

Rigorous Model for Predicting the Behavior of CO₂ Absorption into AMP in Packed-Bed Absorption Columns

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A rigorous computer model was developed for the simulation of the absorption of CO₂ in aqueous 2-amino-2-methyl-1-propanol (AMP) solutions in a packed absorption column that takes into account the heat effects. This model predicts the concentration and the temperature profiles along the packed column for the CO₂–AMP system. These profiles were compared with the experimental data that were obtained from two pilot-plant studies. The first study was with a column packed with 12.7-mm Berl Saddles, and the second study was with a high-efficiency structured packed absorber. The predicted results were found to be in close agreement with the measured values. For the experimental data from University of British Columbia, the average absolute deviations between the predicted and measured data in terms of concentration and temperature profiles are 9.7% and 2.3%, respectively. For the experimental data from University of Regina, the average absolute deviation between the predicted and measured concentration profiles is 13.8%. The model predictions could be improved by using more accurate physicochemical properties, when available.

1. Introduction

In the gas absorption industry, carbon dioxide removal from gaseous mixtures with alkanolamine solutions is classified as an adiabatic gas absorption process with chemical reaction. The first design technique for gas absorption with chemical reaction in adiabatic packed towers was introduced by Pandya,¹ using CO₂ absorption into monoethanolamine (MEA) solution. This design technique accounts for the major heat effects (absorption, reaction, solvent evaporation, and condensation), chemical reaction in the liquid phase, and mass- and heat-transfer resistance in both phases. A similar procedure for the design and simulation of absorption columns was developed by De Leye and Froment² using CO₂ absorption into MEA and diethanolamine (DEA) solution. They presented some numerical results for a commercial process, but comparisons with pilot-plant or industrial data were not provided. Sanyal et al.,³ using CO₂ absorption into amine-promoted hot potassium carbonate solution (K₂CO₃), developed a mathematical model for the absorption of carbon dioxide in a packed column. Close agreement between the calculated values and experimental results for two sets of plant data was reported. Tontiwachwuthikul et al.⁴ and Pintola et al.⁵ utilized Pandya's model¹ to predict the concentration and temperature profiles along the packed columns for CO₂ absorption into MEA and aqueous sodium hydroxide (NaOH). The model predictions were found to be in good agreement with pilot-plant data and industrial-absorber data.

The above models were applied to CO₂ absorption in packed columns using chemical solutions such as monoethanolamine, sodium hydroxide, and amine-promoted hot potassium carbonate. However, a solution of 2-amino-2-methyl-1-propanol (AMP), which is a sterically hindered amine, was not utilized in those models at that time because sufficient fundamental data had not been reported.⁴ Recently, AMP solution has been introduced as commercially attractive over conventional amines, such as MEA, DEA, and methyldiethanolamine (MDEA), because it has a loading capacity of up to 1 mol of CO₂ per mole of AMP, and it has excellent absorption characteristics, superior stripping qualities, higher degradation resistance, and

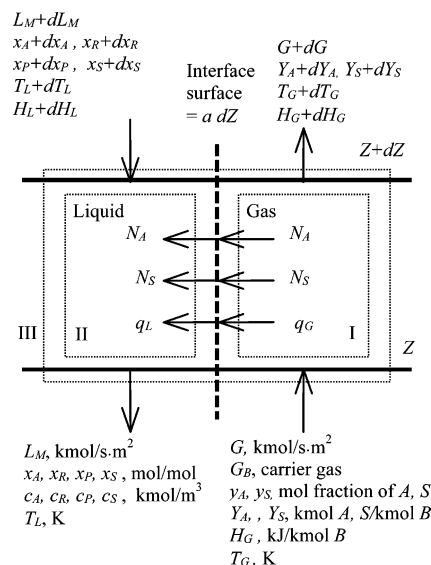


Figure 1. Differential section of the absorber.

a lower corrosion rate. Moreover, the availability of some fundamental data for the CO₂–AMP system has paved the way for simulation of this system. Absorber simulation results in terms of CO₂ partial pressure profiles were reported by Alatiqi et al.⁶ for a CO₂–AMP commercial plant. The model used to simulate the plant was based on a ‘mixing cell’ approach. However, comparisons between the actual and predicted values were not provided.

Using Pandya's procedure¹ and the recent fundamental data for the CO₂–AMP system,^{12–15,19–24} a rigorous computer model for the simulation of CO₂ absorption by aqueous AMP solutions has been developed. The predictions of the model were compared with the experimental data obtained from two pilot-plant studies using random and structured packed absorbers.

2. Mathematical Model

The material and energy balance equations are written around a differential height, dZ , of a packed absorber, as shown in Figure 1. In this figure, L_M , G , H , N , q , x , Y , a , and T refer to the molar liquid flow rate, the total molar gas flow rate, the

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enthalpy, the mass-transfer flux, the heat-transfer flux, the liquid concentration, the gas concentration, the interfacial area, and the temperature, respectively. The subscripts are as follows: A, carbon dioxide; B, inert gas; G, gas phase; S, volatile solvent; and L, liquid phase. Envelop III represents the differential section, which consists of gas and liquid phases denoted by envelopes I and II, respectively. In this process, CO₂ diffuses from the gas phase to the liquid phase and reacts with nonvolatile amine components to produce nonvolatile products.

The major assumptions are as follows: (1) steady-state conditions prevail, (2) the reaction is fast and takes place in the liquid film, (3) CO₂ and H₂O are the only components transported across the interface, (4) the heat- and mass-transfer resistances for H₂O in the liquid phase are negligible, and (5) the interfacial areas for heat and mass transfer are the same. On the basis of these assumptions, the main model equations resulting from mass and energy balances were written and can be presented as follows:

The concentration gradients in each differential section are

$$\frac{dY_A}{dZ} = \frac{-k_{A,G}aP(y_{A,G} - y_{A,i})}{G_B} \quad (1)$$

$$\frac{dY_S}{dZ} = \frac{-k_{S,G}aP(y_{S,G} - y_{S,i})}{G_B} \quad (2)$$

where P and k_G are the pressure and the gas mass-transfer coefficient.

The temperature gradients in each differential section for the gas and liquid phases are given by

$$\frac{dT_G}{dZ} = \frac{-h_G a (T_G - T_L)}{G_B (C_{PB} + Y_A C_{PA} + Y_S C_{PS})} \quad (3)$$

$$\frac{dT_L}{dZ} = \frac{1}{L_M C_{PL}} \left\{ G_B (C_{PB} + Y_A C_{PA} + Y_S C_{PS}) \frac{dT_G}{dZ} + G_B [C_{PS}(T_G - T_0) + \lambda_S] \frac{dY_S}{dZ} + G_B [C_{PA}(T_G - T_0) - \Delta H_R(T_0, P)] \frac{dY_A}{dZ} \right\} \quad (4)$$

where h , C_p , λ , and ΔH_R are the heat-transfer coefficient, the heat capacity, the latent heat of vaporization, and the heat of chemical reaction between the absorbed gas and the amine, respectively.

In each differential section, the gas-phase mole fraction of CO₂ at the interface can be expressed by eq 5, which results from the mass flux balance equations of CO₂ in the gas and liquid phases, and the liquid-phase mole fraction can be expressed by Henry's law ($C_{Ai} = He \cdot p_{Ai}$)

$$p_{Ai} = \frac{p_A + \frac{k_{LA}^0 E}{k_{GA}} C_{Ae}}{1 + \frac{k_{LA}^0 E}{k_{GA}} He} \quad (5)$$

where C_{Ae} , He , k_{LA}^0 , and E are the equilibrium concentration, the Henry's law constant, the physical mass-transfer coefficient, and the enhancement factor, respectively.

The system of differential equations defined by the model is integrated simultaneously to calculate composition and temperature profiles along the column.

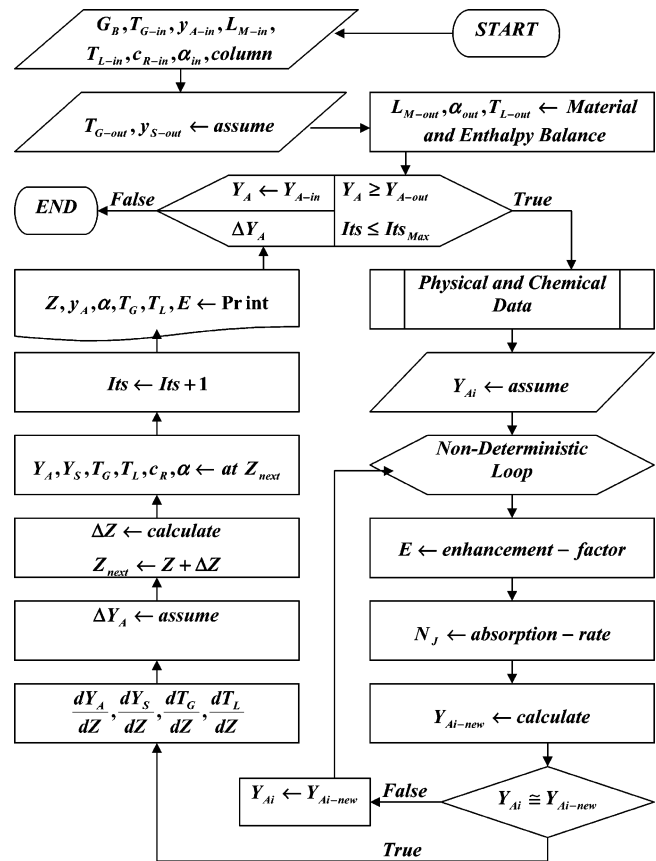


Figure 2. Flowchart for the CO₂-amine simulation model.

For the absorption column simulation, operating in counter-current mode, only the inlet gas and liquid flow conditions are known. The outlet gas and liquid conditions are, at best, partially specified. This leads to a two-point boundary value problem, for which the shooting method of solution is recommended.^{3,4} Usually, the CO₂ concentration of the outlet gas stream is specified; however, the temperature and moisture content are not. A good initial assumption is that the temperature and moisture content of the exit gas are assumed to be in equilibrium with the inlet liquid. Using this assumption, the outlet liquid conditions can be determined by applying overall mass and energy balances around the column. Then, the shooting method procedure begins at the bottom of the column and moves upward, computing the temperature and concentration profiles along the column, until the specified CO₂ concentration in the outlet gas stream is achieved within 1% accuracy. The obtained conditions at the top of the column are compared with the assumed values to test the preset convergence. If the convergence criteria are not met, then new guesses of the outlet gas conditions are made, and the procedure is repeated. The simplified flowchart of Figure 2 represents these procedures, and a FORTRAN 90 computer program was developed to solve the model equations (eqs 1–5). The parameters demanded by the model for each absorption case are obtained from the available experimental measurements or correlations. These parameters are programmed in subroutines and called by the main program at each operating condition. Table 1 lists the main references utilized in determining the main parameters. The parameters in Table 1 include density, viscosity, surface tension, diffusivity, solubility, reaction rate constants, enhancement factor, effective interfacial area, and mass-transfer coefficients. The second column in this table contains the references to the correlations, methods, and procedures for calculating these

Table 1. References Used to Estimate the Main Parameters Required by the Simulation Program

parameter	MEA–CO ₂ system	AMP–CO ₂ system
liquid density	Littel et al. ¹¹	Saha et al., ¹² Henni et al. ²⁴
liquid viscosity	Littel et al., ¹¹ Chenlo et al., ²⁵ Versteeg and Swaaij ¹³	Xu et al., ¹⁴ Henni et al. ²⁴
liquid surface tension	Vazquez et al. ^{15,23}	Vazquez et al. ^{15,23}
diffusivity	Snijder et al., ¹⁶ Ko et al., ²⁶ Versteeg and Swaaij ¹³	Saha et al., ¹² Ko et al., ²⁶ Versteeg and Swaaij ¹³
solubility	Wang et al. ¹⁷ , Mandal et al. ²² , Versteeg et al. ¹⁸	Xu et al., ¹⁴ Saha et al., ¹² Mandal et al. ²² Saha et al. ¹⁹
second-order reaction rate constant	Wellek et al. ²⁰	Wellek et al. ²⁰
enhancement factor	Onda et al. ²¹	Onda et al. ²¹
effective interfacial area, gas-side and physical liquid mass-transfer coefficients		

parameters for the MEA–CO₂ absorption system, and the third column contains such references for the AMP–CO₂ absorption system.

3. Source of Experimental Data

Experimental data from two pilot-plant studies were used to examine the model predictions. The first set of data was reported by Tontiwachwuthikul et al.⁴ for CO₂ absorption from simulated flue gas (mixture of air and CO₂) using MEA and AMP solutions. The absorber, located at the University of British Columbia (UBC), Canada, consisted of six sections each 1.2 m in height and 0.1 m in diameter. The packed height of each section was about 1.1 m of 12.7-mm ceramic Berl Saddles. At steady-state operation, the CO₂ concentration in the gas and liquid phases and the liquid temperature were sampled at the inlet and the outlet of each section. The flow rates of the liquid and simulated flue gas (air and CO₂) were measured and reported.

The second set of data was reported by Aroonwilas,⁷ University of Regina (UR), Canada, for CO₂ absorption from simulated flue gas using AMP. The absorption experiments were performed in a 1.77-m-high, 0.019-m-diameter absorber column. The column was packed with EX-type laboratory structured packing to a total height of 1.10 m. At steady-state operation, the CO₂ concentrations in the gas phase were sampled every 0.33 m along the column. The CO₂ concentrations in the liquid phase were measured at the inlet and the outlet; however, the intermediate concentrations along the column were calculated from the material balance. The liquid and simulated flue gas (CO₂ and air) flow rates are reported, and there are no records of the temperature profiles.

4. Simulation Results and Discussion

The validity of the developed computer model was confirmed by comparing the predictions with the experimental data published by Tontiwachwuthikul et al.⁴ for the well-known CO₂–MEA system. The operating conditions of the pilot plant were as follows: simulated flue gas flow rate = 14.8 mol/m²·s, inlet gas temperature = 288 K, liquid flow rate = 9.5 m³/m²·h, inlet liquid temperature = 292 K, MEA concentration = 3.0 kmol/m³, pressure = 101.3 kPa, and inlet gas composition = 19.1% CO₂, and CO₂ removal = 100.0%.

A comparison between the experimental results and the model predictions under these operating conditions is shown in Figure 3. The agreement between the actual and predicted CO₂ concentration profiles in the gas and liquid phases, as well as with the liquid temperature profile, is very good. The average absolute deviation of the predicted concentration from the

measured concentration is 6.7%. For the temperature profile, the average absolute deviation between the predicted and measured temperatures is 7.5%. In addition, the gas-phase temperature profile along the column was predicted by the model and is shown together with the liquid temperature profile in Figure 3. In this figure, it can be seen that there is a slight temperature crossover at about 30 cm from the bottom of the column where the gas temperature becomes slightly greater than liquid temperature. Because the main exothermic reactions are taking place in the liquid phase, the heat is transferred mainly from liquid phase toward the gas phase. Thus, logically, the gas temperature should be less than the liquid temperature, all along the column and even in equilibrium state. This anomalous behavior can be attributed to the uncertainties in the model input parameters in eqs 3 and 4, mainly the heat capacities of the solutions as well as the heat of chemical reaction between the absorbed gas and the reactants.

After the validity of the developed computer model was confirmed, the model predictions were compared with the experimental data obtained from two different pilot-plant studies

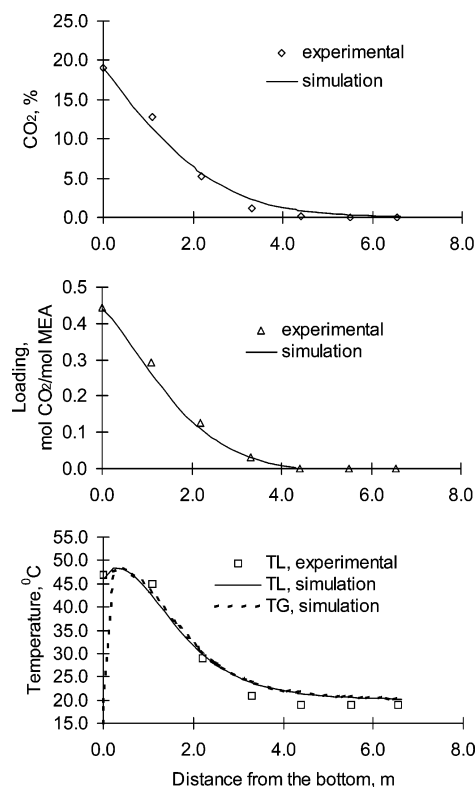


Figure 3. UBC pilot plant: Simulation and actual experimental results for the CO₂–MEA system.

Table 2. Process Conditions for the CO₂-AMP Absorption System

parameter	UBC	UR
simulated flue gas flow rate, mol/m ² ·s	14.8	26.9
inlet gas temp, K	288	298 ^a
liquid flow rate, m ³ /m ² ·h	13.5	5.93
inlet liquid temp, K	287	300 ^a
AMP concentration, kmol/m ³	2.0	2.0
pressure, kPa	101.3	101.3
inlet gas composition, % CO ₂	19.0	14.0
CO ₂ removal, %	73.0	60.1

^a Assumption/not reported experimentally.

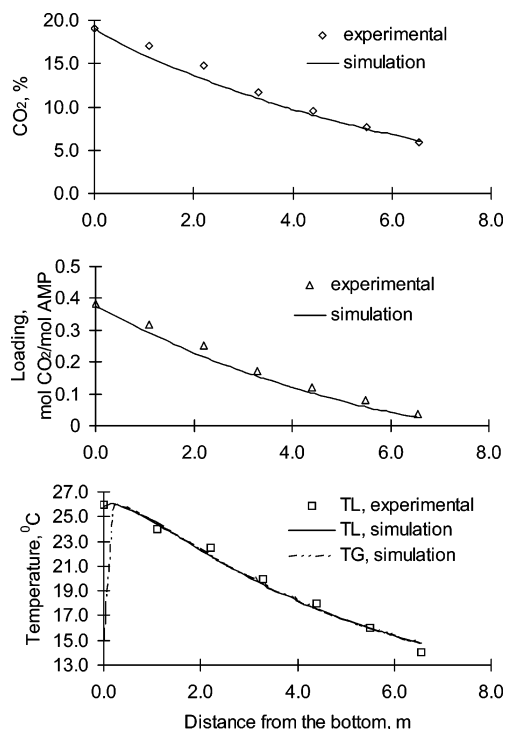


Figure 4. UBC pilot plant: Simulation and actual experimental results for the CO₂-AMP system.

for the CO₂-AMP absorption system.^{4,7} The operating conditions of the pilot plants are presented in Table 2. The actual and predicted profiles are shown in Figures 4 and 5 for the UBC and UR pilot plants, respectively. The predicted results, without using any adjustable parameters, were in good agreement with the obtained values from the UBC pilot plant, which is randomly packed with Berl Saddles, as shown in Figure 4. The average absolute deviation of the predicted concentrations from the measured concentrations is 9.7%. For the temperature profile, the average absolute deviation between the predicted and measured temperatures is 2.3%.

For the UR pilot plant, which is packed with EX-type laboratory structured packing, close agreement is achieved by using the interfacial area as an adjustable parameter, as shown in Figure 5. This is a common practice when the existing equations for predicting the interfacial area are found to be inadequate for certain cases of gas absorption processes, such as using new packings or new solvents.⁸⁻¹⁰ The average absolute deviation of the predicted concentrations from the measured concentrations is 13.8%. For the CO₂-AMP system, deviations between reported parameters such as solubility, diffusivity, and reaction rate constant by different studies exist.¹⁸ Selecting the best correlations or experimental data for predicting these parameters could improve the model predictions.

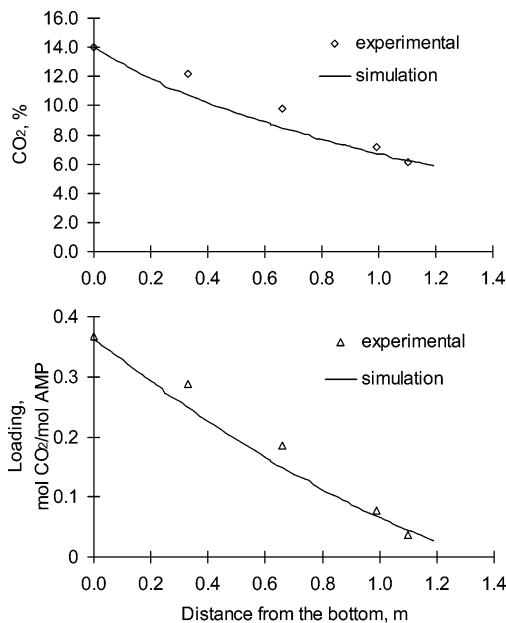


Figure 5. UR pilot plant: Simulation and actual experimental results for the CO₂-AMP system.

5. Conclusion

Judging from the results obtained, the developed computer model can be used successfully to predict the behavior of CO₂ absorption in 2-amino-2-methyl-1-propanol solutions in adiabatic packed columns. For the randomly packed column at UBC, the average absolute deviations between the predicted and measured data in terms of concentration and temperature profiles are 9.7% and 2.3%, respectively. For the structured packed column at UR, the average absolute deviation between the predicted and measured concentration profiles is 13.8%.

Nomenclature

- a = effective interfacial area per unit volume of packing, m²/m³
- AMP = 2-amino-2-methyl-1-propanol
- C_j = concentration of component j in the liquid, kmol/m³
- $C_{p,j}$ = heat capacity of solution j , kJ/kmol·K
- $C_{p,L}$ = heat capacity of solution, kJ/m³·K
- E = enhancement factor
- G = total molar gas flow rate, kmol/m²·s
- G_j = molar gas flow rate of component j , kmol/m²·s
- h = heat-transfer coefficient, kJ/s·cm²·K
- He = Henry's law constant, kmol/m³·kPa
- H_G = gas enthalpy per mole of carrier gas B, kJ/(kmol of B)
- H_L = liquid enthalpy, kJ/(kmol of solution)
- Its = number of iterations
- $k_{G,j}$ = physical gas mass-transfer coefficient for component j , kmol/m²·s·kPa
- k_L^0 = physical mass-transfer coefficient, m/s
- L_M = molar liquid flow rate, kmol/m²·s
- MEA = monoethanolamine
- N_j = mass-transfer flux of j , kmol/s·(m² of interfacial area)
- P = total pressure, kPa
- p_j = partial pressure of j , kPa
- q_j = flux of heat transfer j , kJ/s·(m² of interfacial area)
- T = temperature, K
- x_j = liquid concentration of component j , mol fraction
- Y_j = gas concentration of component j , (kmol of j)/(kmol of B)
- y_j = gas concentration of component j , mole fraction

Z = packing height measured from the bottom, m
 ΔH_R = heat of chemical reaction between A and R, kJ/(kmol of A absorbed)

Greek Letters

λ_j = latent heat of vaporization of j , kJ/(kmol of j)
 α = loading, (mol of A)/(mol of R)

Subscripts

A = carbon dioxide
 B = inert gas, in simulated flue gas
 e = equilibrium
 G = gas
 i = interface
 in = inlet
 j = generalized component j
 L = liquid
 max = maximum value
 new = new value for the variable
 out = outlet
 P = nonvolatile product
 R = amine
 S = volatile solvent, H₂O

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