

## Carbonation of Barium Sulfide in a Foam-bed Reactor

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### Abstract

Carbonation of barium sulfide to barium carbonate has been experimentally investigated in a semi-batch foam-bed reactor. Experimental data have been generated and analyzed to assess the role of the reverse diffusional flux of the desorbed gas (hydrogen sulfide) in the actual performance of the foam-bed reactor. The experiments are carried out using lean carbon dioxide gas. The variables studied are height of foam bed, initial concentration of barium sulfide in aqueous solution, gas flow rate, concentration of carbon dioxide in mixture with nitrogen (diluent gas), volume of the barium-sulfide solution charged into the reactor, surfactant concentration in the aqueous solution, and the nature of surfactant. Effect of addition of different concentrations of salt (sodium chloride) is also studied. A simplified single-stage model based on the concept of resistances-in-series has been proposed to explain the experimental data in terms of an overall mass-transfer coefficient or resistance. The experimental data on conversion of barium sulfide are compared with the single-stage model of foam-bed reactor available in the literature (Bhaskarwar and Kumar, 1984), and found to be consistently lower than those provided by the model.

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### 1. Introduction

Over the last two decades, foam-bed contactor has emerged as a novel gas-liquid reactor. This reactor offers a very large interfacial area which makes it suitable for carrying out a gas-liquid reaction. It also offers a low liquid hold-up and a large contact time at the expense of a moderate pressure drop.

Gas absorption with chemical reaction, in a foam-bed reactor, has been analyzed in some detail in the past two decades (Biswas and Kumar, 1981; Bhaskarwar and Kumar, 1984, 1986; Bhaskarwar, 1987; Bhaskarwar et al., 1987, 1990; Bhaskarwar and Kumar, 1995; Bhaskarwar, 1997; Subramanyam et al., 1999; Varshney et al., 2003; Sharma et al., 2005). All these investigations dealt with a non-volatile product. Subramanyam et al. (1999) developed a strategy for designing a foam-bed reactor system for first or pseudo-first order gas-liquid reaction kinetics.

There are many industrial applications wherein a volatile product gas desorbs back into the gas phase. The primary purpose of desorption performed in practice is either to recover the gaseous product(s) formed or in some cases to remove the undesirable gaseous by-product(s). Desorption of the product into the gas phase generally alters the performance of any reactor, and will certainly affect the performance of a foam-bed reactor too. No experimental information on this effect is however available in literature till date for the latter.

Shah and Sharma (1976) reviewed and analyzed the process of desorption, with and without chemical reaction, with the help of film and penetration theories. They dealt with the systems wherein a gas is absorbed into a liquid followed by a series of chemical reactions, and subsequent desorption of a gaseous volatile product. Astarita and Savage (1980) gave a general approach to the analysis of chemical desorption based on film theory. Landau (1992) developed an analysis of desorption with chemical reaction in which reaction in both film and bulk phase was considered.

In the past, experimental investigations have been performed to understand the desorption phenomena (Schweitzer and Szebehely, 1950; Burrows and Preece, 1954; Pasiuk-Bronikowska and Rudzinski, 1981; Ishikawa et al., 1986; Hikita et al., 1990; Jeelani et al., 1990; Fidi et al., 1993). Jeelani et al. (1990) investigated the behavior of foams formed during the desorption of carbon-dioxide gas from a supersaturated aqueous surfactant solution involving mechanical agitation with vortex formation. A model allowing for the coalescence of gas bubbles was presented for the variation in foam height, above the liquid surface, with time during and after desorption. Fidi et al. (1993) also studied the behavior of foam formed during the desorption of carbon dioxide from batch supersaturated aqueous surfactant solution. Carbon-dioxide gas was desorbed by using submerged water and nitrogen jets issuing from a nozzle. The desorption was so rapid that above the liquid pool both froth and foam formed one above the other. This fact was taken into account while developing a model, to predict the variation in foam height with time during and after desorption, similar to that proposed by Jeelani et al. (1990).

The present experimental investigation is the first attempt to study the gas absorption, chemical reaction, and desorption in a foam-bed reactor. Carbonation of barium sulfide (BaS) was carried out in a semi-batch foam-bed reactor to produce barium carbonate ( $\text{BaCO}_3$ ) and hydrogen-sulfide gas ( $\text{H}_2\text{S}$ ) to assess the role of the reverse diffusional flux of the desorbed gas in the actual performance of the foam-bed reactor.

## **2. Experimental**

### *Preparation of reactant solution*

Commercial grade barium sulfide (nearly 60% BaS) was used as the raw material for the preparation of the reactant solution for carrying out the experiments. Distilled water used for preparing the solutions was first boiled to remove any dissolved oxygen and carbon dioxide present. Barium-sulfide powder was added to the distilled

water and the resulting slurry mixed thoroughly in an air-tight stirred cell for leaching of barium sulfide. Fresh solutions, filtered to clarity, were always used for experimentation, as it is known that barium-sulfide solution undergoes slow oxidation in air, forming elemental sulphur and a family of oxidized sulphur species including sulfite, thiosulfite, polythionates, and sulfate. A known amount of surfactant (Triton X-100 or CTAB) was added to the barium-sulfide solution before carrying out the gas-liquid reaction.

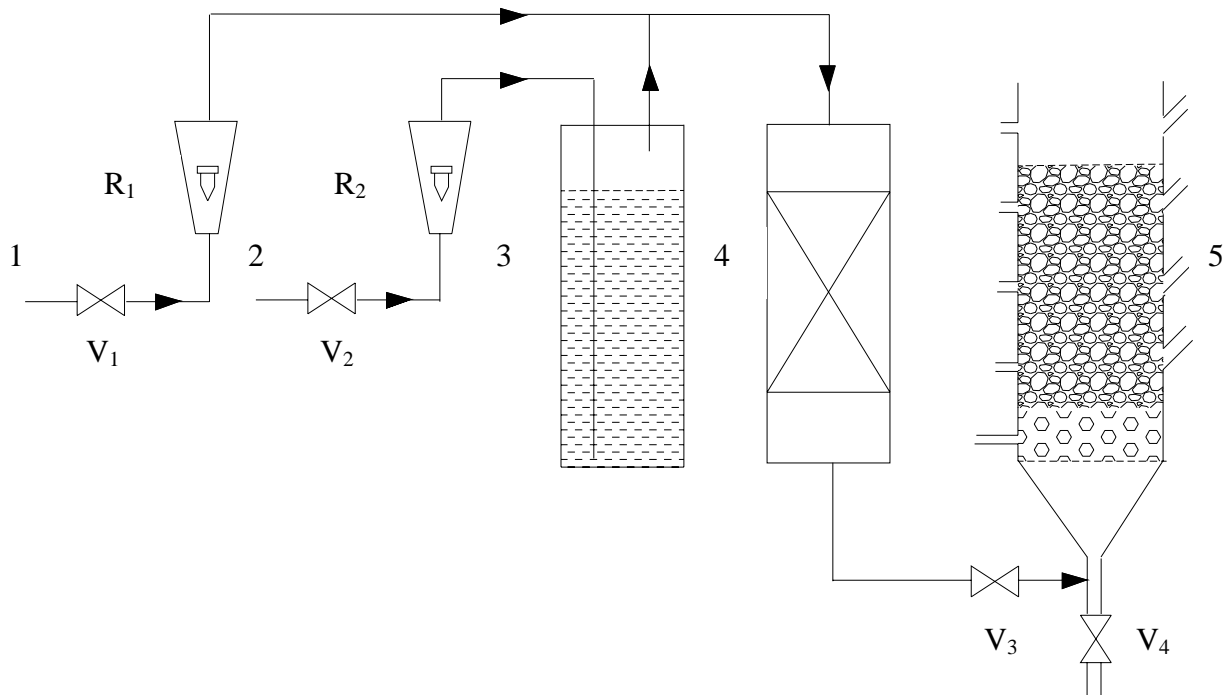
### *Set-up*

Carbonation of barium sulfide was carried out in a semi-batch foam-bed reactor. The experimental set-up and the details of the reactor are shown in figures 1 and 2(a). The foam-bed reactor comprises of a glass column with a conical bottom and a distributor plate. The column is provided with four manometer tappings at various heights to measure the liquid hold-up in the foam. U-tube manometers filled with water are used for measuring the hydrostatic head exerted by foam. The head indicated by the manometer divided by the foam height above the tapping directly gives the average liquid hold-up for foam above that point. The reactant solution is introduced into the reactor through the inlet port and the sample for analysis is collected from the bottom of the column at the end of a particular time of run. The measurements are repeated for different run times to obtain data on the performance of the reactor with time.

A glass distributor plate is placed between the cylindrical part and the conical section of the foam-bed reactor. The conical section ensures a uniform distribution of the stabilized flow of gaseous mixture through the distributor holes. The fabrication details of the distributor plate and the foam column are given in table 1.

### *Experimental procedure*

At the beginning of an experimental run, the glass column was thoroughly rinsed with distilled water. Flow rates of nitrogen (diluent gas) and carbon dioxide (gas-phase reactant) were measured separately, using calibrated rotameters. Nitrogen gas was first saturated with water vapor by bubbling it through a packed saturator. The saturated nitrogen gas was then mixed with a small stream of carbon dioxide in a packed bed, which also helped in removing any entrained water droplets. The mixture was then introduced into the foam-bed reactor. A batch of known volume of barium-sulfide solution, with known concentrations of sulfide and surfactant, was poured into the column through the inlet port after ensuring that the gas mixture passing continuously through the reactor had attained a steady flow rate. The solution started foaming and the foam began rising through the cylindrical reactor column. A direct contact with a layer of 1-butanol applied on a sieve plate suspended from the top was effectively employed to break the foam at a definite height. Samples of the reaction mixture were withdrawn from the bottom of the column from the sampling port at different time intervals till the reaction was complete and were analyzed iodometrically to determine the unreacted barium sulfide (Vogel, 1989).

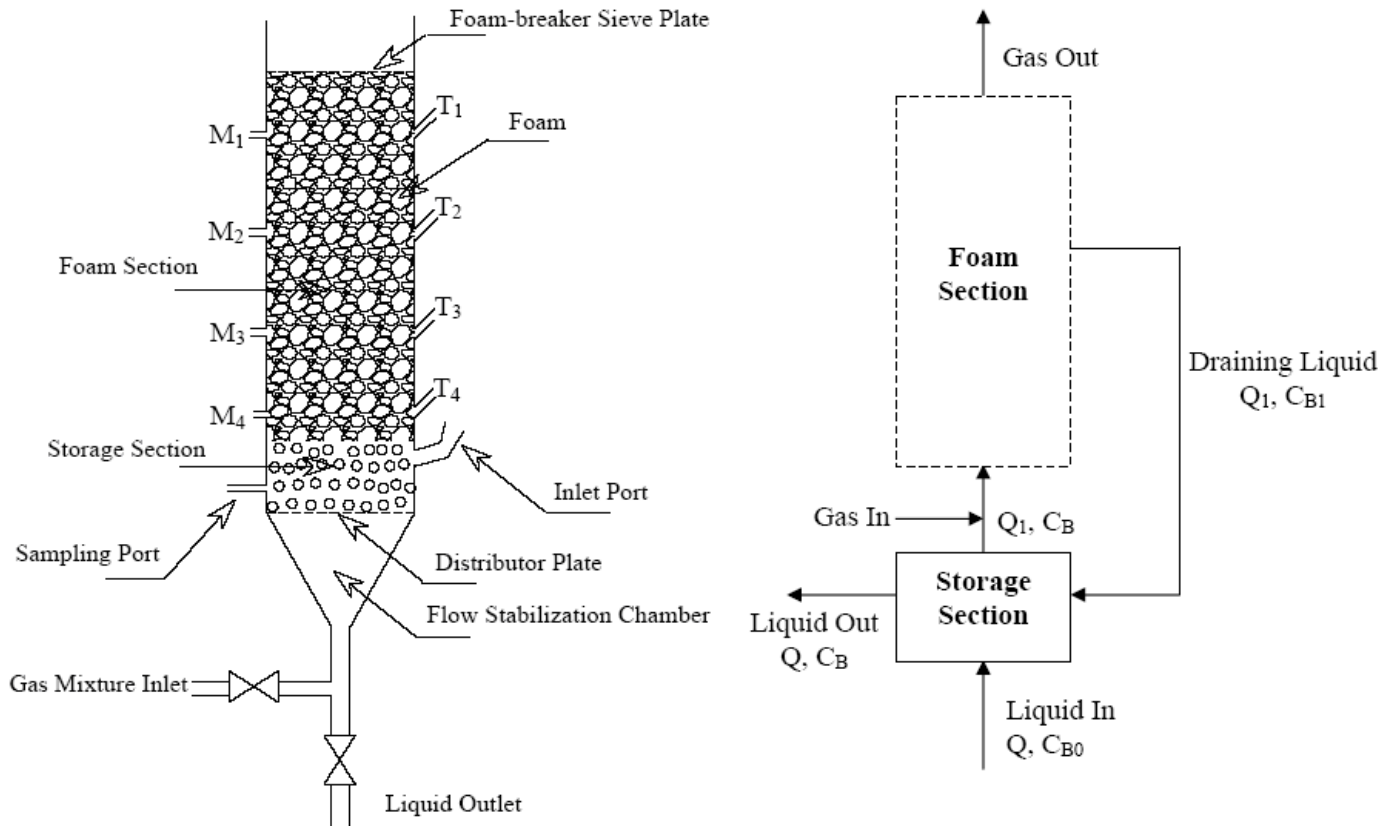


1: CO<sub>2</sub> supply. 2: N<sub>2</sub> supply. 3: Saturator. 4: Packed bed. 5: Foam-bed reactor. R<sub>1</sub> and R<sub>2</sub>: Rotameters. V<sub>1</sub>, V<sub>2</sub>, V<sub>3</sub>, and V<sub>4</sub>: Valves.

**Figure 1. Schematic Diagram of Experimental Set-up.**

**Table 1. Dimensions of the foam-bed reactor.**

<b>Distributor</b>	Diameter of distributor plate = 57 mm Thickness of distributor plate = 3 mm Number of holes = 12 Diameter of each hole = 2 mm Material of construction = Glass
<b>Column</b>	Diameter of the foam-bed reactor = 57 mm Height of the foam-bed reactor = 1100 mm Material of construction = Glass



( $M_1$ - $M_4$ ): (inclined) manometer tapplings.  
 $T_1$ - $T_4$ : Thermometer ports)

(a) (b)  
**Figure 2. Details of the Foam-bed Reactor with corresponding Single-stage model.**

### 3. Mathematical Model

Biswas et al. (1981) studied the absorption of  $CO_2$  from mixture with air in sodium-hydroxide solution containing surfactants like Teepol, sodium lauryl sulphate (SLS), and Triton X-100. A model was developed which took into account the interfacial resistance offered by the surface-active agents.

Bhaskarwar and Kumar (1984) proposed a simplified one-stage model of a foam-bed contactor wherein they visualized the entire foam section as a single section with a uniform liquid hold-up equal to the average value  $\bar{\varepsilon}$ . They studied the effect of surfactants like sodium dodecyl sulphate and octyl phenoxy polyethoxyethanol. It was found that during sodium-sulfide oxidation the resistance offered by the surfactants was negligible.

Asolekar et al. (1985) showed that the effect of surface resistance (or interfacial resistance), due to the presence of surface-active agents, on interphase mass transfer was too high to be neglected for  $CO_2$  absorption with chemical reaction in sodium-

hydroxide solution in a semi-batch foam-bed reactor. The presence of surfactants at the gas-liquid interface retards the transfer rate of solute from the gas to the liquid, and this effect becomes significant when the gas-liquid reaction is very fast.

All these models assumed the gas-phase resistance to be negligible with the sole exception of the model by Bhaskarwar and Kumar (1995) which dealt with the gas-phase controlled absorption of ammonia with instantaneous reaction in solutions of sulfuric acid in a foam-bed reactor. A new single-stage model based on the concept of resistances-in-series is proposed in this paper which incorporates the gas-phase, interface, and liquid-phase resistances into an overall mass-transfer resistance. This model can be used to organize and express the experimental measurements in terms of the overall mass-transfer coefficients.

A schematic diagram of the single-stage model of a foam-bed reactor is shown in figure 2(b). The assumptions involved are:

1. There is no accumulation of gas-phase species A in the storage section.
2. The reaction between gaseous reactant A and liquid-phase reactant B is fast and irreversible. Further, it displays pseudo-first order kinetics.
3. Overall mass-transfer resistance has contributions from the gas, liquid, and interfacial surfactant layer.
4. Due to the motion of buoyant bubbles and the recirculation of liquid draining from the foam section, the shallow storage section is completely backmixed.
5. There is no entrainment of liquid from the foam bed because the superficial gas velocity through the column is low enough ( $u_c < 5-7$  cm/s).
6. Liquid hold-up is constant in the entire foam section (applicable to foams made of low-viscosity liquids).
7. Bubbles in the foam section do not undergo backmixing, coalescence, breakage, expansion, or contraction.
8. The gas bubbles change instantaneously from spherical to regular pentagonal dodecahedral shape (figure 3) while emerging out of the storage section to enter the foam section.
9. Transport and physico-chemical properties/parameters are constant and independent of composition.
10. Isothermal conditions are maintained throughout the operation of the foam-bed reactor.

Based on these assumptions, the following material-balance equations are obtained.

Material balance for liquid-phase species B in the storage section:

$$-V \frac{dC_B}{dt} = \frac{Y_A A_i K_{OV}}{H} \int_0^H (C_{Ag} - 0) dz \quad (1)$$

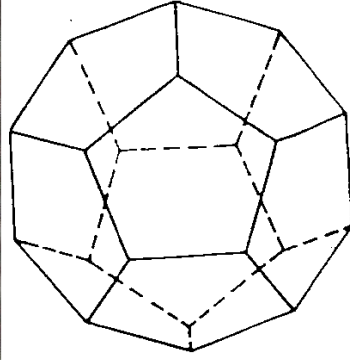
Initial condition:

$$\text{At } t=0; C_B=C_{B0} \quad (i)$$

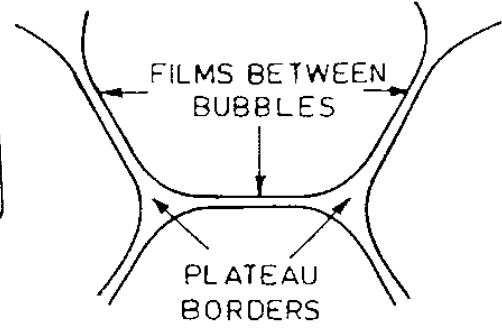
The overall mass-transfer coefficient is obtained from



**a. Actual foam**



**b. Idealization of a foam bubble**



**c. Elements of foam structure**

**Figure 3. A regular pentagonal dodecahedral foam bubble along with the films and Plateau borders.**

$$\frac{1}{K_{OV}} = \frac{1}{K_g} + \frac{K_e}{K_l} + \frac{K_e}{K_s} \quad (2)$$

where

$K_e$  = equilibrium distribution factor for A between the gas and liquid phases,

$$\frac{K_g d_B}{D_A} = Sh = 6.58 \dots (\text{for gas in foam bubble}), \quad (3)$$

$$K_l = \sqrt{D_A \lambda} \dots (\text{for liquid in storage in contact with a rising bubble}),$$

$$\text{or } K_l = 2 \sqrt{\frac{D_A}{\pi t_c^*}}; t_c^* = \frac{H}{u_B} \dots (\text{for liquid in foam in contact with the gas}). \quad (4)$$

Material balance for gas-phase species A in the foam bubble:

$$-V_B \frac{dC_{Ag}}{dt_c} = K_{OV} a_B (C_{Ag} - 0) \quad (5)$$

Initial condition:

$$\text{At } t_c=0; C_{Ag}=C_{Agi} \quad (ii)$$

Integrating equation (5), and using the initial condition (ii), we obtain (for  $t_c = \frac{z}{u_B}$ )

$$C_{Ag} = C_{Agi} e^{-\frac{K_{OV} a_B z}{u_B V_B}} \quad (6)$$

The integral in equation (1) is obtained as

$$\int_0^H C_{Ag} dz = \frac{C_{Agi} u_B V_B}{K_{OV} a_B} \left[ 1 - e^{-\frac{K_{OV} a_B H}{u_B V_B}} \right] \quad (7)$$

Substituting this integral in equation (1) and solving the latter, subject to the initial condition (i), we obtain

$$C_B = C_{B0} - \frac{Y_A A_i C_{Agi} u_B V_B}{H V a_B} \left[ 1 - e^{-\frac{K_{OV} a_B H}{u_B V_B}} \right] t \quad (8)$$

The value of slope obtained from the experimental plot of concentration of barium-sulfide solution in storage versus time may now be compared with the theoretical value anticipated from the above equation, i.e.

$$-\frac{Y_A A_i C_{Agi} u_B V_B}{H V a_B} \left[ 1 - e^{-\frac{K_{OV} a_B H}{u_B V_B}} \right]$$

The overall mass-transfer coefficient,  $K_{OV}$ , may thus be obtained from the data on the performance of a foam-bed reactor.

#### 4. Results and Discussion

The variables influencing the carbonation of barium sulfide in a semi-batch foam-bed reactor are height of foam bed, initial concentration of barium sulfide in aqueous solution, gas-flow rate, concentration of carbon dioxide in mixture with nitrogen (diluent gas), volume of the barium-sulfide solution charged into the reactor, surfactant concentration in the aqueous solution, and the nature of surfactant. Effect of addition of salt (sodium chloride) at different concentrations was also studied. An effort was made during the experimentation to vary only one variable at a time, keeping all other variables and parameters constant to the extent possible. The experimental data corresponding to CTAB are not reported in this paper and all the experimental results correspond to Triton X-100 (1000 ppm concentration) only, unless specified.

##### *Effect of height of foam bed on conversion*

As the foam height was increased from 0.1 to 0.4 m (figure 4), the conversion increased due to the increase in the interfacial area available for mass transfer as well as to the larger time of contact. At a foam height of 0.4 m, the maximum conversion of barium sulfide was obtained. Beyond this height, the conversion decreased as the reverse diffusional flux of desorbing hydrogen-sulfide gas overwhelmed the advantages of larger interfacial areas and contact times. At any given time, for Triton X-100, the conversions at 0.1 m and 0.7 m of foam height were on an average 28% and 17% (respectively) less than the conversions at 0.4 m of foam height. For CTAB, the conversions reduced by 21% for both of these heights relative to the maximum observed at 0.4 m.

##### *Effect of initial concentration of barium sulfide on conversion*

Figure 5 correspond to the effect of initial concentration of barium sulfide on conversion. The conversion at any time increased as the initial concentration of barium



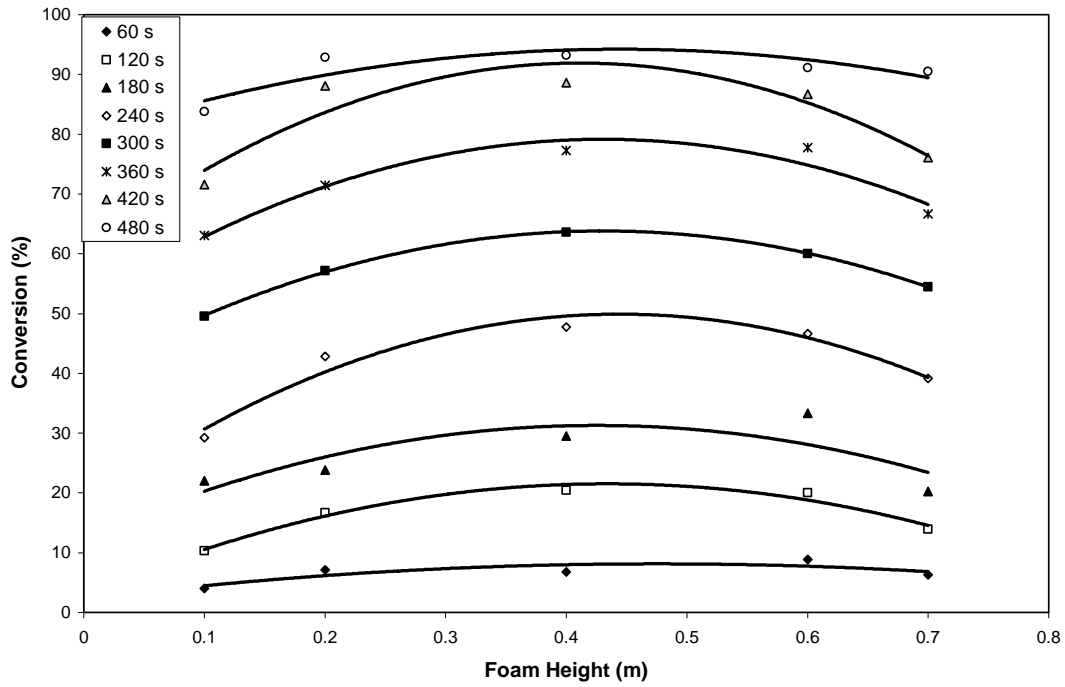


Figure 4. Variation of conversion with foam height at different times of contact.

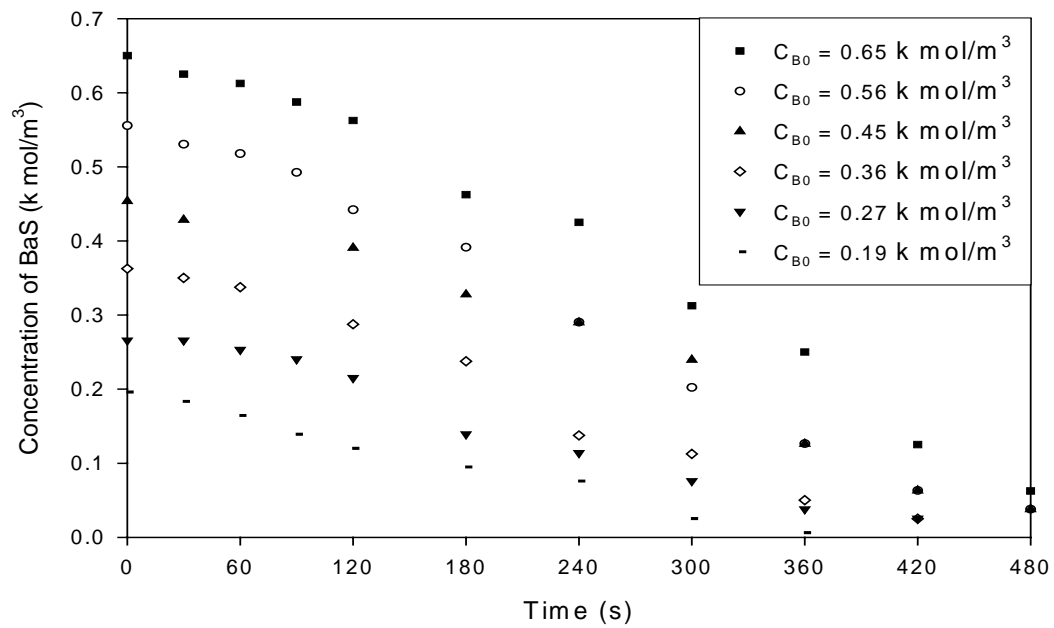


Figure 5. Effect of initial concentration of BaS on concentration vs time profiles.

sulfide was increased from  $0.19 \text{ k mol/m}^3$  to  $0.65 \text{ k mol/m}^3$ , with Triton X-100 as a surfactant. Higher initial concentration of barium sulfide implies a higher magnitude of the pseudo-first order reaction rate constant which results in the higher observed rates of reaction in the foam-bed reactor. At the lower initial BaS concentration ( $C_{B0}$ ) of  $0.19 \text{ k mol/m}^3$ , the rate of reaction of barium sulfide was  $0.0326 \text{ k mol/(m}^3\cdot\text{min)}$  which increased to  $0.069 \text{ k mol/(m}^3\cdot\text{min)}$  at  $0.65 \text{ k mol/m}^3$ . Thus, a three-fold increase in the initial concentration of barium sulfide produced a two-fold increase in the rate of reaction. For CTAB as a surfactant, the barium-sulfide concentration was varied from  $0.16 \text{ k mol/m}^3$  to  $0.66 \text{ k mol/m}^3$ , and the rate of reaction increased from  $0.0269 \text{ k mol/(m}^3\cdot\text{min)}$  to  $0.0783 \text{ k mol/(m}^3\cdot\text{min)}$ , i.e. a four-fold increase in the initial concentration brought about a three-fold increase in the rate of reaction of barium sulfide. This lower-than-linear increase in the observed reaction rate with  $C_{B0}$  is probably due to the retarding influence of desorption of  $\text{H}_2\text{S}$ , at least in part.

#### *Effect of gas-flow rate on conversion*

Figure 6 show the effect of gas-flow rate on conversion of barium sulfide in the foam-bed reactor. As the air-flow rate was increased from  $4.17 \times 10^{-5} \text{ m}^3/\text{s}$  to  $12.5 \times 10^{-5} \text{ m}^3/\text{s}$ , it was observed that the conversion increased almost by a factor of 2.5 to 3.0 for Triton X-100; perhaps due to the fact that the liquid hold-up also increased from 0.0242 to 0.0605 (0.0144 to 0.0928 for CTAB). At any given time during the first three minutes of reactor operation, the conversion increased six-fold (three-fold for CTAB) when the air-flow rate was changed from  $4.17 \times 10^{-5} \text{ m}^3/\text{s}$  to  $12.5 \times 10^{-5} \text{ m}^3/\text{s}$ . During the 4<sup>th</sup>-to-6<sup>th</sup> minute of reactor operation, however, for Triton X-100 the increase was three-fold (two fold for CTAB). In the initial stages of the gas-liquid reaction, the liquid-phase concentration of  $\text{H}_2\text{S}$  produced was small hence as large as a six-fold increase in conversion was observed. At larger times of reactor operation, the amount of  $\text{H}_2\text{S}$  produced in the liquid and its desorption rate was higher, and thus lowered the conversions in the foam reactor by its retarding effect on the  $\text{CO}_2$  gas absorption.

#### *Effect of concentration of carbon dioxide in the gas mixture on conversion*

Figure 7 show the effect of gas-phase concentration on barium-sulfide conversion for Triton X-100 based foam. The  $\text{CO}_2$  concentration was increased from  $1 \times 10^{-2} \text{ k mol/m}^3$  to  $2.5 \times 10^{-2} \text{ k mol/m}^3$ . With increase in the gas-phase reactant concentration, the driving force for absorption of  $\text{CO}_2$  in foam films containing dissolved reactant BaS increased, as the interfacial concentration increased proportionately. Hence the reaction rate and the conversion increased. A 2.5 times increase in the concentration of  $\text{CO}_2$  in gas brought about a two fold increase in the conversion in the foam-bed reactor at any given time upto about 3 minutes. The increase in conversions at greater times of operation of the reactor were lower for similar reasons as that cited earlier.

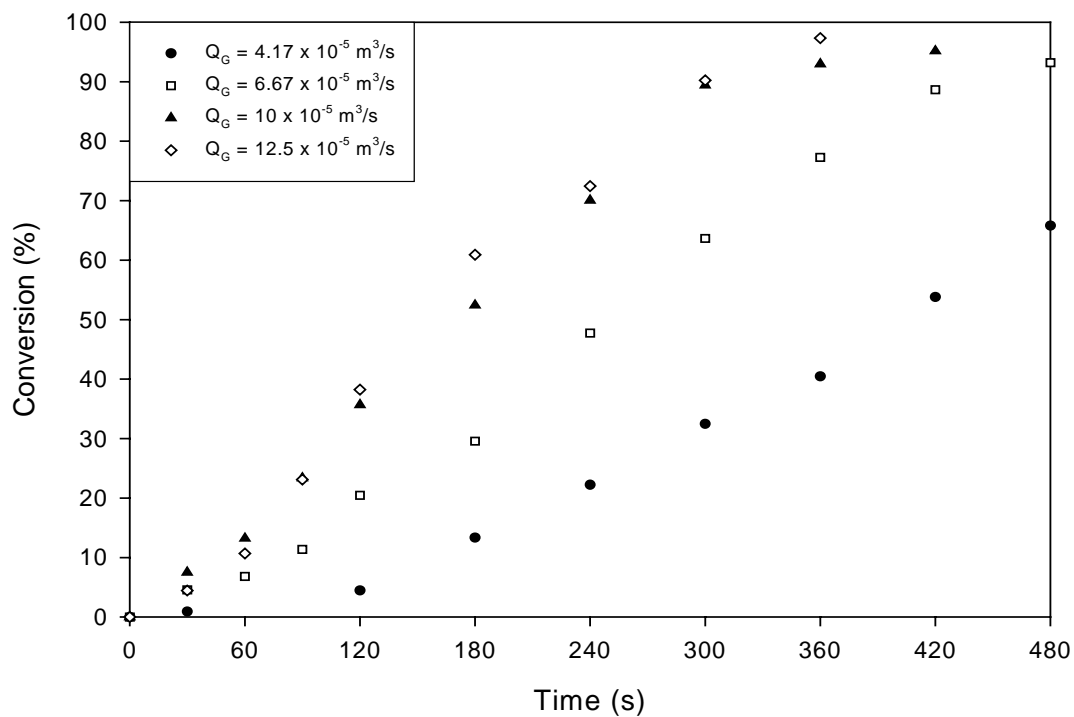


Figure 6. Effect of gas-flow rate on conversion.

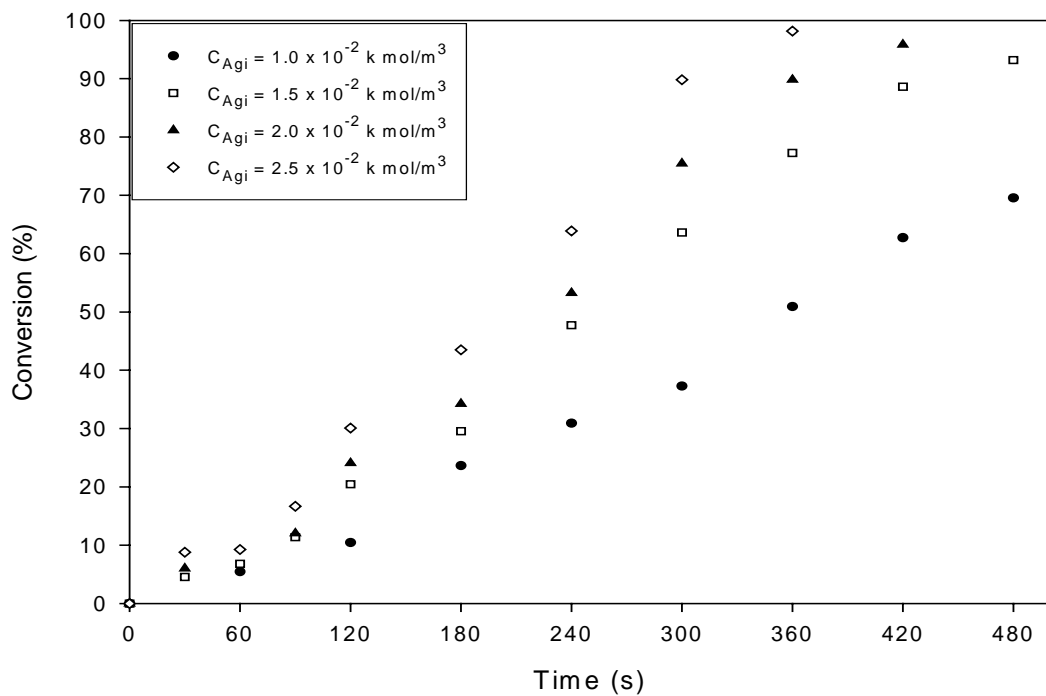
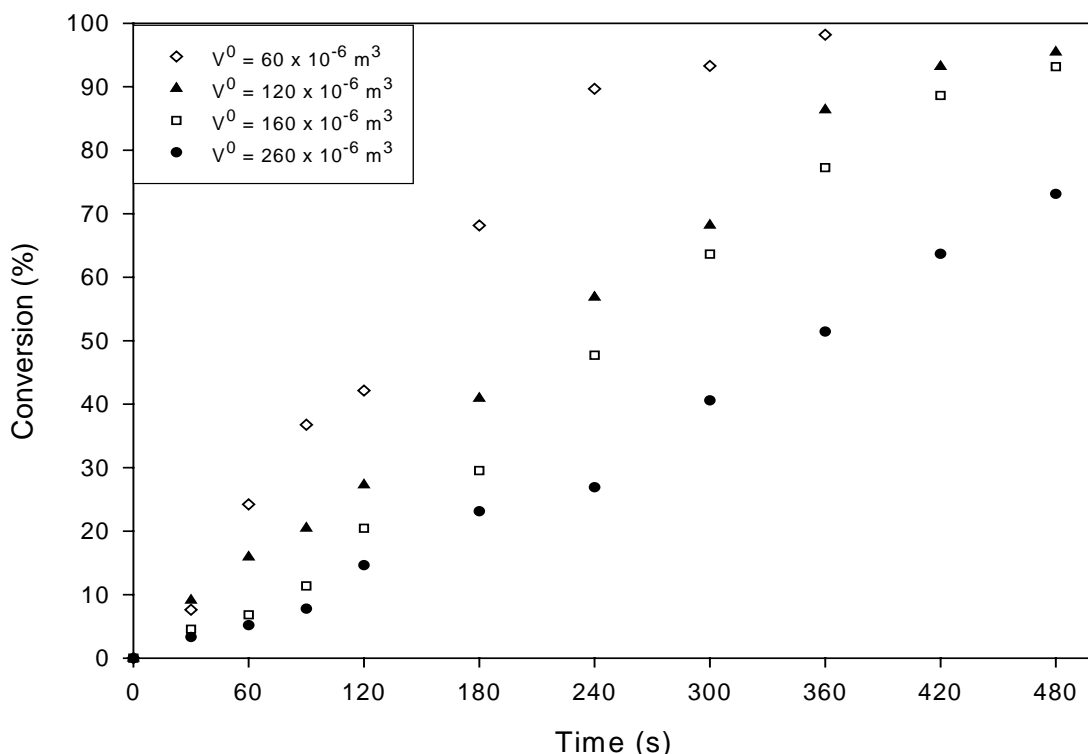


Figure 7. Effect of  $\text{CO}_2$  concentration on conversion.

### Effect of volume of reactant charged into the reactor

Figure 8 show the effect of volume of reactant charged into the reactor. The reactant volume was varied from  $60 \times 10^{-6} \text{ m}^3$  to  $260 \times 10^{-6} \text{ m}^3$ . As the volume of the batch of BaS solution increases, the conversion achieved in a given time decreases. Less volume of reactant in the storage section implies a more intense agitation of the liquid pool by the gas sparged as well as corresponds to lesser moles of the reactant (BaS) in the storage section. Greater extent of absorption of  $\text{CO}_2$  under these conditions leads to higher conversions. At any given time, about a 4 times greater volume of BaS solution charged into the reactor led to about 60% reduction in conversion when using Triton X-100 as a surfactant and about 50% reduction for CTAB.



**Figure 8. Effect of volume of reactant solution charged on conversion.**

### Effect of surfactant concentration and nature of surfactant on conversion

Three different types of surfactant were used during the experimentation, namely, Triton X-100 (non-ionic), CTAB (cationic), and the anionic surfactants like SDS, LABS, stearic acid, sodium-lauryl alcohol, Monoxol OT and Teepol. The aqueous solutions of barium sulfide did not foam with any of the anionic surfactants tried. The reason for this observation is however not known. Comparison of the performance of the non-ionic and cationic surfactants shows that the nature of surfactant does not affect the performance of the foam-bed reactor (figure 9). Comparison between Triton

X-100 and CTAB at nearly the same  $C_s/CMC$  value, however, shows that CTAB gives greater conversions compared to Triton X-100 beyond conversions of about 23%.

The optimum conversion is obtained at a surfactant concentration of 1000 ppm as shown in figure 10. The CMC values for both these surfactants are less than 1000 ppm, and these surfactants reduce the surface tension of the solution to a value less than 35 dynes/cm. The reason for the reduced conversion of barium sulfide, for the concentration of surfactant of 500 ppm, lies in the fact that the small number of surfactant molecules adsorbed at the gas-liquid interface results in high initial diffusional fluxes of  $CO_2$  into the liquid phase. This in turn leads to higher reaction rates and consequently to increased reverse diffusional fluxes of the product gas,  $H_2S$ , at later times. The overall diffusional flux of  $CO_2$  is therefore reduced by the bulk flow induced by desorption of  $H_2S$ , and hence lower conversions result. On the other hand, when the surfactant concentration is made as high as 10000 ppm, the number of surfactant molecules embedded in the film-gas interface is much higher resulting in a tightly packed multilayer with very little free interfacial area available for the diffusion of  $CO_2$ . The multilayer of surfactant molecules also offers a much greater diffusional resistance. Both these factors contribute to the reduced fluxes of  $CO_2$  into the foam, and hence the conversions of barium sulfide in the reactor are lowered.

#### *Effect of addition of sodium chloride*

Experiments were also performed for different concentrations of sodium chloride added to the aqueous solution of barium sulfide. As shown in figure 11, as the concentration of salt in the solution was increased, the conversion decreased. Barium sulfide is essentially monopolar in nature (Gallardo et al., 2000), i.e. it shows electron-donor character as demonstrated by the essentially zero value of the electron-acceptor component of its surface free energy. Pretreatment of the aqueous solution with sodium chloride significantly increases the electron-donor component and hence barium sulfide is repelled away from the interface which contains the nonionic surfactant Triton X-100. Thus, due to the lowered concentration of barium sulfide near the interface, the conversion decreases as the sodium-chloride concentration is increased.

When all experimental data are combined together on a single plot of fractional conversion vs dimensionless time, a best-fit straight line ( $y=0.9871x$ ) with a high correlation coefficient of 0.9382 results, as shown in figure 12. Thus, the gas absorption with chemical reaction in a foam-bed reactor is surprisingly reminiscent of dissolution accompanied by chemical reaction making us trivially state: "Just as in the dissolution process (Bhaskarwar, 1988), where finely divided solid particles dissolve in a solvent and subsequently undergo chemical reaction in the bulk liquid, gas phase in the foam-bed reactor dissolves in the liquid and subsequently undergoes a chemical reaction in the liquid phase". From the mathematical perspective, under the kinetically controlled regime, the two situations are remarkably similar.

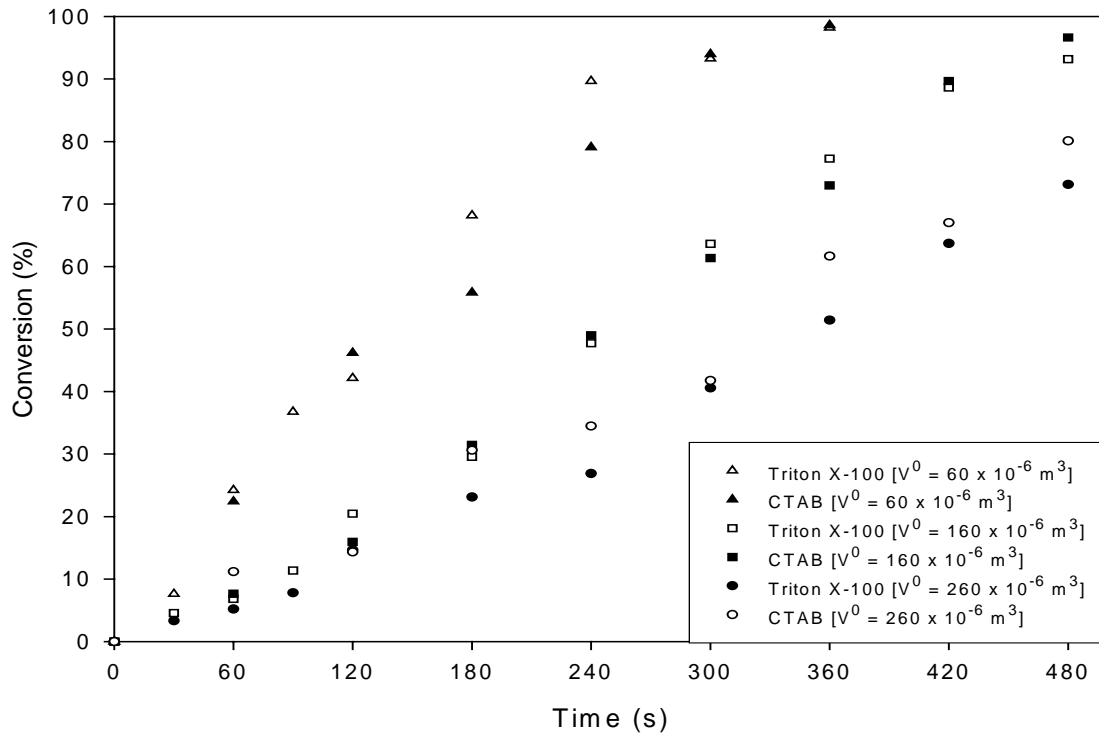


Figure 9. Comparison between Triton X-100 and CTAB at a concentration of 1000 ppm (effect of  $V^0$  variation).

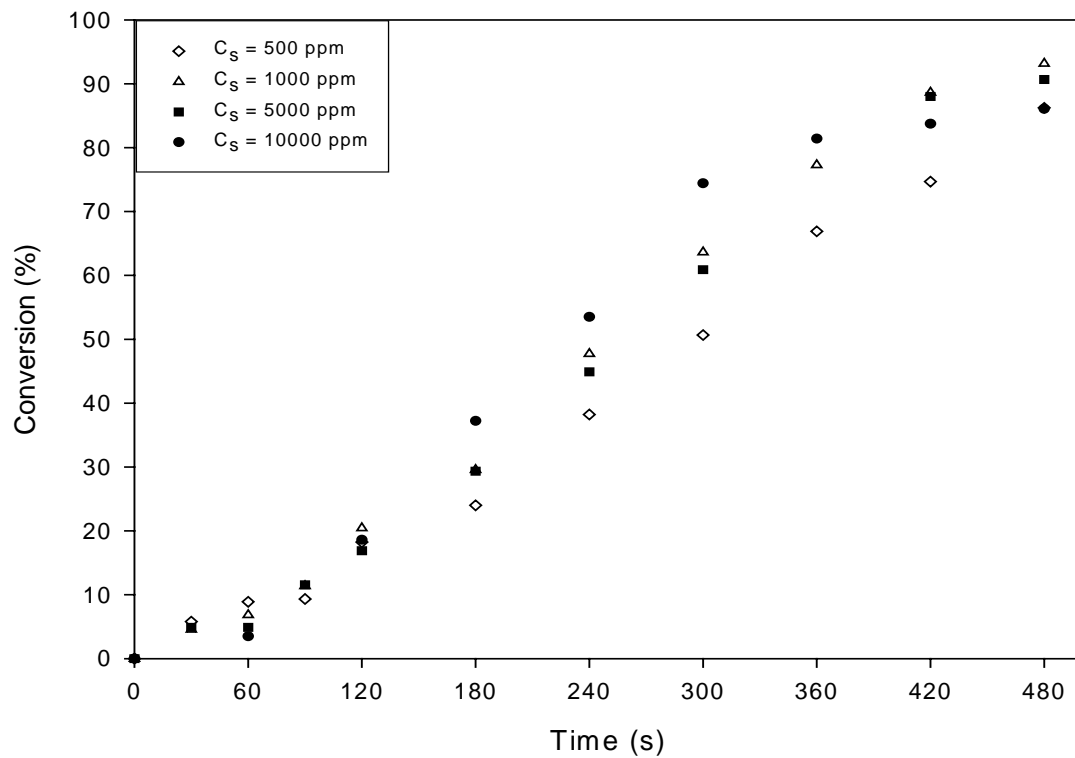
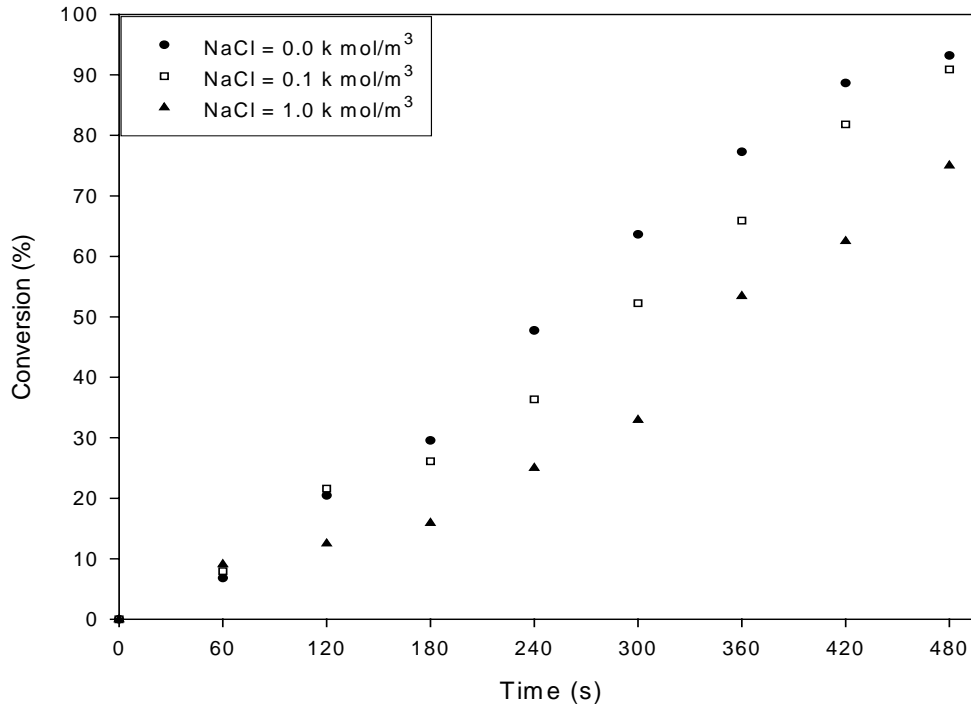


Figure 10. Effect of Triton X-100 concentration on conversion.



**Figure 11. Effect of addition of NaCl on conversion.**

Bhaskarwar and Kumar (1984) proposed the single-stage model of a foam-bed reactor. They derived the following expressions to predict the concentrations in a semi-batch foam-bed reactor, for the case of gas absorption with chemical reaction.

$$C_B = C_{B,ti} - \frac{2Y_A Q_1 M}{VV_1} (t - t_i) \quad (9)$$

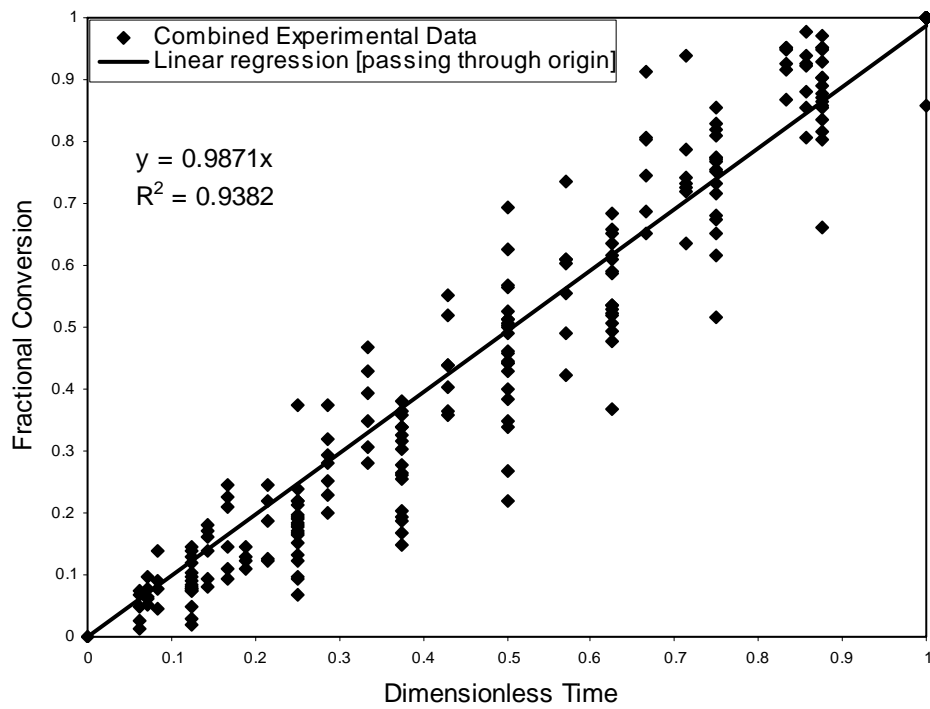
where,

$$M = M_\infty \left[ 1 - \sum_{n=1}^{\infty} \frac{\exp(p_n t_c^*)}{\left[ 1 + \frac{a}{2l} + \frac{p_n}{2D_A k_n^2} + \frac{p_n^2 l a}{2D_A^2 k_n^2} \right]} \right] \quad (10)$$

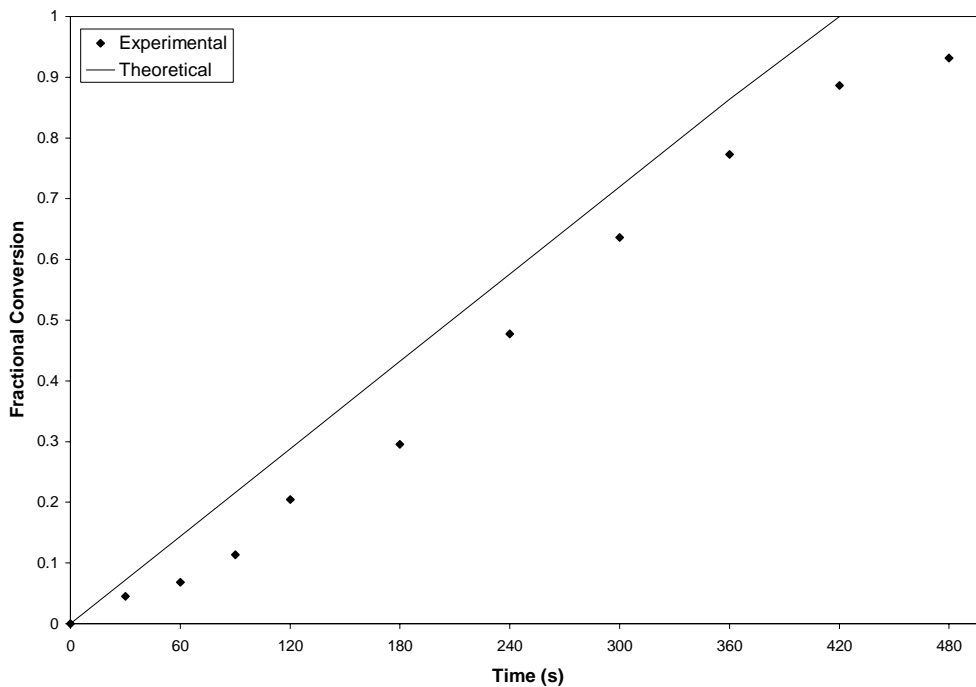
and  $p_n$ 's are the non-zero roots of

$$\frac{lp_n}{D_A} = k_n \tan k_n a \quad \text{and} \quad k_n^2 = -\frac{p_n + \lambda}{D_A} \quad (11)$$

Comparison of the experimental data with the single-stage model of the foam-bed reactor shows that the conversions obtained experimentally are smaller than those predicted by the model (figure 13). This figure clearly indicates that the conversion of barium sulfide is significantly affected by the reverse diffusional flux of hydrogen



**Figure 12. Combined experimental data points for all lean-gas experiments.**



**Figure 13. Comparison of experimental data with the single-stage model of a foam-bed reactor without desorption.**



sulfide, and highlights the importance of desorption of the volatile product accompanying gas absorption with chemical reaction.

*Calculation of the overall mass-transfer coefficient,  $K_{OV}$*

The semi-empirical resistances-in-series model was used to calculate the overall mass-transfer coefficient from the experimental data generated using Triton X-100 as a surfactant. The values of the gas-phase mass-transfer coefficient and overall mass-transfer coefficient are reported in table 2 for different parameters varied.

**Table 2. Values of gas-phase mass-transfer coefficients and overall mass-transfer coefficients for various parameters.**

S.No.	Parameter (unit)	Value of Parameter	$K_g \times 10^2$ (m/s)	$K_{OV} \times 10^2$ (m/s)
1	H (m)	0.1	1.073	1.07
		0.4	0.3704	0.37
		0.7	0.6111	0.61
2	$C_{B0}$ (k mol/m <sup>3</sup> )	0.15	1.033	1.03
		0.35	0.141	0.14
		0.55	5.934	5.81
3	Q (m <sup>3</sup> /s)	$4.17 \times 10^{-5}$	5.767	5.67
		$6.67 \times 10^{-5}$	8.722	8.47
		$12.5 \times 10^{-5}$	5.647	5.54
4	$C_{Agi}$ (k mol/m <sup>3</sup> )	$1.5 \times 10^{-2}$	2.136	2.12
		$2.0 \times 10^{-2}$	0.2803	0.28
		$2.5 \times 10^{-2}$	0.6716	0.67
5	$C_s$ (ppm)	500	0.01	0.01
		1000	2.227	2.12
		5000	1.003	1.00
6	$V^0$ (m <sup>3</sup> )	$60 \times 10^{-6}$	1.031	1.015
		$160 \times 10^{-6}$	5.435	5.113
		$260 \times 10^{-6}$	2.034	1.973

**5. Conclusions**

The variation of the two main parameters, viz. the height of foam bed and concentration of surfactant, reveal the important role of desorption of hydrogen-sulfide gas in governing the observed performance of a foam-bed reactor. The optimum foam height was found to be 0.4 m, and the optimum surfactant concentration to be 1000 ppm. The performance of a foam-bed reactor, in case of carbonation of BaS solutions, does not depend appreciably upon the nature of surfactant used with the notable exception that the aqueous barium-sulfide solutions inexplicably did not foam at all with anionic surfactants. Addition of sodium chloride to aqueous barium-sulfide solutions reduced conversions in the foam-bed reactor. Gas absorption with chemical reaction in a foam-bed reactor may be viewed mathematically as being strikingly similar to the

dissolution accompanied by chemical reaction of solids in liquids under kinetically controlled regime. There is a need to develop a comprehensive model addressing absorption, reaction, and reverse desorption in a fully-coupled formulation of the foam-bed reactor in view of the present experimental data and the recently published theory (Sharma et al., 2005).

## Nomenclature

$a$  = half thickness of a foam film, m

$a_B$  = area of bubble,  $m^2$

$A$  = species present in the gas phase

$A_i$  = overall interfacial area,  $m^2$

$B$  = species present in the liquid phase

$C_{Ag}$  = concentration of species A in the gas pockets surrounding the liquid film, k mol/ $m^3$

$C_{Agi}$  = initial concentration of species A in the gas entering the foam section, k mol/ $m^3$

$C_B$  = concentration of reactant B in the liquid phase in the storage section at time  $t$ , k mol/ $m^3$

$C_{B0}$  = inlet concentration of reactant B in the liquid stream entering the storage section, k mol/ $m^3$

$C_S$  = concentration of surfactant, ppm

$D_A$  = diffusivity of species A in the liquid phase,  $m^2/s$

$d_B$  = bubble diameter, m

$H$  = height of foam section, m

$K_2$  = second-order reaction rate constant,  $m^3/k \text{ mol} \cdot s$

$K_e$  = equilibrium distribution factor for A between gas and liquid phases, dimensionless

$K_g$  = gas-side mass-transfer coefficient, m/s

$K_l$  = liquid-side mass-transfer coefficient, m/s

$k_n$  = defined in equation (11),  $m^{-1}$

$K_s$  = interfacial mass-transfer coefficient, m/s

$K_{OV}$  = overall mass-transfer coefficient, m/s

$l$  = equals  $V_B/12K_e s$ , m

$M$  = total amount of reactant A, both free to diffuse and immobilized, in half the liquid film of surface area  $s$  at contact time  $t_c^*$ , k mol

$M_\infty$  = total amount of reactant A, both free to diffuse and immobilized, in half the liquid film of surface area  $s$  after infinite time, k mol

$n$  = integer number 1, 2, 3, ...

$p_n$  = defined in equation (11),  $s^{-1}$

$Q_1$  = flow rate of the liquid draining into the storage section from the foam section,  $m^3/s$

$Q_G$  = total gas flow rate,  $m^3/s$

$s$  = surface area of the liquid film.  $m^2$

$Sh$  = Sherwood number, dimensionless

$t$  = run time, s

$t_c$  = gas-liquid contact time in foam section, s

$t_c^*$  = total gas-liquid contact time in foam section, s  
 $t_i$  = time node corresponding to  $i^{\text{th}}$  interval, s  
 $u_B$  = bubble velocity, m/s  
 $V$  = volume of liquid in the storage section,  $\text{m}^3$   
 $V_1$  = volume of a liquid film in the foam section,  $\text{m}^3$   
 $V_B$  = volume of bubble,  $\text{m}^3$   
 $V^0$  = volume of barium-sulfide solution initially added to the reactor,  $\text{m}^3$   
 $Y_A$  = stoichiometric coefficient, i.e. moles of liquid-phase reactant B consumed / mole of gas-phase reactant A, dimensionless  
 $z$  = axial position coordinate in the reactor, m

#### Greek symbols

$\lambda$  = pseudo-first order reaction rate constant ( $=K_2C_B$ ),  $\text{s}^{-1}$   
 $\bar{\varepsilon}$  = average value of liquid hold-up in the foam section, dimensionless

#### References

1. Asolekar, S.R., Desai, D., Deshpande, P.K., and Kumar, R., 1985, Effect of surface resistance on gas absorption accompanied by a chemical reaction in a gas-liquid contactor. *The Can. J. Chem. Engng* **63**, 336-339.
2. Astarita, G., and Savage, D.W., 1980, Theory of chemical desorption. *Chem. Engng Sci.* **35**, 649-656.
3. Bhaskarwar, A.N., 1987, Analysis of gas absorption accompanied by a zero-order chemical reaction in a liquid-foam film surrounded by limited gas pockets. *J. Chem. Tech. Biotechnol.* **37**, 183-187.
4. Bhaskarwar, A.N., Desai, D., and Kumar, R., 1990, General model of a foam bed reactor. *Chem. Engng Sci.* **45**(5), 1151-1159.
5. Bhaskarwar, A.N., and Kumar, R., 1986, Oxidation of sodium sulphide in the presence of fine activated carbon particles in a foam bed contactor. *Chem. Engng Sci.* **41**(2), 399-404.
6. Bhaskarwar, A.N., and Kumar, R., 1984, Oxidation of sodium sulphide in a foam bed contactor. *Chem. Engng Sci.* **39**(9), 1393-1399.
7. Bhaskarwar, A.N., Kumar, R., and Gandhi, K.S., 1987, Mass transfer accompanied by a chemical reaction in an emulsion foam bed reactor. *AIChE J.* **33**(2), 331-335.
8. Bhaskarwar, A.N., and Kumar, R., 1995, Gas-phase controlled mass transfer in a foam-bed reactor. *Chem. Engng Comm.* **131**, 115-124.
9. Bhaskarwar, A.N., 1997, Mathematical modelling of foam-bed reactors, in: Nigam, K.D.P. and Schumpe, A. (Eds.), *Three Phase Sparged Reactors*. Gordon and Breach Science Publishers, Australia.
10. Bhaskarwar, A.N., 1988, On application of the method of kinetic invariants to the description of dissolution accompanied by a chemical reaction. *Chem. Eng. Comm.* **72**, 25-34.
10. Biswas, J., and Kumar, R., 1981, Mass transfer with chemical reaction in a foam bed reactor. *Chem. Engng Sci.* **36**, 1547-1556.

11. Burrows, G., and Preece, F.H., 1954, The process of gas evolution from low vapor pressure liquids upon reduction of pressure. *Chem. Engng Sci.* **32**, 99-114.
12. Fidi, N., Jeelani, S.A.K., May, K., and Hartland, S., 1993, Use of submerged jets in gas desorption from supersaturated solutions, *Chem. Engng Sci.* **48**(10), 1833-1842.
14. Gallardo, V., Zurita, L., Ontiveros, A., Durán, J.D.G., Interfacial properties of barium sulfate suspensions. Implications in their stability, *Journal of Pharmaceutical Sciences* **89**(9), 1134-1142.
13. Hikita, H., Ishimi, K., and Koroyasu, S., 1990, Gas desorption from falling liquid films in entrance region of inclined wetted-wall columns with an overflow-type distributor. *Chem. Engng Sci.* **45**(2), 437-442.
14. Ishikawa, H., Miki, T., Okamoto, M., and Hikita, H., 1986, Gas desorption from liquids: Mass transfer and drag coefficients for single bubbles in free rise through Newtonian liquids. *Chem. Engng Sci.* **41**(9), 2309-2319.
15. Jeelani, S.A.K., Fidi, N., and Hartland, S., 1990, Foam formation during CO<sub>2</sub> desorption from agitated supersaturated aqueous surfactant solutions. *Chem. Engng Sci.* **45**(4), 1043-1048.
16. Landau, J., 1992, Desorption with chemical reaction. *Chem. Engng Sci.* **47**(7), 1601-1606.
17. Pasiuk-Bronikowska, W., and Rudzinski, K. J., 1981, Gas desorption from liquids. *Chem. Engng Sci.* **36**, 1218-1224.
18. Schweitzer, P.R., and Szebehely, V.G., 1950, Gas evolution in liquids and cavitation. *J. Appl. Phys.* **21**, 1218-1224.
19. Shah, Y.T., and Sharma, M.M., 1976, Desorption with or without chemical reaction. *Trans. Instn. Chem. Engrs.* **54**, 1-41.
20. Sharma, R.K., Gaikwad, A., and Bhaskarwar, A.N., 2005, Gas absorption with chemical reaction and desorption in a foam-bed reactor. *Chem. Engng Comm.* **192**(4-6), 597-619.
21. Subramanyam, R., Katyal, P., and Bhaskarwar, A.N., 1999, Design of a foam-bed reactor system. *ACH--Models in Chemistry* **136**(1-2), 23-30.
22. Varshney, A., Agrawal, P., and Bhaskarwar, A.N., 2003, Gas absorption with zero-order chemical reaction in a foam-bed reactor. *Chem Engng Sci.* **58**(15), 3413-3424.
23. Vogel, A.I., 1989, *Textbook of quantitative chemical analysis*. Longman Scientific and Technical, England.