

## ABSTRACT

The present investigation concerns itself with the re-analyses of mathematical models reported in the literature for mass-transfer accompanied by chemical reaction in gas liquid and gas-liquid-solid foam-bed reactors for typically two different reaction systems, development of new models and their experimental verification. The systems chosen for studies are, absorption of CO<sub>2</sub> in NaOH solution under conditions of pseudo-first order reaction and the other, for a gas-liquid-solid system: carbonation of hydrated lime slurry using lean CO<sub>2</sub> gas. The former system corresponds to a fast chemical reaction and it occurs in a zone within the liquid film close to the gas-liquid interface. The latter reaction is moderately fast and occurs in the bulk of the liquid. Carbonation of hydrated lime in slurry using carbon-dioxide gas is an industrially important process for the manufacture of precipitated calcium carbonate (PCC). The performance of a short slurry bubblecolumn reactor has been compared with that of the slurry-foam reactor using experimental data collected for the above-mentioned reaction. Mathematical models for these two systems have been reported in the literature for carrying out the reactions in a foam-bed reactor. This reactor comprises of two sections, (i) the lower section, called the storage, is a shallow pool of liquid containing a surfactant through which gas bubbles rise and (ii) the upper section is a tall column of foam, called the foam section. The total amount of liquid contained in the foam, for the typical foam heights reported in the literature, is normally less than 15 percent of the total liquid fed to the reactor. In spite of this fact, models reported in the literature for the two systems assume extent of gas absorption and reaction in the storage section to be negligible. The above mentioned work was therefore undertaken in the present work. Models have been developed for absorption of lean carbon dioxide gas, 0.22% to 0.49%, from its mixture with air in sodium hydroxide solution, 0.23 to 0.87 (N) in semi-batch bubble column- and foam-bed reactors. Experimental studies with this low concentration of CO<sub>2</sub> and relatively high concentration of NaOH were performed with the objective of verifying the contribution of the storage section of a foam bed reactor towards conversion of reactants which was considered negligible in the previous studies, developing a new model, verifying its validity with the data generated and at the same time comparing the Analyses of gas-liquid and gas-liquid-solid foam-bed reactors ii present model with that already reported in the literature in which about the same concentrations of CO<sub>2</sub> and NaOH were used in the gas and liquid phase respectively. Mass transfer with chemical reaction is treated using the principle of absorption into agitated liquids for the development of models for the bubble column. Model for the storage section of a foam-bed reactor is developed following a similar concept to that of the bubble column. In the foam section, on the other hand, mass transfer occurs into the foam films primarily by molecular diffusion and the model is developed using the theories of absorption into quiescent liquids. Concentration of reactant B (i.e., NaOH) in the bulk of the liquid is maintained substantially high compared to a low concentration of dissolved CO<sub>2</sub>. Reactant B diffuses from the bulk of liquid to the reaction zone located close to the gas-liquid interface to nullify its depletion by reaction and maintain the same concentration of B upto the reaction zone as that existed in the bulk liquid. Rate of consumption of B is obtained by using the reaction stoichiometry and the average flux equation for CO<sub>2</sub> (component A). Calculations for concentration of component B in the storage section of a foam-bed reactor proceed by repeating the process over a small time step. For the development of model for the foam section, it is assumed that all the A absorbed in the storage section get reacted there itself and none of it goes to the foam section and vis-à-vis. Predictions for the extent of reaction over a small time interval in storage and foam sections are made using separate modules. The resulting concentration of component B in the storage section is estimated and the calculations are repeated over small time interval till the desired time of reactor operation. For validation of the models developed, experiments in the bubble column reactor were performed on absorption of CO<sub>2</sub> in NaOH solution without any surfactant added to the reaction mixture. Similar experiments were conducted

under otherwise identical operating conditions in a foam reactor with the addition of cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant (0.054% w/w) as the foaming agent. The variables and parameters studied include, effects of initial concentration of NaOH, superficial velocity of gas, volume of solution charged into the reactor and concentration of CO<sub>2</sub> gas on conversion of NaOH. After 2 minutes of reactor operation, a conversion 6 to 20 percent higher than that obtained in a bubble column reactor, was obtained in the foam reactor. Conversion of sodium hydroxide reduces with an increase in the concentration of NaOH in the feed solution when other variables are kept unchanged. This is attributed to the reduced solubility of CO<sub>2</sub> with an increase in the concentration of NaOH in the solution and that the fraction of the total initial mass of NaOH reacted during the same time interval reduced with each successive increment in concentration and caused a reduction in conversion. Conversions of sodium hydroxide after a definite time of reactor operation and under otherwise similar experimental conditions are found to be substantially higher in a foam-bed reactor than that in the bubble column reactor. Large increase in the interfacial area is considered to be the primary reason for this increase in conversion of NaOH. With an increase in the superficial velocity of gas, conversion of NaOH is found to increase. Larger size of bubbles and higher bubble-rise velocity at higher superficial velocity of gas reduce the specific interfacial area and gas-liquid contact time in the bubble column or in the storage section of the foam reactor. These lead to a reduction in the level of conversion. On the contrary, turbulence in the bubble column increases with an increase in the superficial velocity of gas and leads to higher values of gas-liquid mass transfer coefficient in the column. These result in higher rates of gas absorption, reaction and conversion. Percent conversion of NaOH reduces as volume of solution fed to the reactor is increased, concentration and all the other variables being kept unchanged. Total amount of NaOH is larger in the larger volume of solution fed to the reactor and conversion is found to reduce mainly because of the higher total initial mass appearing in the denominator in the definition used for conversion calculation. Conversion of NaOH increases with an increase in the concentration of CO<sub>2</sub> gas. Interfacial concentration of CO<sub>2</sub> in the liquid phase increases and the increased driving force for mass transfer causes an increase in the rates of gas absorption, reaction and therefore the conversion. Model for the bubble column slurry reactor has been developed for simultaneous dissolution of sparingly soluble hydrated lime particles and reaction with the dissolved gaseous species in the liquid phase. The slurry in the reactor is assumed to be well mixed by the rising gas bubbles. The reaction between hydroxide ions in solution and dissolved carbon-dioxide occurs in accordance with a second-order kinetics (Danckwerts and Sharma, 1966). Particle-size distribution has been incorporated in the model for evaluation of the reactor performance as lime samples having different initial particle-size distributions have been used in the experiments and the rate of dissolution of particles in liquid depends on its surface area. In the development of the slurry-foam reactor model, combined contributions of both the storage and foam sections towards gas absorption and reaction have been taken into account. That the storage section contributes significantly have been verified through experiments. The entire foam section is assumed to be equivalent to a single stage with an average liquid hold-up (Bhaskarwar and Kumar, 1984). In the course of reaction, as the dissolved species B gets consumed by reaction with component A absorbed in the liquid phase, concentration of B tends to reduce and more solid (B) dissolves into the liquid phase. There being a continuous transformation from solid to liquid phase, total loading of B in the slurry, both dissolved in solution and that present as particles, is incorporated in writing the material-balance equations for estimation of conversion of component B with the propagation of reaction time. The expressions for evaluation of performance of the slurry-foam reactor remain the same as those used for a slurry reactor, except that in the former case the total loading of component B and the instantaneous values of particle diameters have to be estimated by considering the conversions in both the sections, i.e. storage and foam simultaneously. For evaluation

of performance of the slurry-foam reactor, component A balances in foam and storage sections, component B balance over the storage section, and the mass balance of particles over the storage section are written. Again for writing the component A balance over the storage section, the instantaneous concentration of component A in the liquid stream, for this moderately fast reaction, draining from the foam to the storage section is needed. This concentration is obtained by writing a pseudo-steady state material balance for component A over the foam section. Simultaneous solution of these material-balance equations also needs an expression for the instantaneous volume of particles in the drainage stream from foam section expressed in terms of that in the storage section. For this purpose a mass-balance equation is written assuming that the rate of dissolution of particles in the foam section equals that reacted in this section, so that the concentration of dissolved calcium hydroxide in the liquid entering the foam section and that in the drainage stream from this section are the same, conforming to the pseudo-first order reaction with respect to A in the foam section. Analyses of gas-liquid and gas-liquid-solid foam-bed reactors v In order to validate the models developed, experiments on carbonation of hydrated lime in slurry with lean carbon-dioxide gas, 10 to 50 percent by volume, were performed in a short slurry bubble column reactor, without any surfactant added to the slurry as well as in a foam-bed reactor using different types of surfactants, cationic: cetyl trimethyl ammonium bromide, anionic: sodium dodecyl sulphate, and non-ionic: Triton X-100 as the foaming agents. Under identical conditions of experiments, after 20 minutes of the reactor operation, a higher conversion, about 18 to 42 percent higher than that in a slurry reactor, was obtained in the foam reactor using a cationic or an anionic surfactant as the foaming agent. The variables and parameters studied include, nature of surfactant used in generating stable foam, initial loading of hydrated lime in slurry, superficial velocity of gas, height of foam column, volume of slurry charged into the reactor, initial size distribution of lime particles (samples received from different manufacturers), concentration of each of the surfactants mentioned above, and, concentration of CO<sub>2</sub> in the feed gas. Other essential or supplementary experiments performed are (i) particle-size distribution analysis of calcium-hydroxide samples used as reactant as well as that of the product CaCO<sub>3</sub> (ii) chemical analysis of hydrated lime samples received from different manufacturers and used in the experiments (iii) liquid hold-up measurements in the foam column for all the experimental conditions used in obtaining the different sets of data (iv) Thermo-gravimetric Analysis (TGA) and X-ray diffraction (XRD) studies of calcium hydroxide samples received from different suppliers and that of product calcium carbonate obtained after complete carbonation of lime samples and (v) Scanning Electron Micrograph (SEM) analysis of calcium hydroxide samples and product calcium carbonate particles. Percentage of lime present in samples was found, through chemical analyses, to vary from 94.76 to 95.27 percent. XRD analyses indicate that major impurity is CaCO<sub>3</sub>. Particle-size distributions (PSDs) of reactant Ca(OH)<sub>2</sub> have been measured using CILAS- 940 and MALVERN MASTERSIZER 2000E particle-size analyzers. These play a significant role in governing the reactor performance and incorporated in the models. For Analyses of gas-liquid and gas-liquid-solid foam-bed reactors vi simulation purposes, the total amount of lime sample taken in an experiment was divided into twelve volume fractions. For slow to moderately fast reactions, liquid hold-up is known to govern the performance of a foam-bed reactor. In the present investigation, it has been measured at different heights of the foam column, for all the experimental conditions used, by suction of foam into an evacuated glass bulb of a known volume. Average value of the liquid hold-up over foam column height is then estimated from the knowledge of volume of bulb, the extent of vacuum in the bulb, and the volume of slurry obtained from the condensed foam. Conversions obtained in the slurry-foam reactor with ionic surfactants used as foaming agents after 10 minutes of reactor operation are found to be about 7 to 17 per cent higher than those obtained with non-ionic surfactants. The higher conversions obtained with ionic surfactants over those with a non-ionic surfactant are attributed to the higher gas-liquid interfacial areas and liquid hold-up values obtained experimentally. With an increase in the

initial solids loading, solid-liquid interfacial area increases and results in increased rates of solid dissolution and rate of reaction. However, conversion of lime reduces because initial solids loading appearing in the denominator in the conversion calculation. Superficial velocity of gas is observed to be the second most important variable which bring about maximum variation in the conversion of lime. Increase in the superficial velocity of gas causes higher liquid hold-up, higher drainage rate within the foam column, and an increased turbulence intensity in the storage section. These result in higher rates of mass transfer and of conversion of the two reactants. With an increase in the height of slurry-foam column, the total gas-liquid interfacial area for gas absorption in the foam section, gas-liquid contact time, and the total amount of liquid in the foam section increase. These factors together contribute to higher conversion of lime. With increased volume of feed slurry at constant values of slurry concentration and other variables, a reduction in the conversion of lime is observed. With an increase in the volume of slurry, at constant gas-flow rate and other variables, the intensity of agitation in the storage section reduces with the consequent reduction in the mass-transfer coefficient. The rates of dissolution of solids and that of absorption of gas in the liquid reduce. Analyses of gas-liquid and gas-liquid-solid foam-bed reactors vii Besides, solids loading being constant, the total amount of solids present is more in a larger volume of slurry, and the calculated values of conversion is found to reduce primarily because of the definition used for its calculation. With an increase in the concentration of surfactants, viz. SDS; CTAB and Triton X-100; at constant values of all other variables, the conversion of lime is seen first to increase and then to reduce at still higher concentrations. Increased surfactant concentration render the foam to be more stable and thus liquid hold-up in the foam column increases. The total volume of liquid in the storage section reduces with the consequent increase in turbulence. These beneficial effects, along with the larger interfacial area in the foam section for the reasons cited earlier, off set any retarding effect the surface resistance may have on gas absorption, and a small increase in the conversion is thus obtained. However, at higher concentration levels of the surfactant, the particle surfaces get appreciably covered with the surfactant molecules (Stangle and Mahalingam, 1990), reducing the rate of dissolution of solids. These phenomena, therefore, cause a decrease in the conversion of lime at higher surfactant concentrations. Effect of initial particle-size distribution of lime particles on conversion of lime has also been studied maintaining all other parameters at constant values. For a given solids loading, the sample of solids having a larger population of finer particles would have a larger interfacial area per unit volume of slurry. The dissolution rate of solid particles being proportional to solid-liquid interfacial area, samples of hydrated lime with higher population of finer particles results in higher conversion of lime. The model also predicts the effect. Effect of concentration of CO<sub>2</sub> gas on conversion of lime has been studied by varying the CO<sub>2</sub> concentration from 10 to 50 percent by volume. Rates of absorption of CO<sub>2</sub> gas in hydrated lime slurry and the reaction rates are enhanced significantly with the increase in concentration of CO<sub>2</sub> in the feed gas mixture, the equilibrium interface concentration of dissolved CO<sub>2</sub> being increased. For a given value of particle loading and at a given temperature, total solid-liquid interfacial area and interface concentration  $C_B^*$  remains invariant. Rate of dissolution of lime is enhanced for the reaction to proceed at a higher rate as CO<sub>2</sub> concentration in the feed gas is increased. This is possible only if solid-liquid mass-transfer coefficient value is increased. A dimensionless correlation has been developed using the experimental data collected for carbonation of hydrated lime slurry Analyses of as functions of concentration of carbon-dioxide gas and other variables/parameters pertinent to the experiments performed.