A Model for a Foam-Bed Slurry Reactor

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A typical foam-bed reactor is a shallow pool of liquid above a gas distributor with a tall column of foam above it. Foam is generated by passing a gas through the pool of liquid, which is either self-foaming or contains a surfactant. Such a foam-bed reactor can be operated in various modes: semibatch, continuous flow, refluxed, and countercurrent. In all these modes, the distorted foam bubbles rise upward along with the liquid films surrounding them. The films of liquid drain continuously in the process and attain, in certain cases, a thickness at which the foam breaks and the gas escapes. Alternatively, foam has to be broken mechanically to separate gas from the liquid. Many investigators (Helsby and Birt, 1955; Metzner and Brown, 1956; Jackson, 1963; Zurakowski and Glaser, 1966; Sieu and Wasilewski, 1972; Shah and Mahalingam, 1984), have developed correlations involving physical characteristics of foam-bed and mass-transfer coefficients. Other models based on the idealized dodecahedral structure of cellular foam involving absorption of a gas accompanied by a chemical reaction in a foam matrix, have been proposed by Biswas and Kumar (1981) and Bhaskarwar and Kumar (1984, 1986). These investigators have essentially used the semibatch mode of operation.

The carbonation of lime slurries is encountered in the manufacture of precipitated calcium carbonate. Slurry reactions are also usefully employed in a variety of chemical industries and in pollution control. By virtue of such large interfacial areas available for mass transfer in foam beds, it may be advantageous to employ these reactors to carry out some of the slurry reactions. An attempt has been made to develop a model for such a situation and verify it experimentally.

The Model

A typical slurry foam-bed reactor can be divided into two sections, a storage section and a foam section. The storage section is a small pool of slurry containing a surfactant to enhance foaming above the gas distributor plate. The gas bubbles rise through the pool of slurry and reach the top of the storage section. At the slurry-foam interface, the spherical bubbles of gas attain a pentagonal dodecahedral shape and move upward until they reach the top of the foam section. In the process of upward movement of the bubbles, the films continuously drain the slurry downward through the Plateau borders. At a certain thickness of slurry films, the films break and a foam-gas interface is formed at the top of the foam section. The bubbles travel a fixed distance in the foam section and the entrapped gas in the bubbles remains in contact with the slurry films for a fixed time, t_c. The gas contains the species A, which gets absorbed into the slurry films in the foam section. The physicochemical processes are:

$$\begin{aligned} &A\ (\text{gas}) \rightarrow A\ (\text{aqueous}) \\ &B\ (\text{solid}) \rightarrow B\ (\text{aqueous}) \\ &A\ (\text{aqueous}) + Y.B\ (\text{aqueous}) \rightarrow \text{Products} \qquad (1) \end{aligned}$$

The following assumptions have been made.

- Bubbles do not undergo either backmixing, breakage or coalescence.
- The foam section has a constant slurry holdup throughout its height. This has been shown to be reasonably correct for liquids of low viscosity (Desai and Kumar, 1983).
- The volume fraction of the solid reactant in the slurry is low and the particles are spherical and have a discrete size distribution.
- Absorption of gas taking place in the storage section is neglected, as it turns out to be too low. The gas absorption takes place solely in the pentagonal slurry films of foam matrix.
- The surfactant used offers an additional resistance to mass transfer process occurring at the gas-slurry film interface, since the surface-active chemical molecules accumulate there.
- The fast irreversible reaction between the absorbed gaseous species A and dissolved solid species B is pseudofirst-order with respect to species A. This has been confirmed using an analysis based on an approach similar to that of Ramachandran and Sharma (1969) and Sada et. al., (1977).

The material balance equation for the species B written over the storage section, based on the single-stage model as shown in

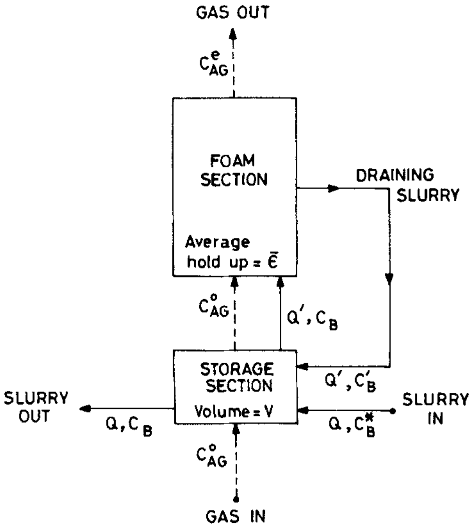

Figure 1. Single-stage model for slurry foam-bed reactor.

Figure 1 can be written as

$$\frac{dC_B}{dt} = \frac{Q}{V}(C^*_B - C_B) - \frac{Q'}{V}(C_B - C'_B) + \sum_i \left(\frac{4\pi n_{pi} K_{SLi}}{V}\right) r_i^2 (C^*_B - C_B) \quad (2)$$

where i indicates the ith size in the particle size distribution.

The last term in Eq. 2 represents the rate of solid dissolution in the storage. Equation 2 is applicable in continuous feed to storage. For the semibatch mode of operation of the foam-bed reactor, Q is equal to zero. The mass transfer coefficient K_{SLi} was calculated using Sherwood number equal to two.

Equation 2 cannot be solved unless C'_B and r are expressed in terms of C_B. The relationship between the instantaneous radius of particle r and the instantaneous concentration of B is:

$$\frac{dr_i}{dt} = -\left(\frac{K_{SLi}}{\rho_B}\right)(C^*_B - C_B) \quad (3)$$

In order to be able to compute C'_B, the diffusion equation for species A into slurry films of foam matrix needs to be written. Each pentagonal film of slurry is shared by two pyramidal gas pockets of $V_b/12$ volume, Figure 2. The diffusion equation for species A is:

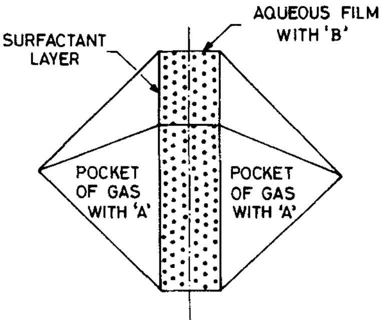

Figure 2. Slurry film associated with gas pockets.

$$\frac{\partial C_A}{\partial t_c} = D_A \frac{\partial^2 C_A}{\partial x^2} - \lambda C_A \quad (4)$$

The initial and boundary conditions are,

$$\text{At } t_c = 0 \quad \text{and} \quad -a \leq x \leq +a$$

$$C_A = 0$$

$$\text{At } t_c > 0 \quad \text{and} \quad x = \pm a \quad (5)$$

$$1\frac{\partial C_{AG}}{\partial t_c} = \mp D_A \frac{\partial C_A}{\partial x} = -K(C^*_A - C_A) \quad (6)$$

where

$$1 = V_b/12s \text{ and } C^*_A = kC_{AG} \quad (7)$$

Equation 4, subject to the conditions of Eqs. 5 and 6, has been solved using Laplace transform method and yields:

$$C_A(x, t_c) = \sum_{n=1}^{\infty} K_s \cos(k_n x) e^{(p_n t_c)} \Bigg/ \Bigg\{ \cos(k_n a) \cdot \left[1 - \frac{Lp_n}{(Lp_n + K_s)} + \left(\frac{1}{L} + \frac{p_n}{K_s}\right)\left\{\frac{a}{2} + \frac{Lp_n K_s}{[2D_A k_n^2 (Lp_n + K_s)]}\right\} + \frac{aLp_n^2 K_s}{[2D_A^2 k_n^2 (Lp_n + K_s)]}\right]\Bigg\} \quad (8)$$

where $L = 1/k$ and $p_n s$ are the nonzero roots of:

$$\frac{Lp_n K_s}{D_A(Lp_n + K_s)} = k_n \tan(k_n a),\ k_n^2 = -\frac{p_n + \lambda}{D_A} \quad (9)$$

Representing by M' the total amount of solute gas diffused in half the liquid film during contact time t_c and M_∞ for the corresponding quantity attainable theoretically after infinite time, we obtain

$$\frac{M'}{M_\infty} = 1 - \sum_{n=1}^{\infty} K_s e^{(p_n t_c)} \Bigg/ \Bigg((Lp_n + K_s) \Bigg\{ 1 - \frac{Lp_n}{(Lp_n + K_s)} + \left(\frac{1}{L} + \frac{p_n}{K_s}\right)\left[\frac{a}{2} + \frac{Lp_n K_s}{(2D_A k_n^2 (Lp_n + K_s)}\right] + \frac{aLp_n^2 K_s}{[2D_A^2 k_n^2 (Lp_n + K_s]}\Bigg\}\Bigg) \quad (10)$$

where

$$M_\infty = (C^0_{AG} V_b)/12 \quad (11)$$

Equation 10 simplifies to the case for a film without surfactant when $K_s \rightarrow \infty$. The ratio M'/M_∞ is a measure of fractional absorption of species A during contact time t_c in the foam section. Further, from stoichiometry,

$$C'_B = C_B - \frac{YM'}{(V_1/2)} \quad (12)$$

The values of t_c, V_b, V_1, L, a, and Q' were obtained using relations given by Biswas and Kumar (1981).

If the final outlet gas concentration C^e_{AG} at any time t is desired, it could be obtained easily from:

$$C^e_{AG}(t) = C^0_{AG}\left(1 - \frac{M'}{M_\infty}\right) \tag{13}$$

Equations 2 and 3 need to be solved simultaneously to obtain C_B values with respect to time t. These are solved numerically using a fourth-order Runge-Kutta method with modification due to Gill.

Experimental Method

Laboratory setup

The foam-bed reactor comprises a glass column of 1.35 m height and 0.047 m ID. The bottom of the column is flanged with a metal cone with a gas distributor in between. The gas distributor is a sieve plate made out of stainless steel with 15 holes of 1.5×10^{-3} m dia.

Compressed air at constant pressure is passed through a CO_2 scrubber in order to remove atmospheric carbon dioxide. The air stream is further passed through a dust remover packed with glass wool. Carbon dioxide gas from a cylinder is metered with a capillary flowmeter and mixed with the air steam. The mixture of air and carbon dioxide is further metered with an orifice meter before it enters the reactor.

Technique

The flow of known composition air-carbon dioxide mixture is started at the desired rate in the empty column. A slurry of calcium hydroxide is prepared using 0.5×10^{-3} m^3 distilled water and a known weight of calcium hydroxide powder of about 7 μm radius average particle size. A known amount of specific surfactant is added to the slurry to impart foamability, and the slurry charged into the reactor. A stopwatch is started at this point to measure the run time.

Slurry samples of nearly 5×10^{-6} m^3 volume are removed at predetermined intervals. All the samples (around eight per run) are analyzed iodometrically.

For a particular concentration of a surfactant and a particular flow rate and composition of the gas, at least four runs are conducted using different slurry compositions. Such a group of experiments is referred to as a set. A total of nine sets of experiments were conducted using combinations of three surfactants and three gas compositions.

Estimation of parameter K_s

It is felt that the most relevant way of estimating K_s would be to use a foam-bed reactor itself, which would offer similar times of contact. The system of reaction has to be chosen so that it is self-foaming. From the difference in conversion between the results obtained with and without surfactant, the values of K_s could be determined. Biswas and Kumar (1981) have used the system of carbonation of sodium hydroxide solutions in the absence of surfactant and found that their model could predict the experimental results quite well. The same system has been used in the present work and three surfactants were added to sodium hydroxide solutions. Keeping all other parameters same, the difference in the rates of carbonation in the presence and absence of surfactant was used to estimate parameter K_s. For 140 ppm of Triton X-100, 240 ppm of sodium lauryl sulfate, and 1,260 ppm of Teepol, K_s values have been estimated as 0.375×10^{-2}, 0.157×10^{-2}, and 0.319×10^{-3} m/s respectively.

Results and Discussion

The equipment and system parameters and operating variables studied in the present investigation are given in Table 1. The following effects have been studied.

Effect of run time on consumption rates of $Ca(OH)_2$

The experimental results for a typical experimental set are presented in Figure 3. The actual conditions of the experiment are given in the figure. A typical curve can be divided into two parts, the constant rate period and the falling rate period. The dotted line represents the constant rate period calculated for the case where surface resistance is absent (i.e., $K_s = \infty$).

The constant rate is observed as the particles of calcium hydroxide offer enough surface area to keep the liquid at virtually saturated condition. However, the calcium hydroxide particles continuously diminish in size with time and the area offered by all these is not enough to maintain saturation of

Table 1. System Parameters and Operating Variables

Variables	Codes for Experimental Sets								
	1.1	2.1	3.1	1.2	2.2	3.2	1.3	2.3	3.3
	Triton X-100			Na-L-S			Teepol		
Surfactant conc., ppm	140	140	140	240	240	240	1,260	1,260	1,260
$C_B^* \times 10^2$, kmol/m^3	4.0	4.0	4.0	3.89	3.89	3.89	3.59	3.59	3.59
$\bar{\epsilon}$	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027
$C^o_{AG} \times 10^3$, kmol/m^3	1.343	0.759	0.467	1.343	0.759	0.467	1.343	0.759	0.467
$Q_G \times 10^4$, m^3/s	5.55	5.45	5.40	5.55	5.45	5.40	5.55	5.45	5.40
No. runs conducted	8	7	7	8	7	7	5	5	4

Equipment parameters: $r_c = 0.047$ m; $H_N = 15$
System parameters: $D_A = 1.96 \times 10^{-9}$ m^2/s; $K_2 = 1.24 \times 10^4$ m^3/kmol · s
Operating variables: $H = 0.42$ m; $V_o = 5 \times 10^{-4}$ m^3; $r^o = 7 \times 10^{-6}$ m

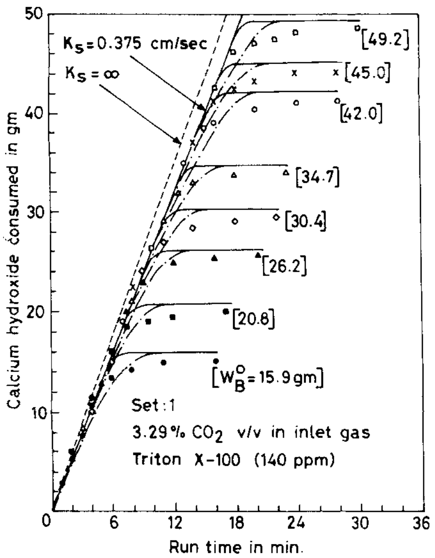

Figure 3. Lime slurry consumption vs. run time for experimental set 1.

hydroxide in the liquid. At this point the consumption v. time curve branches off from the straight line and the falling rate curve is generated. The calculations made by taking uniform particles of radius 7 μm are shown as solid lines. The model is able to predict the calcium hydroxide consumed during the constant rate period within ±2% of the observed values. However the variable rate could not be predicted. The calculated and observed values of $Ca(OH)_2$ consumed were different by as much as 15%. An attempt was made to take a particle size distribution containing particles of 2, 7, and 30 μm sizes. The 7 and 30 μm particles constituted 0.4 and 0.45 mass fraction, the rest were of radius 2 μm. The dotted lines show these calculations. The deviations now have been reduced to a maximum of 9%. However this deviation is systematic. Thus, the introduction of particle size distribution offers a partial explanation for the discrepancy. It is found that during the falling rate period, the dissolved B in the film is significantly reduced during time t_c and hence the pseudofirst-order condition is not satisfied, therefore making the model inapplicable there.

Effect of slurry compositions on consumption rates

For a fixed set of variables, such as inlet gas composition, foam height, and concentration of the surfactant in the slurry, various slurry compositions have been studied. For a typical experimental set, the plots of slurry consumption ($W_B^0 - W_B$) v. run time t are shown in Figure 4. It is interesting to observe from the figure that the constant rate line is the same for all the slurry concentrations studied. This is due to the saturated condition being maintained in the contactor. The branching-off for the falling rate periods occurs at different times. The comparison with the model is shown and is found to be excellent for the constant rate period. For the falling rate period, the arguments given earlier hold.

Effect of surfactants on consumption rates

It can be seen from Figures 3 through 5 that the constant rate periods for all the slurry compositions in a set of experiments follow a unique line. The dotted lines in the figures are obtained by simulation of constant rate period when surface resistance effects are not considered ($K_s = \infty$). It is evident that the slope of the dotted line is higher in all the sets than that given by the experimental data points, showing significant effect of surface resistance. This has been also pointed out by Shah and Mahalingam (1984). When appropriate K_s values obtained from independent experiments are used, the model predicts the experimentally observed lime slurry consumption rates quite well.

It is also seen that Triton X-100 gives the desired foamability and offers the least resistance among the three surfactants. If it is necessary to employ a foaming agent, its choice can be crucial for obtaining higher conversion. Otherwise the advantage of higher interfacial area could be nullified.

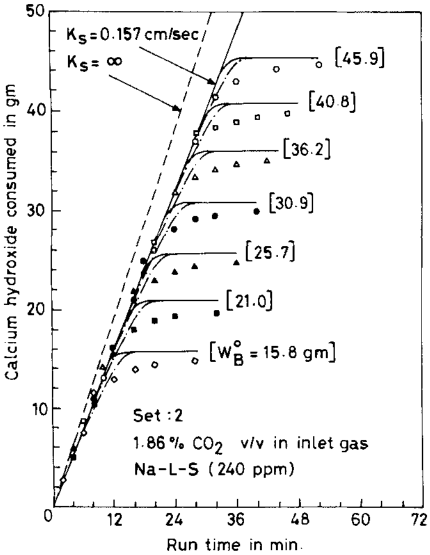

Figure 4. Lime slurry consumption vs. run time for experimental set 2.

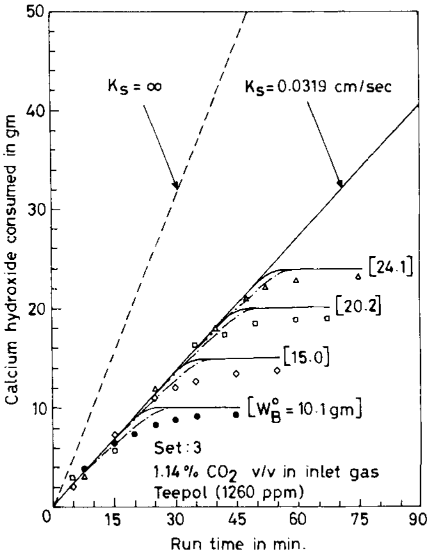

Figure 5. Lime slurry consumption vs. run time for experimental set 3.

Notation

A = species present in gas phase
$2a$ = thickness of a liquid film in foam section, m
a_p = external surface area of a single catalyst/slurry particle, m^2
B = species present in liquid phase or dissolving particulate species in slurry
C_A = concentration of A in liquid phase, kmol/m^3
C_A^* = concentration of A in liquid phase at gas-liquid interface in equilibrium with C_{AG} in foam section, kmol/m^3
C_{AG} = concentration of A in gas phase kmol/m^3
C_{AG}^0 = concentration of A in gas phase at $t_c = 0$, kmol/cm^3
C_{AG}^e = concentration of A in gas phase at exit of reactor, kmol/m^3
C_B = concentration of B in liquid phase kmol/m^3
C_B' = concentration of B in liquid draining from foam section, kmol/m^3
C_B^* = saturation concentration of B in liquid phase, kmol/m^3
D_A = diffusivity in liquid phase of species A, m^2/s
g = acceleration due to gravity, m/s^2
H = height of foam, m
H_N = number of holes in the distributor
K_s = liquid-side mass transfer coefficient for film at gas-liquid interface in presence of surface resistance and a chemical reaction, m/s
K_{SL} = mass transfer coefficient for solid dissolution, m/s
K_2 = second-order reaction rate constant, m^3/kmol · s
k = Henry factor
k_n = defined in Eq. 9
L = representative length of gas pocket, m
l = actual length of gas pocket, m
M' = total amount of reactant A, both free to diffuse and immobilized, in liquid film of thickness a and area s in time t_c in absence and presence of surface resistance, respectively, kmol
M_∞ = total amount of reactant A, both free to diffuse and immobilized, in a liquid film of thickness a and area s after infinite time, kmol
M'/M_∞ = fraction of A absorbed from gas phase in time t_c in absence and presence of surface resistance, respectively
n_p = number of dissolving slurry particles
p_n = defined in Eq. 9
Q = flow rate of liquid entering the foam-bed reactor, m^3/s
Q' = flow rate of the liquid draining from foam section, m^3/s
Q_G = flow rate of gas, m^3/s
r = radius of slurry particle of species B, m
r_c = internal radius of foam column, m
r^o = initial radius of slurry particle, m
s = surface area of a pentagonal liquid film, m^2
t = run time, s
t_c = contact time of gas with liquid in the foam section, s
V = storage section volume, m^3
V_1 = volume of a pentagonal liquid film of thickness $2a$ and area s, m^3
V_o = liquid volume in foam and storage, m^3
W_B = weight of reactant B in slurry phase at time t in reactor, kg
W_B^0 = initial weight of reactant B in slurry phase in reactor, kg
x = distance from center of a liquid film, m
Y = stoichiometric constant

Greek letters

λ = pseudofirst-order reaction rate constant, s^{-1}
ρ_B = density of solid species B, kg/m^3
$\bar{\epsilon}$ = average liquid holdup in foam

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