SHORT COMMUNICATION

SEPARATION OF OIL CONTAMINANTS BY SURFACTANT-AIDED FOAM FRACTIONATION

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Abstract – The separation of oily contaminants out of aqueous/non-aqueous phases using foam fractionation with a surfactant was investigated. In the separation of the light oil (hexadecane), the eluted amount of oil and the o/w (oil/water) ratio increased with the weight percentage of SDS (sodium dodecyl sulfate); and the ratio actually remained the same above the CMC (critical micelle concentration) point (0.23 wt% of SDS). Most of the oil was eluted even at 49:1 initial o/w ratio with the surfactant. For the heavy oil (carbon tetrachloride), the eluted o/w ratio and the oil recovery had maxima at 0.05 and 0.1 wt% of SDS solution, respectively, even though the overall recovery of 20-30% was much lower than that of 80-100% in the light oil. It was speculated that emulsion formation might affect oil entrapment in the foams. Higher gas flow rates, in general, increased the oil recovery, but did not increase the o/w ratio in the effluents.

Key words : Foam Fractionation, NAPL Separation, Surfactant

INTRODUCTION

Groundwater or soil near manufacturing industries is apt to be contaminated with waste solvents and hydrocarbon which are called NAPL (non-aqueous phase liquid). If it is lighter than water, NAPL is classified into LNAPL, and DNAPL if it is heavier than water. For decades stripping or sparging of air has been frequently used for remediation of soil and/ or groundwater with removal of VOC's and toxic organic chemicals [Valsaraj et al., 1992; Norris and Matthews, 1994]. Peters et al. [1996] have shown that low air flow followed by foaming with an surface active agent can provide an alternative cure to the removal of NAPL's in the groundwater wells.

Foam separation, which is characterized as a low cost process, has been developed for decades to separate heavy metal, enzymes, surfactants, biological polymer, etc. [Charm et al., 1966; Rubin et al., 1970; Sarkar et al., 1987]. Foaming in underground wells removes the hydrocarbon or oil phase out of two immiscible phases physically. Firstly, the oil phase is solubilized into the water phase with surfactants; then it is migrated to the interfaces to form emulsion or microemulsion due to low interfacial tension [Pennell et al., 1993; McDermott et al., 1989; Park et al.,, 1997]. Secondly, foams formed continuously by gas injection entrap a certain portion of oil phase along with water phase, and they are withdrawn out of the mixture phases. Since gravity and stability of the foams

control the whole process, the separation is known to depend on wall characteristics of the foam pathway, composition of the mixture liquid, and physical properties of the liquid such as specific gravity and viscosity [Bhakta and Ruckenstein, 1997; Narsimhan and Ruckenstein, 1986; Pennell et al., 1993]. Similar examples are found in surfactant-based oil recovery processes, which have been widely used to recover petroleum oil trapped among the rocks. They are, however, focused on solubilization of the oil phase and pumping rather than foaming [Davis, 1994; Eicke et al., 1996; Peters et al., 1992; Oh et al., 1987].

In this paper we present the results of foaming through aqueous/surfactant/non-aqueous phases in a glass column in order to show its ability of oil removal and selective separation (oil/water ratio, abbreviated as o/w). Low operation cost (without pumping) and high selectivity are expected as potential advantages.

EXPERIMENTS

1. Materials and Apparatus

n-Hexadecane (purity, 99%; sp. gravity, 0.77; Sigma Chemical), carbon tetrachloride (>96%; sp. gravity, 1.59; Kanto Chemical), and triple distilled water were used for all the experiments. To activate foams, sodium dodecyl sulfate (SDS, 99% of purity; Sigma Chemical) was used in the range of 0.05-0.3 wt%, whereas critical micelle concentration (CMC) of SDS is 0.23 wt%.

A Pyrex glass column (ID, 18 mm; 220 mm long) equipped with a foam collector was set up for experiments that mimic a field remediation as shown in Fig. 1. For bubble generation, compressed gas (nitrogen) was injected from the bot-

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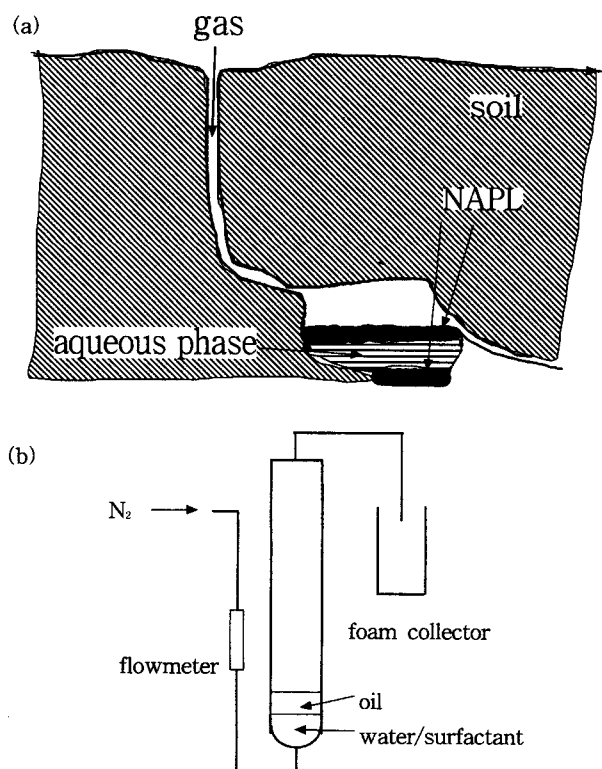
(a)

(b)

Fig. 1. (a) Schematic of a field well contaminated with NAPLs. (b) Laboratory scale experimental setup.

tom of the column (bubbling inlet diameter, 2 mm) through a flowmeter at ambient condition.

2. Experimental Method

n-Hexadecane was chosen as a model compound for LNAPL (light non-aqueous phase liquid) separation. Carbon tetrachloride as one of the heaviest oil (sp. gravity, 1.59) was used for DNAPL (dense non-aqueous phase liquid) separation. A mixture of hexadecane and an SDS solution or a mixture of CCl_4 and an SDS solution was placed without stirring in the column. With N_2 gas injected through the column, foams were generated from the surface of the lighter liquid, and it was collected in a vial for 5 min. Gas flow rate (Gv) was changed from 1.0 to 4.0 ml/s. The volumes of oil in collected samples were measured within 25 μl error using water-soluble black ink (as indicator of water phase). In some cases, the volumes of oil/water were measured after a long time (1 h or so) or all the mixture was eluted.

RESULTS AND DISCUSSION

1. Separation of LNAPL

1-1. Effect of SDS, an Ionic Surfactant

Two milliliters of hexadecane and three milliliters of SDS-aqueous solution were placed in the vertical column. N_2 was blown at 1.5 ml/s for 5 min. The concentrations of SDS solution were 0.05 to 0.3 wt%. Initial foaming was unstable for a short time (about 10-50 s), resulting in collapse during the growth. This tendency was pronounced with lower concentration of SDS solution, which indicates dispersion of the surfactant in oil phase was not as good as that in aqueous phase
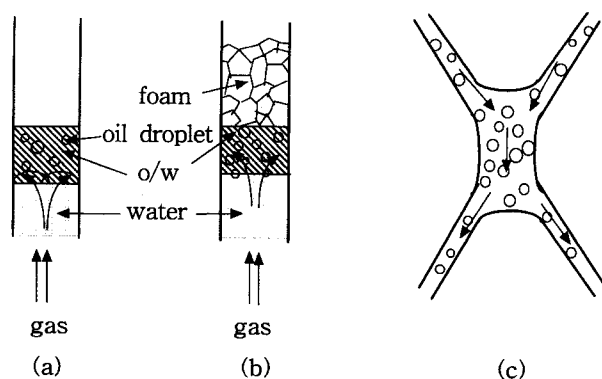
Fig. 2. An illustration for oil elution process by foaming: (a) formation of oil droplets by water intrusion, (b) foam formation and growing, (c) oil in water entrapped inside the plateau borders (arrow indicates direction of the drainage).
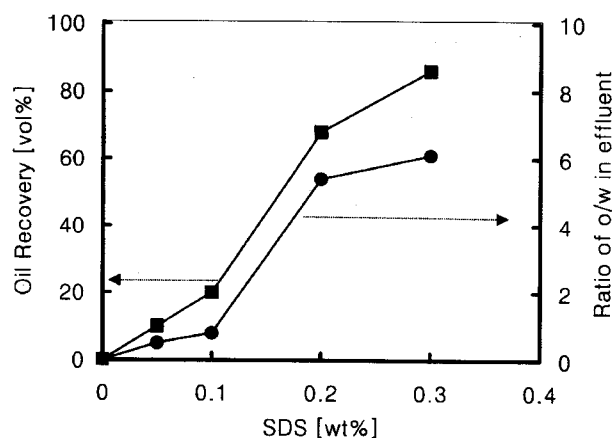

Fig. 3. Oil recovery and o/w ratio in effluents for LNAPL with different SDS concentrations (Gv=1.5 ml/s, initial o/w= 2/3 (v/v), and total volume of the mixture=5 ml).

due to temporarily incomplete mixing by gas. After the short induction periods, bubbling caused emulsion (oil droplets trapped in water phase) due to mature mixing followed by foam growing and drainage as illustrated in Fig. 2. The oil recovery and the oil/water ratio in the effluents were plotted in Fig. 3. This figure shows the positive effect of the surfactant on increase in selectivity and amount of oil recovered. As the SDS concentration approaches near the CMC (0.23 wt%), the oil recovery ratio soars drastically. This implies that a sufficient amount of the surfactant keeps the foams stable with suppressed drainage of the dispersed phase (oil) in the foam plateau.

1-2. Effect of Gas Flow Rate

Gas flow needs to be maintained above the minimum for entrapping oil and water in form of foam against gravity. At Gv<0.2 no effluent was observed. As shown in Fig. 4, the total effluent increased as gas flow rate became higher. The highest ratio of oil/water in the effluent was found at Gv= 1.5 ml/s.

1-3. Initial Volume Ratio of Hexadecane/Water

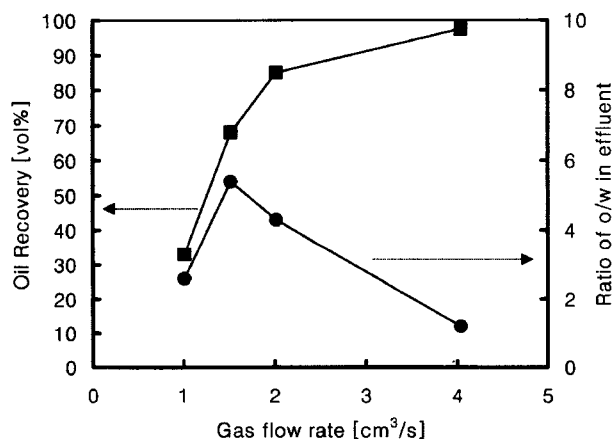The initial volume ratio of oil/water did not affect foam

Fig. 4. Oil recovery and o/w ratio in effluents for LNAPL with different gas flow rates (0.2 wt% of SDS solution, initial o/w=2/3 (v/v), and total volume of the mixture=5 ml).

Table 1. Compositions of effluents by foaming with various initial oil/water ratios for hexadecane (0.2 wt% of SDS solution, Gv=1.5 ml/s, total volume=5 ml)

Initial oil/water ratio (v:v)	Amount of SDS (g)	Ratio and volume (μl) of oil/water in effluent	Oil recovery (%)
4:1	0.002 (0.2 wt%)	6.3 (2250/355)	56
4.9:0.1	0.0002 (0.2 wt%)	none	0
4.9:0.1	0.002 (2.0 wt%)	1.0 (150/150)	4

generation and oil recovery rate while it was kept above 20 %. However, ten percent reduction of the initial water content greatly lowered foam generation and oil recovery rate as shown in Table 1. There also could be a minimum of water content in order to erect and support the polyhedral structure of the foams. This is only true if the surfactant is sufficient enough to stabilize the foams (Table 1).

2. Separation of DNAPL

2-1. Effect of SDS and Gas Flow Rate

Heavy oil like carbon tetrachloride is hard to be entrained by gas because of its large gravity effect (specific gravity is about 1.6). Therefore, the oil resides beneath the water layer. Since most of the water-soluble surfactant exists in the upper aqueous phase, gas blowing may not be so effective in mixing as well as in stabilizing foams in comparison with that of the light oil 'removal. Moreover, increased oil drainage leads to rapid collapse of the foam bed.

The effect of SDS appeared in two different ways as shown in Fig. 5. At lower SDS concentrations the o/w ratio from the effluents was unexpectedly high, whereas the ratio was uniformly kept low at higher SDS concentrations of 0.2 or greater. This unusual finding is probably due to reduction in oil drop size of the formed emulsion. The more surfactant is added, the finer the emulsion oil droplets become. It is also well known that oil and water entrapped in the plateau borders between foams are fairly stabilized with sufficient emulsifiers [Barnes, 1994]. In other words, the foams did not rupture or coalesce. Since the droplets are still heavy enough not
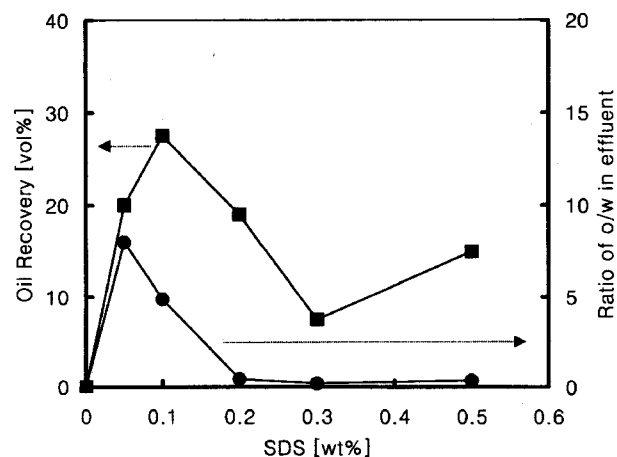

Fig. 5. Oil recovery and o/w ratio in effluents for DNAPL with different SDS concentrations (Gv=2.0 ml/s, initial o/w= 2/3 (v/v), and total volume of the mixture=5 ml).
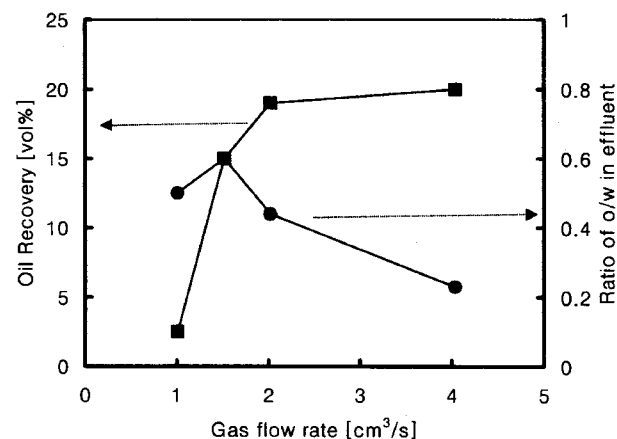

Fig. 6. Oil recovery and o/w ratio in effluents for DNAPL with different gas flow rates (0.2 wt% of SDS solution, initial o/w=2/3 (v/v), and total volume of the mixture=5 ml).

Table 2. Effect on oil removal with increase in surfactant concentration and gas flow rate for both NAPLs

Oil phase	Gas flowrate (ml/s)	SDS %	Ratio and volume (μl) of oil/water in effluent	Oil recovery (%)
LNAPL	0.75	0.1	0.8 (400/500)	20
	1.0	0.2	4.3 (1700/400)	85
DNAPL	0.75	0.1	2.2 (225/100)	11
	1.0	0.2	0.44 (375/850)	19

to be easily entrained by gas, the foams overloaded with many of the finer droplets tend to experience fast collapse caused by a large drainage through the plateau borders during entrainment. This strengthened drainage unavoidably accelerates destruction of newly formed foams. In a long-term operation of 1.5 h at 0.1 wt% of SDS (data not shown), total oil recovery was improved as much as 82 %, but the oil/water ratio was reduced to 1.4. With different gas flow rates the oil removal in the effluent remained as low as 20 % or less and

the maximum oil/water ratio was 0.6, respectively (Fig. 6). The trend was very similar to that of LNAPL shown in Fig. 4, but the values were much lower.

Table 2 compares oil removals for both LNAPL and DNAPL with different SDS concentrations and gas velocities. Increases in SDS content and gas flow rate brought in additively higher oil separation and recovery for the LNAPL mixtures. The data for DNAPL, however, suggests the possibility of low operation cost despite the low recovery.

CONCLUSIONS

Four main results to be pointed out in this work are that: i) there was an optimum concentration of SDS solution for each oil (hexadecane and carbon tetrachloride) to be eluted with the best o/w ratio; ii) for the CCl_4/H_2O system, the absolute amount of the eluted oil as well as the o/w ratio decreased as the SDS concentration increased above the CMC, which indicates that oil entrapment of the foams is closely related to the characteristics of the o/w emulsion formed during bubbling; iii) the light oil was successfully recovered even with a small amount of water (initially o/w=49) when the surfactant was sufficiently added in the aqueous phase; and iv) with increased gas flow rates the accumulated amount of oil increased, but its rate gradually decreased regardless of SDS concentration and the kind of oil.

The o/w ratio and the amounts of elution for the heavy oil were found to be low, whereas those for the light oil remained high in a practical sense.

NOMENCLATURE

Gv: gas flow rate [ml/s]

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