aromaticity	Yes	Yes	No
Molecular weight	154.20	92.13	100.20
Color/form	White scales or leaflets	Colorless liquid	Colorless liquid
Boiling point, °C	254–255	111	98.4
Melting point, °C	67–71	−95	−91
Density, g/cm³	1.041	0.8661	0.684
Aqueous solubility, mg/L	1–2	515	2–3
Vapor pressure, mmHg	1 (at 71°C)	40 (at 31.8°C)	40 (at 20°C)
Vapor density (air = 1)	5.31	3.14	3.45
log K_{ow}[b]	3.16–4.33	1.83–2.94	4.66
log K_{oc}[c]	3.15–5.58	1.12–3.28	N.P.
K_H (Pa·m³/mol)[d]	13.68–157	680	2.035 atm·m³/mol

[a] Sources: *CRC Handbook of Chemistry and Physics*, 65th ed. (R. C. West et al., Eds.), CRC Press, Boca Raton, Florida, 1984. *The Merck Index*, 10th ed., (M. Windholz et al., Eds.), Merck & Co., Rahway, New Jersey, 1983. Hazardous Substances Data Bank, National Library of Medicine. *Groundwater Chemicals Desk Reference*, J. H. Montgomery and L. M. Welkom, Lewis Publishers, Chelsea, Michigan, 1990.

[b] K_{ow} is the octanol water coefficient.

[c] K_{oc} is the soil/water distribution coefficient referenced to soil organic content.

[d] K_H is Henry's law constant.

was selected since it is not aromatic and, therefore, does not interfere with the various UV analyses. A full-scale operation would most likely use less expensive, mixed commercial solvents such as Stoddard solvent or other petroleum cut solvents. However, there is a relatively high degree of aromaticity in these mixed solvents (from naturally occurring aromatic hydrocarbons) which would preclude the use of UV spectrophotometric analysis.

Development of UV Spectrophotometric Analytical Methods

There were several matrices which required analysis for biphenyl and toluene in the execution of the research. Table 3 is a summary of the matrices, the constituents analyzed, and the potential presence of SDS. Given the need for on-going modifications to the testing, data were needed more rapidly than could be obtained from the GC analyses provided by the laboratory. Thus the effort to develop a rapid, reliable analytical protocol was given initial priority.

For the analysis of aqueous SDS samples containing biphenyl or toluene, the samples were extracted with reagent-grade heptane (VWR Scientific) by batch extraction. Batch extraction was carried out by swirling together a 1:2 mixture of aqueous SDS sample and heptane. After a 1-hour contact period, the heptane layer was removed and its volume measured. If a second extraction was necessary, a fresh aliquot of heptane was added to the aqueous phase remaining from the first extraction, and the same extraction procedure was followed again. Any emulsions were broken by adding solid NaCl; NaCl did not interfere with the analysis.

TABLE 3
Various Matrices Requiring Analysis for Biphenyl/Toluene

Matrix	Biphenyl	Toluene	SDS present
Soil	Yes	Yes	Yes[a]
Aqueous solution	Yes	Yes	Yes[a]
Air	No	Yes	No
Heptane	Yes	No[b]	No[b]

[a] Samples analyzed before treatment of the soil should not have SDS present; those analyzed after treatment had been initiated would have SDS present.

[b] Ideally these matrices would not have these constituents present. However, analyses were performed at critical points in the execution of the research to document at which concentrations the constituents were present.

The heptane solutions containing the biphenyl or toluene were analyzed using a Shimadzu UV-1201 split beam spectrophotometer with Spectrosil (a trademark of Starna Cells), far-UV quartz rectangular matched cells with a 10-mm path length, and a flat Teflon cover. Absorbance at the appropriate wavelength was measured for each extract, and concentrations were calculated based on calibration curves constructed from a series of standards prepared from either biphenyl or toluene in heptane. The wavelength for biphenyl's absorbance peak maximum is 247 nm with a detection limit of 1 ppm. See Fig. 7 for the biphenyl UV spectrophotometric absorbance curve and Fig. 8 for the calibration curve. Two wavelengths were used to construct calibration curves for quantitation of toluene, 260 and 216 nm (see Fig. 9 for the toluene absorbance curve). The detection limits for absorbance at 260 and 212 nm were 100 and 2 ppm, respectively. (See Fig. 10 for the toluene calibration curve for concentrations greater than 100 ppm.) Given the high concentration of toluene used in the first test, the more sensitive level calibration curve, derived at 216 nm, was not needed. Figure 11 provides the calibration curve at 216 nm for the lower concentrations of toluene. (This, however, was created at a later time when evaluation of removal efficiencies required lower limits of detection.)

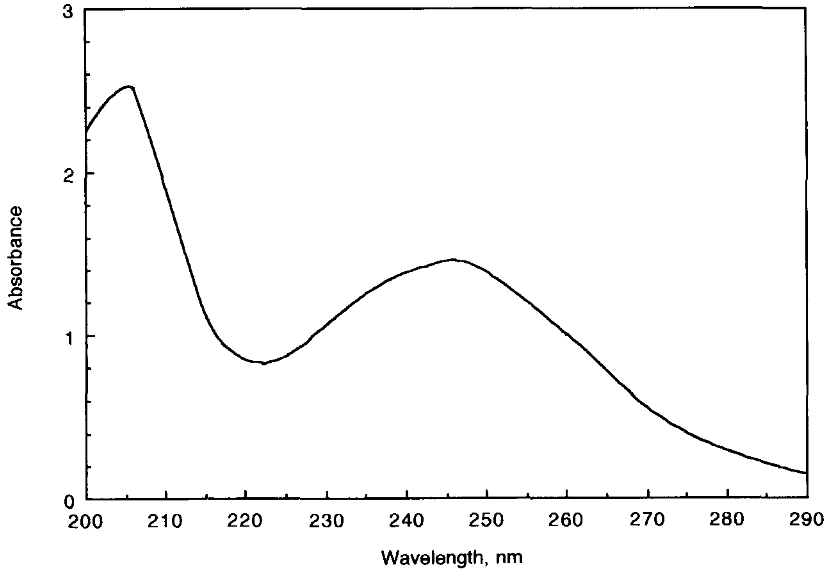


FIG. 7 Typical absorbance curve for 24 ppm biphenyl in heptane.

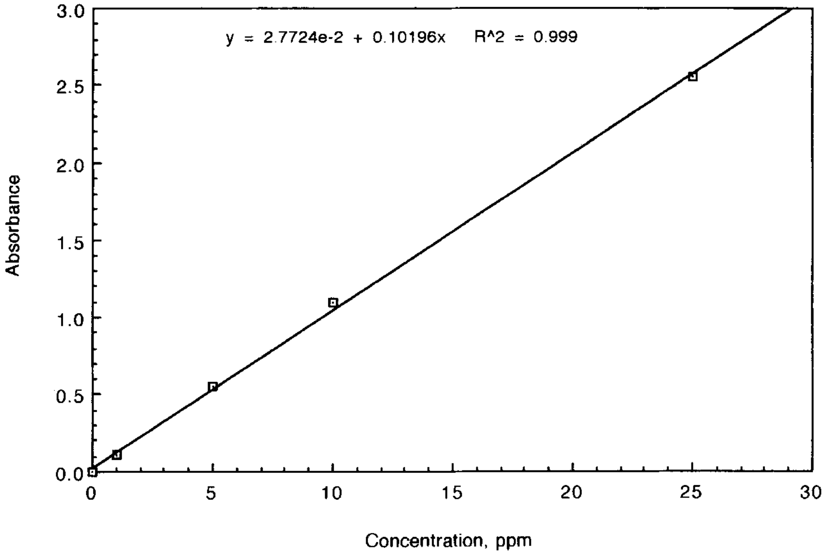


FIG. 8 Calibration curve for biphenyl in heptane with absorbance measured at 247 nm and used for analysis of SDS solutions from laboratory column and solvent extraction column tests.

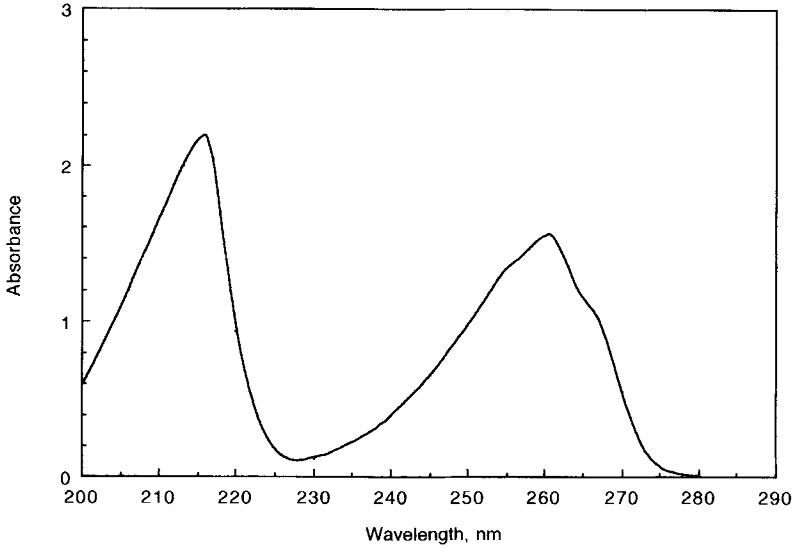


FIG. 9 Typical absorbance curve for 1000 ppm toluene in heptane.

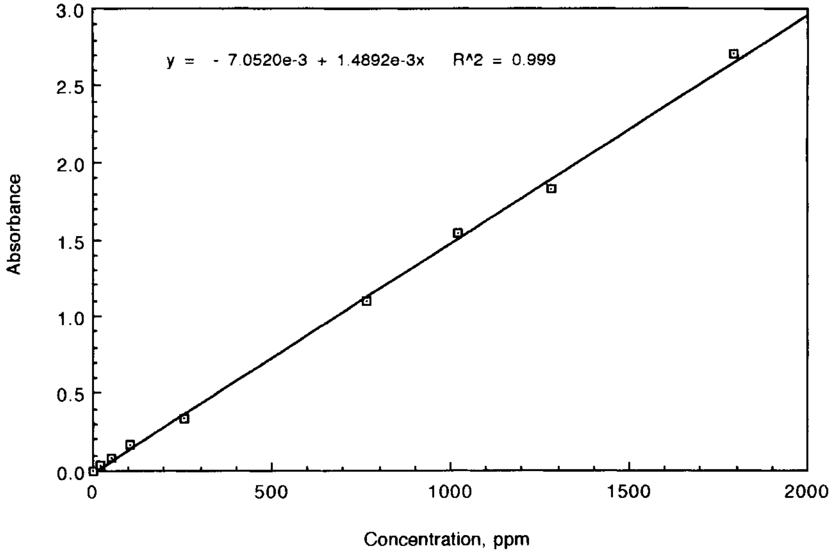


FIG. 10 Calibration curve for toluene in heptane with absorbance measured at 260 nm and used for analysis of SDS solutions from laboratory column test.

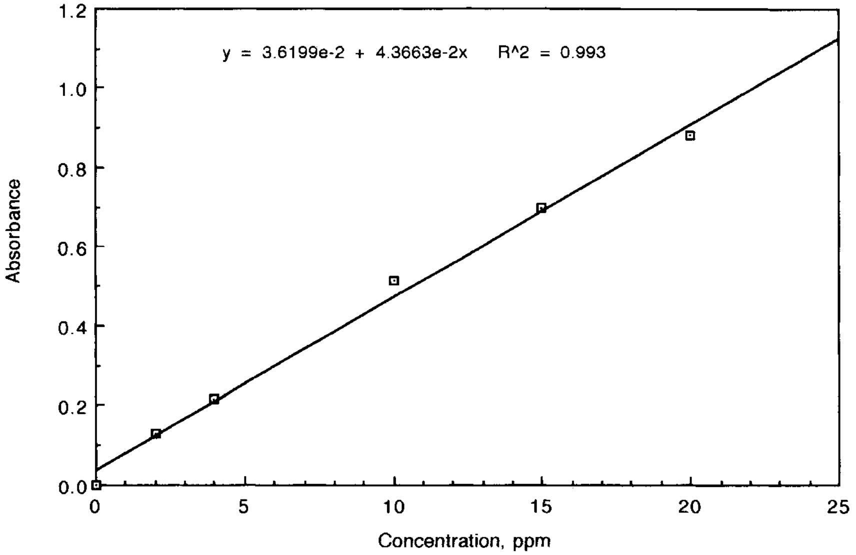


FIG. 11 Calibration curve for toluene in heptane with absorbance measured at 209 to 213 nm and used for analysis of SDS solutions from toluene test bed.

Testing and Evaluation of Process Components Related to the Removal of Nonvolatile Constituents

In order to be time and cost effective, as well as to minimize the waste generated, the laboratory column effluents generated during the development of the UV spectrophotometric analytical method were used as the source of SDS test solution containing the nonvolatile constituent (biphenyl) for the pilot-scale system testing. The effluent was generated from the soil/sand mix columns. The solution (approximately 8 liters) was then used to test the ability of the pilot-scale solvent extraction column to extract the biphenyl into the solvent (i.e., heptane) phase. The heptane (with biphenyl) was then treated in the solvent recovery system (a specially adapted still). The recovered surfactant solution was also treated by the hyperfiltration unit to assess its performance and see if there were any unanticipated problems.

The concentrated surfactant solution and the permeate water generated by the hyperfiltration process were recombined to reconstitute the original surfactant dilution. This recovered surfactant solution was then reapplied to another set of biphenyl-spiked soil columns and the removal efficiency monitored. Similarly, the purified heptane was reused in the solvent extraction column.

Collection of Test Surfactant Solution. The effluent (containing biphenyl) from six laboratory columns was collected and stored in closed amber glass jars. This volume was obtained from approximately 10 pore volumes passing through columns which had initially contained 1000 mg/kg biphenyl. The average biphenyl concentration of the combined effluents was 324 ppm. The average final residual concentration of biphenyl in the column soils was between 0 and 10 ppm for seven pore volumes removed (99% reduction without optimization). This final residual concentration is based on the total mass removed by the surfactant solution, not on a final analysis of soil for biphenyl.

Solvent Recovery System Testing. The solvent recovery system was tested by distilling heptane solvent that was recovered from the solvent extraction column following feed cycle testing. A total of 11.2 L heptane containing 157 ppm biphenyl was placed in the boiling chamber of the solvent recovery system. The chamber was sealed and the power was turned on with the oil bath thermostat set at 135°C (275°F) and the cooling water flow to the condenser set at 1.26 L/min (20 gph). During the test, a maximum condensation recovery rate of 142 mL/min was achieved.

Hyperfiltration Unit Testing

The ability of the hyperfiltration unit to reject excess water while retaining and concentrating SDS was demonstrated using recycled surfactant from the solvent extraction column testing. The unit was tested by pumping the recycled SDS solution from a tank through the hyperfiltration housing at a rate of 14 L/min and a pressure of 1034 kPa (150 psi) and returning the concentrate to the same tank. Water permeate was removed from the aqueous SDS at an average rate of 305 mL/min during the test, which was completed after 40.8 minutes.

Air-Stripping Column Testing

The air stripping column was tested several times with SDS solution that contained toluene. During each test, the air and SDS solution flow rates were established and product SDS solution samples were taken and analyzed for toluene until steady-state operation of the air-stripping column was approached. Air-stripping column performance results were calculated from the data nearest steady state and are presented in Table 4 for five different tests that were conducted. Tests 1, 2, and 3 were conducted using virgin 25 g/L SDS solution spiked with toluene. Tests 4 and 5 were conducted using SDS solution of like concentration that had been passed through a 29.3-kg (65 pound) soil test bed that contained 3000 ppm toluene (based on 29.3 kg dry weight of soil). Air flow rates ranged from 100 to 250 L/min while the SDS solution flow ranged from 200 to 500 mL/min.

The performance of the pilot-scale unit in removing VOCs from soil was evaluated by flushing 25 g/L SDS solution through soil spiked with 3000 ppm toluene, recovering the product SDS solution from the soil, using the air-stripping column to remove toluene from the SDS solution, and then recycling the stripped SDS solution back to the soil test bed as the feed surfactant. No other components of the pilot-scale unit were needed because toluene was the only "contaminant." The test bed of soil

TABLE 4
Air-Stripping Column Test Results—Phase I

	Virgin SDS solution spiked with toluene			SDS solution from soil bed containing toluene	
	Test 1	Test 2	Test 3	Test 4	Test 5
Air flow (L/min)	100	200	250	250	200
SDS solution flow (mL/min)	500	200	250	250	200
Toluene data:					
Concentration in (ppm)	2400	2160	1630	1080	26
Concentration out (ppm)	900	290	280	250	3
Percent removal	63	87	83	77	88

was prepared from 29.3 kg (65 pounds) of the standard soil mixture which had been screened and mixed according to procedures established in the previous column studies. The soil mixture was divided into three equal portions. The first portion was placed in the test bed container, and 50 mL toluene was evenly distributed over the soil surface. A second portion of soil was quickly added, and another 50 mL toluene was added in like manner. The final portion of soil was added, and the container was tightly covered with aluminum foil to prevent toluene loss. Virgin or fresh 25 g/L SDS solution was added to the test bed about 65 hours later; the soil remained covered with a layer of SDS solution almost continuously throughout the test period to minimize any toluene losses due to volatilization. The density of the test bed after settling was 1.14 g/cm^3 with an estimated pore volume of 6207 cm^3. (The pore volume was estimated at 24% of the total volume occupied by the soil based upon the average percent of total volume that was determined for the soil columns studies.)

Although the test was conducted over a 10-day period, the actual run time in which SDS solution was moved through the soil test bed was only 27 hours. Figure 12 shows the recovered SDS product flow rate as a function of actual run time; down times in which there was no product flow are shown at the top of the graph. In general there were three average flow rates: 244 mL/min for the first 4.7 hours run time, 200 mL/min through 18.4 hours run time, and 100 mL/min through 27.1 hours run time, at

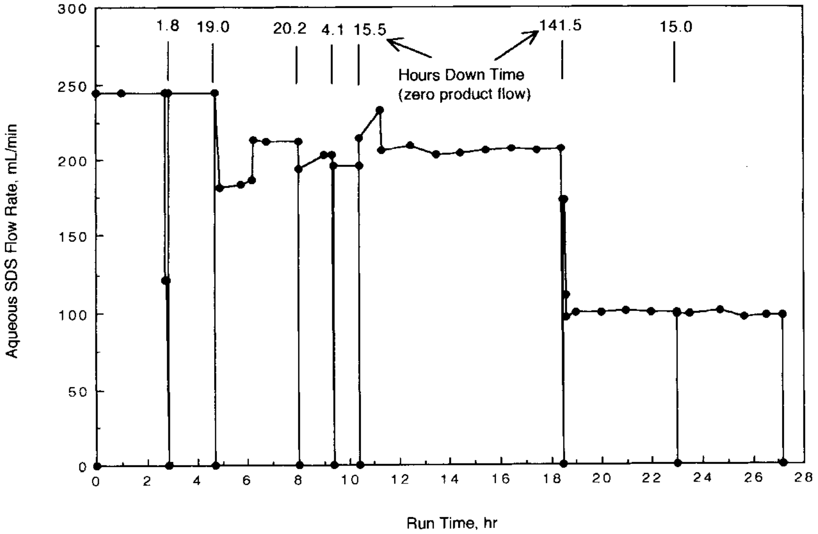


FIG. 12 Pilot-scale toluene removal test: Aqueous SDS flow rate through soil test bed.

TABLE 5
SDS Feed Data for Pilot-Scale Toluene Removal Test

SDS feed	Run time, (h)	Elapsed time, (h)	Number of pore volumes	Total volume (L)
Virgin	0–2.9	2.9	0–6.8	42.2
Recycled	2.9–18.5	15.6	6.8–38.2	194.9
Virgin	18.5–27.2	8.7	38.2–46.7	52.8

which point the test was discontinued. These flows were controlled by the product recovery pump setting.

The run times, pore volumes, and total volumes of virgin and recycled SDS solutions are summarized in Table 5. The addition of virgin SDS solution at the end of the test was necessary because the concentration of toluene in the feed approximately equaled the concentration in the product toward the end of the addition of the recycled SDS solution. If the air-stripping column efficiency were improved by providing a longer SDS solution residence time and/or by multiple passes of the SDS product stream, the addition of virgin SDS solution may not have been necessary.

Foaming within the air-stripping column occurred when recovered SDS solution was used that had been passed through the soil bed containing toluene. The air-stripping column completely filled with foam after processing a total of 61.5 L aqueous SDS solution. The foam slowly started to collect in the air-stripping column discharge cone, and once it had built up to a sufficient level, the upward air flow pushed it rapidly up the column to the top of the packing, totally blocking the column air pathways. At this point, the air-stripping column had to be shut down. This problem was effectively dealt with by adding about 20 ppm of an antifoam agent to the SDS solution being fed to the air-stripping column. A total of 96 L aqueous SDS solution was effectively treated by the air-stripping column without any process-limiting foaming once the antifoam agent was used. The antifoam agent was AF 9020 by General Electric. No attempt was made to optimize the antifoam concentration or to test other antifoam agents.

RESULTS

Results from UV Spectrophotometric Analytical Method

The precision of the UV spectrophotometric procedure was evaluated by analyzing duplicates of variously selected samples. Results for duplicate samples containing biphenyl were typically within 5% of each other. For the most part, two extractions were adequate to recover the great bulk of the biphenyl. Several samples were extracted three times as proof of this. The third extraction accounted for an average of less than 5% of the total mass of biphenyl estimated.

The accuracy of this procedure was evaluated by Eckenfelder Inc.'s Analytical and Testing Services Division using USEPA Method 8015 with a gas chromatograph/flame ionization detector (GC/FID) in which duplicate aqueous surfactant samples containing biphenyl or toluene were injected directly onto the GC column. Figure 13 illustrates the correlation between UV spectrophotometric data and GC/FID data. Correlation of the analytical results was better for the biphenyl-containing samples than for the more volatile toluene-containing samples. This difference was anticipated because of the inherent problems associated with toluene analysis in general in the UV analytical procedure since there is no way to perform the procedure with zero headspace. Table 6 summarizes the results of the toluene reproducibility testing by comparison of UV spectrophotometry data and GC/FID data.

Results from Solvent Extraction Column Testing to Remove Nonvolatile Constituents

The SDS solution containing biphenyl was processed through the solvent extraction column four times (feed cycles 1, 2, 3, and 4) in order to

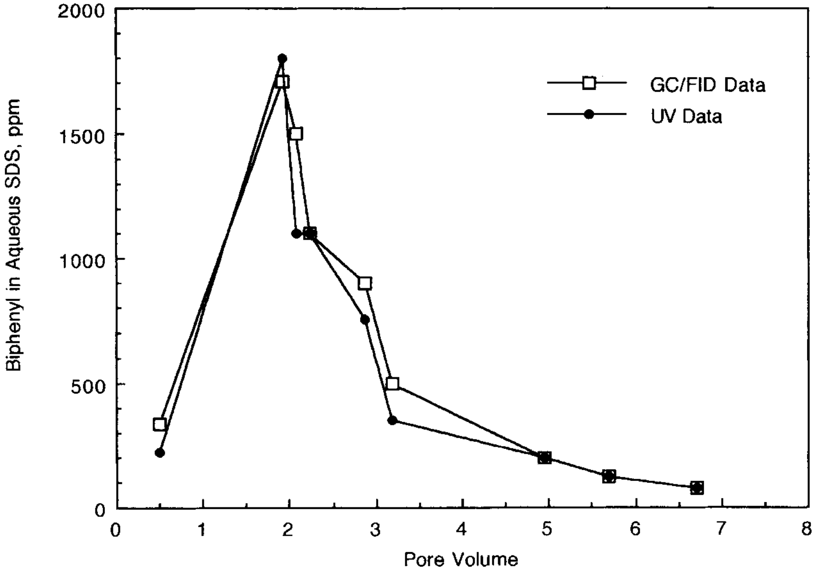


FIG. 13 Comparison of UV spectrophotometric data and GC/FID data for biphenyl analysis of effluent from column 16 (initial biphenyl concentration in soil was approximately 1000 mg/kg).

TABLE 6
Summary of Results from Analysis of SDS Solutions Containing Toluene by Comparison of UV Spectrophotometry Data and GC/FID Data

Sample[a]	Toluene concentration (mg/L)	
	UV spectrophotometry[b]	GC/FID[c]
ASF-04D	890	850
ASF-15D	39	26
SF-15D	3.5	3.0
SP-03D	2900	4500
SP-39D	12	9.9

[a] Samples are all SDS solution with toluene from Phase I pilot-scale testing with toluene soil test bed. ASF was the designation for air-stripping column feed. SF was the designation for recycled SDS solution feed to the soil test bed. SP was the designation for SDS solution product from the air-stripping column.

[b] Calibration curve for concentrations greater than 100 ppm is given in Fig. 10; calibration curve for concentrations less than 50 ppm is given in Fig. 11. Concentrations greater than 25 ppm and less than 100 ppm were quantified by extrapolation of the curve in Fig. 11.

[c] Analysis by USEPA Method 8015 with a method detection limit of 1.0 mg/L.

obtain a high overall biphenyl removal. Fresh heptane solvent was used during feed cycle 1. During feed cycles 2, 3, and 4, the solvent recovery system was operated to remove and concentrate the extracted biphenyl from the heptane, and the recycled heptane was used.

Figure 14 shows the aqueous biphenyl concentrations in the SDS feed to the solvent extraction column and in the SDS product from the solvent extraction column during feed cycle 1. As can be seen, the column was approaching steady-state operations at about 0.7 hour run time, and the overall biphenyl removal efficiency was 67%. Column operating parameters for feed cycle 1 were as follows:

Initial biphenyl concentration	324	ppm
SDS feed rate to column	155	mL/min (average)
SDS residence time in column	~20	min
Heptane solvent rate to column	141	mL/min (average)
Plate reciprocation rate	25	cycles/min
Final biphenyl concentration (SDS solution)	57	ppm (composite of product)

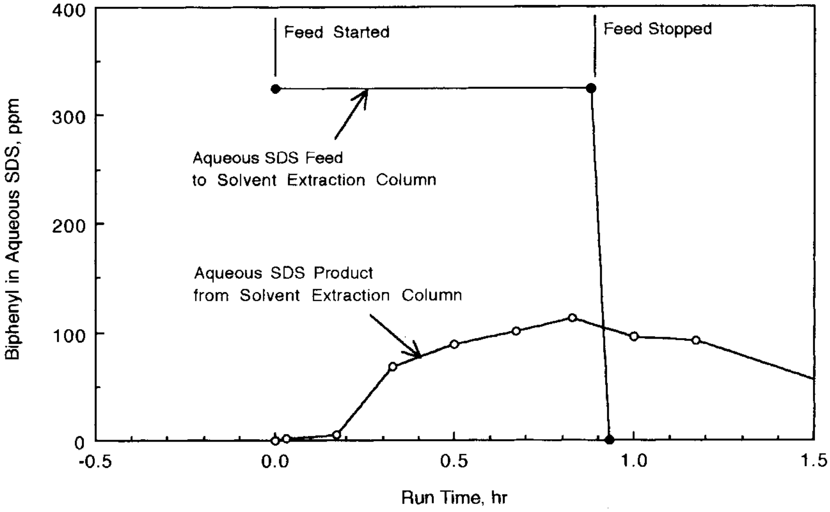


FIG. 14 Solvent extraction column test: Feed cycle 1 (virgin heptane).

The SDS/biphenyl product from the solvent extraction column was recycled three additional times consecutively through the column at a reduced flow rate (target of 100 mL/min). Figure 15 presents the solvent extraction column SDS feed and product biphenyl concentrations for feed cycles 2, 3, and 4. The column operating parameters were as follows:

Initial biphenyl concentration (SDS solution)	57	ppm
SDS feed rate to column	100	mL/min (average)
SDS residence time in column	~30	min
Heptane solvent rate to column	100	mL/min (average)
Plate reciprocation rate	52	cycles/min, increased to 74 cycles/min at 2 hours run time
Final biphenyl concentration (SDS solution)	~5	ppm

Figure 15 illustrates that the extraction efficiency was high during feed cycle 2, and subsequently decreased with each successive feed cycle. Table 7 provides a summary of the biphenyl removal efficiencies for each feed cycle. The removal efficiency declined notably during feed cycle 4 as the overall biphenyl concentration in the SDS solution decreased. The

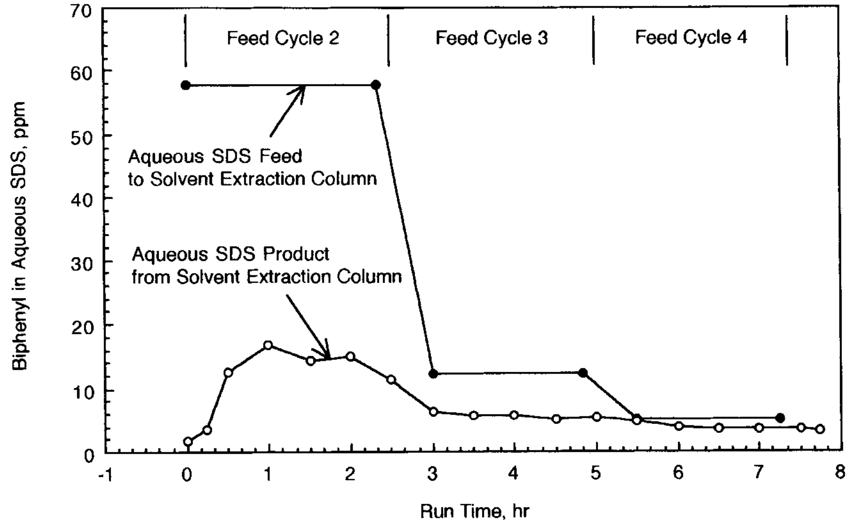


FIG. 15 Solvent extraction column test: Feed cycles 2, 3, and 4 (recycled heptane).

heptane solvent contained residual biphenyl from the solvent recovery step. The residual biphenyl in the heptane (~8 ppm) became proportionally higher as the biphenyl concentration in SDS decreased, therefore limiting the mass transfer of biphenyl from the SDS solution to the solvent. All four cycles combined resulted in an overall biphenyl removal efficiency of 98%.

Figure 16 shows the biphenyl concentrations in the heptane extract from the solvent extraction column and shows the heptane condensate concentration from the solvent recovery system for feed cycles 2, 3, and 4.

TABLE 7
Solvent Extraction Column Biphenyl Removal Efficiency

Feed cycle	Biphenyl mass (g)		Percent removal of biphenyl from SDS solution[a] (%)
	Feed	Product	
Cycle 1	2.626	0.861	67
Cycle 2	0.861	0.198	77
Cycle 3	0.198	0.082	59
Cycle 4	0.082	0.059	28

[a] An overall biphenyl removal efficiency of 98% was achieved by the end of cycle 4.

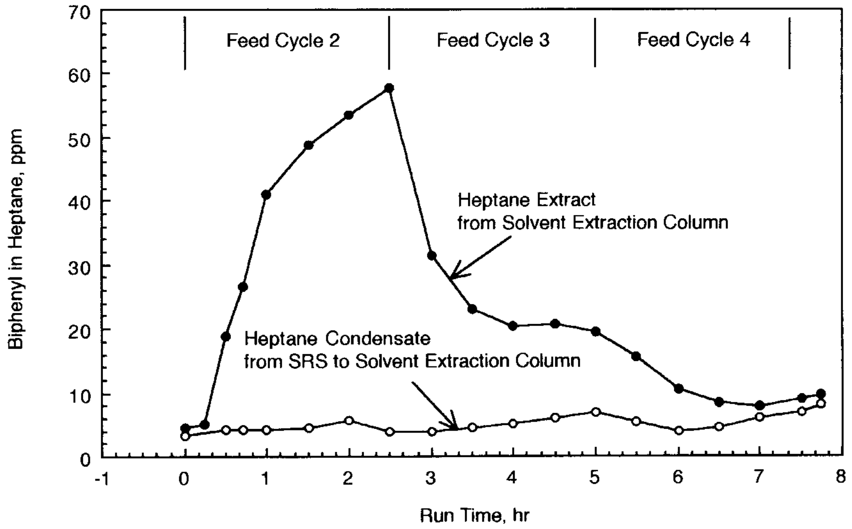


FIG. 16 Solvent extraction test: Feed cycles 2, 3, and 4.

During the fourth feed cycle, the concentration of biphenyl in the solvent recovery system had built up to the point that the heptane condensate had about 8 ppm biphenyl and the heptane extract from the solvent extraction column had about 10 ppm biphenyl. The biphenyl present in the heptane condensate from the solvent recovery system has a limiting effect on the biphenyl removal efficiency at lower biphenyl concentrations, as is evident from the removal efficiency data in Table 7.

Results from Hyperfiltration Unit

Figure 17 shows the volumes of water filtrate and SDS concentration versus run time. The water removal rate remained essentially constant throughout the test period and resulted in a 78% volume reduction of the SDS solution, which corresponds to an increase in SDS concentration of 4.5 times the original concentration. The SDS concentrate and water filtrate were both measured for conductivity as a function of run time. The results are plotted in Fig. 18. The conductivities of the SDS concentrate and water filtrate are used here to demonstrate that SDS was retained within the concentrate. As can be seen from Fig. 18 data, the SDS concentrate conductivity was about 50 to 70 times higher than that of the water filtrate, which indicated good retention of the SDS by the hyperfiltration membrane. The conductivity of the water filtrate ranged from 59 to 143

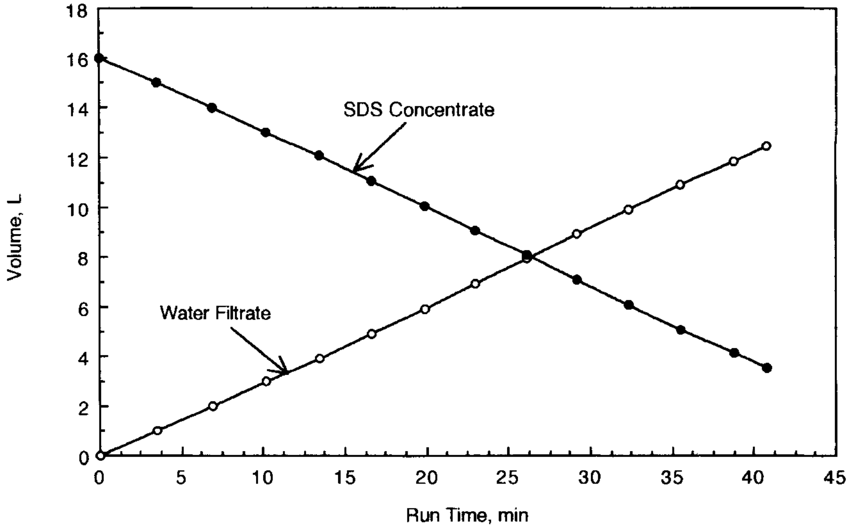


FIG. 17 Hyperfiltration unit test: Aqueous volumes.

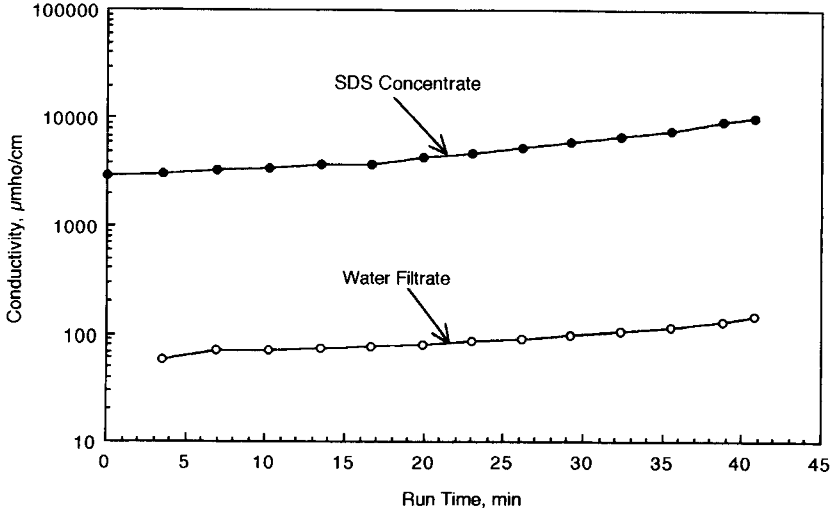


FIG. 18 Hyperfiltration unit test: Aqueous conductivities.

μmho/cm. This is lower than the conductivity of tap water (average of about 210 μmho/cm) which was used originally to make up the SDS surfactant solution.

The recycled surfactant produced by this test contained a small amount of residual biphenyl (about 4.9 ppm). The water filtrate was analyzed for biphenyl, and there was none detected (detection limit = 1 ppm), again indicating effective operation of the hyperfiltration unit.

Results from Solvent Recovery Testing

A total of 98.5% of the biphenyl was retained in the concentrated still bottoms following the test. The condensate volume collected was 8.1 L with a biphenyl concentration of 3.3 ppm. The concentrated still bottoms accounted for 3.1 L and contained 565 ppm biphenyl. During this test, the volume of the still bottoms was reduced by 72%. It is estimated that this could be improved to between 80 and 90% volume reduction after minor system adjustments are made.

Results from Air Stripping Testing

Despite the wide test ranges used in the experiment (see Table 4), the toluene removal efficiencies remained within a relatively narrow range of 63 to 88% (average 80% with standard deviation of 10%). The removal efficiency was not reduced with lower toluene concentrations, as indicated by the Test 5 data. These results indicate that with the high air flow rates tested (100 to 250 L/min) and with this particular column design, the removal of toluene may be diffusion limited. If this is correct, improved performance could be obtained by increasing the column height (and SDS solution residence time) or by passing the SDS solution through the column multiple times. The existing column is sufficiently overdesigned that the aqueous SDS film thickness and residence time are probably relatively constant for the SDS solution flow range tested, 200 to 500 mL/min.

The toluene concentration in the SDS product stream from the soil test bed is shown as a function of run time in Fig. 19 and as a function of the number of pore volumes through the test bed in Fig. 20. The spikes in the toluene concentration occurred when there was a cessation of flow through the test bed, which allowed more toluene to be solubilized in the SDS solution through desorption/diffusion mechanisms. Figure 19 also shows the concentration of toluene present in the recycled SDS solution from the air stripping column which was used as feed to the test bed during the middle portion of the test; the average concentration of toluene in the recycled SDS solution was 170 ppm (generally the concentration de-

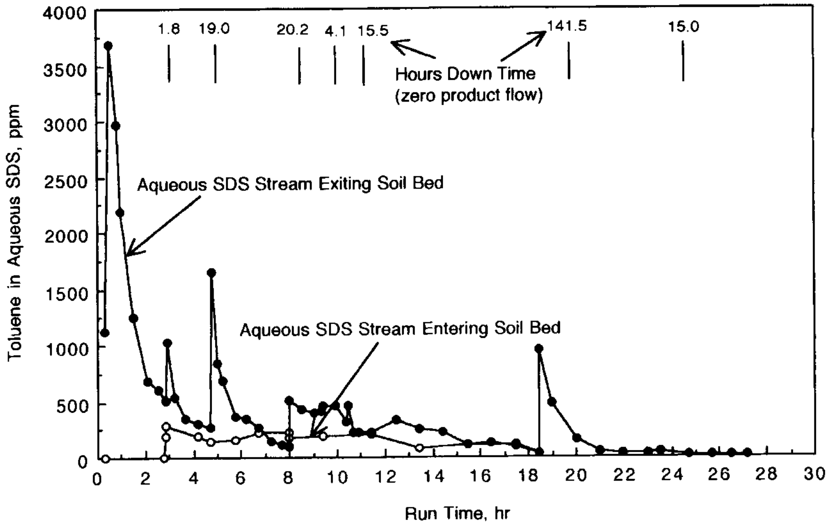


FIG. 19 Pilot-scale toluene removal test: Toluene concentration in aqueous SDS.

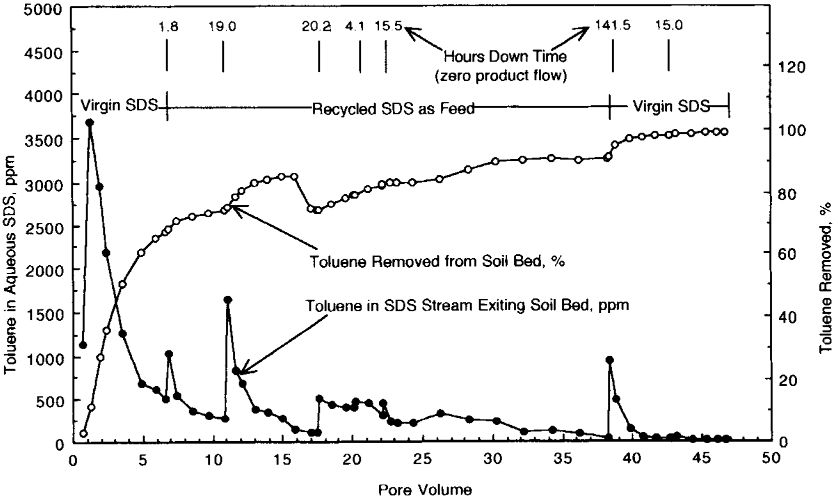


FIG. 20 Pilot-scale toluene removal test: Toluene removal from test bed.

creased with time). This acted to extend the cleanup time by reintroducing toluene back into the partially cleaned soil.

The percent of toluene removed from the soil test bed is also shown in Fig. 20. The toluene removed was calculated by subtracting the amount of toluene added to the soil test bed via the recycled SDS solution (shown in Fig. 19) from the amount of toluene in the SDS product stream from the test bed. Percent removal was then calculated by dividing the amount of toluene removed from the test bed by the total initial toluene in the soil test bed. For each point, flow rates and run times were included in the calculations.

SUMMARY AND CONCLUSIONS

A summary of the results from the treatment of the nonvolatile and volatile compounds in the recycle system is provided in Tables 8 and 9, respectively.

There was essentially no difference in the removal of biphenyl from soil using either virgin or recycled SDS solution (see Fig. 21). Also, there was

TABLE 8
Summary of Key Pilot-Scale Results from Phase I Treatment of Nonvolatile Compounds[a]

Testing component	Performance measure
Biphenyl removal from SDS solution by solvent extraction column:	
Removal per feed cycle	28 to 77%
Overall removal after four feed cycles	98%
Residual biphenyl in SDS solution after four feed cycles	~1 ppm
Biphenyl removal from heptane by solvent recovery system	98.5%
Biphenyl removal from laboratory column:[b]	
Removal using virgin SDS solution	90% (± 7%)
Removal using recycled SDS solution	94% (± 7%)
Hyperfiltration testing:	
Volume reduction factor	78%
Concentration factor	4.5
Initial conductivity of water used (average)	210 μmho/cm
Conductivity of water filtrate (range)	55–143 μmho/cm
Biphenyl concentration in SDS concentrate	4.9 ppm
Biphenyl concentration in water filtrate	BMDL[c]

[a] Test results represent performance under reasonable operating conditions and do not represent optimized operating conditions.

[b] Initial biphenyl concentration in soil: 1000 ppm.

[c] Below method detection limit of 1 ppm.

TABLE 9
Summary of Key Pilot-Scale Results from Treatment of Volatile Components[a] during Phase I Testing

Testing component	Performance measure
Toluene removal from soil in test bed:[b]	98%
Toluene removal from SDS solution by air-stripping column:	
Removal using virgin SDS solution	63 to 87%
Removal using recycled SDS solution	77 to 88%
Residual toluene in SDS solution (after air stripping)	~3 ppm

[a] Test results represent performance under reasonable operating conditions and do not represent optimized operating conditions.

[b] Initial toluene concentration in soil: 3000 ppm.

essentially no difference in the performance of recycled heptane compared to virgin heptane.

The air-stripping column averaged 80% removal per cycle of toluene from an SDS solution. The removal efficiency appeared independent of air or liquid flow rates and of initial toluene concentration and, therefore, may be diffusion limited. Use of the diffusion-limited model confirmed the suspicions. (See Table 10.) Air-stripping column efficiency could be improved by providing a larger residence time for the SDS solution and/or by providing multiple passes of the SDS solution through the column.

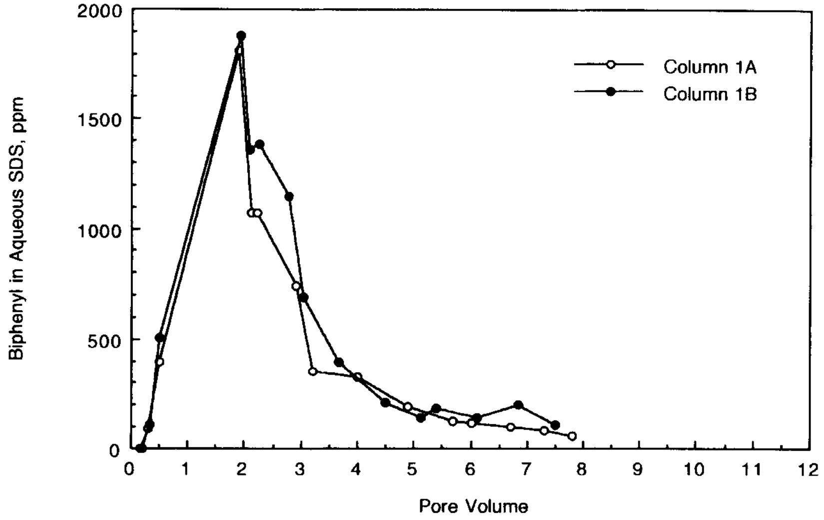
Foaming problems in the air-stripping column were overcome by the addition of an antifoam agent to the column SDS feed solution.

The air used in the column during Phase I was dry and below room temperature. This leads to evaporation and cooling inside the air-stripping

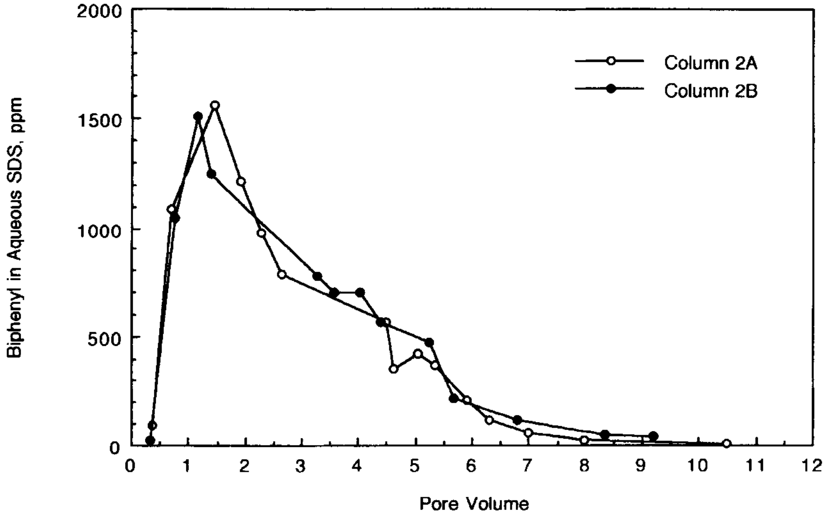
TABLE 10
Results of Modeling the Air Stripping of Toluene during Phase I Testing

Test number[a]	Experimental effluent concentration (mg/L)	Experimental percent removal	Modeled effluent concentration (mg/L)	Modeled percent removal
1	900	63	830	51
2	290	87	292	86
3	280	83	296	82
4	250	77	197	82
5	3	88	3.5	87

[a] See Table 4 for operating conditions.



a. Virgin Surfactant Solution



b. Recycled Surfactant Solution

FIG. 21 Recycled surfactant column test: Comparison of virgin and recycled surfactant for removal of biphenyl from soil.

column. Phase II incorporated design modifications to permit the air to be humidified (saturated) and warmed prior to contact with the SDS solution in the air-stripping column. Also, an antifoam agent was employed when necessary.

Given the temperature-related behavior of SDS solution (it thickens considerably below 20°C), a heating unit within the soil test bed container was incorporated into the Phase II design. The noncontact heating unit would maintain the soil temperatures above 20°C and preclude flow problems with the SDS solution.

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