MODELING OF FOAM FRACTIONATION COLUMN FOR REMOVAL OF NON-AQUEOUS CONTAMINANTS

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Abstract: A phenomenological model was developed in order to describe the phenomena in which oily phases are separated from abundant aqueous phase using foam fractionation. The liquid mixture containing water and non-aqueous phase liquid (NAPL) was in emulsion state (oil in water) for easy foam generation using sodium lauryl sulfate (SLS), a popular anionic surfactant. Two physically operable factors, gas velocity and surfactant concentration, were investigated via the simulation. The numerical results were compared to the results of previous experiments. It was found that separation of light NAPL was good enough in terms of amount of elution and its selectivity, which rise up to 20 at 5.5 cm/s of gas velocity and 1.0 wt% of SLS concentration. On the other hand, poor separation for dense NAPL mixtures was shown, which is usually far less than 1.0 in selectivity. Comparison between numerical simulation and experiments showed that there was a relatively good agreement for lighter oil-water mixtures while dominating gravity force in DNAPL resulted in opposite to actual trend. It is recommended to consider “bubble rupture or collapse” as well as liquid drainage and suction effect in plateau borders for better model prediction.

Key Words: foam fractionation, NAPL, modeling

INTRODUCTION

Groundwater or soil near the manufacturing industries, military bases, and agricultural area is easily contaminated with waste solvents and hydrocarbons which are called NAPLs (non-aqueous phase liquids). Heavily or lightly contaminated wells could be remediated via various clean-up processes using gas flow. For example, stripping or sparging of air through the soil has significantly contributed to remediation of soil and/or groundwater with removal of VOCs (volatile organic compounds) and toxic organic chemicals \(^{12}\). Low air flow followed by foaming with an surface active agent, on the other hand, can provide an alternative cure for the contaminated groundwater wells which are filled with NAPLs\(^{11}\). Especially, foam separation, which is characterized as a low cost process, has been successfully applied to separate heavy metals, enzymes, surfactants, biological polymers, etc.\(^{4-6}\). Basically foaming works by physically removing the hydrocarbon or oil phase out of two immiscible phases: 1) 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\(^ {7,8}\), 2) and then, 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.

From the fact that gravity and stability of the foams control the whole process, a few models were presented regarding foam drainage in a hollow cylinder\(^ {9-11}\). The previous models were dedicated only to standing foams, not continuously growing foams, so that liquid drainage
only applied. Also liquids inside foams in those reports were confined to a single phase which is not very common in many real separations. In order to fully simulate a continuous generation and drainage of foam, causing separation, we here present a comprehensive mathematical model for continuous, foamy separation of oil/water mixtures. The simulated results were, then, compared with the experimental data out of our previous work\textsuperscript{12}.

**DESCRIPTION OF FOAMING**

Two immiscible liquid phases (n-hexadecane or carbon tetrachloride as NAPLs and water) with sodium dodecyl sulfate are placed in a cylindrical glass tube (ID, 18 mm; 220 mm long). Then an inert gas (N\textsubscript{2}) is blown in the range from 1.0 to 4.0 cm\textsuperscript{3}/s through the sintered glass plate positioned at the bottom of the tube. Grown foams rise up to the open end of the tube and then they are collected in a bottle as collapsed. The details of the experiments can be referred to the previous work\textsuperscript{12}.

**THEORETICAL DEVELOPMENT OF A FOAMING MODEL**

Figure 1 is a schematic diagram showing foam bed formed during bubbling and its structure with plateau borders (PB hereafter) between bubbles. As shown in the figure, volume of the liquid entrapped by blowing remains captured or drained out by gravity in the plateau borders.

Some assumptions are introduced to build a mathematical model: those are i) that the foams are uniform pentagonal dodecahedral, ii) that the drainage takes place only on plateau borders, and iii) that the plateau borders form at the intersection of three cylinders in contact. Foams are known to be a structure of pentagonal dodecahedrals as many analyzed images of them become available\textsuperscript{9,11}. Liquid holdup in a foam structure comes from plateau borders and bubble films, but the amount of the confined liquid on the films is negligible in many real cases if high mobility attributed by low surface viscosity applies. Assumptions of bubbles' uniformity and triangular intersections of PB are necessary for rigorous calculations in the model even if they are still unrealistic. For a unit volume of the foam bed, $\Delta V (=A \Delta z)$ during a unit time $\Delta t$, a simple mass balance holds as follows (see Figure 2):

\[ [\text{Liquid trapped in PB}] = [\text{Liquid entrained by Gas}] - [\text{Liquid drained by Gravity}] \]
\[
\left( N_B n_p a_{p l} \right)_{|z+\Delta z} - \left( N_B n_p a_{p l} \right)_{|z} \Delta Z \cdot A
\]
\[
= \left( \frac{G}{V} n_p a_{p l} \right)_{|z+\Delta z} - \frac{G}{V} n_p a_{p l} \right)_{|z} \Delta t
\]
\[
- \frac{3}{15} \left( N_B n_p a_{p} \bar{u}_g R_{|z+\Delta z} - N_B n_p a_{p} \bar{u}_g R_{|z} \right) \Delta t
\]
\[
\text{(1)}
\]

Dividing Eq.(1) by \(A \Delta z \Delta t\), then we have
\[
\left( \frac{N_B n_p a_{p l} \left|_{t+\Delta t} - N_B n_p a_{p l} \left|_{t} \right.}{\Delta t} \right)
\]
\[
= \left( \frac{G}{V} n_p a_{p l} \right)_{|z+\Delta z} - \frac{G}{V} n_p a_{p l} \right)_{|z} \Delta z
\]
\[
- \frac{3}{15} \left( \frac{N_B n_p a_{p} \bar{u}_g R_{|z+\Delta z} - N_B n_p a_{p} \bar{u}_g R_{|z}}{\Delta z} \right)
\]
\[
\frac{\partial (N_B n_p a_{p l})}{\partial t} = \frac{\partial}{\partial z} \left( \frac{G}{V} n_p a_{p l} \right) - \frac{\partial}{\partial z} (n_p a \bar{u}_g R)
\]
\[
\text{(2)}
\]

where the variables are defined as follows:

- \(N_B\), the number of bubbles per unit volume; \(n_p\), the number of PB per bubble; \(a_p\), the average cross-sectional area of a PB; \(l_p\), the length of a PB; \(V\), volume of a bubble; \(R\), the radius of a bubble if it were a sphere; \(A\), cross-sectional area of the glass tube; \(z\), the direction where foam grows; \(G\), superficial gas velocity.

The velocity of the drained liquid \(\bar{u}_g\) has been calculated for a single phase liquid\(^{(1)}\).

\[
\bar{u}_g = \frac{C_V a_p}{20 \sqrt{3} \mu} \left( \rho g + \sigma \frac{\partial}{\partial z} \left( \frac{1}{r_p} \right) \right)
\]
\[
\text{(4)}
\]

In Eq. (4), \(\rho\), \(g\), \(\mu\), \(\sigma\), and \(r_p\) refer to the density of the liquid, gravitational acceleration, viscosity, surface tension, and radius of curvature of PB walls, respectively. The factor \(C_V\) is the velocity coefficient which accounts for the effect of finite surface viscosity as Desai and Kumar have calculated from the relation between surface viscosity and bulk viscosity of the liquid\(^{(1)}\). Also Eq. (4) comprises two driving forces due to gravity \((\rho g)\) and gradient of PB suction \(\left[ \sigma \frac{\partial}{\partial z} \left( \frac{1}{r_p} \right) \right]\) as Narsimhan has first considered\(^{(1)}\).

Assuming that foams are pentagonal do-

decahedral we have the following relations:

\[
n_p = 10, \quad l_p = 0.816R
\]
\[
\text{(5)}
\]

Employing the liquid fraction in the foam bed, \(e\), we get

\[
e = N_B n_p a_{p l} \rho
\]
\[
N_B = \frac{1 - e}{V}, \quad a_p = \frac{V}{n_p l_p} \left( \frac{e}{1 - e} \right),
\]
\[
r_p = \left[ \frac{V}{a_n l_p} \left( \frac{e}{1 - e} \right) \right]^\frac{1}{2}
\]
\[
\text{(6)}
\]

where \(\alpha = 0.161\).

All variables are then rewritten in terms of \(e\). Eq. (3) can be, then

\[
\frac{\partial e}{\partial t} = \frac{\partial}{\partial z} \left( \frac{Ge}{1 - e} \right) - \frac{3}{15 (0.816)} \frac{\partial}{\partial z} (e \bar{u}_g)
\]
\[
\text{(8)}
\]

As we deal with two immiscible liquids, A (water) and B (hydrocarbon), Eq. (8) just holds for each phase;

\[
\frac{\partial e_i}{\partial t} = \frac{\partial}{\partial z} \left( G_i \cdot \frac{e_i}{1 - e} \right) - \frac{3}{15 (0.816)} \frac{\partial}{\partial z} (e \bar{u}_g)
\]
\[
\text{for } i = A, \ B
\]
\[
\text{(8')}
\]

Also, \(\bar{u}_g\) in Eq. (8) is a "mixed" velocity for the two liquid phases.

\[
\bar{u}_g = \frac{e_A}{e} u_A + \frac{e_B}{e} u_B
\]
\[
\text{(9)}
\]

Since water is the dominant phase in the mixed emulsion, the individual velocity can be described as follows. \(\sigma_A\) in Eq. (10b) is rather correct than \(\sigma_A\) since A is the bulk phase in "B in A" type emulsion.

\[
u_A = \frac{C_V a_p}{20 \sqrt{3} \mu A} \left( \rho g + \sigma_A \frac{\partial}{\partial z} \left( \frac{1}{r_p} \right) \right)
\]
\[
\text{(10a)}
\]

\[
u_B = \frac{C_V a_p}{20 \sqrt{3} \mu A} \left( \rho g + \sigma_A \frac{\partial}{\partial z} \left( \frac{1}{r_p} \right) \right)
\]
\[
\text{(10b)}
\]

The following initial and boundary conditions are needed for solving Eq. (8);
\[ e=0 \text{ at } t=0 \] (11a)

Once foam starts to develop

\[ e=0.26 \text{ at } z=0 \] (11b)
\[ \bar{u}_e=0 \text{ at } z=M \gg 1 \text{ where } M \text{ is a constant} \] (11c)

Eq. (11b) generally holds for stabilized foams. When the drainage stops with balanced two forces, i.e., gravity and PB suction, \( \bar{u}_e \) is reasonably assumed to be zero at an equilibrium position in infinite dimension of \( z \) (Eq. (11b)). As the condition (11b) depicts a moving boundary, it is necessary to develop another equation for \( H(t) \) to resolve the problem.

Volumetric gas flow rate, \( \frac{dV_g}{dt} \) becomes

\[ \frac{dV_g}{dt} = \frac{d}{dt} \int_0^{R(t)} (1-e) Adz = G \cdot A \] (12)

Eq. (12) can be rearranged as

\[ \frac{d}{dt} \int_0^{R(t)} dz - \frac{d}{dt} \int_0^{R(t)} e dz = G \]

or

\[ \frac{dH(t)}{dt} - \int_0^{R(t)} \frac{\partial e}{\partial t} dz - e|_{z=R(t)} \cdot \frac{dH(t)}{dt} = G \]

and Eq. (13) reduces to

\[ \frac{dH(t)}{dt} = \left(1-e|_{z=R(t)}\right) (G + \int_0^{R(t)} \frac{\partial e}{\partial t} dz) \] (14)

Eqs. (8) and (14) then can be solved simultaneously using the IMSL computing routine MOLCH\textsuperscript{13}. Since \( H(t) \) is the front line of foam generated, we will have effluent out of the column when \( H(t) > H_{\max} \).

\[ H_{\max} = L_0 - LP(t) \] (15)

Liquid balance results

\[ A \cdot e \cdot H(t) + A \cdot LP(t) = A \cdot LP_0 \] (16)

Therefore, the amount of effluent at a time \( t \), \( e \cdot (H(t)-H_{\max})A \) will be

\[ e \cdot (H(t)-H_{\max})A = A \cdot e \cdot (1-e) \cdot H(t) + e \cdot (LP_0-L_0) \] (17)

Table 1 summarizes the values of parameters used in the simulation.

**RESULTS AND DISCUSSION**

Figure 3 shows the profiles of foam effluents with different gas velocities for the lighter liquid mixture (hexadecane/water). The y-axis, \( eA(H(t)-H_{\max})/V_0 \) stands for the fraction of eluted liquid of the initial liquid volume, i.e., recovery of liquid by foaming. Logarithmic increase of the total liquid effluent was observed up to 200 s. The initial startup was followed by almost linear rate of foam growth. Overall the effect of gas velocity ranging from 0.8 to 5.5 cm\(^3\)/s implies that foam created by the anion surfactant, possesses reasonably strong stability itself in the specified conditions. Complete removal of the liquid pool was simply predicted in some cases of simulation (recovery of liquid is greater than 1). Even at the highest

| Table 1. Values of parameters used in the model calculations |
|-----------------|-----------------|---------------|
| \( L_0 \)       | 220 mm          | \( \rho \) (hexadecane) | 0.77 g/cm\(^3\)\textsuperscript{14} |
| \( A \)         | 254.3 mm\(^3\) | \( \rho \) (tetrachloromethane) | 1.59 g/cm\(^3\)\textsuperscript{14} |
| \( R \)         | 0.2 mm          | \( \mu \) (hexadecane) | 3.03 mPa.s\textsuperscript{14} |
| \( V_0 \)       | 5 cm\(^3\)      | \( \mu \) (tetrachloromethane) | 0.908 mPa.s\textsuperscript{14} |
| Initial o/w(v/v)| 2/3             | \( \sigma \) | \( \infty \) |

\textsuperscript{14} Refer to CRC Handbook\textsuperscript{14}

\textsuperscript{14} Use an empirical equation: \( \sigma = 40-46.13 \times \log[\text{SLS wt%}/0.23] \)\textsuperscript{14}
Figure 3. Time evolution of total LNAPL effluent at different gas velocities with 0.2 wt% of SLS solution. Curves 1 through 7 stand for 5.5, 5.0, 4.0, 3.0, 2.0, 1.0, and 0.8 cm³/s of G, respectively.

Figure 4. Time evolution of total LNAPL effluent at different SLS concentrations in the conditions of G=1.0 cm³/s. Curves 1 through 7 stand for 0.5, 0.2, 0.15, 0.1, 0.05, 0.02, and 0.01 wt% of SLS concentrations, respectively.

gas velocity ever tested there was no sign of foam collapse, just like observations in the previous experiments.\(^{11}\)

With different SLS concentrations (0.01, 0.02, 0.05, 0.1, 0.15, 0.2 and 0.5 wt%) at G=1.0 cm³/s, the effluent volumes are shown in Figure 4 in which lower SLS concentrations lead to relatively high removal of the liquid mixture. In other words, there were no substantial increases for SLS solutions of 0.1 through 0.5 wt% which is over the CMC (critical micelle concentration, 0.23 wt% in this case). The difference between the two classes of concentrations would be reasonably explained when one considers that even if the change of surface tension with surfactant concentration was large (σ changed from 70 dyn/cm to 40 dyn/cm for aqueous solution), which leads to reduction of PB suction at a linear rate, the influence of surface viscosity is not so large that the drainage velocity, \(u_d\) as depicted in Eqs. (4), (10a) and (10b) is negligibly affected. This result also implies that micelles in the bulk aqueous solution did not play effective roles in order to enhance or at least maintain the stabilized structure of foams perceiving oil-in-water emulsion.

In Figure 5, eluted amounts for both phases separated at G=1.0 cm³/s are all shown. Separation selectivity grows with SLS concentration as much like total amount of liquid does. However, gaps among the selectivities are relatively large if compared to those in total amounts. It is obvious that the velocity of drainage, \(u_d\) is dominantly controlled by the density difference(water, \(\rho =1.0\ g/cm^3\); hexadecane, \(\rho =0.770\ g/cm^3\)). Also this is partly because of PB stability imparted by the surfactant and PB suction which will increase with surface tension inside PB as well. Rough
estimation in the simulation resulted in almost equal contribution in order of magnitude for the two factors stated above.

In DNAPL (dense non-aqueous phase liquid) experiments (carbon tetrachloride/water\textsuperscript{12}), unlike Figures 3 through 5, ratios of oil in water in most effluents were less than 1.0. Density of carbon tetrachloride is known to be 1.59 g/cm\textsuperscript{3} at room temperature. That means that gravity force of oil itself is so high as to accelerate the drainage of the liquid regardless of its mixture-like characteristics. Figure 6 shows the reversed ratio of oil in water in the effluent even at the largest gas velocity. Also changing rates of cumulated effluents with time drop more rapidly than those do for LNAPL. This result manifests stronger gravitational effect (PB suction and surface viscosity are less important for DNAPL). Composition of the oil ranges from 0.2 to 0.6 by volume. As stated earlier initial logarithmic evolution of effluent continues for about 200 seconds and it is followed by semi-linear increase. That increase was too moderate to reach the point where all liquid is completely taken out of the column within our simulation time-scale for DNAPL. Similarly, in Figure 7, composition of oil and water in the effluents resemble with that in Figure 6 although the total amounts of effluents hardly differentiate each other since liquid loading by gas is believed to be a limiting factor under the given conditions. It was found that the highest SLS concentration gave the highest ratio of oil to water as expected. That was not, however, in agreement with experimental observation in which the highest ratio of oil to water was obtained at 0.05 wt\% of SLS solution. This discrepancy arises partly from our "no collapse or no rupture" assumption. In reality, such incidents frequently happen in foaming experiments, especially for heavy liquid.

Figures 8 and 9 show two sample comparisons of simulated results with experimental data. Data presented in Figures 8 and 9 was obtained in 5 mins' and 20 mins' foam collection, respectively. For lighter oil, the simulation agrees well with experimental points, especially at lower surfactant concentrations (Figure 8). It is believed that oil like hexadecane, fully surrounded by water phase in emulsion, mostly remains captured in the entrained water phase in PB during bubbling when some portion of the water is drained out by gravity. That explains why ratio of oil to water becomes larger with higher SLS concentrations. Case of dense oil (Figure 9) turns to a different story.
CONCLUSIONS

A mathematical model dictating foam generation and drainage only by gravity and plateau border suction effects was developed in order to predict the behavior of oily contaminants trapped in cylindrical wells. The model could predict the experimental results within reasonable precision for mixtures of lighter oil and water whereas it needs to reflect realistic situation including physical rupture or collapse of bubbles once generated for better agreement with experiments. Higher gas velocity and surfactant addition influenced positively on increase in oil recovery for both of LNAPL and DNAPL. However, for DNAPL separation predominant effect of gravity led to at most 40% of oil recovery and low selectivity (<1.0).

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