

A METHOD FOR ESTIMATING MASS TRANSFER COEFFICIENTS IN A PACKED COLUMN USING REACTIVE ABSORPTION DATA

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This paper is devoted to the development of a new method for estimating mass transfer coefficients and effective area in packed columns in the case of reactive absorption. The method is based on a plug-flow model of reactive absorption of carbon dioxide with sodium hydroxide solution. The parameter estimation problem is solved using an optimization technique. Some mass transfer parameters are found to be correlated. Global sensitivity analysis by Sobol's technique showed that the unit model with the defined objective function is sensitive to the estimated parameter. Case studies of reactive absorption with different packings illustrate application of the proposed method for estimating mass transfer coefficients and effective area from column operation data. The model calculations are compared with experimental data obtained by other authors. The concentration profiles calculated by the unit model with the estimated parameters are shown to match well with experimental profiles from literature. A good agreement between estimated values and experimental data from literature confirms the applicability of this method.

Keywords: Packed column; Mass transfer coefficient; Reactive absorption; Phase equilibria; Reaction kinetics; Carbon dioxide; Sodium hydroxide.

Reactive absorption in packed column is widely used to remove acid gases (such as CO₂) from refinery gases. In order to accurately design a column unit, a rigorous model of gas absorption with chemical reaction must be used and information on mass transfer coefficients and effective area is necessary for the calculation. The methods for studying mass transfer can be divided into two groups. The first group is based on individual measurements of the mass transfer parameters¹⁻⁴. Mass transfer in gas phase is usually studied with physical absorption of freely soluble gases. Reactive absorption is used for studying effective area and mass transfer in liquid phase. It should be noted that the last methods are based on generalization of experimental data according to the hypothesis of plug flow in both phases to provide design correlations³.

The second group of the methods allows estimating parameters simultaneously. These methods are widely used to obtain parameters of a unit model. Linek et al.⁵ and Perrin et al.⁶ used an optimization technique for estimating dispersion model parameters from tracer experiments. Ji et al.⁷ applied an optimization technique for determining mass transfer coefficients and effective area from concentration profiles in a pilot plant.

The basic difficulty is the ill-posed nature of the parameter estimation problem due to the sensitivity of the solution to noise in measurements⁸. Understanding the processes in packed columns requires further development of models and methods for successful prediction of the performance of real absorbers. The purpose of the present work is to develop a new method for estimating mass transfer coefficients and the effective mass transfer area from column operating data in the case of reactive absorption. To increase the sensitivity of the model we decreased the number of fitting parameters by using additional relationships for coupled parameters. The main principles are discussed in our previous works^{9,10}.

Unit Model Formulation

The following assumptions were made in deriving the unit model: (i) mass transfer coefficient is constant along the column; (ii) radial concentration is uniform in both phases; (iii) absorption is assumed to be isothermal; (iv) the flow rates of both phases are constant along the packed column. Figure 1 illustrates a typical gas-liquid contacting packed column.

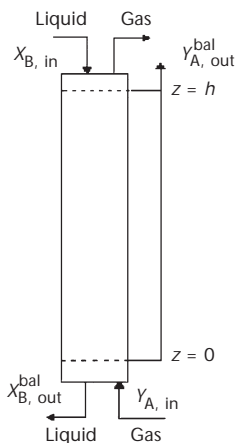


FIG. 1
One-dimensional model of a packed bed

The gas mixture enters the column at molar flow rate G_{in} and composition Y_{in} . It contacts a liquid, which enters the packed bed at flow rate L_{in} and composition $X_{B,in}$. The solute gas crosses the interface into liquid phase with molar flow rate N_A . The reaction between the absorbed gas and liquid is assumed to be complete within liquid film.

The accompanying irreversible chemical reaction between CO_2 (A) and NaOH (B) follows the stoichiometric equation



where A is transfer component (CO_2); B, chemisorbent (NaOH); P, reaction products; q , stoichiometric coefficient ($q = 2$).

The plug-flow model of reactive absorption in a packed bed is proposed by Treybal¹¹ and Danckwerts¹². They considered overall chemical reaction (1) for five-component system containing an inert carrier gas, an acid gas, an inert liquid solvent, a reactant in the liquid and a reaction product. Taking into account the above assumptions the model equations are written as follows¹³

$$G_I dY_A = S_{col} \rho_{m,G} \beta_{f,G}^* a_w (y_A - y_{A,s}) dz \quad (2)$$

$$L dx_B = q S_{col} \rho_{m,L} E \beta_{f,L}^* a_w (x_{A,s} - x_A) dz, \quad (3)$$

where G_I is inert gas molar flow rate and $Y_A = y_A/(1 - y_A)$ is molar ratio of component A.

Integrating (2) over column height gives

$$M_A = G_I (Y_{A,in} - Y_{A,out}) = \beta_{f,G}^* V \rho_{m,G} a_w \Delta \bar{y}_A. \quad (4)$$

Thus, the mass transfer coefficients and effective area are considered as parameters of the unit model. We need to define an objective function and to establish a computation consequence of the problem.

Phase Equilibria and Reaction Kinetics

The unit model is based on the concept of gas absorption with irreversible reaction (1). The experimental data needed for a unit model are solubility, diffusion coefficients, density, viscosity, phase equilibrium data and reaction kinetics. Enhancement factor (E) is defined as ratio of the rate of absorption with chemical reaction to the rate of physical absorption. For a simple irreversible chemical reaction of the second order (1), the enhancement factor can be calculated from the equation¹⁴

$$E = \frac{2(M_x + 1)}{1 + (1 + 4(M_x/R_x)^2)^{1/2}}, \quad (5)$$

where $M_x = \frac{x_B D_A}{q x_{A,s} D_B}$, $R_x = \frac{1}{\beta_{f,L}} \left(\frac{2}{m+1} D_A k_2 C_{A,s}^{m-1} C_B^n \right)^{1/2}$, m and n show the or-

der of chemical reaction ($m = 1$, $n = 1$). The accompanying reaction between NaOH and CO₂ is sufficiently fast so that gas is consumed within liquid film. Kinetic data for the reaction of CO₂ with NaOH in aqueous solution were reported by Pohorecki and Moniuk¹⁵

$$\log k_2 = 11.895 - 2382/T + 0.221I_c - 0.016I_c^2. \quad (6)$$

Henry's constant for CO₂-aqueous NaOH solution can be estimated from equation¹²

$$\log \left(\frac{H_A}{H_w} \right) = \sum (I_i h_i), \quad (7)$$

where h_i is sum of the contributions of a cation, an anion and a gas, $h_i = h_+ + h_- + h_g$, I_i is ionic strength. Solubility of CO₂ in water according to Danckwerts¹²

$$\log H_w = 7.30572 - 1140/T. \quad (8)$$

The diffusion coefficient for CO₂ in NaOH solution was calculated analogously to N₂O as presented by Versteeg and van Swaaij¹⁶. The diffusion coefficient of NaOH was taken from Danckwerts¹².

Mass Transfer Model

The calculations of transport processes are very important in the design and rating of separation equipment. We have used the well-known method¹⁷ to calculate mass transfer rates. For a binary mixture, the finite flux mass transfer coefficient is defined as

$$\beta^{\bullet} = \frac{N - \bar{x}N_t}{\rho_m \Delta \bar{x}} \quad (9)$$

The finite flux coefficient β^{\bullet} is related to the zero-flux coefficient β by the equation¹⁷: $\beta^{\bullet} = \beta \Xi$, where β^{\bullet} is transfer coefficient corresponding to conditions of finite mass transfer rates and β is mass transfer coefficient at $N_t \rightarrow 0$. The correction factor Ξ that accounts for the effect of finite rates of mass transfer is given by

$$\Xi = \psi(\exp \psi - 1)^{-1}, \quad \psi = \frac{N_t}{\rho_m} \beta^{-1} \quad (10)$$

According to the plug-flow model, the mass transfer coefficient in gas phase is

$$\beta_{f,G} = \frac{M_A}{\Xi_G V \rho_{m,G} a_w \Delta \bar{y}_A} \quad (11)$$

Mass transfer area can be estimated as follows

$$a_w = \frac{M_A}{\bar{J}_A} \quad (12)$$

where $\bar{J}_A = \frac{1}{h} \int_0^h \rho_{m,G} \beta_{f,G}^{\bullet} (y_A - y_{A,s}) dz$.

Analysis of the above equations shows that some mass transfer parameters are correlated. The plug-flow model of reactive absorption in a packed column has three parameters ($\beta_{f,L}$, $\beta_{f,G}$, a_w) where two parameters of the set are correlated. Assuming mass transfer coefficient in liquid phase $\beta_{f,L}$ is an independent parameter, mass transfer coefficient in gas phase $\beta_{f,G}$ and effective area a_w are correlated to the independent parameter with Eqs (11) and (12). Employment of the established correlations allows increasing sensitivity and validity of the parameter estimation method. The next step is to formulate a parameter estimation problem for the unit model.

A New Parameter Estimation Method

The unit model consists of a set of differential and algebraic equations, which describes gas absorption with sodium hydroxide solution in a packed bed column. We take up the problem of estimating the unit model parameters from column operating data in the case of reactive absorption. Input data needed for solving the parameter estimation problem are

- liquid flow rate and composition at inlet and outlet section of the packed bed;
- vapor flow rate and composition at inlet and outlet section of the packed bed;
- phase equilibria, reaction kinetics.

According to the material balance, molar flow rate of CO_2 transferred to liquid phase is

$$W_A^{\text{bal}} = G_{\text{in}} y_{A,\text{in}} - G_{\text{out}} y_{A,\text{out}} \quad (13)$$

where G_{in} is flow rate of gas entering packed bed; G_{out} , flow rate of gas leaving packed bed; $y_{A,\text{in}}$, concentration of CO_2 component in inlet stream; $y_{A,\text{out}}$, concentration of CO_2 component in outlet gas stream. The total mass transfer rate is $W_t^{\text{bal}} = G_{\text{out}} - G_{\text{in}}$. For the plug-flow model, diffusive part of mass transfer rate is given by

$$M_A^{\text{bal}} = G_1 (Y_{A,\text{in}} - Y_{A,\text{out}}) \quad (14)$$

We need to evaluate the mass transfer coefficient and effective mass transfer area in a packed column for the plug-flow model using column operation data. Reliability of the estimated parameters in many respects depends on sensitivity of the model. Beck and Woodbory⁸ proposed to increase sensitivity of a model by eliminating the coupled parameters. In the case of the plug-flow model the number of fitting parameters can be reduced by using additional relationships for mass transfer coefficient in gas phase (11) and effective area (12). The resulting parameter estimation problem is

$$\min_{\beta_{r,L}} (F_{\text{obj}}) = \sum_1^n \left(\frac{W_{A,i}^{\text{bal}} - W_A^{\text{calc}}}{W_{A,i}^{\text{bal}}} \right)^2 \quad (15)$$

subject to (16)

$$L \frac{dx_B}{dz} = qE\beta_{f,L}^* a_w S_{col} \rho_{m,L} (x_{A,s} - x_A) \quad (16)$$

$$G_I \frac{dY_A}{dz} = \beta_{f,G}^* a_w S_{col} \rho_{m,G} (y_{A,s} - y_A) \quad (17)$$

$$z = h, \quad x_B = x_{B,in} \quad (18)$$

$$z = 0, \quad y_A = y_{A,in} \quad (19)$$

$$W_A^{calc} = \bar{N}_A^{calc} a_w V, \quad (20)$$

$$\beta_{f,L}^* = \beta_{f,L} \Xi_L, \quad \Xi_L = \psi_L (\exp \psi_L - 1)^{-1}, \quad \psi_L = \frac{N_t^{calc}}{\rho_{m,L} \beta_{f,L}} \quad (21)$$

$$\beta_{f,G}^* = \beta_{f,G} \Xi_G, \quad \Xi_G = \psi_G (\exp \psi_G - 1)^{-1}, \quad \psi_G = \frac{N_t^{calc}}{\rho_{m,G} \beta_{f,G}} \quad (22)$$

$$\beta_{f,G} = \frac{M_A^{bal}}{\bar{\Xi}_G V \rho_{m,G} a_w \Delta \bar{y}_A}, \quad a_w = \frac{M_A^{bal}}{\bar{J}_A^{calc}}, \quad \bar{J}_A^{calc} = \frac{1}{h} \int_0^h \rho_{m,G} \beta_{f,G}^* (y_A - y_{A,s}) dz \quad (23)$$

$$N_A^{calc} = \rho_{m,G} \beta_{f,G}^* \frac{(y_A - y_{A,s})}{1 - y_{A,s}} = \rho_{m,L} E \beta_{f,L}^* \frac{(x_{A,s} - x_A)}{1 - x_{A,s}}, \quad N_t^{calc} = N_A^{calc} \quad (24)$$

$$\bar{\Xi}_G = \frac{1}{h} \int_0^h \Xi_G dz, \quad \Delta \bar{y}_A = \frac{1}{h} \int_0^h (y_A - y_{A,s}) dz \quad (25)$$

$$\beta_{f,L,min} < \beta_{f,L} < \beta_{f,L,max}, \quad (26)$$

where x_A is concentration of A component in liquid phase, $x_A = 0$; n is number of observations under the same operating conditions.

The model equation (16) is written for the chemisorbent, as concentration of CO_2 in liquid phase is equal to zero, $x_A = 0$. The source of mass in Eq. (16) is estimated with CO_2 component according to the chemical reaction (1). The interface concentration of CO_2 is calculated from the corresponding continuity equation of the component molar flux at the interface (24). Enhancement factor ($E = E(z)$) is found from Eq. (5) with the given mass transfer coefficient in liquid phase ($\beta_{f,L}$) and concentrations ($x_{A,s} = x_{A,s}(z)$, $x_B = x_B(z)$). It is assumed that there is phase equilibrium at interface.

The problems (15)–(26) require global iterations of mass transfer coefficient in gas phase $\beta_{f,G}$. In each iteration mass transfer coefficient in the gas phase from Eq. (23) is improved taking into account the mass transfer driving force Eq. (25). The iterations are repeated until the concentration profile convergence is achieved. This means that mass transfer coefficient used in the model equation (17) coincides with the coefficient computed from (23) with driving force (25). The convergence of concentration profiles also provides the convergence of iterations of mass transfer coefficient in gas phase.

After the objective function has been found it must be minimized with respect to the selected parameters. The conventional approach to solve an optimization problem is to apply the well-known discretization technique transforming DAE constraints into a large set of algebraic constraints. The outlet parameters and variables resulting from solving the parameter estimation problem (15)–(26) are

- concentration profiles along the packed bed height in liquid phase $x_B = x_B(z)$;
- concentration profiles along the packed bed height in gas phase $y_A = y_A(z)$;
- effective mass transfer area a_w ;
- mass transfer coefficients $\beta_{f,L}, \beta_{f,G}$;
- enhancement factor $E = E(z)$.

In this unit model, there are two differential equations and three unknown parameters ($\beta_{f,L}$, $\beta_{f,G}$, a_w) which are determined from column operation data by applying the parameter estimation technique. The solution of the problem and confidence range for estimated parameters are found by using Monte Carlo (MC) simulation. The optimization problems (15)–(26) are solved using the commercial package MATLAB.

Sensitivity Analysis

The purpose of sensitivity analysis is to apportion the uncertainty in the output variables to uncertainty in input variables. Such knowledge is important for (i) evaluating the applicability of the model, (ii) determining parameters for which it is important to have more accurate values, and (iii) understanding the behavior of the system. MC methods are the most widely used means for sensitivity analysis. Optimization and parameter estimation problems are often solved using MC simulations¹⁸.

We used Sobol's sensitivity indices for global MC-based sensitivity analysis. The total sensitivity index (TSI) is defined as sum of all indices involving the factor in question. TSI is given by

$$\text{TSI}_i = 1 - \frac{D_{-i}}{D}, \quad (27)$$

where D is the total variance of the output, D_{-i} is the total variance complement to factor i .

The conventional MC method involves the following steps: (i) obtaining random samples from the probability distributions of the inputs, (ii) performing model simulations for the combination of the sampled inputs, and (iii) statistically analyzing the model outputs. Sobol's sensitivity indexes help to identify parameters having larger influence on unit model outputs.

The output function was defined by Eqs (15)–(26). In the case of plug-flow model we need to study the sensitivity of the outlet function (15) with model equations (16)–(26) to input variables of the model such as liquid flow rate, gas flow rate and mass transfer coefficient into liquid phase. Input variables randomly changed in simulations were flow rate, molar density and mass transfer coefficient in liquid phase. The ranges for input variables are shown in Table I.

TABLE I
Ranges of parameters and total sensitivity indexes

Parameter	Min	Max	Mean	Std	TSI, %
G, kmol/s	4.18×10^{-6}	4.22×10^{-6}	4.2×10^{-6}	1.22×10^{-8}	45.4
$\rho_{m,L}$, kmol/m ³	54.51	59.84	57.31	1.51	0
$\rho_{m,G}$, kmol/m ³	0.040	0.044	0.0424	1.17×10^{-3}	0
$\beta_{f,L}$, m/s	1.0×10^{-5}	8.0×10^{-4}	4.05×10^{-4}	3.95×10^{-4}	54.6
F_{obj}^a	0.01	0.1	0.055	0.045	

^a Outlet function Eq. (15), $L/G = 9.92$.

The estimates of TSI for these cases were evaluated with the results obtained from 10 000 MC simulations. This guarantees that the error in the sensitivity values is not larger than 3%. It should be noted that changing gas flow rate affects the convection term on the right-hand side and source term on the left-hand side of Eq. (17). We assume that there is no measurements error in the concentrations and the ratio of liquid and gas flow rates is fixed in the analysis. The liquid flow rate was found from the condition $L/G = \text{const}$. The equality of TSI to 0% for some input variables means that their uncertainty ranges do not affect the output function variance. The gas flow rate (G) with TSI of 45% accounts for 45% of the total output function variance (D). Uncertainty in the gas flow rate can also be related to an inaccuracy of mass balance. Decrease in an inaccuracy of mass balance leads to the increase in TSI and sensitivity to the mass transfer coefficient ($\beta_{f,L}$). We conclude that an inaccuracy of mass balance less than 3% can be neglected and higher than 3% should be taken into account in parameter estimation. For example, mass balance inaccuracy in experiments reported by Aroonwilas et al.¹⁹ was in the range of 0 to $\pm 4.5\%$. Sensitivity analysis by Sobol's technique reveals that the unit model equations (16)–(26) with the outlet function (15) is sensitive to parameter $\beta_{f,L}$ with TSI of 54%. This means that the last parameter can be estimated from solving the parameter estimation problem. Solution of the parameter estimation problem, Eqs (15)–(26), and confidence intervals are found using the MC method. In this case, the varied input parameter was mass transfer coefficient in liquid phase $\beta_{f,L}$. The range for the input parameter is the same as in sensitivity analysis (Table I).

Case Study of Absorber with EX Structured Packing

To verify the new parameter estimation method and mass transfer prediction of the proposed unit model, simulation results of CO_2 absorption with chemical reaction in aqueous solution of sodium hydroxide (NaOH) were compared with the experimental data obtained by Aroonwilas from a pilot plant. Aroonwilas et al.¹⁹ provided experimental data on the performance of structured packing in an 0.019 m pilot plant with the EX-type Sulzer structured packing. The height of packing section was 1.77 m.

Taking operating data from run¹⁹ TH-103 as the input data, we applied the developed method for estimating the unit model parameters from the pilot plant column. The estimated parameters with confidence intervals found from MC simulation are given in Table II. Liquid and gas streams entering the packed bed (Table II) had the following characteristics for run¹⁹

TH-103: Temperature 24 °C, liquid flow rate 0.2189 kmol/h, gas flow rate 0.02978 kmol/h, NaOH solution mole fraction 0.022038, CO₂ gas mole fraction 0.07493.

Concentration profiles calculated by the unit model allow direct comparison with the experimental results, reported by Aroonwilas¹⁹ as concentrations in different positions of the column. Figure 2 shows comparison between calculated and experimental profiles for run¹⁹ TH-103. Experimental values in Fig. 2 are given by points and the profiles calculated with the estimated parameters in Table II are plotted as a solid line.

TABLE II
Unit model parameters estimated from pilot plant data for run¹⁹ TH-103 with EX structured packing

Parameter	Estimated ^a	Empirical
Mass transfer coefficient in gas phase, m/s	$(1.01 \pm 0.53) \times 10^{-2}$	1.68×10^{-2}
Mass transfer coefficient in liquid phase, m/s	$(2.7 \pm 0.6) \times 10^{-5}$	1.9×10^{-4}
Effective area, m ² /m ³	536.6 ± 48.6	935

^a 95% confidence level.

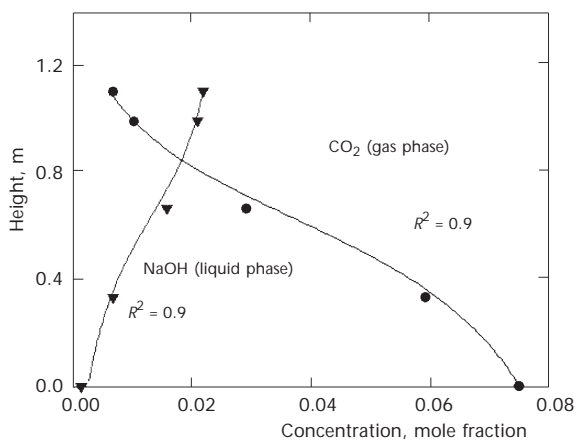


FIG. 2

Comparison of experimental and predicted concentration fields in the packed column for the air (CO₂)-NaOH system. Points, experimental run¹⁹ TH-103; solid line, predicted profiles with estimated parameters from Table II. Liquid flow rate 0.2189 kmol/h, gas flow rate 0.02978 kmol/h, column diameter 0.019 m, EX structured packing

For run¹⁹ TL-103 and run¹⁹ TL-105 with the same operation conditions, a solution to the parameter estimation problem is given in Table III. Liquid and gas streams entering the packed bed (Table III) had the following characteristics: Temperature 24 °C; liquid flow rate 9.73 m³/m² h; air flow rate 12.84 mol/m² s; NaOH solution mole fraction 0.0288 (run¹⁹ TL-105), 0.0263 (run¹⁹ TL-103); CO₂ gas mole fraction 0.1296 (run¹⁹ TL-105), 0.1229 (run¹⁹ TL-103).

Empirical correlations for mass transfer coefficients and the effective area²⁰ were utilized to set an initial estimate of the parameters. Confidence intervals for the estimated parameters in Table III were obtained using a MC simulation study. A comparison of experimental and predicted profiles with parameters in Table III is shown in Figs 3 and 4.

TABLE III

Unit model parameters estimated from pilot plant data for run¹⁹ TL-103 and run¹⁹ TL-105 with EX structured packing

Parameter	Estimated ^a	Empirical
Mass transfer coefficient in gas phase, m/s	0.053 ± 0.014	1.025 × 10 ⁻²
Mass transfer coefficient in liquid phase, m/s	(6.0 ± 1.5) × 10 ⁻⁵	1.79 × 10 ⁻⁴
Effective area, m ² /m ³	146.5 ± 15.5	986

^a 95% confidence level.

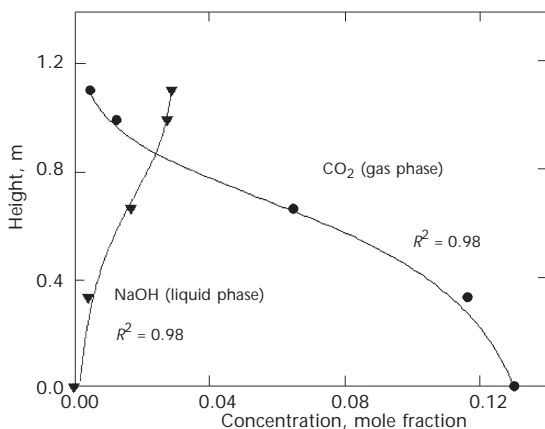


FIG. 3

Comparison of experimental and predicted concentration fields in the packed column for the air (CO₂)-NaOH system. Points, experimental run¹⁹ TL-105; solid line, predicted profiles with estimated parameters from Table III. Liquid flow rate 0.1498 kmol/h, gas flow rate 0.015 kmol/h, column diameter 0.019 m, EX structured packing

It should be noted that liquid and gas streams in run¹⁹ TL-103 and run¹⁹ TL-105 had the same flow rates but they differed in composition. According to the theory, mass transfer coefficients and specific area are the same under similar hydrodynamic conditions. Comparing simulation results for

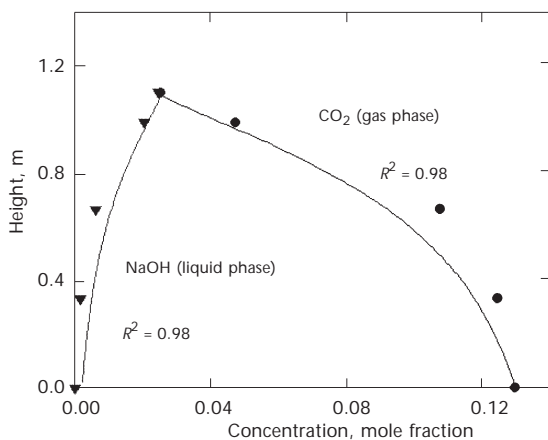


FIG. 4

Comparison of experimental and predicted concentration fields in the packed column for the air (CO₂)-NaOH system. Points, experimental run¹⁹ TL-103; solid line, predicted profiles with estimated parameters from Table III. Liquid flow rate 0.1498 kmol/h, gas flow rate 0.015 kmol/h, column diameter 0.019 m, EX structured packing

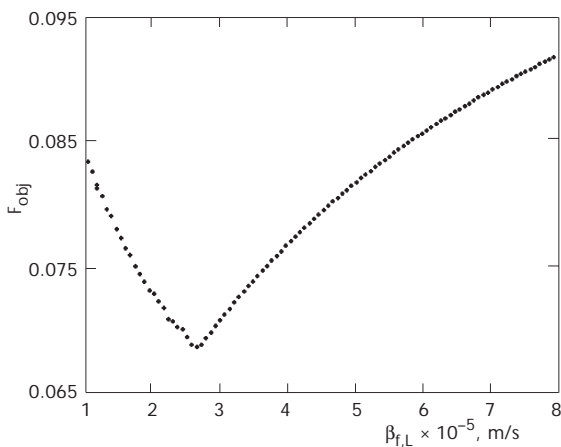


FIG. 5

Dependence of objective function Eq. (15) on parameter $\beta_{f,L}$ for operation conditions of run¹⁹ TH-103 with EX structured packing

run¹⁹ TL-103 and run¹⁹ TL-105 with the same estimated parameters, we can conclude that there is a satisfactory fit of experimental and predicted concentration profiles taking into account the inaccuracy of the method. It may be expected that processing of large quantity of operation data will allow estimating the parameter values which are close to the actual ones. A databank on mass transfer for different packings developed in future will promote deeper understanding of the linkage between hydrodynamics and mass transfer in packed columns.

The dependence of objective function (15) on parameter $\beta_{f,L}$ is shown in Fig. 5. Simulation results were obtained with 1000 input sample points. As seen in Fig. 5 the parameter estimation problem is nonlinear. This is caused by the model equations for reactive absorption being nonlinear. It should be noted that the mass transfer coefficient in gas phase and effective area were found to be correlated parameters; they are computed from additional relationships.

Case Study of Absorber with Mellapak Structured Packing

For additional testing of the unit model and the parameter estimation method, we used experimental data on the effective mass transfer area reported by Siminiceanu et al.²¹ They used the absorption of CO₂ diluted with air in NaOH solutions as a model reaction for determining the effective mass transfer area of Mellapak structured packing. The absorption rates enable determination of the effective mass transfer area independently of mass transfer coefficients. Tables IV and V show a comparison of the experimental mass transfer area and effective area estimated by the developed method. The effective mass transfer area is usually not identical to the wetted area of the packing. Conventional technique for measuring mass transfer area is based on chemical methods. Estimated values of the effective mass

TABLE IV
Comparison of experimental²¹ and estimated mass transfer area for Mellapak packing under different operating conditions

Parameter	Run N2	Run N4
Liquid flow rate, l/h	120	200
Experimental effective area, m ² /m ³	95.25	126.75
Effective area calculated by the model, m ² /m ³	102 ± 14.3	115.6 ± 7.5

transfer area agree well with experimental values reported by Siminiceanu et al.²¹ which correspond to a chemical method.

Operation conditions for absorber with Mellapak structured packing were as follows: Temperature 25 °C; liquid flow rate 100, 120, 160, 200 l/h; air flow rate 10 m³/h; NaOH solution 0.5 mol/l; CO₂ gas mole fraction 0.05.

Simulation results show that the proposed unit model predicts well the mass transfer performance of the packed column with parameters estimated from pilot plant by an optimization technique. The use of mass transfer coefficients allowed a suitable interpretation of operating data obtained from the packed bed column. The method implemented and the unit model can be used to simulate and to analyze the performance of packed columns.

TABLE V
Unit model parameters estimated from pilot plant data²¹ for run N2 with Mellapak 750Y packing

Parameter	Estimated ^a	Empirical
Mass transfer coefficient in gas phase, m/s	0.00656 ± 0.002	9.93 × 10 ⁻³
Mass transfer coefficient in liquid phase, m/s	(2.38 ± 0.54) × 10 ⁻⁵	1.93 × 10 ⁻⁴
Effective area, m ² /m ³	102 ± 14.3	405

Column diameter 0.1 m, height of packing 0.518 m, geometric surface area 750 m²/m³.

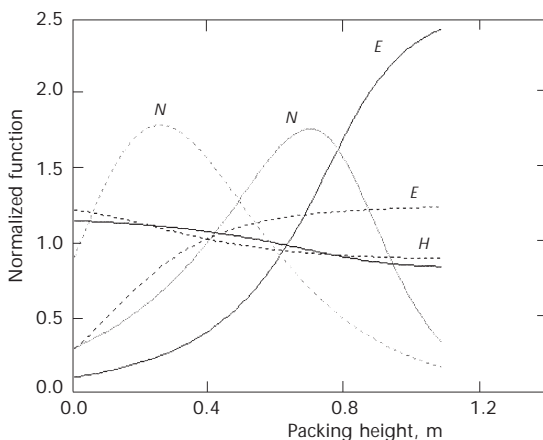


FIG. 6
Distribution of CO₂ molar flux (*N*), enhancement factor (*E*) and Henry constant (*H*) in the packed column with different mass transfer coefficient in liquid phase. Column diameter 0.019 m, EX structured packing

The distribution of CO₂ molar flux with a corresponding Henry constant and enhancement factor along the column height in Fig. 6 illustrates a possibility of estimating mass transfer coefficients in a packed column. Solid lines in Fig. 6 correspond to calculation results with estimated parameters in Table III and dotted lines are the profiles computed by the plug-flow model with empirical values of the mass transfer coefficient in liquid phase. Results in Fig. 6 reflect that the enhancement factor and fluxes are significantly changed along the packed bed. It is evident that the integral of the molar flux over the packing height and mass transfer rate varied with the mass transfer coefficient in liquid phase. As a result, the objective function (15) has a minimum corresponding to the estimated mass transfer coefficient in liquid phase with a certain confidence range.

RESULTS AND DISCUSSION

We have performed the parameter estimation by using the proposed method based on an optimization technique. The parameters to be estimated were mass transfer coefficients ($\beta_{f,L}$, $\beta_{f,G}$) and effective interfacial area (a_w). Input data for starting the parameter estimation are liquid and vapor molar flow rates and composition at inlet and outlet sections of the packed bed. The parameter estimation problem (15)–(26) was solved by the MC method. Differential equations of the unit model have been solved using the finite difference method. The initial value of the mass transfer coefficient in gas phase was set from an empirical equation. The results of solving the parameter estimation problem provide the information on mass transfer coefficients, specific area and concentration profiles in a packed column.

Ji et al.⁷ estimated the mass transfer coefficients and effective area by fitting the computed mass transfer rate to the experimental one, resulting from component concentrations in gas and liquid phases along the column height. In contrast to the last method, we used an objective function defined as squared deviation of the measured and predicted component flow rates. The component flow rate, as well as concentration profiles, depend on the parameters of the model. The main difficulty in parameter estimation is that the problem is usually underdetermined. The proposed approach is based on the idea of increasing sensitivity of the parameter estimation method by revealing the coupled parameters. Some parameters of the unit model are found to be correlated. To increase the sensitivity of the model we decreased the number of the fitting parameters by using additional relationships for the coupled parameters. We added equations for the mass transfer coefficient in gas phase and the effective area to the well-

known equation set, Eqs (2) and (3). This modification of the unit model allows to eliminate fitting of the correlated parameters. As a result, the unit model, Eqs (16)–(26), has a single estimated parameter (mass transfer coefficient in liquid phase). Analysis of the molar component flux along the packed bed also proved the dependence of mass transfer rates on mass transfer coefficient in liquid phase. The sensitivity of the model to the parameter was shown to be 54%.

The proposed method allows realizing the most complete analysis of operation data on reactive absorption using the plug-flow model. The estimated mass transfer coefficients and specific area give quantitative information on the intensity of mass transfer and efficiency of the separation process in packed columns. The method can be extended to distillation and absorption processes for studying mass transfer in packed columns.

CONCLUSIONS

This paper focuses on developing a new method for estimating mass transfer coefficients in packed columns using reactive absorption data. The method is based on the plug-flow model of reactive absorption in a packed column. Sensitivity analysis by Sobol's technique revealed that the developed unit model with a defined objective function is sensitive to the estimated parameter. The MC simulation method has been selected as the optimization technique for estimation of parameters. Solution of the parameter estimation problem provides information on mass transfer coefficients, specific area and concentration profiles in the column. The unit model has been tested by using experimental data obtained by Aroonwilas et al.¹⁹ and Siminiceanu et al.²¹ from pilot plant tests. The results show quantitative agreement between calculated component profiles using estimated parameters with those reported by Aroonwilas et al.¹⁹ The method allows studying mass transfer in columns of different scales, when application of the conventional methods is limited. The model proposed is physically realistic, including all relevant phenomena and it affords results that agree well with reliable measurement. The model can be used to optimize packing designs and shorten the time to commercial application.

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LIST OF SYMBOLS

a_v	interfacial area, m^2/m^3
a_w	effective mass transfer area, m^2/m^3
$C_{A,s}$	the local concentration of CO_2 at interface in the liquid film, kmol/m^3
C_B	chemisorbent concentration, kmol/m^3
D	the total variance of the output function
D_A	diffusivity of dissolved component, m^2/s
D_B	diffusivity of reactant, m^2/s
E	enhancement factor
F_{obj}	objective function; outlet function
G	gas flow rate, mol/s
h	gas flow path length, m
h_g	contributions of a gas, m^3/kmol
h_+	sum of the contributions of a cation, an anion and a gas
h_+	contributions of a cation, m^3/kmol
h_-	contributions of an anion, m^3/kmol
H	Henry's constant, $\text{kmol}/(\text{m}^3 \text{ kPa})$
H_w	Henry's constant for CO_2 -water system, $\text{kmol}/(\text{m}^3 \text{ kPa})$
I_c	ionic strength of the solution, $(\text{kg ion})/\text{m}^3$
I_i	ionic strength
J	diffusive flux of CO_2 component, $\text{mol}/(\text{m}^2 \text{ s})$
k_2	second-order reaction rate constant, $\text{m}^3/(\text{kmol s})$
L	liquid flow rate, mol/s
M	diffusive part of mass transfer rate, mol/s
N_A	molar flux of CO_2 component, $\text{mol}/(\text{m}^2 \text{ s})$
N_t	total molar flux, $\text{mol}/(\text{m}^2 \text{ s})$
q	stoichiometric coefficient
S_{col}	area, m^2
Std	standard deviation
T	temperature, K
TSI	total sensitivity index
V	packed bed volume, m^3
W_A	molar flow rate of CO_2 component, mol/s
W_t	total molar flow rate, mol/s
x_A	mole fraction of CO_2 in liquid bulk
x_B	mole fraction of NaOH in liquid bulk
X_B	molar ratio of B component
$\Delta \bar{x}_A$	mean mass transfer driving force of CO_2 in liquid phase
y_A	mole fraction of CO_2 in gas bulk, mole fraction
Y_A	molar ratio of component A
$\Delta \bar{y}_A$	mean mass transfer driving force of CO_2 component in gas phase, mole fraction
z	coordinate of gas flow path, m
β_t	the mass transfer coefficient, m/s
ρ	phase density, kg/m^3
ρ_m	molar phase density, mol/m^3

Ξ	correction factor
Ψ	rate factor

Subscripts and superscripts

A	dissolved component (CO ₂)
B	reactant (NaOH)
bal	balance
c	solution
calc	calculated
col	column
f	surface
g	gas
G	gas phase
i	index
in	inlet
I	inert gas
L	liquid phase
m	molar
m, n	order of chemical reaction
max	maximum
min	minimum
obj	objective
out	outlet
s	interface
t	total
v	volumetric
w	wetted
•	finite mass transfer rate

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