Recovery of coal tar in 1-D column test using surfactant enhanced aquifer remediation (SEAR)

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Abstract

This paper presents the results of flow-through column testing using a new surfactant, Alfo–terra 123-8 PO sulfate, for the recovery of coal–tar from contaminated soil. Coal tar is a dense, non-aqueous phase liquid (DNAPL) that is difficult to recover due to its hydrophobic behavior and its high viscosity. Preliminary testing (phase behavior–batch tests) revealed a high degree of coal tar solubilization using a formulation of 12 wt.% Alfo–terra 123-8 PO sulfate surfactant, 4 wt.% secondary butanol, and 200 mg/L calcium chloride (as calcium). The formulation also exhibited rapid equilibration, without forming anisotropic gels. The column test was performed to verify compatibility of the formulation with the field-obtained DNAPL and soil. The column test was successful, resulting in low pressure drop, over 97 % coal tar recovery, with no visible gel formation nor any coal tar mobilized. This experiment showed good compatibility of the selected surfactant using field soil and field DNAPL, and should be studied further and considered for use in the field.

1 Introduction

Generally, coal tar is a by-product from operations at manufactured gas, gas purification, gas storage, gas distribution, and coke production facilities [1, 2]. Coal tar—a mixture of compounds—is a black, gooey, sludge-like material that smells like mothballs [1, 2]. Coal tar has proven difficult to remove from soil due to its hydrophobic behavior and its high viscosity. It dose not easily dissolve in water, yet there is concern for potential ground water contamination because the presence of poly aromatic hydrocarbons (PAHs) that make-up coal tar have been
linked to cancer. In the United States, coal–tar contaminated sites are found in such places as South Chattanooga, TN, Columbia, PA, Brooklyn, NY, Newport, NJ, and so on [3,4,5]. Currently, the most common remediation methods for coal tar contamination is pump and treat, solvent extraction, bioremediation, and excavation.

In this column experiment, the selected surfactant solution showed promise for the recovery of coal tar by virtue of solubilizing large quantities when mixed in test tubes and by the absence of viscous gels and other anisotropic behavior. However, before use in the field, the surfactant solution must be tested to ensure compatibility with the field soil as well. Therefore, it is important to note that this objective is accomplished by recording the pressure–drop across the column during the surfactant flood. The second indication of compatibility between surfactant solution, field coal tar, and field soil is found in the recovery profile of the surfactant flood. A high recovery percentage (around 100 %) is an indication of good compatibility.

2 Experimental Equipment and Material

2.1 Experimental Equipment

A Kimble–Kontes® Chromaflex chromatography column (model # 426870-2560), 2.5–cm diameter and 60–cm length, was used in the column experiment. An end piece (model # 426876-0025) with an adjustable bed length was used to keep soil confined after placement. During the flood, a fluid reservoir was used to hold injected fluids (de–aired water and surfactant solution). The reservoir was a 10–liter capacity and was custom–made of Plexiglass. The column set–up was made using Swagelok® valves fittings and tubing with Perforax® (PFA) tubing of 1/8–inch diameter, fittings and ferrules made of either nylon or stainless steel in the same size. A dual–action piston pump (model # AA 100-S made by Eldex) was used to inject fluids during the experiment. The pump is capable of delivering constant flow rates from 0.2 to 10.0 mL/min and 5000–psi maximum pressure. A fraction collector was assembled with the column set–up for the collecting samples at timed intervals during the surfactant flood experiment. The fraction collector (model # 68-3870-002) has a capacity of 144 tubes (13mm diameter), made by Instrument Specialties Company (ISCO). Corning® glass tubes with a 5–ml capacity and 13–mm diameter were used in the fraction collector.

The pressure drop between the injection and production points of the soil column was measured using a Cole–Parmer® pressure transducer (model # EW07354-22). This transducer uses a solid–state sensor to convert a 24–Volt DC excitation to a 20–mA current. Inside the transducer, a 150–Ohm and a 100–Ohm resistor are connected in series (total of 250–Ohm) between the output terminals and a voltage meter (Cat. No. 22-801 Digital Multimeter made by Radioshack®), measures the transducer response. A DC power supply of 24 Volts by an Omega (model # U24Y101) is used to excite the transducer. After the collecting the samples, a gas chromatograph, an Agilent (formerly Hewlett
Packard) 6890 series equipped with a flame ionization detector (FID), was used for analyzing sample concentration. An HP5 capillary column 30 m–long (diameter 0.32 mm) with a film thickness of 0.25μm was installed in the chromatograph.

2.2 Experimental Material

The surfactant formulation consisted of surfactant, calcium chloride, secondary butanol, and de–ionized water. Alfo–terra® 123-8 PO sulfate, made by Condea Vista Corporation, Austin, TX, was the surfactant used. It is a branched alcohol pro–poxylate sulfate sodium salt. Calcium chloride, made by Fisher Scientific Company, was used as the electrolyte. Secondary butanol, from Fisher Scientific Company, of 99 % purity was used in the surfactant solution as a co–solvent. The water de–ionizer was a Nanopure Infinity UV/Reverse Osmosis System (model # D8971/9011), made by Barnstead Thermolyne Corporation. In the osmosis system, the membrane rejected 93 % of monovalent ions, polyvalent ions, particles, microorganisms and dissolved organics; the UV system’s production rate was 18.0–MΩ-cm.

3 Experimental Method

3.1 Mixing Surfactant

Surfactant solutions were made on a percentage by weight basis as–received. Distinction must be made between surfactant concentrations that are reported on an “active” basis or “as received.” The column experiment was performed using a solution of 12 wt.% as received (4 wt.% active), 4 wt.% secondary butanol, 200 mg/L calcium chloride (as Ca). The surfactant solution was prepared using two solutions, one consisting of 40 mL secondary butanol with 200 mL water (de–ionized), and a second of 0.735 g calcium chloride in 200mL water. These two solutions were added to a 1L volumetric flask containing 133.3 g Alfo–terra surfactant, and water added to the 1–liter mark.

3.2 Column preparation

The glass column was jacketed and surfactant flood was performed at the aquifer temperature (17 °C) using a cold water bath. After weighing the dry, empty column set–up (including end pieces, tubing, and valves), it was packed with the field soil that was contaminated with field NAPL at a ratio of 0.05 g NAPL per 1 g soil. Before contaminating the soil, particles larger than No. 10 mesh and smaller than No. 200 mesh, including organic matter were removed. The end pieces were added and the column re–weighed. Each end piece had two screens—a 60–mesh toward the soil to prevent the movement of fines and then a 120–mesh screen to distribute flow uniformly across the column diameter. The dead volume of the end piece assembly was 2.7 mL.
Once the column was assembled and pressure-tested, it was water-saturated and re-weighed. The data was used to estimate the reduced pore volume of the pack before surfactant injection.

3.3 Surfactant flood

The initial surfactant injection rate was set to 2 mL/min, about 50 ft/day. After examination for any produced NAPL, the samples were covered with aluminum foil and refrigerated to prevent evaporation losses while awaiting GC analysis. GC analysis of the effluent samples was made to determine the concentration of coal tar, and calculate the total mass recovered. During the initial stage of the surfactant flood, pressure measurements were recorded every 2 minutes.

During the initial flood, a shut-in period was made after 5 pore volumes of surfactant were injected into the column. The initial flow rate was determined to be too high to reflect field conditions and there was concern that the contact time between the surfactant solution and the coal tar may be too short to allow the solubilization to reach equilibrium. The shut-in period allowed for greater contact time between surfactant solution and coal tar in order to determine whether equilibrium conditions were reached. After several weeks, the surfactant flood was re-started until complete recovery of the coal tar, 13.59 g, was attained. The new flow rate was 0.13 mL/min, about 3.5 ft/day, which reflects a flow rate that can be reasonably attained in the field. Using this slower flow rate, both sampling and pressure measurement intervals were increased to about 20 minutes. A total of 18.65 PV of surfactant were injected into the column.

After the column test, a water flood was performed to remove any remaining surfactant solution from the pack. Then, the column was re-weighed and the gravimetric data used to compute the mass of coal tar recovered. The column was then opened and the contents extruded into a beaker of methylene chloride. Since coal tar is completely soluble in methylene chloride, we hoped to extract any remaining coal tar from the soil. After stirring for 24 hours to allow any possible coal tar remaining in the soil to dissolve into the methylene chloride, an aliquot was analyzed by gas chromatography.

3.4 Gas Chromatograph analysis

An Agilent 6890 gas chromatograph with flame ionization detector (FID) was used to analyze effluent collected from the column. The GC was equipped with an HP5 capillary column that is 30–m long, 0.32–mm diameter, with a film thickness of 0.25 m. Since the coal tar is a mixture of hydrocarbons that results in several peaks when analyzing with a GC, one peak with a retention time of 4.996 minutes was used as an indicator compound. All coal tar measurements were reported using this indicator compound.
4 Results

4.1 Pressure drop as a function of volume produced

Before contaminating soil, a pressure drop of 0.9 psig was measured for the clean soil. During most of the surfactant flood, the pressure drop across the column remained low, below 2 psig; note that in Figure 1, the pressure drop rose sharply at 450 ml produced after the surfactant solution was shut–in. When the pumps were re–started, the pressure increased temporarily and quickly returned to normal. The final pressure drop across the column was 0.9 psig. This value is the same as the initial pressure drop measured for clean soil.

![Pressure Drop Profile of Surfactant Flood](image)

Figure 1: Pressure drop as function of volume produced (1PV = 89mL)

4.2 Visual observation

During the surfactant flood, no viscous nor anisotropic gels were observed. Also, the samples produced had some color (such as light orange, dark orange, brown, and dark brown). This color is probably related to the degree of solubilization of coal tar in the surfactant solution. The initial samples were light orange, similar to those from the water flood. Then, the samples darkened to brown, and the final sample color was again light orange. It appears that the darker colored samples high concentration of coal tar and the lighter color sample had low concentration of coal tar.

4.3 Coal tar recovery

The produced effluent was analyzed for coal tar and the concentration profile is plotted in Figure 2. The surfactant solution was shut–in after 5 pore volumes (450mL) produced. The surfactant flood was re–started after one month at a flow rate of 0.13 mL/min (3.5 ft/day), which was slower than the initial flow rate of 2 mL/min (50 ft/day). The slower flow rate allowed for longer contact time between surfactant solution and coal tar, and is more realistic of flow rates
attainable in the field. During the column experiment, the solubilization of coal tar was quite high coal tar but no coal tar was mobilized. The initial solubilization of coal tar was 30,000 mg/L, about 20 times greater than the aqueous solubility of coal tar. In Figure 2, note that after 5 pore volumes of surfactant flooding, the concentration of coal tar dropped from 30,000 mg/L; however, the concentration remained above 5,000 mg/L until 12 pore volumes. At this point, as can be seen in Figure 3, the recovery percentage was over 80%, or 13.59 g of coal tar recovered from the soil column. Finally, after 18.65 pore volumes of surfactant flooding, the cumulative recovery of coal tar was over 97%. After the surfactant flood was stopped, water was used to remove any surfactant solution and the column was re-weighed. Gravimetric data indicated that the remaining amount of coal tar was 0.5 g. Then, the remaining amount of coal tar in the soil column was checked using a methylene chloride extraction. The analysis of the methylene chloride indicated that less than 0.5 g of coal tar were remaining in the soil. Based the results of the methylene chloride extraction, the estimated coal tar recovery is 97%.

![Coal Tar Concentration History of Surfactant Flood](image)

Figure 2: Coal tar concentration as function of volume produced (1PV = 89 mL)
5 Conclusions

Based on the results obtained from this experimental study, the following conclusions can be drawn:

A. Pressure drop across the column were low, indicating good compatibility between the selected surfactant solution, the coal tar, and the field soil.

B. No viscous gels or other anisotropic behavior were noted in the produced effluent. These results indicate a suitable formulation for use in a pilot–scale test.

C. The formulation of 12 wt. % surfactant, 4 wt. % secondary butanol, 200 mg/L calcium chloride (as calcium) performed well in the flow–through column test: 1) coal tar was not mobilized, 2) the solubilization of coal tar in the effluent was quite high, initially about 30,000 mg/L (about 20 times the aqueous solubility of the coal tar), 3) pressure drop was low, usually less than 1 psig.

D. The total recovery percentage of coal tar was high, about 97 %, using 18.65 pore volume of surfactant solution. This result leads to the conclusion that the use of Alfo–terra 123-8 PO sulfate surfactant® solution could be an aid in recovering coal tar in the field when compared to a pump–and–treat approach using only water.

The formulation of 12 wt. % surfactant (as received), 4 wt. % secondary butanol, 200 mg/L calcium chloride (as calcium) solution had high solubilization capacity for coal tar in the field soil and good compatibility with coal tar. In the future, an experiment with a surfactant formulation designed to solubilize higher amounts of coal tar will be performed. If successful, this future column
experiment would recover the DNAPL with fewer pore volumes of throughput, making the field application of this surfactant more economically attractive.

6 References