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Absorption of pure carbon-dioxide gas in a foam-bed reactor

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Abstract

Carbon dioxide is the most important of greenhouse gases. Removal of carbon-dioxide gas from large-scale gaseous emissions as from thermal power plants, etc. is a real challenge. Foam-bed reactor offers a novel method of removal of carbon-dioxide gas. Removal of carbon-dioxide gas by treating it with aqueous barium-sulfide solution has been experimentally investigated here in a semi-batch foam-bed reactor. Experimental data have been generated and analyzed in this investigation to assess the role of the reverse diffusional flux of the desorbed hydrogen-sulfide gas in the actual performance of a foam-bed reactor. The experiments are carried out using pure carbon-dioxide gas, to focus on liquid-phase and interfacial resistances. The variables studied are height of foam bed, initial concentration of barium sulfide in aqueous solution, gas-flow rate, volume of the barium-sulfide solution charged into the reactor, and the surfactant type, and its concentration in the aqueous solution. The variation of two main parameters, viz. the height of foam bed and concentration of surfactant, reveals the important role of desorption of hydrogen-sulfide gas in governing the observed performance of the foam-bed reactor.

Keywords: absorption, desorption, pure gas, foam-bed reactor, carbonation

1. Introduction

Prior to 1939, foams were subject of interest to physicists and chemists. The concept of foam-bed reactor was first put forward by Luchinsky (1939) who proposed the absorption of gases such as nitrogen oxides in foams made of aqueous solutions of hydrogen peroxide, hydrogen iodide, etc. Luchinsky realized that the enormous gas-liquid interfacial areas in foams could be exploited for the purpose of gas absorption.

When the chemical reaction is fast, the rate of absorption depends largely on the interfacial area available for the mass transfer. Thus the choice of reactor becomes very important. Compared to all conventional gas-liquid reactors, foam-bed reactors offer higher interfacial area per unit volume of the liquid (table 1). Foam-bed reactor now seems to be the promising gas-liquid reactor by virtue of its additional

characteristics of moderate pressure drop, high gas-to-liquid ratio, low liquid hold-ups, and defiant life of foam bubbles which makes the contact times long. All these characteristics are very desirable for the treatment of large quantities of lean gases, as in the case of smoke stack furnaces or power-plant exhausts or contaminated separation from toxic gas streams.

Numerous investigations have been reported in the area of absorption with chemical reaction in a foam-bed reactor (Biswas and Kumar, 1981; Bhaskarwar, 1986; Asolekar et al., 1988; Varshney et al., 2003) which have demonstrated that foam-bed reactors perform better than conventional reactors under certain conditions. All these investigations dealt with the products which were non-volatile. But 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. Very few investigations are available which deal with the simultaneous gas absorption with chemical reaction and desorption in a foam-bed reactor (Subbarao, 1984; Challapalli, 1997; Wadhwa, 1999; Sharma et al., 2005). But all these used lean gas to study the performance of the foam-bed reactor.

The objective of the present work was to study the performance of a foam-bed reactor, operated in semi-batch mode, for the case of pure gas absorption with chemical reaction and desorption, by conducting experiments with respect to various operating parameters. To achieve this objective, the system chosen was the carbonation of barium sulfide. This carbonation reaction involves the simultaneous absorption of carbon-dioxide gas into the aqueous barium-sulfide solution, fast chemical reaction between dissolved gas-phase species and the reactive species in the liquid phase, leading to the formation of a precipitate of barium carbonate and desorption of hydrogen-sulfide gas produced by the chemical reaction.

2. Theory
Foam-bed reactor consists of a shallow pool of liquid (containing surfactant) above a distributor plate. Foam is generated by sparging the gas from the bottom of the distributor plate into the liquid as shown in figure 1. The shallow pool of liquid is called as the storage section and the section above it, which contains the foam, is termed as the foam section. When the gas is continuously passed through the batch of liquid, the reactor is said to operate in a semi-batch mode and in the second case when both the gas and the liquid flow continuously along and across the reactor, the reactor is said to operate in the continuous mode.

In both the modes of operation, the gas in the form of predominantly spherical gas bubbles traverses through the storage section. As these bubbles leave the top of the liquid pool they get distorted in shape into polyhedrons and are identified as foam matrix. The liquid in the foam is present in the form of films and Plateau borders. In a foam matrix, two adjacent bubbles are separated by a liquid film of pentagonal shape whereas a Plateau border is formed at the junction of three liquid films. The Plateau

borders not only separate the liquid films from each other, but also form an interconnected network of their own. As more gas is passed, the foam bubbles along with the associated films and Plateau borders move upward through the foam column. During this movement, the liquid films drain into Plateau borders which in turn drain into the liquid pool, through their network, due to gravity. The rising films eventually become so thin that they are no longer stable. As a result, they break at the top of the foam bed and the released liquid returns to the storage through the Plateau borders.

Mass transfer with chemical reaction occurs both during the passage of the gas bubbles through the liquid pool and in the foam. The liquid is assumed to be carried into the foam section from the storage by bubbles, to partially react there and to return to the storage section with a concentration different from the one at which it entered the foam section. Thus liquid is recycled from the foam section, through the Plateau borders, back to the storage section. This continuous recirculation of the liquid further enhances the backmixing of the liquid in the pool of liquid which is mainly induced by the upward motion of the buoyant gas bubbles. In the foam, the reaction is assumed to occur in the liquid films surrounded by limited amounts of gaseous reactant (figure 2). No mass transfer is assumed to occur in the Plateau borders because of the negligible area offered by them.

For the case of pure gas absorption, the gas-phase resistance is zero. The foam bubbles generated using pure gas shrink as they travel up in the foam section. These shrinking bubbles are assumed to retain an idealized regular pentagonal, dodecahedral shape throughout the time of contact. During shrinkage, the pentagonal films are assumed to reduce in area, but to maintain a constant average thickness. It is also assumed that vaporization of liquid does not occur from the film surface and that the gas in the bubble remains pure while it rises through the column.

3. Experimental

The carbonation of barium sulfide has been experimentally studied in a semi-batch foam-bed reactor at about 30 ^{o}C using pure carbon-dioxide gas. The reaction is,

$$BaS + CO_2 + H_2O \longrightarrow BaCO_3 + H_2S \qquad (1)$$
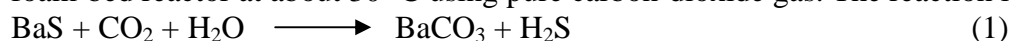
3.1 Mechanism and Kinetics

Solid barium sulfide dissolves readily in water to give a highly alkaline solution that is substantially 10% dissociated into the hydroxide and hydrosulfide.

$$2BaS + 2H_2O \longrightarrow Ba(OH)_2 + Ba(SH)_2 \qquad (2)$$
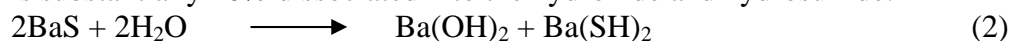
Barium hydroxide is much more soluble in hot water than in cold, whereas the solubility of hydrosulfide is relatively unaffected by temperature.

Barium sulfide solutions undergo slow oxidation in air, forming elemental sulfur and a family of oxidized sulfur species including sulfite, thiosulfate, polythionates, and sulfate. The elemental sulfur is retained in the dissolved liquor in the form of polysulfide ions, which are responsible for the yellow color of most barium-sulfide solutions (Kirk and Othmer, 2004).

If carbon-dioxide gas is added to the aqueous barium-sulfide solution, the following reactions will occur as the first steps at higher pH (in the strongly alkaline region).

$$CO_2 + 2OH^- + 2H_2O \longrightarrow CO_3^{2-} + 2H_2O \qquad (3)$$

$$Ba^{2+} + CO_3^{2-} \longrightarrow BaCO_3 \qquad (4)$$
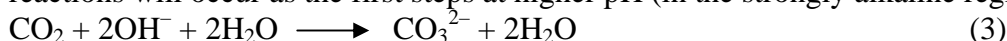
As the reactions proceeds, the pH will be decreased and the following reactions will occur in a weakly alkaline region, evolving hydrogen-sulfide gas (Kubota et al., 1990).

$$CO_2 + 2SH^- + H_2O \longrightarrow CO_3^{2-} + 2 H_2S \qquad (5)$$

$$Ba^{2+} + CO_3^{2-} \longrightarrow BaCO_3 \qquad (6)$$
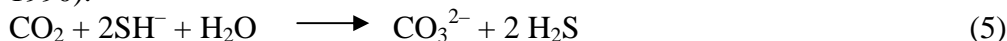
The kinetics of the reaction was reported by Gupta and Sharma (1967). They studied the absorption of carbon dioxide into aqueous barium-sulfide solution in a bubbler reactor and a continuous stirred cell. The absorption was accompanied by a fast reaction between dissolved carbon-dioxide gas and the reactive species in the solution. The overall mass-transfer coefficients found for the system in the bubbler reactor (typical value was about 3 x 10^{-3} k mol/s.atm.m^3) were an order of magnitude less than those for completely gas-film controlled system (typical value was 2.8 x 10^{-2} k mol/s.atm.m^3), indicating that diffusion and kinetic factors are likely to play an important role in the carbonation reaction. They reported a second-order rate constant of 11000 m^3/k mol.s. The hydration of carbon dioxide, which is the rate controlling step, is known to be catalyzed by anions of weak acids. The sulfide ion acts as catalyst and the rate of catalyzed reaction is proportional to the concentration of catalytic species.

3.2 Experimental set-up

The experimental set-up is shown in figure 3. The regulator of carbon-dioxide gas cylinder was heated using two infra-red lamps to avoid formation of dry ice and consequent plugging of the supply line. Calibrated rotameter was provided to measure the flow rate of the reactant gas before the gas enters the foam-bed reactor.

The foam-bed reactor comprises of a glass column and a distributor plate assembly (figure 1). The glass column was provided with four tappings at various heights to measure the liquid hold-up in the foam. The tappings were connected to inclined-tube manometers using rubber tubings. These manometers were filled with water and used for measuring the hydrostatic head exerted by foam. Similarly four thermometer ports were provided to monitor the temperature inside the reactor at various heights. The inlet for reactant solution was provided at a height of 0.03 m above the gas-distributor plate. The outlet for the reaction mixture, provided just above the distributor plate, was used to collect samples for chemical analysis. The distributor plate made of glass was placed between the cylindrical part and the conical section of the foam-bed reactor. The conical section ensured a uniform distribution of the stabilized flow of gaseous mixture through the distributor holes. A foam-breaker sieve plate coated with n-butanol was suspended from the top and was used to break the foam at a desired height. Table 2 shows the dimensions of the reactor and details of the distributor plate.

3.3 Experimental procedure

Commercial grade barium sulfide (nearly 60% BaS) was used as the reactant for the study. Distilled water used for preparing the solutions was first boiled to remove any dissolved gases, like oxygen and carbon dioxide. Barium-sulfide powder was added to the carbon dioxide free distilled water and the resulting slurry mixed thoroughly in an air-tight stirred cell for leaching of barium sulfide.

At the beginning of an experimental run, the glass column was thoroughly rinsed with distilled water. Flow rate of carbon-dioxide gas was measured using calibrated rotameter and the gas was then introduced into the foam-bed reactor. A batch of known volume of barium-sulfide solution, with known concentrations of barium sulfide and surfactant, was poured into the column through the inlet port after ensuring that the gas passing continuously through the reactor had already attained a steady flow rate. The barium-sulfide solution started foaming and the foam began rising through the cylindrical reactor column. A direct contact with a layer of n-butanol applied on to a sieve plate suspended from the top was effectively employed to break and maintain the foam at a definite height. Samples of the reaction mixture were withdrawn from the storage section of the reactor through the sampling port at different time intervals till the reaction was complete. These samples were analyzed iodometrically (Vogel, 1989) to determine the concentration of unreacted barium sulfide. The measurements were repeated for different run times to obtain the data on the performance of the reactor over time.

4. Results and Discussion

Effect of various parameters like height of the foam bed (H), initial concentration of aqueous barium-sulfide solution (C_{B0}), flow rate of the gas mixture (Q_G), volume of the liquid-phase reactant charged into the reactor (V^0), initial concentration of the surfactant added to the liquid phase (C_s), and the nature of the surfactant [Non-ionic (Triton X-100, Tween 80), Cationic (CTAB)] were 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 results were plotted as concentration-time profiles. The greater the slope of the curve, the higher is the conversion attained in a given time.

The experimental data were compared with the model of Acharya (1994) which is applicable for pure gas absorption with chemical reaction. As shown in figure 4, the model predicted much higher conversions than the experimental data, indicating that desorption of product gas was causing the conversions to reduce.

4.1 Effect of height of foam bed

As the foam height was increased from 0.1 to 0.4 m (figure 5), the conversion increased due to the increase in the interfacial area available for mass transfer as well as due 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 longer contact times. The drainage rate from the foam section also decreased at higher foam heights. Since the

drainage occurred from the foam films, the film surface is renewed at a slower rate. A smaller drainage rate at a higher foam height manifests itself in the decreased flux of carbon-dioxide gas into the foam films and hence in the lower conversions.

4.2 Effect of initial concentration of aqueous barium-sulfide solution
Figure 6 corresponds to the effect of initial concentration of barium sulfide in aqueous solution on concentration-time profiles in the foam-bed reactor. The conversion at any time increased as the initial concentration of barium sulfide was increased. Higher initial concentration of barium sulfide implies a higher magnitude of the pseudo-first order reaction-rate constant which results in the higher observed rate of reaction in the reactor.

4.3 Effect of gas-flow rate
Figure 7 show the effect of gas-flow rate on the variation of concentration of barium sulfide in storage section with time. With the increase in gas-flow rate, the liquid hold-up increased, which results in the formation of thicker foam films. Thicker foam films imply higher effective liquid-phase concentration gradient of unreacted carbon dioxide at each face of the film (Bhaskarwar and Kumar, 1984) and hence higher rates of mass transfer. The drainage rate from the foam section also increased. Since the drainage occurred from the foam films, the film surface is renewed at a faster rate and the intensity of interfacial turbulence lost due to the presence of surfactant (Springer and Pigford, 1970) is partially recovered. A greater drainage rate at a higher gas-flow rate manifests itself in the increased flux of carbon-dioxide gas into the foam films and hence in the higher conversions. Further, the intensity of agitation of storage increased with the increase in gas-flow rate. On the other hand, the residence time of gas in the reactor decreased thus allowing lesser time for mass transfer with reaction, and the volume of the polyhedral gas bubble increased with a consequent decrease in the specific interfacial area.

As the gas-flow rate was increased from 2.50×10^{-5} m^3/s to 4.67×10^{-5} m^3/s, it was observed that the conversion actually increased. Thus the effects of increase in values of liquid hold-up and intensity of agitation suppressed those of the lesser times of contact and lesser interfacial area.

4.4 Effect of volume of aqueous barium-sulfide solution charged into the reactor
Figure 8 show the effect of volume of barium-sulfide solution charged into the reactor on its performance. The aqueous phase reactant volume was varied from 60×10^{-6} m^3 to 260×10^{-6} m^3. For a greater volume of the batch of barium-sulfide solution, the conversion achieved in a given time decreased. Lesser volume of reactant in the storage section implies a more intense agitation of the liquid pool by the gas sparged, besides the fewer moles of barium sulfide in the storage section. The greater extent of absorption of carbon dioxide possible under these more intense turbulent conditions leads to the higher conversions observed.

4.5 Effect of concentration of surfactant
The concentration of surfactant in aqueous barium-sulfide solution was varied from 500 ppm to 10000 ppm. Once again an interesting result was uncovered; this time in

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the form of existence of an optimum concentration of surfactant. One might have expected the conversion to gradually decrease with an increase in the surfactant concentration. Instead, an optimum conversion was obtained at a surfactant concentration of 1000 ppm as shown in figure 9. The reason for the reduced conversion of barium sulfide, at a low concentration of surfactant, of say 500 ppm, lies in the fact that the small number of surfactant molecules adsorbed at the gas-liquid interface resulted in high initial diffusional fluxes of carbon-dioxide gas into the liquid phase. These, in turn, led to higher reaction rates and consequently to increased reverse diffusional fluxes of the product gas, hydrogen sulfide, at later times in foam films, which are the location of maximum gas absorption in the reactor. The overall diffusional flux of carbon dioxide into foam liquid was therefore reduced by the bulk flow induced by the desorbing hydrogen-sulfide gas, and hence the lower conversions observed. Antithetically, when the surfactant concentration was made as high as 10000 ppm, the number of surfactant molecules embedded in the film-gas interface was much larger resulting in a tightly packed multi-molecular layer which left a very little free interfacial area for the diffusion of carbon-dioxide molecules into the foam liquid. The multilayer would also result in a much lower solubility of carbon-dioxide gas in the surface phase, i.e. at the interface. Both these factors contributed synchronously to the reduced fluxes of carbon-dioxide gas into the continuous liquid phase in foam, respectively through the greater diffusional resistance and the reduced driving force. Consequently, the conversions of barium sulfide obtained in the reactor at high surfactant concentrations were again lower than the optimal.

4.6 Effect of nature of surfactant
Three different types of surfactants were tried out in the experimental work, namely,
 i. Non-ionic – Triton X-100 and Tween 80,
 ii. Cationic – CTAB, and
iii. Anionic – SDS, Monoxol OT, Teepol, sodium lauryl alcohol, LABS, and stearic acid

The aqueous solutions of barium sulfide did not foam properly with any of the anionic surfactants. When these surfactants were tried, the foaming was non-uniform. Foam was not stable and collapsed due to coalescence of bubbles. This non-uniformity may be due to the formation of a solid complex and the insufficient wetting ability of these surfactants with respect to the solid formed. It is indicated in literature (Bikerman, 1973) that a medium wetting ability of surfactants is necessary for good stability of foam containing solid particles.

The non-ionic and cationic surfactants did not appreciably alter the performance of the foam-bed reactor indicating that the resistance offered by these surfactants was nearly the same (figure 10).

5. Conclusions
Simultaneous pure gas absorption, chemical reaction, and desorption was experimentally studied in a semi-batch foam-bed reactor for the carbonation of barium sulfide. It was found that the conversion in a foam-bed reactor was significantly affected by the reverse diffusional flux of gas-phase product H_2S. The

conversion in a foam-bed reactor increased with the increase in the initial concentration of liquid-phase reactant BaS, decrease in the volume of reactant charged in the reactor, and increase in the total gas-flow rate. There was an optimum surfactant concentration (1000 ppm) and an optimum foam height (0.4 m) at which maximum conversion was achieved. Anionic surfactants did not foam aqueous BaS, while the nature of surfactant (cationic/ non-ionic) was not significantly affecting the performance of the reactor as the surfactants offered similar resistances to mass transfer.

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Notation

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

C_s = concentration of surfactant, ppm

H = height of foam section, m

K_s = surfactant-film mass-transfer coefficient, m/s

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

t = time of operation of the foam-bed reactor, s

V^0 = volume of liquid charged into the reactor, m^3

Greek Letters

ε = Average liquid hold-up in the foam section, dimensionless
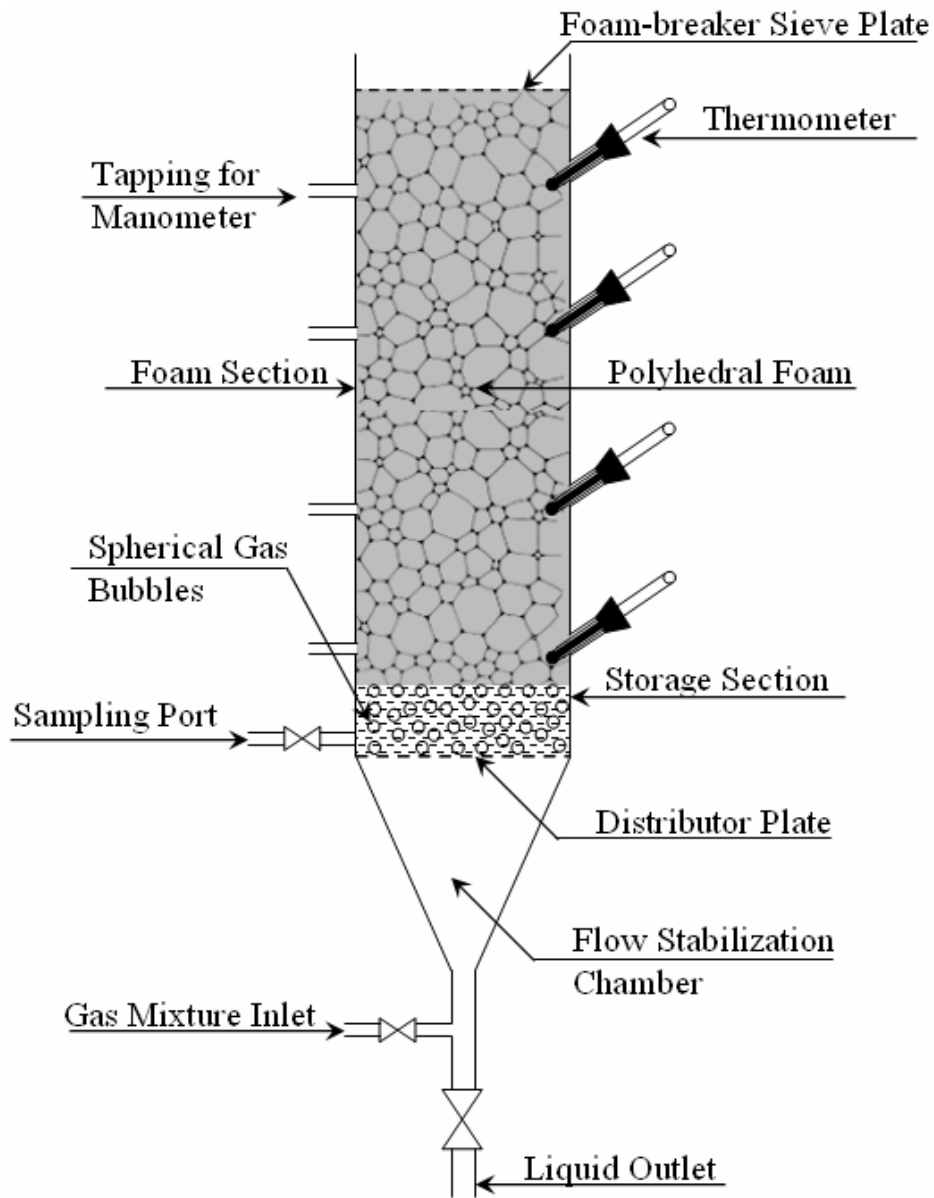
Figure 1. Details of the semi-batch foam-bed reactor.
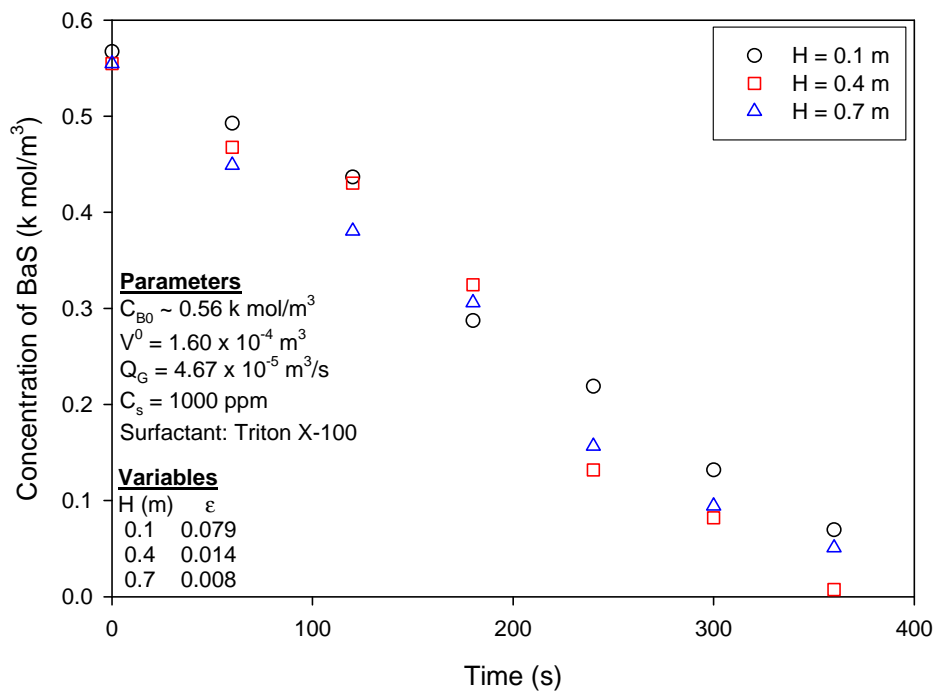
(a) End view

(b) Elevation
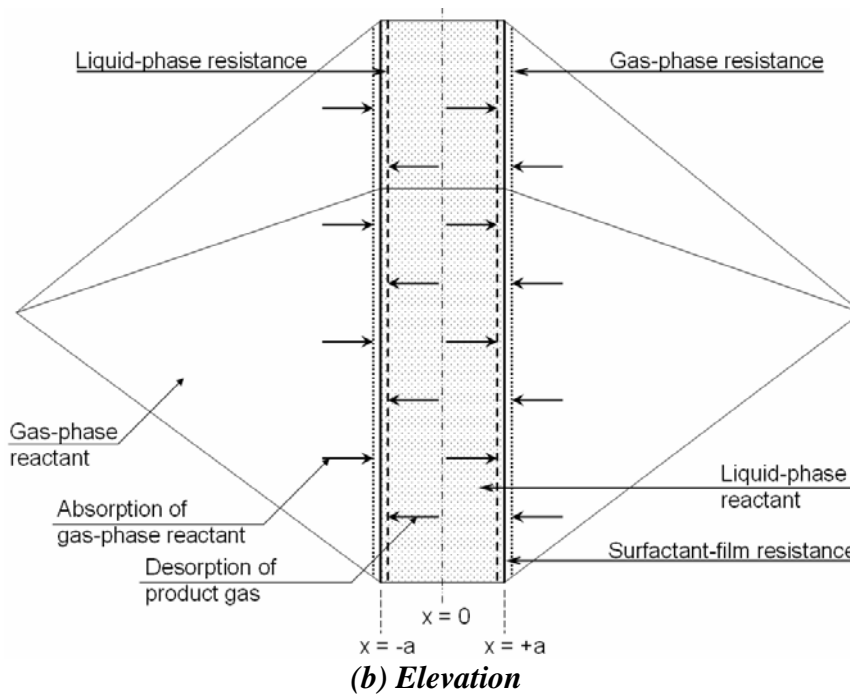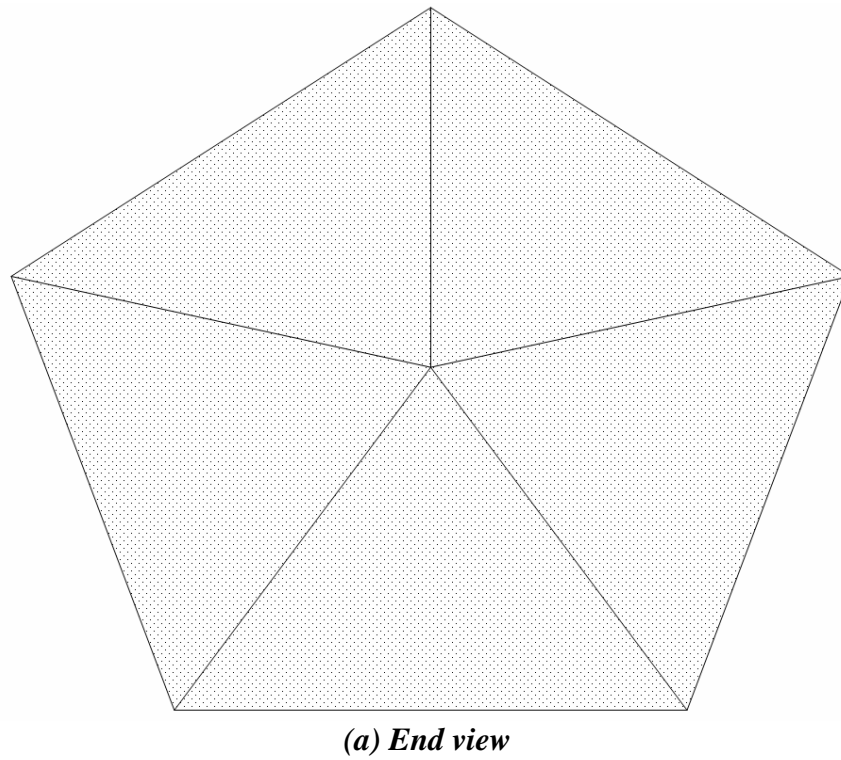
**Figure 2. Liquid-foam film with associated gas pockets.**
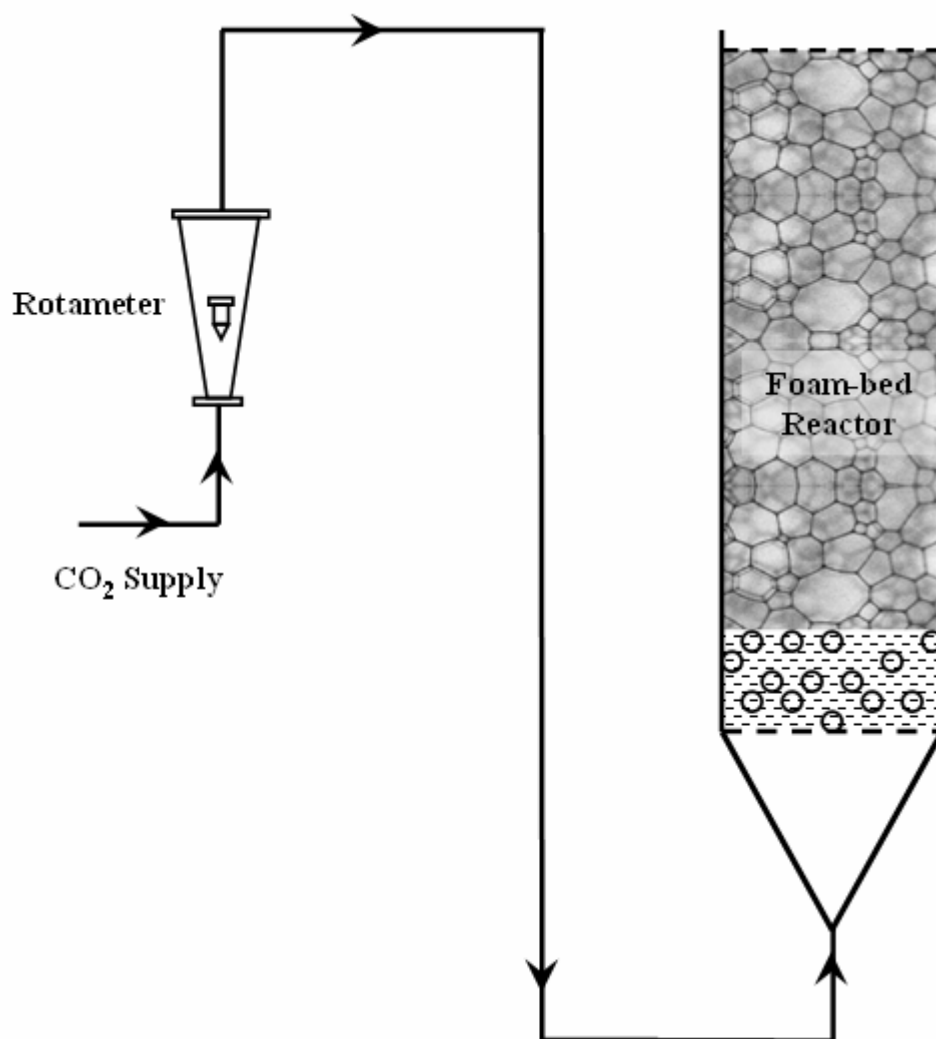
Figure 3. Schematic diagram of the experimental set-up for the carbonation of barium sulfide using pure carbon-dioxide gas in a semi-batch foam-bed reactor.
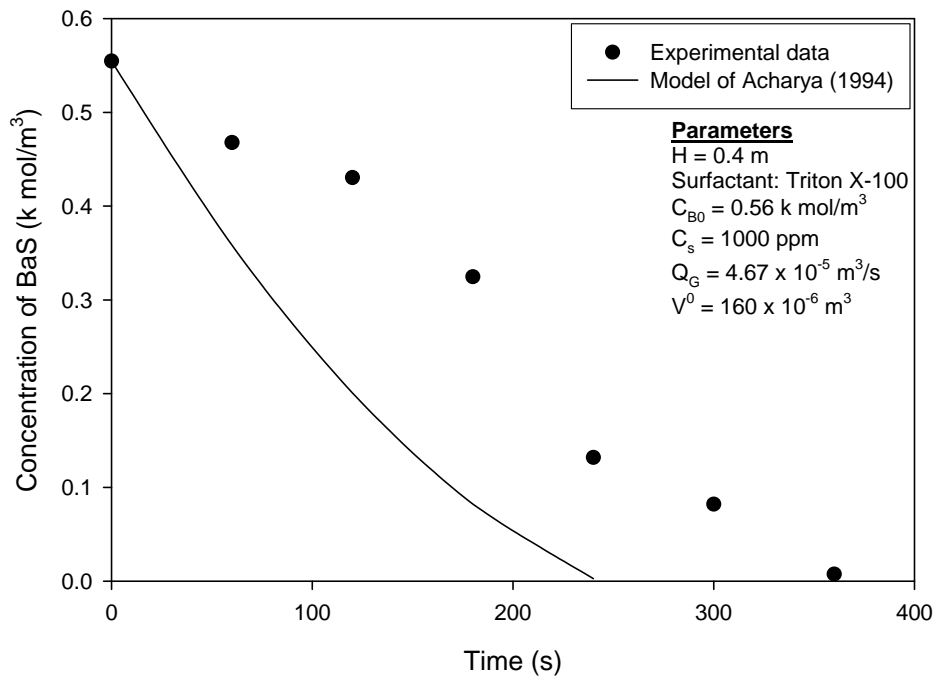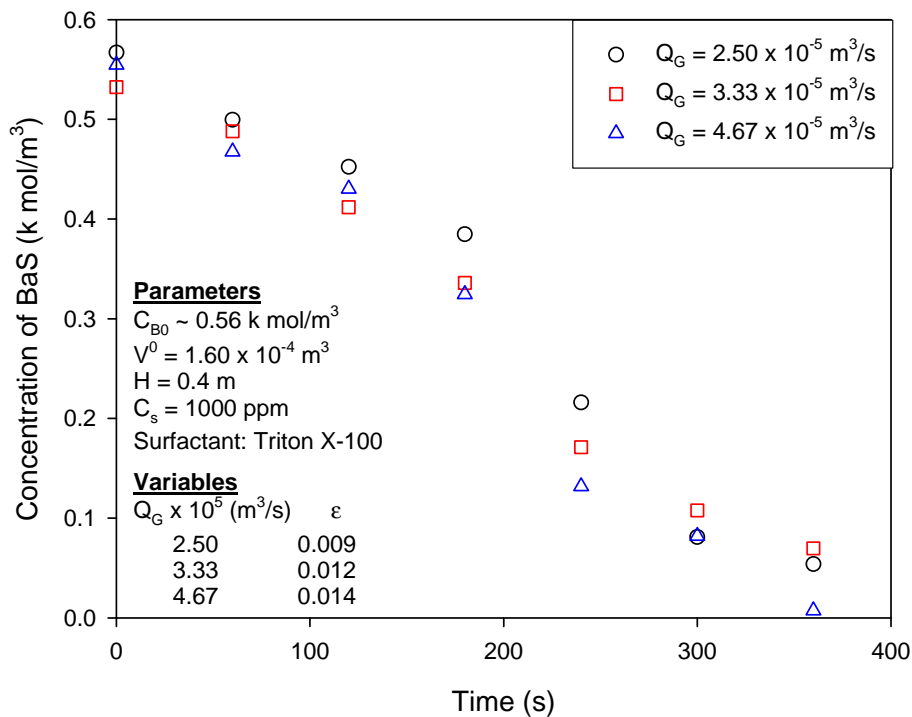
Figure 4. Comparison of the model of Acharya (1994) with the experimental data on carbonation of barium sulfide using pure gas.

Figure 5. Effect of foam height on the concentration vs. time profiles.
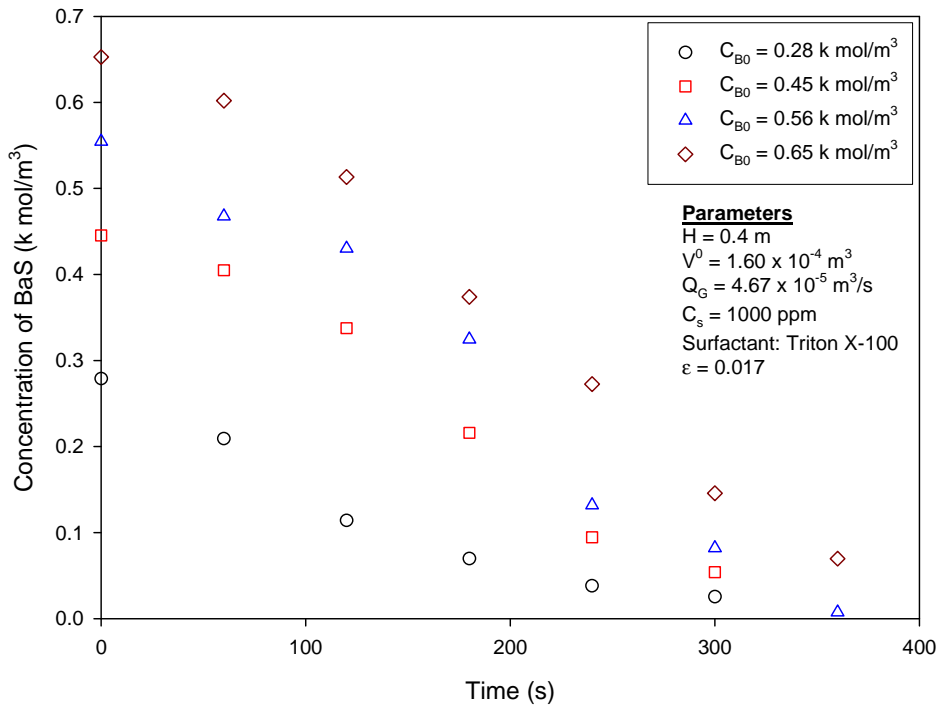
Figure 6. Effect of initial concentration of aqueous barium-sulfide solution on the concentration vs. time profiles.

Figure 7. Effect of gas-flow rate on the concentration vs. time profiles.
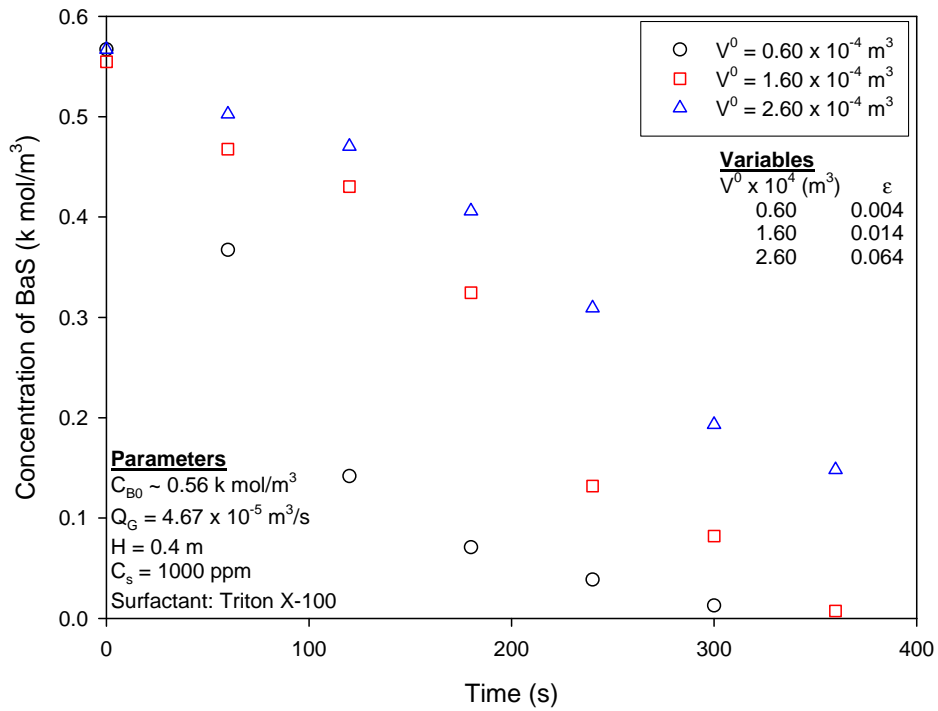
Figure 8. Effect of volume of aqueous barium-sulfide solution charged into the reactor on the concentration vs. time profiles.
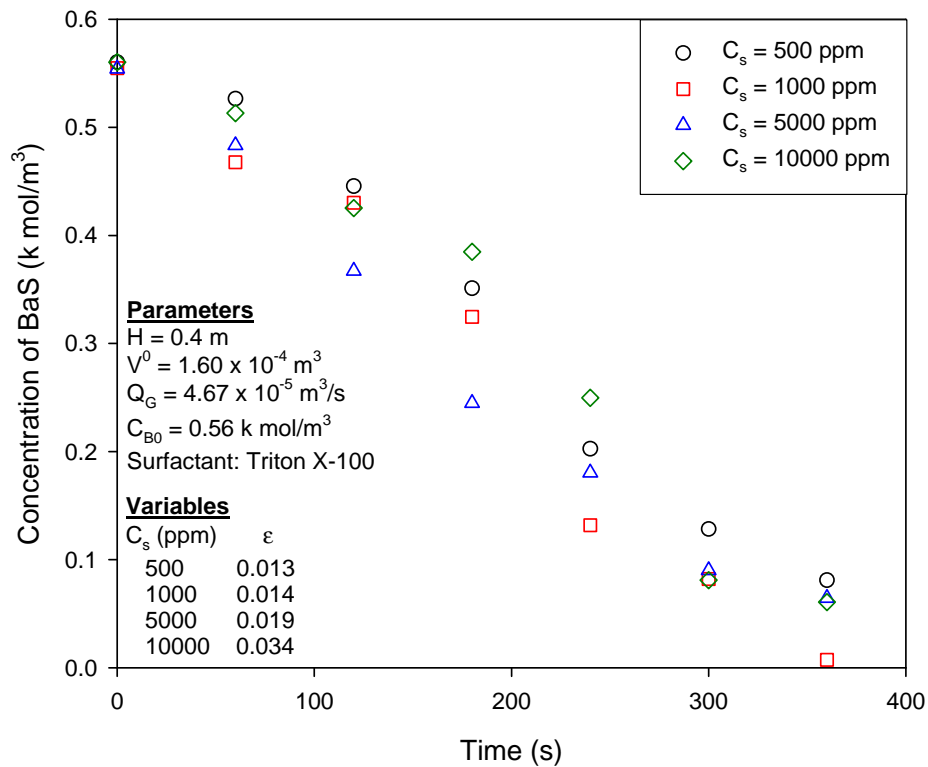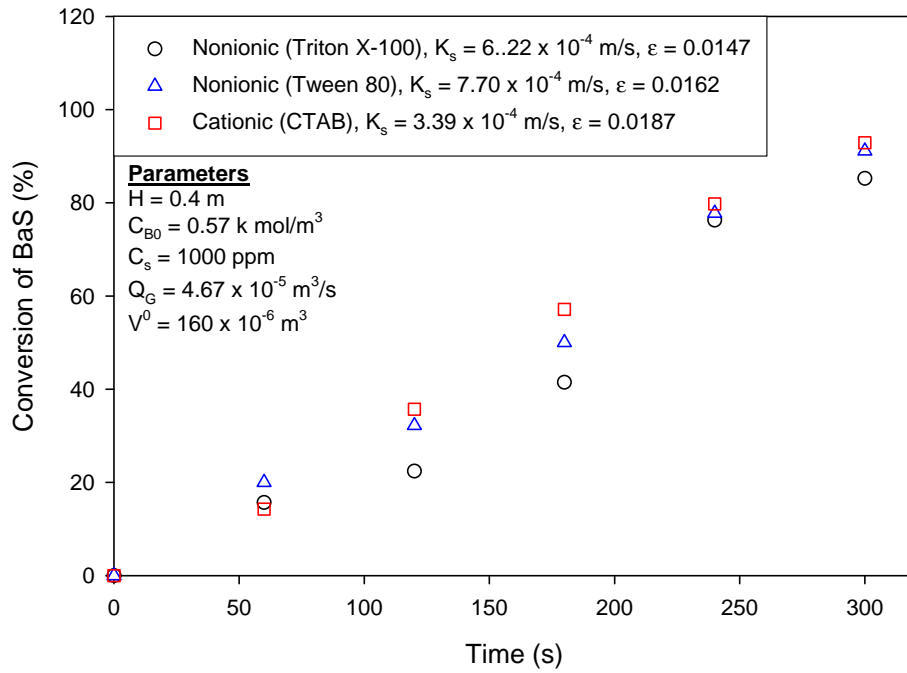

Figure 9. Effect of concentration of surfactant on the concentration vs. time profiles.

Figure 10. Effect of nature of surfactant on the concentration vs. time profiles.

Table 1. Gas-liquid interfacial area for various reactors (Shah and Mahalingam, 1984).

Gas-liquid contactor	Interfacial area per unit volume of reactor (m^2/m^3 of reactor)
Foam reactor	
Wire mesh size 20	1105
Wire mesh size 60	2070
Wire mesh size 100	2645
Packed columns	
Counter current	10-350
Co-current	10-1700
Plate columns	
Bubble cap	100-400
Sieve plate	100-200
Bubble columns	50-600
Packed bubble columns	50-300
Spray columns	10-100

Table 2. Dimensions of the foam-bed reactor.

Distributor	Diameter of distributor plate = 0.057 m
	Thickness of distributor plate = 0.003 m
	Number of holes = 12
	Diameter of each hole = 0.002 m
	Free area = 1.48 %
	Material of construction: Glass
Column	Diameter of the foam-bed reactor = 0.057 m
	Height of the foam-bed reactor = 1.1 m
	Material of construction: Glass