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Modelling of cross-flow membrane contactors: Mass transfer with chemical reactions

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Abstract

Conventionally, carbon dioxide and hydrogen sulphide are absorbed using aqueous alkanolamines or carbonate solution in column type of equipment. However, in view of the unparallel advantages offered, the use of microporous hollow fiber membrane modules is an attractive alternative. In the present study application of cross-flow membrane contactors for absorption of these gases using aqueous potassium carbonate as a solvent is explored. The carbon dioxide and hydrogen sulphide absorption into aqueous solutions carbonate involves complex chemical reactions. The effect of these chemical reactions on the absorption into a liquid flowing though a hollow fiber membrane may not be described using conventional mass transfer models like e.g. the penetration or surface renewal model due to the lack of a well defined liquid phase bulk and the presence of a laminar velocity profile in the mass transfer zone. Moreover, in the case of cross-flow membrane contactors, the concentrations of both fluids, inside and outside the fibers, vary in both directions i.e. in the direction of flow and in the direction normal to the flow. Hence the theoretical analysis of the cross-flow membrane contactor is more complicated. To describe the effect of the chemical reaction on the absorption rate in the cross-flow hollow fiber contactor, a detailed mathematical model was developed using first principles. A complete scheme of the reversible ionic reactions and equilibria involved was implemented in the model to describe the solute uptake. The experiments were carried out study the effects various parameters such as gas and liquid velocities, bulk concentrations of solute gas and liquid phase reactant. The theoretical predictions were compared with experimental results. An excellent match between experimental results and model predictions was obtained.

Keywords: Hollow fiber membranes; Membrane contactors; Gas treating; Cross-flow; Modelling

1. Introduction

Natural gas, refinery gas contains hydrogen sulphide as a major impurity. Hydrogen sulphide is a highly toxic and corrosive gas and considered as one of the major sources for the environmental problems such as acid rains. Therefore, in order to utilize these fuels for chemical processing or energy generation, the hydrogen sulphide concentration in these gases must be reduced to very low levels; less than 0.0115 g/m^3 is required for certain specific applications [32].

Increasing demand of energy has given more attention to the low quality natural gas containing high percentages of carbon dioxide (up to 30%). In view of high transportation cost and corrosive effects caused by carbon dioxide, it is necessary to reduce the concentration of carbon dioxide to acceptable levels. Typically 2% carbon dioxide is stipulated as a pipeline specification. Carbon dioxide is also produced whenever fossil fuels such as natural gas or coal are burned for energy generation. A typical rate of carbon dioxide generation from a thermal power plant is 5×10^5 kg/h in the case of 600 MW coal fired plant. Emission of carbon dioxide is regarded as a serious potential cause for environmental problems such as global warming. Hence, carbon dioxide capture from these sources is important if the green house effect is to be reduced.

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The most common process for removal of these gases is an absorption into a solvent using conventional gas–liquid contactors such as packed or plate column. Both hydrogen sulphide and carbon dioxide are acidic in nature and are similar in many physical and chemical aspects. Hence, the solvents used for the removal of carbon dioxide in gas treating process also absorb hydrogen sulphide. Compared to physical solvents, enhanced absorption incorporating chemical reaction results into high selectivity and reduced solvent circulation. Therefore, there has been great deal of effort in applying chemical solvents such as aqueous solutions of alkanolamines and aqueous carbonate solutions. In addition to the conventional absorption processes utilizing column type of contactors, the use of microporous hollow fiber membrane contactors is an attractive alternative. In view of the unparallel advantages offered by these hollow fiber membrane contactors, considerable academic and industrial work has been done to develop these contactors for natural gas treating [11]. However, up to now only very few of these processes have been successfully tested on a larger scale. Kvaerner Oil and Gas and W.L. Gore and Associates GmbH have been developing a membrane gas absorption process for the removal of acid gases from natural gas and exhausts of the offshore gas turbines [16]. In this process, PTFE hollow fiber membranes are used in combination with physical (Morphysorb®) or chemical (alkanolamines) solvents. However, PTFE hollow fibers are not available in small diameters (few hundred microns) and are more expensive, making natural gas treating using membrane gas absorption not so attractive as compared to the conventional absorption process. TNO Environment Energy and Process Innovation (the Netherlands) have been developing a membrane gas absorption process for the removal of CO_2 from flue gases using commercially available and cheaper polypropylene hollow fiber membranes. However, the conventional alkanolamine solutions are found to wet the polypropylene membranes. To avoid these wetting problems, TNO has developed a range of new reactive absorption liquids based on the amino acid salt solutions [15]. Nevertheless, these newly developed reactive solvent may suffer from the problem of precipitation of reaction products at high amine concentration and high amine loading [21]. The precipitation of the reaction products may result into a significant increase in the overall mass transfer resistance due to the blockage of the membrane pores.

On the other hand, absorption of carbon dioxide and hydrogen sulphide into aqueous carbonate solutions using polyolefin membranes contactors has been studied experimentally by Nii et al. [24] and Chun and Lee [5] who found that modules made up of polyolefin membranes are ideally suitable for this system. However, the theoretical analysis of this system is more difficult due to complex reactions involved in the system. These investigators used an overall mass transfer coefficient or simple kinetics to describe the system. The more detailed theoretical analysis of carbon dioxide absorption into potassium carbonate system using membrane contactors by Lee et al. [22] lacks experimental validation of the system. It is important to note that all the work was carried out using parallel-flow modules, where the change in the concentration of shell-side fluid is uni-axial (i.e. along the axis of module or in the direction of flow). In case of cross-flow membrane contactors the concentrations of both fluids vary significantly in both directions i.e. in the direction of flow as well as in the direction normal to the flow and thus the change is bi-axial for both fluids. Hence the theoretical analysis of cross-flow membrane contactor is more complex.

In this work, a detailed theoretical analysis is carried out for the removal of carbon dioxide and hydrogen sulphide by absorption into aqueous potassium carbonate solutions using cross-flow hollow fiber membrane contactors. Complete reversible reactions scheme was included in the microscopic theoretical model equations as opposed to the use of overall mass transfer coefficient to describe solute uptake. The theoretical predictions were validated by the experimental analysis carried out using commercial as well as laboratory-made cross-flow membrane contactors.

2. Theory: mass transfer with chemical reactions

2.1. Reactive absorption of carbon dioxide in aqueous carbonate solutions

Absorption of carbon dioxide into the aqueous carbonate solutions has been studied by many investigators [17,30,31]. In these studies most of the work has been carried out using high bicarbonate to the carbonate ratios. In such cases the carbon dioxide into the aqueous carbonate buffer solutions can be treated as absorption accompanied by an irreversible pseudo-first order reaction. The chemical absorption mechanism under the conditions of low or negligible bicarbonate to carbonate ratio is, however, more complex and contains two-step reversible reactions [34].

When the potassium carbonate is dissolved in water it is ionized into the potassium ion (K^+) and carbonate ion ($CO_3{}^{2-}$). The bicarbonate ion ($HCO_3{}^-$) and hydroxyl ion (OH^-) are then generated by the inverse of reaction 2 in following reaction scheme. The various reactions taking place during the absorption of carbon dioxide into the aqueous potassium carbonate solution are given below [17].

$$CO_2 + OH^- \underset{k_{1,2}}{\overset{k_{1,1}}{\longleftrightarrow}} HCO_3{}^- \tag{1}$$

$$HCO_3{}^- + OH^- \underset{k_{2,2}}{\overset{k_{2,1}}{\longleftrightarrow}} CO_3{}^{2-} + H_2O \tag{2}$$

$$2H_2O \underset{k_{3,2}}{\overset{k_{3,1}}{\longleftrightarrow}} H_3O^+ + OH^- \tag{3}$$

$$CO_2 + 2H_2O \underset{k_{4,2}}{\overset{k_{4,1}}{\longleftrightarrow}} HCO_3{}^- + H_3O^+ \tag{4}$$

$$CO_2 + CO_3{}^{2-} + H_2O \leftrightarrow 2HCO_3{}^- \tag{5}$$