

Modelling of Gas Absorbers for Carbon Dioxide Capture Applications

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ABSTRACT

A rate-based process model for the capture of CO₂ from a gas mixture using aqueous solutions of monoethanolamine (MEA) in a packed absorption column is developed in this work. The model is based on the fast second-order kinetics for the CO₂-MEA reaction and takes into account the heat effects associated with the absorption and chemical reaction through energy balances in the gas and liquid phases. Appropriate correlations for the key thermodynamic and physical properties are incorporated to ensure reliable predictions. The model is validated by comparing the predictions with experimental data obtained by Tontiwachwuthikul *et al.* (1992) in a pilot-scale absorption column. Good quality predictions for the gas phase CO₂ and MEA concentrations and the liquid temperature along the column height were obtained.

Keywords: CO₂ scrubbing; reactive absorption; modeling; packed-bed absorber

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INTRODUCTION

In recent times, there have been global environmental concerns for the reduction of greenhouse gas emissions from industrial sources, such as thermal power plants, to alleviate the global warming problem. Generally, global warming results from the emissions of methane, carbon dioxide, nitrous oxide, and chlorofluorocarbons (Davis and Cornwell, 1991). Among these, carbon dioxide (CO_2) is considered to be the principal contributor to the problem, thus being the target of major reductions. Following the 1997 Kyoto Protocol, the European Commission prescribed drastic CO_2 reductions of 20% by the year 2020. Therefore, CO_2 removal from thermal power plant flue gases, which would otherwise be vented to the atmosphere, becomes essential. With existing technologies, CO_2 removal can be achieved by several separation techniques including absorption into liquid solvents, adsorption on solids, permeating through membranes, and chemical conversion. For CO_2 capture from large volume flue gas streams, the absorption into liquid solvents is the most feasible process approach (Kohl and Nielsen, 1997). Conventionally, CO_2 absorption takes place in packed or tray columns that allow direct contact between gas streams containing CO_2 and the liquid absorption solvents. Removal performance of the absorption process can be determined by the degrees of gas-liquid contact provided by column internals. To remove CO_2 from the flue gas streams efficiently, internals that promote good gas-liquid contact are required.

Packed towers using aqueous solutions of monoethanolamine (MEA) are widely used for the separation of acidic constituents, such as CO_2 and H_2S , from industrial waste gases. Treybal (1969) developed the basic theory for steady-state, adiabatic absorption and stripping involving single-solute, non-reactive systems. The heats of absorption, solvent evaporation and condensation, as well as heat and mass transfer resistances in both phases were accounted for in Treybal's model. Rigorous theories for absorption with chemical reaction were well documented by Danckwerts (1970) and Astarita *et al.* (1983). Their efforts were primarily directed towards developing expressions for the local mass transfer coefficients. In contrast, little emphasis was placed on devising design methods for packed towers for chemical absorption. A general design methodology based on the model of Treybal (1969) for gas absorption with chemical reactions was proposed by Pandya (1983). Deleye and Forment (1986) subsequently adopted a similar procedure and presented some numerical results for commercial processes, but comparisons with industrial data were not given. Sanyal *et al.* (1988) have modelled the absorption of CO_2 in hot carbonate solutions and validated their results by comparing with inlet and outlet data obtained from a packed-bed absorber. Tontiwachwuthikul *et al.* (1992) provided extensive experimental data for the CO_2 -MEA system and compared the data with predictions from a mathematical model based on Pandya's (1983) work. Later, Pintola *et al.* (1993) presented an improved mathematical model along with comparisons with data from an industrial absorber.

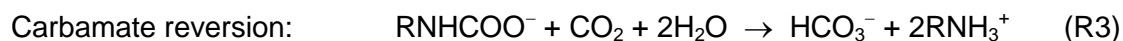
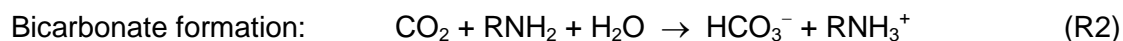
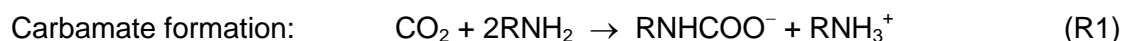
In the present work, a rate-based process model for the chemical absorption of CO_2 into aqueous MEA solutions has been developed. The model predictions are validated against experimental data obtained in a pilot-scale pack-bed absorber by Tontiwachwuthikul *et al.* (1992). Such a process model can be used as an effective tool for the design of absorption columns for CO_2 capture from thermal power plants and for the simulation of the CO_2 capture performance as a function of process operating conditions.

MATHEMATICAL MODEL FORMULATION

To develop a comprehensive mathematical model, it is essential to understand the underlying mechanisms of the chemical absorption process. These encompass reaction mechanisms, reaction kinetics, and mass transfer mechanisms. For the system in question, i.e. CO₂ absorption in aqueous MEA solutions, mass transfer is accompanied by chemical reactions in the liquid phase. The mathematical model developed in this study is based on the earlier work of Treybal (1969) and Panday (1983). An outline of the model is given here; full details may be found in Khan (2009).

Chemistry of CO₂-MEA System

The reactions between CO₂ and amines have been extensively studied for decades (Danckwerts, 1970; Astarita *et al.*, 1983), but very little is actually understood about the process. However, three reaction steps appear to be of principal importance for the CO₂-MEA system:



Astarita *et al.* (1983) have suggested that for the CO₂-MEA absorption system, the rate of bicarbonate formation is insignificant since the stability of MEA carbamate is quite high. The overall absorption rate may be regarded as approximate irreversible. Carbamate formation has also been studied extensively by Astarita *et al.* (1983) for MEA, where its forward rate has been established to be first-order with respect to both CO₂ and MEA, and second-order with respect to overall reaction:

$$r = k_2[\text{CO}_2][\text{RNH}_2] \quad (1)$$

This rate expression is generally valid provided the solution loading is less than 0.5 mol of CO₂ per mole of amine. The second-order rate constant, k_2 , depends on the temperature and is given by:

$$\log(k_2) = 10.99 - 2152/T \quad (2)$$

Reaction Kinetics

One of the most important yet difficult aspects of modelling gas absorption with chemical reaction is the determination of the enhancement factor, E . Danckwerts (1970) defined it as the ratio of the mass transfer coefficient for absorption with chemical reaction, k_L , to the mass transfer coefficient for purely physical absorption, k_L° . In contrast with k_L° , which is fairly constant, k_L and hence E change significantly along the height of the column. The determination of enhancement factor requires the solution of a set of partial differential equations that govern the simultaneous diffusional mass transfer and chemical reactions in the liquid film. As it stands, there are no general analytical solutions. The CO₂-MEA reaction is second-order and approximate solutions have been provided by van Krevelen and Hoftijzer (1948) and Wellek *et al.* (1978). Although the latter authors found the equations derived by van Krevelen and Hoftijzer (1948) to be most accurate, they required an iterative solution procedure to determine E . The explicit equation presented by Wellek *et al.* (1978) in terms of the enhancement factor for an instantaneous reaction, E_i , and Hatta modulus, M , which deviates by less than 3% from the most accurate solution, can be adopted:

$$E = 1 + \frac{1}{\left[\left(\frac{1}{E_i - 1} \right)^{1.35} + \left(\frac{1}{E_1 - 1} \right)^{1.35} \right]^{1/1.35}} \quad (3)$$

$$\text{where } E_i = 1 + \left(\frac{C_{B,L} D_B}{b D_{A,L} C_{A,i}} \right), \quad E_1 = \frac{\sqrt{M}}{\tanh \sqrt{M}} \quad \text{and} \quad M = \frac{D_{A,L} k_2 C_{B,L}}{(k_L^o)^2}$$

Estimation of Thermodynamic and Physical Properties

The calculation of mass transfer rates requires detailed knowledge of the physical properties of the gas and liquid phases, as well as the solubilities and diffusivities of the gas in the liquid phase. Liquid diffusivity has a strong dependence on both temperature and physical properties of the solvent. Therefore, a correlation that relates CO₂ diffusivity to both of these parameters simultaneously is desirable. Versteeg and van Swaaij (1988) suggested the following empirical expression:

$$D_{CO_2,L} = D_{CO_2,water} \left(\frac{\mu_{water}}{\mu_L} \right)^{0.8} \quad (4)$$

$$D_{CO_2,water} = 2.35 \times 10^{-6} \exp\left(-\frac{2119}{T}\right) \quad (5)$$

where $D_{CO_2,L}$ is the diffusion coefficient of CO₂ in liquid solvent, $D_{CO_2,water}$ is the diffusion coefficient of CO₂ in water, μ_L is the viscosity of the liquid solvent, μ_{water} is the viscosity of water, and T is the absolute solvent temperature. Weiland *et al.* (1998) reported an empirical correlation for the solvent viscosity in terms of the percentage mass of amine present in the solution, w , the solvent absolute temperature, T , and CO₂ loading, α :

$$\frac{\mu_L}{\mu_{water}} = \exp\left[\frac{(21.186w + 2373)[\alpha(0.01015w + 0.0093T - 2.2589) + 1]w}{T^2} \right] \quad (6)$$

The CO₂-MEA system obeys Henry's law well due to a relatively low solubility of CO₂ in alkanolamine solutions. The Henry's constant was determined using the correlation developed by Danckwerts (1970) to calculate the solubility of CO₂ in the liquid phase at any given MEA concentration, C_{MEA} , and absolute liquid temperature:

$$H_{CO_2} = 10^{(5.3 - 0.035C_{MEA} - 1140/T)} \quad (7)$$

Material and Energy Balances

The variation of CO₂ concentration in the gas phase along the height of a pack-bed absorption column is given by the following steady-state, one dimensional species conservation equation for constant physical properties:

$$\frac{d(u_z C_{CO_2G})}{dz} = \frac{dN_{CO_2G}}{dz} = S_{CO_2} \quad (8)$$

where C_{CO_2G} is the molar concentration of CO₂ in the gas phase, N_{CO_2G} ($= u_z C_{CO_2G} = G_{Air} Y_{CO_2}$) is the molar flux of CO₂ (kmol/m²s), G_{Air} is the molar flow rate of air per unit

cross-sectional area of column, S_{CO_2} is the source term representing the rate of chemical absorption of CO_2 , u_z is the gas velocity in the z direction along the column height, and Y_{CO_2} is the mole ratio of CO_2 in the gas phase. Equation (8) is discretised over a differential height of the column, Δz , as shown in Fig. 1, to yield:

$$N_{CO_2 G_{i+1}} = N_{CO_2 G_i} - S_{CO_2} \Delta z \quad (9)$$

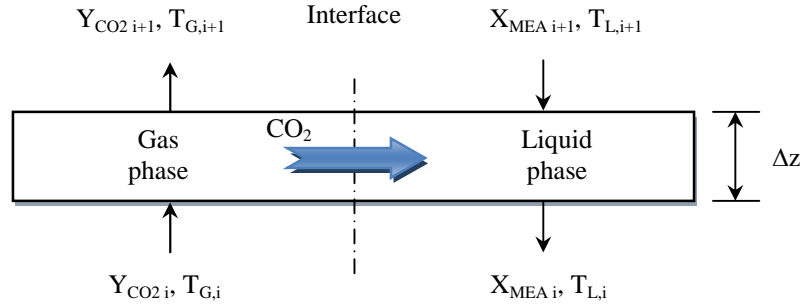


Figure 1. A differential element of the column.

The MEA concentration in the solution can be obtained by performing an overall material balance over the differential element:

$$X_{MEA_i} = X_{MEA_{i+1}} + (Y_{CO_2 i} - Y_{CO_2 i+1}) b G_{Air} / L_{water} \quad (10)$$

where b is the stoichiometric factor, X_{MEA} is the mole ratio of MEA in water, and L_{water} is the molar flow rate of water.

The source term is obtained for a fast second-order reaction using the two-film mass transfer theory as (Levenspiel, 1999):

$$S_{CO_2} = \frac{p_{CO_2}}{\frac{1}{k_{CO_2 G} a} + \frac{H_{CO_2}}{k_{CO_2 L} a E}} \quad (11)$$

where a is the gas-liquid interfacial area per unit volume of column, $k_{CO_2 G}$ and $k_{CO_2 L}$ are the gas- and liquid-film physical mass transfer coefficients, respectively, and p_{CO_2} is the partial pressure of CO_2 . The enhancement factor, E , is given by Eq. (3) and the Henry's constant, H_{CO_2} , by Eq. (7). The parameters, a , $k_{CO_2 G}$ and $k_{CO_2 L}$ were obtained from the correlations given by Onda *et al.* (1968).

The absorption of CO_2 in the solvent results in the release of heat of solution. Following absorption, exothermic chemical reactions take place between MEA and CO_2 . Both of these mechanisms increase the liquid temperature, and consequently the gas temperature due to it being in direct contact with the liquid, from the inlet to the outlet of the column. The variations of temperature in the gas and liquid phases are determined from the thermal energy equations provided below.

Gas phase energy balance:

$$G_{Air} Y_{CO_2} C_{p,G} \frac{dT_G}{dz} = h_G a (T_G - T_L) \quad (12)$$

Liquid phase energy balance:

$$LC_{p,L} \frac{dT_L}{dz} = G_{Air} Y_{CO_2} C_{p,G} \frac{dT_G}{dz} + G_{Air} (H_R + H_S) \frac{dY_{CO_2}}{dz} \quad (13)$$

where T_G and T_L are the gas and liquid temperature, respectively, and H_R and H_S are the heat of reaction and heat of solution, respectively. Equations (12) and (13) were discretised over the differential height as shown in Fig. (1).

The absorption column was divided into 30 differential elements and the discretised species conservation and thermal energy equations were solved for each element using the MATLAB program. Due to the implicit relationship between the material and energy balances, an iterative procedure is adapted to determine the compositions and temperatures in each element of the absorber.

THE EXPERIMENTAL CASE

The rate-based model developed for the purpose of simulation of CO₂ absorption by aqueous MEA solutions was validated by simulating a series of experiments carried out by Tontiwachwuthikul *et al.* (1992), as mentioned earlier in the introduction. The experiments were carried out in a pilot-scale packed absorption column with 6.55 m height of packing and 0.1 m in internal diameter, as shown schematically in Figure 2. The column was packed with 12.7 mm ceramic Berl saddles and the operating pressure was 103.15 kPa. The gas mixture, air-CO₂, which was introduced into the column at a desired height, flowed upwards and counter currently to the solvent which was introduced at the top of the column. Having reached steady-states, the exact compositions and temperatures were measured along the column height. The conditions of the trial run simulated here are given in Figure 2.

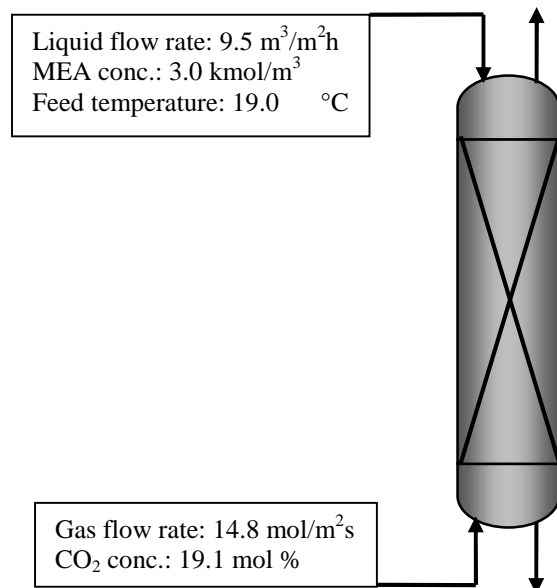


Figure 2. Schematic of the pilot-plant CO₂ absorber with process conditions

RESULTS AND DISCUSSION

A number of experiments covering wide-ranging operating conditions (Tontiwachwuthikul *et al.*, 1992) were simulated to validate the model predictions, however because of the space limitation only selected results are presented here. Figure 3 shows the comparison between the experimental and predicted gas phase

CO₂ concentrations along the column height. The predictions were obtained for both pseudo first-order and second-order reaction kinetics. It should be noted that in some of the previous modelling studies on the CO₂-MEA system the former reaction regime was used in order to simplify the calculation. As can be seen, the agreement between the predictions obtained using the second-order kinetics and experimental data are very good, as compared with the pseudo first-order simulation results, thereby confirming the validity of the mathematical model based on the second-order kinetics. However, quantitatively there are minor deviations between the second-order simulation and experimental results. The CO₂ concentration is slightly under-predicted in the initial 2.5 m of the column. This may be due to the use of empirical correlations for the gas- and liquid-film coefficients and the interfacial area in the absorption rate equation (11). The predicted, using both the kinetic regimes, and measured MEA concentration distributions along the column are show in Figure 4. The level of agreement between the predicted and measured CO₂ concentrations revealed in Figure 3 is also reflected here. The predicted output concentrations for both CO₂ and MEA exactly match the experimental measurements. It is evident from both figures that the concentrations decrease rapidly in the bottom part of the column, indicating that most of CO₂ removal from gas takes place in that particular region. The remaining height of the column serves to further reduce the CO₂ concentration to a very small value.

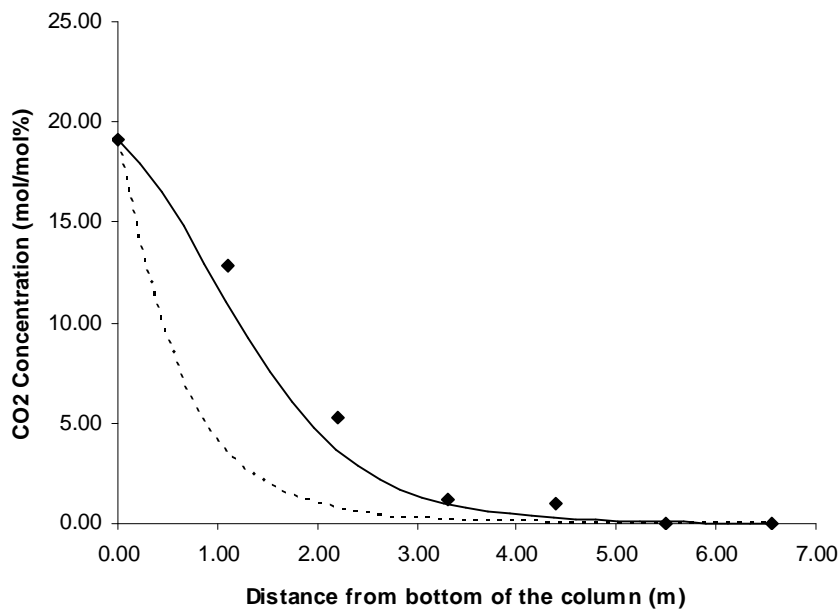


Figure 3. Comparison between the predicted and measured gas phase CO₂ concentration profiles as a function of the column height (----- 1st order kinetics, _____ 2nd order kinetics, ◆ Expt.data).

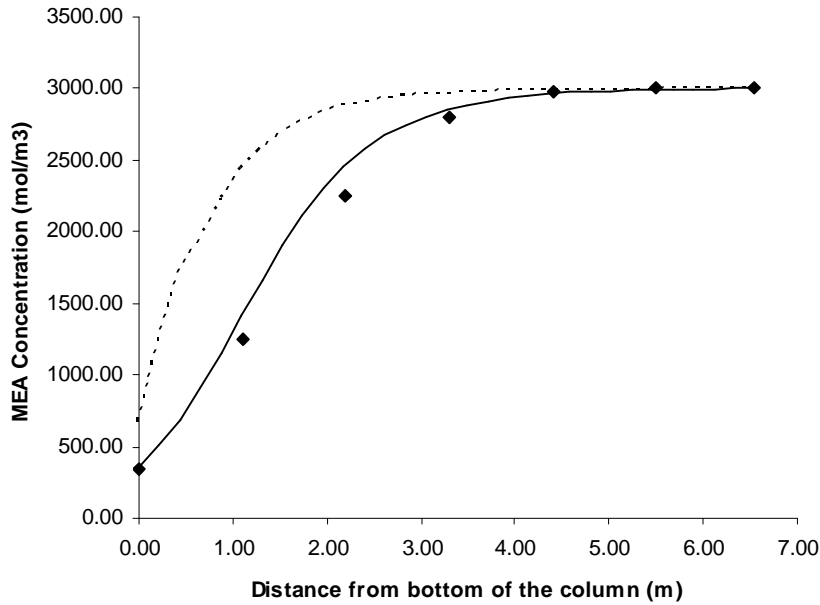


Figure 4. Comparison between the predicted and measured MEA concentration profiles as a function of column height (----- 1st order kinetics, _____ 2nd order kinetics, ◆ Expt.data).

The variation of temperature within the absorber is important and should not be neglected. The rate of reaction between the solvent and solute gas as well as the solubility of solute gas is a strong function of temperature. Figure 5 shows a comparison between the predicted liquid temperature profile using the second-order kinetics with experimental measurements as a function of column height. The overall agreement is reasonably good. However, there are discrepancies in the bottom section of the column where most CO_2 absorption occurs. As shown in the figure, the heat effects due to CO_2 absorption and reaction with MEA can cause a maximum in the temperature of the liquid phase near the bottom of the column. Higher up the column, the liquid temperature is fairly constant and is close to the inlet temperature of the solvent.

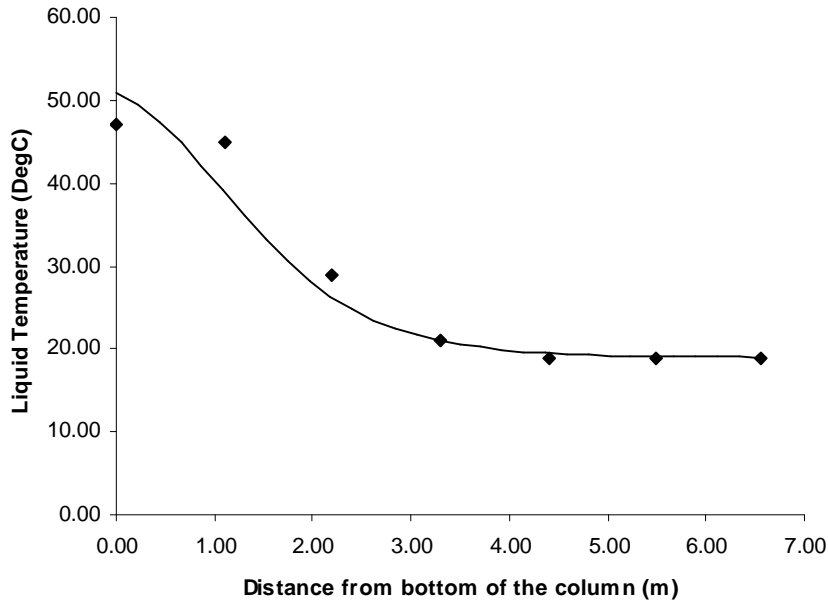


Figure 5. Comparison between the predicted and measured liquid temperature profiles as a function of column height (_____ 2nd order kinetics, ♦ Expt.data).

CONCLUSIONS

The following principal conclusions may be drawn from the present study. Good agreements were found between the experimental measurements and the model predictions based on the second-order kinetics for a pilot scale CO₂ absorption column. The variation of the enhancement factor along the column must be accurately taken into account for reliable modelling. The heat of chemical reaction and variations in physical properties render chemical absorption quite complex. All of these factors must be included in the mathematical model in order to obtain accurate predictions. Model validation should be based on concentration and temperature profiles along the whole length of column and not just the conditions at the absorber top and bottom. Most CO₂ removal typically occurs in the bottom region of the absorber. The top region merely reduced the CO₂ concentration down to very low levels. The present study demonstrates that a rate-based process model can generate accurate predictions of the key process parameters for the chemical absorption of CO₂ by an MEA solution in a pilot-scale packed bed absorber. However, further validation of such models using data from large scale columns is needed before they can be used reliably for the design and simulation of absorption columns for CO₂ capture from power plant flue gases.

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