# How Bubbly Mixtures Foam and Foam Control Using a Fluidized Bed by <br> José Guitián ${ }^{\ddagger}$ Daniel Joseph* 

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#### Abstract

In hydrocracking and other foaming reactors, the foam rises to the top because it has a higher gas fraction than the bubbly mixture from which it comes. The high gas hold-up in foams is undesirable in chemical reactors because it strongly decreases the liquid residence time and in hydrocracking reactors also promotes the formation of coke. To study foams we built a cold slit bubble reactor which when used with aqueous anionic surfactants gives rise to foam. This reactor reproduces the foaming processes which are characteristic of the commercial system CANMET from Petrocanada. We discovered a critical condition for foaming; when the gas velocity exceeds a critical value which depends on the liquid velocity, a foam interface appears at the top of the reactor, with foam above and bubbly mixture below. The interface is very sharp and it moves down the reactor as the gas velocity is increased at a constant liquid velocity. This is the way reactors foam, with the bubbly mixture being consumed by foam.

The foam may be destroyed by increasing the liquid velocity backing up against the foaming threshold. The reactor partitions into two phase, two phase flow with bubbly mixture below and foam above. The bubbly mixture is dispersed gas in water plus surfactant; the phase above is a foam through which large gas bubbles rise. Constant state theories for the bubbly mixture, the foam and the position of the foam interface are derived and semiempirical correlations are presented.

Foaming may be strongly suppressed by fluidizing hydrophilic particles in the bubbly mixture below the foam. The suppression is achieved by increasing the liquid holdup by bed expansion; by increasing the wetted area of solid surface (walls and particles) and by decreasing the gas hold-up by increasing the effective density of the liquid-solid mixture.


## Industrial foaming reactors

Applications of foams and foaming are found in many industries like the flotation of minerals, enhanced oil recovery drilling in oil reservoirs, insulation, construction and refining processes such as Vacuum distillation and Delay-Coker
reactors. However, foaming and defoaming are not yet well understood. The modern theory of foams could be said to start with [1973] study of Bikerman. A consolidation of the advances in the study of foams and foaming is in the collection edited by Prud'homme and Khan [1995]. Foams trap gas and are not wanted in many applications; Garrett [1993] has edited a collection of papers on defoaming. Our application area is to unwanted foaming in foaming bubble reactors and the practical application of our study is the suppression of foaming. To achieve this goal we propose fundamental studies of recent observations which we have made in foam suppression studies in the slit bubble reactor described in section two below.

Pruden [1993] has reported $80 \mathrm{v} \%$ gas hold-up in the reactor of the commercial demonstration plant used in the CANMET process for a wide range of gas velocities and reactor temperatures. The overall gas hold-up values which were observed are consistent with a severe foaming condition in the reactor using a typical commercial gas velocity. In the CANMET process, foam formation was detected in the commercial unit only because of the higher gas velocities employed. Under typical hydrocracking conditions using catalytic slurry reactors of the bubble column type and catalysts, foam may be present in the reaction zone. Foaming can occur at temperatures higher than $400^{\circ} \mathrm{C}$ which are typical in industrial reactors.


Figure 1: Diagram of the bubble column: height 170 cm , width 26 cm and depth 1.3 cm . Flow lines are clearly visible through the thin Plexiglas column. The metal screen at the top of the column which is used to hold solid particles in the reactor does not have a major effect on the flow below.

## Slit bubble reactor.

To evaluate the fluid dynamics of a foaming bubble column with a continuous gas/liquid input, we constructed apparatus shown in Figure 1. Nine highly accurate pressure transducers were installed. The output of each pressure transducer is in the mV range and is amplified to the $0-10 \mathrm{~V}$ range. This signal is fed into a PC, where the signal is converted to pressure and a time average is constructed. The total and local average gas hold-up in the column is calculated using the pressure obtained at different times. Measurements were taken at a rate of 30 per second for a period of 3 minutes after reaching a stable state. The time required for transients to decay depends on the operating conditions and the foaming capacity of the surfactant mixtures. Steady states are recognized in foaming systems by the stabilization in the pressure values in the column and by visual observation of the foam interface. The time required to reach steady state was between 30 min . and 60 min . depending basically on the liquid and gas velocities.

The superficial gas velocity $U_{g}$ and liquid velocity $U_{l}$ are prescribed data which we control in our bubble column. Figure 1 shows the experimental equipment in the foaming mode. The total average gas fraction $\epsilon_{g}=1-V_{l} / V$ in steady flow was determined by direct measurement of the liquid volume $V_{l}$ after the gas and liquid flows were stopped simultaneously and by a second method based on the pressure drop $\left(\Delta P_{t}\right)$ which is the sum of the static pressure drop $\left(\Delta P_{s}\right)$ and the pressure drop due to friction between two points separated by a distance $(\Delta H)$. However, at gas and liquid velocities normally employed in bubble columns, the pressure drop due to the friction is relatively small and the local gas fraction between the two points is given by

$$
\begin{equation*}
\epsilon_{g}=1-\frac{\Delta P_{s}}{g \rho_{l} \Delta H} \tag{1}
\end{equation*}
$$

The two methods agree when $\Delta H=L$ showing that the pressure drop due to friction is negligible. The variation of the total gas fraction with gas velocity, using foaming systems, in the laboratory reactor in Figure 1 is in astonishing agreement with published data for the CANMET reactor (see Figure 6).

## Part 1: Foam formation at an interface

When the superficial velocity of the gas exceeds a critical value which depends on the foaming properties of the liquid and its superficial velocity, a foam/bubbly mixture interface appears at the top of the reactor as shown in Figures 1 and 3. The interface is very sharp and it moves down the reactor as the gas velocity is increased at a constant liquid velocity. This is the way the reactor foams, with the bubbly mixture being consumed by foam. You can eliminate foam entirely by increasing the liquid velocity beyond a threshold set by the


Figure 2: Plots of equation (2) giving $U_{g}$ and $U_{l}$ for the inception of foaming. The constants $a$ and $b$ in (2) depend on the properties of the surfactant solution.


Figure 3: Foam regions in two phase foaming systems. $f=h / H$, where $H$ is the total height of the reactor and $h$ is the height of the foam.

## gas velocity.

The interface defines a change of phase of a two-phase, twophase flow; the bubbly mixture is a two phase flow of gas and surfactant in water; the foam is also two phase flow of gas and surfactant in water but is better characterized as a foam though which large gas bubbles rise. When characterized in this way, gas bubbles are always the dispersed phase; surfactant in water is the continuous phase in the bubbly mixture and the foam is continuous in the foamy mixture. The interface marks a phase change for the continuous phase from surfactant in water to foam.

The reader should maintain distinction between the foam which is a structure of fluid with films and plateau borders and foamy mixture in which large gas bubbles rise though the foam. However, in the sequel we shall not always call attention to this distinction between foam and foam though which large gas bubbles rise.
$U_{g}$ for different liquid velocities $U_{l}$. Foaming does not occur in
 as $U_{g}$ is increased past the critical value, more and more of
the bubbly mixture is consumed by foam.
 рәұеледәs si weof әЧL •лоұәеәл әчұ јо doұ әчұ ұе sлeәdde ueof foam in the reactor; the reactor will be filled to the top with
bubbly mixture. When $U_{g}$ reaches the critical value in $(2)$


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> reactor is 2 meters in diameter witn a capacity operates at a temperature greater than $400^{\circ} \mathrm{C}$. Water/SDS/1-Pentanol Systems. The CANMET hydrocracking cess and cold model experimental results (Figure 1) using Figure 6: Comparison between gas fraction in CANMET pro-
can be simulated using pentanol/water systems. [1987] have noted the gas hold-up in coal liquifaction reactor function of gas velocity of such commercial unit. Fan et al laboratory reactor reproduces the gas fraction behavior as a of heavy crudes using bubble column reactors. The cold [1993]), owned by Petrocanada, for the hydroconversion

 also an increasing function of $U_{g}$ as shown in Figure 5 . foaming is shown in Figure 4 ; the foam height $f=h / H$ is The increase in the total gas fraction in the reactor due to when $U_{l}$ decreases. The maximum gas fraction for this foam
is slightly above $80 \%$ which can be considered a typical value with $(2)$ is the fact that there is more gas for a given $U_{g}$
when $U_{l}$ decreases. The maximum gas fraction for this foam branches bifurcate from the non-foaming branch. Consistent
 begins when $U_{g}$ goes critical. This occurs for smaller values 4 is for a non-foaming high liquid flow situation. Foaming threshold value defined by (2). The bottom curve in Figure pure liquids without surfactants. Foaming also does not occur
in foaming liquids when the liquid velocity is larger than the
where $U_{b \infty}$ is the terminal velocity of a single bubble and $\Phi\left(\epsilon_{g}\right)$ depends only on $\epsilon_{g}$.
The terminal velocity of a spherical bubble which rises freely as a hard sphere in a liquid/surfactant has been calculated by Matsumoto and Morooka [1989] and is given by

$$
\begin{equation*}
\frac{U_{b \infty} D_{b} \rho_{l}}{\mu_{l}}=\frac{G a}{\left[18^{4 / 5}+(G a / 3)^{2 / 5}\right]^{5 / 4}} \tag{4}
\end{equation*}
$$

where $G a$ is the Galilei number $\left(D_{l}^{3} \rho_{l}\left(\rho_{l}-\rho_{g}\right) g / \mu_{l}^{2}\right)$. Linear regression of our data using (4) gives $\Phi\left(\epsilon_{g}\right)\left(1-\epsilon_{g}\right)=1$. Hence the fraction in the bubbly mixture can be explicitly obtained from (3) as

$$
\begin{equation*}
\epsilon_{g b}=\frac{U_{g}}{U_{g}+U_{l}+\left[\frac{\mu_{l} G a}{D_{b} \rho_{l}\left[18^{4 / 5}+(G a / 3)^{2 / 5}\right]^{5 / 4}}\right]} \tag{5}
\end{equation*}
$$

The computation of the bubble size $D_{b}$ in a bubble column is rather complicated and is described in the appendix.

To predict the gas fraction in the foam we use (3) again written as

$$
\begin{equation*}
\frac{\nu_{g}}{\nu_{l}}=\frac{U_{g}}{\epsilon_{g f}} \frac{\left(1-\epsilon_{g f}\right)}{U_{l}}=\frac{U_{b \infty} \Phi\left(\epsilon_{g f}\right)\left(1-\epsilon_{g f}\right)}{U_{l}}+1 \tag{6}
\end{equation*}
$$

In the limiting case of very dry foams, the gas is trapped in the foam; the water and gas move in lock step on $\nu_{g} / \nu_{l}=1$; the $\operatorname{term} U_{b \infty} \Phi\left(\epsilon_{g f}\right)\left(1-\epsilon_{g f}\right) / U_{l}$ in equation (6) is equal to zero. Regression analysis of our data shows that $U_{b \infty} \Phi\left(\epsilon_{g f}\right)(1-$ $\left.\epsilon_{g f}\right) / U_{l}$ is constant for all foams. This is a surprising result which implies that equation (6) can be simplified to

$$
\begin{equation*}
\frac{U_{g}}{\epsilon_{g f}} \frac{\left(1-\epsilon_{g f}\right)}{U_{l}}=\frac{\nu_{g}}{\nu_{l}}=\Omega \tag{7}
\end{equation*}
$$

The two equations (7) may be solved for

$$
\begin{equation*}
U_{g}=\frac{U_{l} \epsilon_{g f}}{1-\epsilon_{g f}} \Omega \tag{7}
\end{equation*}
$$

where

$$
\begin{equation*}
\epsilon_{g f}=1-\frac{U_{l}(\Omega-1)}{\nu_{g}-\nu_{l}} \tag{7}
\end{equation*}
$$

showing that $\epsilon_{g f}$ and then $U_{g}$ are determined by the slip velocity $\nu_{g}=\nu_{l}$ in the foam and the superficial velocity $U_{l}$. We may also replace $U_{g}$ in (5) with $(7)_{1}$; this shows that $\epsilon_{g b}$ also is determined by $\nu_{g}-\nu_{l}$ and $U_{l}$.

The constant $\Omega$ in this equation should be a function of the foaminess of each foaming system. Some typical values of $\Omega$ are ( $7.4,7.6,6.5$ ) for aqueous $(0.04 \mathrm{wt} \% \mathrm{SDS}$, $0.04 \mathrm{wt} \% \mathrm{SDS} / 1 \mathrm{wt} \% 1-$ Pentanol, $\quad 0.02 \mathrm{wt} \% \mathrm{SDS} / 1 \mathrm{wt} \% 1-$ Pentanol) solutions. Relaxing our assumption of constant states for the moment, we note that the gas in the foam is partitioned into a fast moving part which rises through
the foam and a trapped part which moves with the foam. Neglecting drainage, the foam velocity $\nu_{f}=\nu_{l}$. Then $\nu_{g}$ is apparently associated with fast rising large gas bubbles since $\nu_{g}=\Omega \nu_{l}$ and the slip velocity $\nu_{g}-\nu_{l}$. may then also be regarded as the difference between the velocity of fast rising gas bubbles through the foam and the foam itself.

## Phase change Interface

The two constant states are greatly different; the gas fraction $\epsilon_{g}$ is much larger and the gas velocity $\nu_{g}=U_{g} / \epsilon_{g}$ is much smaller in the foam than in the bubbly mixture. We find it remarkable that these two constant states are separated by a sharp interface shown in Figure 3 at the critical condition (2) and moves down the column as $U_{g}$ increases. We do not pretend to understand the physics which gives rise to this interface and we have only an ad hoc theory to predict its position.

The existence of two constant states with greatly different gas fractions separated by a sharp interface occurs in counterflow bubble reactors and has been analyzed using a drift flux theory (Wallis [1969]). This theory gives rise to two solutions for the gas fraction corresponding to observations with systems that are not able to produce foam, but does not predict the position of the interface.

The physics of a counterflow bubble reactor with rising bubbles and falling liquid is very different than foaming reactors because surfactants are not involved and the discontinuity in the gas fraction does not involve a change of phase at a boundary separating two two-phase flows (bubbly mixture and foam). This latter transition involves morphological transformation analogous to phase change in crystalline solids. Another way to think of the phase change from bubbly mixture to foam is in analogy to evaporation with an equilibrium "temperature" $U_{g}$ and "pressure" $U_{l}$ satisfying a vapor-liquid like phase change equation (2).
We could say that the system allows two solutions, one without foam, and the foaming solution which has a lower energy.

To predict $f$, we looked at the mechanical energy dissipation, following Gidaspow's [1994] treatment of transient one dimensional particulate flow. In the constant state theory, all derivatives except $d p / d x$ are put to zero. Since we found in experiments that at the operating conditions normally used in bubble columns, (moderate values $U_{g}$ and $U_{l}$ ), the pressure drop is balanced by the static pressure head, we can neglect the gas wall friction and liquid wall friction. Therefore, the liquid momentum balance is given by

$$
\begin{equation*}
-\left(1-\epsilon_{g}\right) \frac{d p}{d x}-\left(1-\epsilon_{g}\right) \rho_{l} g+\beta\left(\nu_{g}-\nu_{l}\right)=0 \tag{8}
\end{equation*}
$$

and the gas momentum balance by

$$
\begin{equation*}
-\epsilon_{g} \frac{d p}{d x}-\epsilon_{g} \rho_{g} g-\beta\left(\nu_{g}-\nu_{l}\right)=0 \tag{9}
\end{equation*}
$$

after eliminating $d p / d x$, we get

$$
\begin{equation*}
g\left(\rho_{l}-\rho_{g}\right)=\frac{\beta\left(\nu_{g}-\nu_{l}\right)}{\epsilon_{g}\left(1-\epsilon_{g}\right)} \tag{10}
\end{equation*}
$$

The friction factor parameter $\beta$ can be related to the drag coefficient by the balance of buoyancy and drag

$$
\begin{equation*}
\frac{4}{3} \pi\left(\frac{d_{b}}{2}\right)^{3} g\left(\rho_{l}-\rho_{g}\right)=\pi\left(\frac{d_{b}}{2}\right)^{2} \frac{1}{2} \rho_{l}\left(\nu_{g}-\nu_{l}\right)^{2} C_{D} \tag{11}
\end{equation*}
$$

where $C_{D}$ is the drag coefficient. From (10) and (11) we find that

$$
\begin{equation*}
\beta=\frac{3}{4} \frac{\rho_{l} \epsilon_{g}\left(1-\epsilon_{g}\right) C_{D}\left(\nu_{g}-\nu_{l}\right)}{d_{b}} \tag{12}
\end{equation*}
$$

The mechanical energy equation for the gas/liquid mixture can be obtained by multiplying the liquid momentum balance (8) by $\nu_{l}$ and dividing by $\left(1-\epsilon_{g}\right)$, multiplying the gas momentum balance (9) by $\nu_{g}$ and dividing by $\epsilon_{g}$ and adding both equations. After writing

$$
\begin{equation*}
d p / d x=-\rho_{l}\left(1-\epsilon_{g}\right) g \tag{13}
\end{equation*}
$$

the energy equation is given by

$$
\begin{equation*}
\rho_{l} g\left(1-\epsilon_{g}\right)\left(U_{g}+U_{l}\right)-\rho_{l} g U_{l}-\rho_{g} g U_{g}=\beta\left(\nu_{g}-\nu_{l}\right)^{2} \tag{14}
\end{equation*}
$$

where $\rho_{g} U_{g}$ is much smaller than $\rho_{l} U_{l}$ and may be neglected. Equation (13) indicates that the input power to the column is dissipated by the friction associated with gas bubbles rising through the liquid.

After substituting (12) into (14) we get

$$
\begin{gather*}
I=\rho_{l} g\left(1-\epsilon_{g}\right)\left(U_{g}+U_{l}\right)-\rho_{l} g U_{l}-\rho_{g} g U_{g} \\
=\frac{3}{4} \frac{\rho_{l} \epsilon_{g}\left(1-\epsilon_{g}\right) C_{D}\left(\nu_{g}-\nu_{l}\right)^{3}}{d_{b}}=D \tag{15}
\end{gather*}
$$

Equation (15) relates the power input per unit volume of column $(I)$ on the left to the power dissipated per unit volume of column due to the friction between the phases $(D)$ on the right. An expression for the bubble size in a foam has been determined by Haas [1967] using different type of surfactants

$$
\begin{equation*}
d_{b}^{2}=\alpha \frac{U_{g}}{\left(1-\epsilon_{g f}\right)} \tag{16}
\end{equation*}
$$

where $\alpha$ is a constant function only of the foaming system employed.

To determine $\alpha$ it is necessary to obtain additional information. We did visual measurements of the bubble size of the foam using high speed filming in two different foaming systems and we found that the foam bubble size is between 2 mm and 4 mm when $6 \mathrm{~cm} / \mathrm{s}<U_{g}<11 \mathrm{~cm} / \mathrm{s}$ and $0.05 \mathrm{~cm} / \mathrm{s}<U_{l}<$ $0.15 \mathrm{~cm} / \mathrm{s}$. This gives rise to the average $\alpha$ values given in Table 1.

When surfactants are present and foam appears we shall assume that the ratio of foam fraction to bubbly mixture

| System | $\begin{gathered} \text { Gas } \\ \text { Velocity } \\ {[\mathrm{cm} / \mathrm{s}]} \end{gathered}$ | Liquid Velocity $[\mathrm{cm} / \mathrm{s}]$ | Average Foam Bubble Diameter [cm] | $\begin{gathered} \text { Average } \alpha \\ \text { from } \\ \text { equation }(16) \\ {[\mathrm{cm} / \mathrm{s}]} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \text { Water/ } \\ 0.04 \mathrm{wt} \% \\ \text { SDS } \end{gathered}$ | 4.9 | 0.05 | 0.2 | $9 \times 10^{-4}$ |
|  | 8.1 | 0.05 | 0.3 |  |
|  | 6.0 | 0.1 | 0.3 |  |
|  | 8.2 | 0.1 | 0.3 |  |
|  | 10.5 | 0.1 | 0.4 |  |
| Water/$0.04 \mathrm{wt} \% \mathrm{SDS} /$$1 \mathrm{wt} \% 1-\mathrm{C} 5$ | 4.9 | 0.154 | 0.2 | $20 \times 10^{-4}$ |
|  | 6.0 | 0.154 | 0.2 |  |
|  | 8.2 | 0.154 | 0.3 |  |

Table 1: Bubble size and constant $a$ from equation (16).
fraction is equal to its power dissipation ratio in each of the phases; in other words

$$
\begin{align*}
& \frac{f}{1-f}=\frac{D_{f} f}{\left(I_{b}(1-f)+I_{f} f\right)-D_{f} f}  \tag{17}\\
&=\frac{\text { Energy dissipated in foam }}{\text { Energy dissipated in bubbly mixture }}
\end{align*}
$$

where $I_{b}$ is the power input per unit volume of the bubble phase $I_{f}$ the power input per unit volume of foam (LHS of equation 15), $D_{f}$ the power dissipated per unit volume of foam (RHS of equation 15 ). Equation (15) implies that the power dissipated per unit volume of foam and the power dissipated per unit volume of bubbly mixture are equal. We don't propose (17) as a correct statement of physics; it is an ad hoc assumption which is true for $f=0$ and $f=1$ and appears not to wander far from the truth for $0<f<1$. After substituting (15) into (17) we find that

$$
\begin{align*}
& f= \\
& \frac{\frac{3 C_{D} \epsilon_{g f}\left(1-\epsilon_{g f}\right)}{4 g d_{b}}\left(\frac{U_{g}}{\epsilon_{g f}}-\frac{U_{l}}{1-\epsilon_{g f}}\right)^{3}-\left(\left(1-\epsilon_{g b}\right)\left(U_{g}+U_{l}\right)-U_{l}\right)}{\left(1-\epsilon_{g f}\right)\left(U_{g}+U_{l}\right)-\left(1-\epsilon_{g b}\right)\left(U_{g}+U_{l}\right)} \tag{18}
\end{align*}
$$

where, following the discussion of (7), slip velocity in the foam

$$
\begin{equation*}
\nu_{g}-\nu_{l}=\frac{U_{g}}{\epsilon_{g f}}-\frac{U_{l}}{\left(1-\epsilon_{g f}\right)} \tag{19}
\end{equation*}
$$

may also be regarded as the difference in the velocity of the large gas bubbles which rise through the foam and the foam itself. Equations (7) show that $f / C_{D}$ is a function of $\nu_{g}-\nu_{l}, U_{l}$ and material parameters.

The drag coefficient for a solid sphere moving through an unbounded liquid depends on the Reynolds number (see for example Dallavalle [1948], Churchill [1988]), alone and is given by empirical formulas with good accuracy. We shall assume that the same formula

$$
\begin{equation*}
C_{D}=\left(0.63+4.8 R e_{f}^{-1 / 2}\right)^{2} \tag{20}
\end{equation*}
$$

holds for a bubble rising through foam when

$$
\begin{equation*}
R e_{f}=\frac{\left(1-\epsilon_{g f}\right) \rho_{l}\left(\nu_{g}-\nu_{l}\right) d_{b}}{\mu_{f}} \tag{21}
\end{equation*}
$$

where $\mu_{f}$ is the unknown viscosity of the foam. Equations (16) and (18), together with measured values of $f$, determine the drag coefficient $C_{D}$; then (20) and (21) determine $R_{e f}$ and $\mu_{f}$. Equations (16)-(21) determine the foam viscosity in terms of $U_{l}$ and the slip velocity, but the calculation illustrated in Figure 7 shows that $\mu_{f}$ is essentially independent of $U_{l}$.

Princen and Kiss [1989] derived an expression for the foam viscosity depends on the slip velocity and $\epsilon_{g f}$. If we use the foam of their analytic expression for $\mu_{f}$ and fit their constants and exponents by nonlinear regression using our data for water $/ 0.04 \%$ SDS we get

$$
\begin{equation*}
\mu_{f}=\frac{0.8177 \epsilon_{g f}^{0.76}}{d_{b} \dot{\gamma}}+\frac{60.08\left(\epsilon_{g f}-0.69\right)}{\left[d_{b} \dot{\gamma}\right]^{2.96}} \tag{22}
\end{equation*}
$$

with a regression coefficient of $R^{2}=0.98$. Equation (22) can be compared with a similar equation in the abstract of the paper by Princen \& Kiss [1989]. In their formula $d_{b} \dot{\gamma}=\nu_{g}-\nu_{l}$ but $\epsilon_{g f}$ is assumed to be given and is not computed from dynamics.


Figure 7: Foam viscosity as determined by equation (21). The derivation of this equation shows that in principle the foam viscosity depends on flow variable $\nu_{g}-\nu_{l}$ and $U_{l}$, but this figure shows that $\mu_{f}$ can be well approximated by a function of the slip velocity alone; regression of the data gives $\mu_{f}=8.0\left(\nu_{g}-\nu_{l}\right)^{-2.151}$ with a regression coefficient $R^{2}=0.9893$.

## Part 2. Foam control using a fluidized bed

## 1. Fluidization of particles in the bubbly mixture

Particles in batch may be fluidized in the bubbly mixture, but not in the foam. Since the particles are loaded in batch, the initial solids fraction $\epsilon_{p}=\frac{4 n \pi}{3} a^{3} / V$, where $n$ is the number of particles, $a$ is the radius and $V$ is the volume of the reactor, does not change once the solids are loaded into the reactor. The volume fractions (or hold-ups) of liquid $\epsilon_{l}$ and gas $\epsilon_{g}$ are also fractions relative to $V$, but these continuous variables depend on input velocities $U_{l}$ and $U_{g}$.

Since no particles or a very small number of particles enter the foam, the effective concentration of particles is the ratio $\frac{4}{3} \pi a^{3} n$ of solids to $V_{s}$ which is the volume in the bubbly mixture occupied by the slurry (see figure 10).

## 2. Foam rheology and the foam barrier

The foam is an elastic network of films and plateau borders which maintains a locked grid structure as it moves slowly and uniformly through the bed. Large gas bubbles rise rapidly through the foam, but the foam itself does not circulate as an ordinary fluid and particles which are driven into the foam are either trapped there or fall out, but they do not circulate. The trapped particles show that the foam has a yield stress; the slow motion of the locked grid shows that the foam yields at the walls and the flow can be associated with a viscosity and the fact that particles which fall out of the foam draft, kiss and chain as in a viscoelastic fluid (figure 1) rather than draft, kiss and tumble as in a Newtonian fluid shows that the falling particles see a viscoelastic fluid (see Joseph et al. [1994] and [1996]).


Figure 8: Particles falling in the foam tend to chain as in viscoelastic fluid.

The criterion (1) for foaming is not strongly affected by the presence of particles; the mixture will foam when the gas velocity is high enough even in a fixed bed. The foam at top of the reactor acts as a barrier to further expansion of particles in the fluidized bed and the creation of more foam by increasing the gas input compresses the fluidized bed.

## 3. Foam suppression with glass and plastic spheres

Prior literature (Garret [1993], Bikerman [1973], Prud'homme \& Khan [1996]) on the use of particles to destroy foam describe effects of hydrophobic particles which attack the foam. Fluidization of hydrophilic particles to increase the liquid fraction (hold-up) under a foam barrier has not been discussed before.

We found that we could suppress foam by fluidizing hydrophobic particles in the bubbly mixture. This suppression can be framed as a decrease in the gas fraction or an increase in the liquid fraction of the bubbly mixture. Such effects have been reported for gas bubbles rising in pure liquids which dont foam but the decrease in the gas fraction in the pure liquid case is at best $20 \%$ compared to the $75 \%$ reduction which can be achieved in foaming systems.

For a simple mixture the gas fraction in the reactor is a linear combination of the gas fraction in each region.

$$
\begin{equation*}
\epsilon_{g}=\epsilon_{g f} f+(h-f) \epsilon_{g b}+\epsilon_{g s}(1-h) \tag{23}
\end{equation*}
$$

where $f=X_{f} / H, h=X_{p} / H, \epsilon_{g b}$ is given by (5), $\epsilon_{g f}$ is given by (7) and we propose that

$$
\begin{equation*}
\epsilon_{g s}=\epsilon_{g o} \Phi+\epsilon_{g b}(1-\Phi) \tag{24}
\end{equation*}
$$

where $\epsilon_{g o}$ is the gas fraction in the packed bed formed from all the particles in the slurry and $\Phi=C_{s} / C_{o}$ is the ratio of the volume concentration of spheres $C_{s}=\frac{4}{3} \pi n a^{3} / V_{s}$ in the expanded slurry to the concentration $C_{o}=\frac{4}{3} \pi n a^{2} / V_{o}$ in the packed bed. Here $V_{s}$ is the volume of the fully expanded slurry under foam (figures 9 and 10) and $V_{o}$ is the volume of the packed bed. When $C_{s}=C_{o}, \epsilon_{g s}=\epsilon_{g o}$; when $C_{s}$ tends to zero for a very expanded bed, $\epsilon_{g s} \rightarrow \epsilon_{g b}$. There is at present no theory giving the volume fraction $C_{s}$ of fluidized spheres fully expanded under a foam barrier. A typical case giving the foam fraction $f$ as a function of $U_{g}$ for a fixed $U_{l}$ is shown in figure 9 and in the explanatory cartoon shown in figure 10. Most of the data points in the figures below are for the fully expanded case $h=f$.

The control variables entering into the description of the effects on foam height of fluidizing spheres of one size are the size, density and initial solids fraction of spheres $\epsilon_{p}$ which is determined once and for all by the number of spheres which are loaded into and remain in the reactor. We have already noted that the effective concentration $C_{s}$ of spheres in a fully expanded bed under the foam is determined by the dynamics of the bed and cannot be given a-priori. At first, the solids


Figure 9: Effect of $532 \mu \mathrm{~m}$ glass particles on foam formation in a reactor of height $H$ with $U_{l}=0.257 \mathrm{~cm} / \mathrm{s}$. The fluidized particles in the slurry suppress the formation of foam even when the slurry is not expanded, $X_{f}<X_{p}$. For $U_{g}>U_{g}^{*}(\approx 7.5 \mathrm{~cm} / \mathrm{s})$, the bed is fully expanded $X_{f}=X_{p}$ and its further expansion for increasing $U_{g}$ appears to be inhibited by the foam.
in bubbly mixture expand in the usual way independent of the initial solids fraction. As the gas velocity is increased the bed expands more and the foam barrier falls until they touch. Then the bed is fully expanded under foam.

In section 5 we shall show that the gas fraction $\epsilon_{g}$ in a foaming reactor is decreased when (1) the initial solids fraction $\epsilon_{p}$ of particles of fixed size and density is increased (figures $11 \& 12$ ), (2) the size of particles at fixed $\epsilon_{p}$ and density is decreased (figures $13 \& 14$ )and (3) the density of particles of fixed size and concentration is decreased. To explain these trends we need first to discuss the mechanisms of foam suppression.


Figure 10: Particles in the bubbly mixture suppress foam even when they are not fully expanded as in (a) and (b). In (c) and (d) the fluidized bed and foam both expand against each other as the gas velocity is increased (cf. figure 9).

## 4. Mechanisms of foam suppression

The suppression of foam may be explained as an increase in the liquid hold-up in bubbly mixture by fluidized particles or by a decrease in gas hold-up. These effects are associated with increases in (1) the effective density of the liquid-solid mixture, (2) the area of effective wetted walls and (3) bed expansion. Gas bubbles rise faster in the composite liquid because the effective buoyant lift is greater, decreasing gas hold-up. This effect occurs both in foaming and non-foaming bubble columns.

Hydrophilic particles suspended in a bubbly mixture increase the effective area of walls wetted by liquid. Fluidized particles are stationary in an average sense so that liquid on the wall is held back. Another way to say this is that the average forward velocity of liquid is reduced by no-slip relative to an effective stationary wall composed of the reactor walls plus the wetted surface of fluidized particles.

The expansion of a bed of particles without a foam barrier should not depend on the initial batch loading $\epsilon_{p}$. However, the foam barrier prevents the further expansion of a fully expanded bed in the bubbly mixture under the foam trap (see figure 9). The effective concentration of such an expanded bed does depend on the batch loading and $V_{s}$, thus $C_{s}$ is a monotonic function of $\epsilon_{p}$; the effective concentration increases with the batch loading.

The bed expansion is the third and possibly most important mechanism of foam suppression. The more that we can expand a bed of hydrophilic particles, the greater will be the fraction of liquid held in the reactor. Inspection of figures 9 and 10 suggests that the sharply decreased height of foam generated for fluidizing particles struck as a balance between increasing bed expansion and increased foaming generated by increasing the gas velocity $U_{g}$ at fixed liquid velocity $U_{l}$.

## 5. Data for foam suppression by fluidized spheres of different density concentration and size

Figures 11 and 12 show that the gas fraction decreases sharply with the initial solids fraction $\epsilon_{p}$ of spheres for both glass and plastic $532 \mu \mathrm{~m}$ spheres, respectively; the addition of plastic or glass sharply reduces the height of the foam, or increases the height of the bubbly mixture. Comparing figures 11 and 12 for the same $\epsilon_{p}$ and liquid velocity shows that the gas fraction is smaller for the plastic than for the glass spheres. The lower density of plastic spheres will give rise to a greater bed expansion for particles of fixed size, concentration and fluidizing velocity.

We next consider the effects of changing the size of the particles. For spheres of the same density and initial loading $\epsilon_{p}$, the smaller particles are more effective in reducing the foam (gas fraction $\epsilon_{g}$ ) in the reactor. This effect is shown in figure 13 for plastic and in figure 14 for glass particles. We may interpret this effect as an increase in liquid hold-up


Figure 11: Gas fraction as a function of gas velocity for different initial solids fractions $\epsilon_{p}$ of $532 \mu \mathrm{~m}$ glass spheres.
produced by the increase in area of particles contacting liquid which you get when the size of the particles is reduced at fixed solids loading and as an increase in the bed expansion following from the reduction of the buoyant weight of small particles.

The liquid fraction for the largest $3000 \mu \mathrm{~m}$ particles is actually smaller than the liquid fraction with no particles. However, there is less foam, a smaller gas fraction $\left(\epsilon_{g}=1=\epsilon_{l}-\epsilon_{p}\right)$ than in bed with no particles. Hence, the fraction $\left(\epsilon_{l}+\epsilon_{p}\right)$ of liquid plus solid with large particles circulating is greater than with no particles, even though the liquid fraction is smaller (figure 15). If you need liquid in the reactor, overly large particles should not be used. Collapse of the data can be obtained by dividing $\left(1-\epsilon_{g}\right)$ by the area per unit volume of reactor $6 \epsilon_{p} / d_{p}$ (figure 16 ).

## 6. Summary

- A cold model bubble column reactor has been constructed in a narrow slit geometry which reproduces existing data from the literature on non foaming systems and cylindrical bubble columns. The column is equipped for high accuracy measurements of gas hold-up. The slit geometry allows us to observe the flow pattern and bubble size and to determine the presence of foam.
- The gas hold-up in non foaming systems can be correlated using the concept of slip velocity between the gas and liquid phases. The gas hold-up for water/air systems can be obtained from Richardson/Zaki type of correlations.


| 1.- $-U_{l}=0.154 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=9.9 \mathrm{~V} \%$ | 5.- $U_{l}=0.2567 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=19.5 \mathrm{~V} \%$ |
| :--- | :--- | :--- |
| 2.- $U_{l}=0.2567 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=9.9 \mathrm{~V} \%$ | 6. $-U_{l}=0.4621 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=19.5 \mathrm{~V} \%$ |
| 3. $\triangle U_{l}=0.4621 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=9.9 \mathrm{~V} \%$ | 7.- $-U_{l}=0.154 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=29.2 \mathrm{~V} \%$ |
| 4.- $U_{l}=0.154 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=19.5 \mathrm{~V} \%$ | 8.- $U_{l}=0.2567 \mathrm{~cm} / \mathrm{s}-\varepsilon_{p}=29.2 \mathrm{~V} \%$ |

Figure 12: Gas fraction as a function of gas velocity for different initial solids fractions $\epsilon_{p}$ of $532 \mu \mathrm{~m}$ plastic spheres.

- When a mixture water/surfactant is employed in the bubble column, foam can be present depending on the input parameters. Bubble and foam regimes are present at the same time in the column; the foam regime above is separated from the bubbling regime below by a very clear interface that moves down sharply when the gas velocity is increased.
- One of the most important results is that the dynamic response of the slit bubble column is nearly the same as in the large CANMET high temperature and pressure commercial reactor ( 2 m in diameter). This result suggest that detailed studies of the characteristics of such big reactors can be obtained from relatively inexpensive slit reactors. The CANMET process can be simulated using a mixture Water/1-Pentanol/SDS.
- The total gas hold up in foaming systems can be predicted using the slip velocity concept for each of the phases (foam and bubbly mixture) by applying Richardson/Zaki type of correlations. The foam fraction is predicted by an energy balance where the ratio of the volume of foam to volume of bubbly mixture is given by the ratio of the energy dissipated in each of the phases. It is perhaps of interest that the foam height and other features of reactor respond are obtained from this energy balance in which thermodynamic correlations (temperature, interfacial energy, etc.) are totally neglected.
- The viscosity of the foam for a given foaming system is determined by the slip or relative velocity $\nu_{g}=\nu_{l}=d_{b} \dot{\gamma}$ and the foam gas hold up according to (22).
- Marked reduction in the gas hold-up (or foam height) of


| 1. - - No Particles | 5. - $9.9 \mathrm{~V} \% 532 \mu \mathrm{~m}$ [area $\left.=11.2 \mathrm{~cm}^{2} / \mathrm{cc}\right]$ |
| :---: | :---: |
| 2. $\checkmark-10 \mathrm{~V} \% 1068 \mu \mathrm{~m}\left[\right.$ area $\left.=5.6 \mathrm{~cm}^{2} / \mathrm{cc}\right]$ | 6. $-19.5 \mathrm{~V} \% 532 \mu \mathrm{~m}\left[\mathrm{area}=16.9 \mathrm{~cm}^{2} / \mathrm{cc}\right]$ |
| 3. $-\triangle-20 \mathrm{~V} \% 1068 \mu \mathrm{~m}\left[\mathrm{area}=11.2 \mathrm{~cm}^{2} / \mathrm{cc}\right]$ | 7. $\simeq 29.2 \mathrm{~V} \% 532 \mu \mathrm{~m}\left[\mathrm{area}=32.9 \mathrm{~cm}^{2} / \mathrm{cc}\right]$ |
| 4. $-\mathrm{O}-30 \mathrm{~V} \% 1068 \mu \mathrm{~m}\left[\mathrm{area}=16.9 \mathrm{~cm}^{2} / \mathrm{cc}\right]$ |  |

Figure 13: Effect of particle size on the gas fraction for plastic particles. The gas fraction decreases as the area of the particles increase, (size or number).


$$
\begin{array}{ll}
\text { 1. }- \text { NoParticles } & \text { 4. }-\triangle-\text { GLASS } 730 \mu \mathrm{~m}\left[\mathrm{area}=16.4 \mathrm{~cm}^{2} / \mathrm{cc}\right] \\
\text { 2. }- \text { GLASS } 3000 \mu \mathrm{~m}\left[\text { area }=4.0 \mathrm{~cm}^{2} / \mathrm{cc}\right] & \text { 5. }-\mathrm{O}-\mathrm{GLASS} 532 \mu \mathrm{~m}\left[\mathrm{area}=22.6 \mathrm{~cm}^{2} / \mathrm{cc}\right] \\
\text { 3. }- \text { GLASS } 1105 \mu \mathrm{~m}\left[\mathrm{area}=10.9 \mathrm{~cm}^{2} / \mathrm{cc}\right]
\end{array}
$$

Figure 14: Effect of the particle size on the gas fraction for glass particles. The variation is monotonic in the size $\left(\epsilon_{l}+\epsilon_{s}=1-\epsilon_{g}\right)$ increases with area. The largest particles have less gas but also less liquid placing a practical limitation.
up to $75 \%$ can be achieved in a foaming reactor by fluidizing hydrophilic particles in the bubbly mixture below the foam. The gas hold-up is decreased when (1) the number of particles of fixed size and density loaded in batch (the solids loading $\epsilon_{p}$ ) is increased, (2) the size of particles at fixed loading and density is decreased and (3) the density of particles of fixed size and loading is decreased. The decreases in gas hold-up can be associated with an increase in the buoyant lift on bubble due to an increase in the effective density of the solid-liquid mixture, the increased area of wetted walls of fluidized particles and the increases in bed expansion caused by lighter particles and reduced particle size at fixed loading.

- The fluidization of particles always increased the holdup of solids plus liquid; if the particle size is not too large (figure 16) the liquid hold-up itself is increased by


Figure 15: Effect of the particle size on the liquid fraction $\epsilon_{l}$ in the whole reactor. The largest particles reduce the liquid fraction below the value for no particles; however $\epsilon_{l}+\epsilon_{g}$ ( 3000 microns) $>\epsilon_{l}$ (no particles) so that the gas fraction $\epsilon_{g}$ is smaller. The greatest increase in the liquid fraction is produced by the smaller particles (larger area).


Figure 16: Ratio between $\left(\epsilon_{l}+\epsilon_{g}\right)$ and particles per unit volume of reactor as a function of gas velocity.
fluidizing particles.

- The height of foam decreases slightly in a fully expanded bed of particles under foam when the gas velocity is increased at a constant liquid velocity. This foam height is struck as balance of the tendency to increase the bed expansion by increasing the fluidizing gas velocity and to decrease the expansion by greater production of foam.

The foam barrier which keeps hydrophilic particles in a reactor and increases liquid hold-up has a certain technological potential for enhanced liquid-solid contact in commercial reactors (and forms the basis of a patent application presently under consideration).

The trends identified here should be established in greater quantitative detail. The possibility of generating increased solids hold-up in reactors with continuous rather than batch injection of particles is strongly suggested by the results given here.

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## APPENDIX

Calculation of the bubble diameter $d_{b}$ in equations (4) and (5) Deckwer [1992] argued that the bubble size in a bubble column can be related to the energy density by a power law

$$
\begin{equation*}
D_{b}=k\left[\frac{E}{V_{l}}\right]^{m} \tag{A. 1}
\end{equation*}
$$

where $k$ and the exponent $m$ are function of the system. The energy dissipation density per unit volume of liquid term $E / V_{l}$ has to be evaluated in terms of the fluid dynamic parameters. In concurrent up-flow operation of bubble columns the area created and liquid re-circulation is achieved by the turbulence induced by the gas flow. Gas enters at the bottom of the column which is at a higher pressure and leaves the top at lower pressure. The pressure difference between top and bottom is given the liquid head because of pressure losses due to friction are negligible. Therefore, the amount of energy available in the column $E$ can be obtained from the gas and liquid phase energy balance

$$
\begin{equation*}
E=Q_{g} \Delta P \tag{A. 2}
\end{equation*}
$$

where $Q_{g}$ is the total volumetric gas, $\Delta P$ is the pressure difference between the bottom and top of the column.

In a bubble column the pressure difference between the bottom and the top of the column (height $H$ and cross section area $A$ ) can be calculated as follows:

$$
\begin{equation*}
\Delta P=\rho_{l}\left(1-\epsilon_{g}\right) H_{g} \tag{A. 3}
\end{equation*}
$$

Substituting equation (A.1) into 3.5.18 with $Q_{g}=A U_{g}$ and dividing by the liquid volume in the column $V_{l}=A H\left(1-\epsilon_{g}\right)$, finally an expression for the power dissipation in a bubble column is obtained:

$$
\begin{equation*}
\frac{E}{V}=\rho_{l} g U_{g} \tag{A. 4}
\end{equation*}
$$

Therefore, (A.1) can be written as $D_{b}=k\left(E / V_{l}\right)^{m}=$ $k\left(\rho_{l} g U_{g}\right)^{m}$.

The fitting parameters $k, m$ and $n$, in (A.1) were determined in different foaming systems by nonlinear regression. Table 2 gives the values of the fitting parameters $k$ and $m$.

The fitting parameter $n$ was $n=-l$ for the three foaming systems evaluated as has been reported by Davidson et al. [1966] a regression parameter $R^{2}$ higher than 0.99 , shows that a good fitting has been obtained in all the cases.

| System | Fitting Parameters |  | Regression <br> Parameter |
| :---: | :---: | :---: | :---: |
|  | $k$ | $m$ | $R^{2}$ |
| Water/0.04wt\%SDS | 20.255 | -0.55147 | 0.997 |
| Water/0.02wt\%SDS 1wt | 34.057 | -0.6429 | 0.993 |
| Water/0.04wt\%SDS <br> $/ 1 \mathrm{wt} \mathrm{\% 1-Pentanol}$ | 38.778 | -0.7148 | 0.997 |

Table 2: Fitting parameters of gas hold-up in the bubbly mixture from equation (A.1) and (5) for three foaming systems evaluated.

