

Design of surfactant foam flood for NAPL recovery from shallow subsurface

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Abstract

In this paper, the generation of foam using selected surfactant solutions was investigated in relation to the ability to create foam and its stability. The approach used to generate the foam *in-situ* consists of several cycles (7) of Surfactant-Alternating-Gas (SAG) until foam was observed. More specifically, the cycles were performed by injecting 0,25PV surfactant followed by 0,25PV of air. The pressure drop was used to compute the apparent viscosity. Results showed that the selected surfactant blend can be used to generate foam *in-situ* at a contaminated site.

During the flow experiment, no significant visible change of the sand pack was observed but an increase in the differential pressure was measured ($\Delta P=5$ psi) after two cycles. During the third cycle, foam was observed at the first quarter of the column and an additional increase in the differential pressure confirmed the creation of foam within the sand pack. Increases of the pressure drop through the cycles continued. The pressure drop was used to compute the apparent viscosity, which was ranged from 60 to 100cP from the 3rd to 7th cycle, respectively. Foam was collected from the column exit (after three days) as a proof of foam generation and to measure its stability.

Keywords: NAPLs, remediation, foam, surfactant.

1. Introduction

NAPL recovery efficiency is increased significantly with the use of surfactant solutions, which offer two mechanisms: (i) solubilisation and (ii) mobilization. The first relies on increasing the NAPL's apparent aqueous solubility as an enhancement to the commonly-used "pump-and-treat" method (P&T) and has been termed Surfactant Enhanced Aquifer Remediation (SEAR) (Mulligan *et al.*, 2001; NAVFAC, 2002; Sheng, 2011). The second mechanism is achieved by reducing NAPL/water interfacial tension, which allows the NAPL to become mobilize and be recovered faster than either P&T or SEAR. Careful design must be exercised, though, to control the NAPL movement so that it is captured by production wells (Kostarelos et al., 2013; Yoon et al., 2002).

Viscosifiers have been shown to mitigate potential viscous fingering, improve the horizontal sweep efficiency of injected solutions such as surfactants and thus improve overall field performance (Jones *et al.*, 2016). Surfactant foams have been studied for this purpose and have been gaining much attention for their use where large contrasts in permeabilities of the contaminated zone would lower vertical sweep efficiency; foams effectively block highly-permeable layers to deliver injected solutions to the target zone.

The generation of foam with surfactants in homogeneous porous media has attracted the attention of many researchers the last years. It is reported that foaming characteristics are influenced by surfactant concentration and presence of inorganic electrolytes (Yekeen et al., 2017). Generating foam in-situ and transportation of foam in porous media is affected by the microscale structure of pores and vugs (i.e. pore shape, size, connectivity, and distribution) (Ma et al., 2012). Studies regarding the stability and mobility of foam generated by gassolvent/surfactant mixtures under reservoir conditions showed that at a given temperature, foam stability of C_3H_8 foam increases as the surfactant concentration increases until reaching the effective surfactant concentration (effective CMC), above which foam stability remains constant (Wang and Li, 2016). Furthermore, the use of surfactant foam flushing for removal of DNAPLs from shallow soils recovered 34 to 60% of residual DNAPL (Maire and Fatin-Rouge, 2017). The combined use of foam/surfactant polymer (SP) flooding for carbon dioxideenhanced oil recovery (CO₂-EOR) has also been reported (Xu et al., 2017). Foam has been shown to improve reservoir sweep efficiency in gas-injection enhanced oil recovery projects (Hirasaki, 1989; Li et al., 2010). The application of foam in fractured reservoirs was investigated experimentally and the results showed that foam as a mobility-control agent resulted in significantly improved areal sweep and delayed gas breakthrough (Fernø et al., 2016)

In this paper, the generation of foam using selected surfactant solutions is discussed in terms of two parameters: (i) the ability to create foam; and (ii) foam stability. In addition to these batch tests, the selected combination of surfactant solutions was tested in a flow experiment (1-D) and the procedures are discussed.

2. Materials and Methods

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 sand confined after placement. During the flood, a fluid reservoir was used to hold injected fluids (de-aired water and surfactant solution). The column setup was made using Swagelok® valves fittings and tubing with Perforaxy (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 (Shimadzu model LC-20AD) was used to inject fluids during the experiment. The pump is capable of delivering constant flow rates from 0.01 ml/min to 9.99 ml/min at a maximum pressure 10 µPa. The differential pressure between the injection and production points of the column was measured using a differential pressure transducer. The PX26-005DV (0-5 psi) and PX26-001DV (0-1psi) by Omega Company, were used for the column experiments. A DC power supply of 24 volts is required to excite the Omega pressure transducers. This voltage was supplied by an Omega Linear Power Supply, model U24Y101.

2.2. Experimental Material

The surfactant formulation consisted of two surfactant solutions with the addition of sodium choride. Aerosol MA80 (sodium di(1,3-dimethylbutyl)sulfosuccinate, 78-80% activity) and Aerosol OT75-E (sodium dioctyl sulfosuccinate (ethanol; methanol), 73-75% activity), made by Cytec Industries Inc., were the surfactant used. Sodium chloride, made by Merck KGaA Company, was used as the electrolyte. No co-solvent was used. The water de-ionizer used is a Milli-Q Direct 8 Water Purification System (catalogue # ZR0Q00800), made by Millipore S.A.S (France).

The sand used in this study was collected from a contaminated site in Denmark and is mainly silica sand. After drying a grain size analyse was performed and the grain sizes from 150 to 300 μ m were used to fill the column.

2.3. Experimental Method

2.3.1 Mixing Surfactant

Surfactant solutions were made on a percentage by weight basis as-received. The column experiment was performed using a solution of 4 wt.% blend of MA80 and OT75-E, 1:1 mass basis at salinity 20,000 mg/L NaCl.

2.3.2 Column preparation

The glass column was jacketed and surfactant flood was performed at the aquifer temperature (10 °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 (grain size: 150 - 300µm). The end pieces were added and the column re-weighed. Each end piece had two screens-a 120-mesh toward the soil to prevent the movement of fines and then a 20-mesh screen to distribute flow uniformly across the column diameter. The dead volume of the end piece assembly was measured. The column was de-aired and flushed with CO₂ so as to eliminate any trapped air pockets out from the packed column, then was saturated with water and re-weighed. The data was used to estimate the reduced pore volume of the pack before surfactant injection. Then, hydraulic conductivity was measured, permeability, porosity and pore volume was determined.

Soil porosity (n): a measure of the ease with which a fluid can move through a porous material. The soil porosity depends on the consistence and packing of the soil and it is calculated:

$$n = \frac{W_{sat} - W_{dry}}{\pi . r^2 . L} \tag{1}$$

where: W_{sat} and W_{dry} are weights of the column saturated with water and flushed with CO₂ (dry), r is the inner radius of the column and L is the column length.

$$PV = \frac{W_{sat} - W_{dry}}{\rho_w} - V_d \tag{2}$$

where: ρ_w is the water density (0.997 kg/m³) and V_d is the dead volume.

Soil permeability is a measure indicating the capacity of the soil to allow fluids to pass through it. It is often represented by the permeability coefficient (k) through the Darcy's equation:

$$k = \frac{q.\,\mu.\,L}{A.\,\Delta P} = \frac{m.\,\mu.\,L}{A} \tag{3}$$

The permeability(k), [Darcy] is calculated with the dynamic viscosity μ [Pa s], the column length (L) [m] and the cross sectional area of the column (A) [m²]. *m* is the ratio of the volume flow q [m³/s] to the atmospheric pressure difference Δp [Pa] synonymous to the slope of the curve calculated through experimental measurements in the horizontal position at 10 °C before starting the salt and surfactant flushing.

2.3.3. Foam experiments

In field and lab experiments, foam can be generated by coinjection of gas and surfactant or by surfactant-alternatinggas (SAG) injection. SAG injection produce large slugs of liquid and gas, which are injected at maximum allowable pressure, which is an approach where time of injection and gravity override can be minimized (Jones *et al.*, 2016)

The approach used in this study to generate the foam *insitu* consists of several cycles (7) of Surfactant-Alternating-Gas (SAG) until foam was observed. More specifically, the cycles were performed with 0,25PV surfactant flushing and 0,25PV of air flushing. The pressure drop was used to compute the apparent viscosity, as proof for foam generation in the sand packed column.

$$\mu = \frac{k.A.\Delta P}{q.L} \tag{4}$$

3. Results and Discussion

3.1. 1-dimensional flow (column) study

The 1-dimensional flow (column) study results are presented below. In preparing the soil column, the properties of the soil pack (porosity, permeability, hydraulic conductivity) were measured and are shown in Table 1. Results from Figure 1 were used for the calculation of permeability value. Prior to the surfactant flood, the irreducible (or residual) water saturation, residual oil saturation, and the respective endpoint relative permeabilities were measured and are also presented in Table 2.

Dead volume [mL]	V_d	6.85
Pore volume [mL]	PV	101.79
Porosity	n	0.38
Permeability at 100% DI-water saturation [Darcy]	k	46.34
Oil endpoint relative permeability	k _{res,o}	0.8
water endpoint relative permeability	k _{res,w}	0.38



Figure 1. Pressure drop Δp [atm] measured for a range of flow rates and then used to compute the hydraulic conductivity and permeability of the pack.

The selection of a surfactant at a specific concentration to be used for creating foam with high stability in EOR process is very important. Preliminary work showed that the selected surfactant formulation has the ability to foam, and a column test to show that the formulation *can* create foam *in-situ* was investigated.



Figure 2. Preliminary foam "shake" test comparing five formulations to select the best foamer.

During the first two cycles of the flow experiment, no significant visible change was observed within the column but an increase at the differential pressure was observed (ΔP =5psi). During the third cycle, a significant visible change was observed at the first quarter of the column and a significant increase in the differential pressure showing the creation of foam inside the column. Increase of the pressure drop through the cycles continued. The pressure drop was used to compute the apparent viscosity, which was calculated to about 60-100cP from the 3rd to 7th cycle (Figure 2).



Figure 3. Photograph of the 1st part of the column (entry) at the start (1st cycle) of surfactant flushing.



Figure 2. The differential pressure between inlet/outlet of the column is shown for the surfactant flood: 0,25PV surfactant injected followed by 0,25PV of air. The pressure drop was used to compute the apparent viscosity, which was calculated about 60 cP after the 3rd cycle and increased to 100cP during the 7th cycle



Figure 4. Photograph the 1^{st} part of the column (entry) at the end of the 7^{th} cycle of surfactant and air flushing – foam visible (after 3 days).

The column was shut-in (kept closed) for three days and observations regarding foam were made daily, after which the foam was collected from the column exit as a proof of foam generation.

4. Conclusions

The foaming ability of the selected surfactant was achieved. Significant increase in the differential pressure was observed showing the creation of foam inside the column. The apparent viscosity was ranged from about 60 to 100cP from the 3^{rd} to 7^{th} cycle, respectively.

The column, after beinng shut-in (kept closed) for three days and from daily observations regarding foam, not only proved that the foam could be generated *in-situ*, but also that the foam would be stabile for a long period (3 days).



Figure 5. Foam collected from the exit of the column after being shut-in for 3 days as a proof of foam stability.

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