Research Article

Carbon Dioxide Absorption Modeling for Off-Gas Treatment in the Nuclear Fuel Cycle

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The absorption of carbon dioxide is an important process in many practical applications such as reduction of greenhouse gases, separation and purification processes in the chemical and petroleum industries, and capture of radioactive isotopes in the nuclear fuel cycle. The goal of this research is to develop a dynamic model to simulate CO\textsubscript{2} absorption by using different alkanolamines as absorption solvents. The model is based upon transient mass and energy balances for the chemical species commonly present in CO\textsubscript{2} gas-liquid absorption. A computer code has been written to implement the proposed model. Simulation results are discussed. The reported model simulates well the response to dynamic changes in input conditions. The proposed model can be used to optimize and control the separation of carbon-14 in the form of CO\textsubscript{2} in the nuclear industry.

1. Theoretical Considerations

1.1. Introduction. The off-gas stream produced from reprocessing used nuclear fuel containing a host of radioactive gases including tritium, iodine, methyl iodide, krypton, xenon, and carbon dioxide. These gases are hazardous to human health, and some are of considerable economic value. Currently, there is interest in the efficient capture of these gases for recovery or storage purposes [1].

Presently, postcombustion separation of carbon dioxide from flue-gas streams is investigated using membrane separation, low-temperature distillation, physical adsorption by activated carbon and zeolites, chemical absorption by mineral oxides to produce the corresponding carbonates, and chemical absorption by suitable solvents [2]. Chemical absorption by solvents is the most common form of the CO\textsubscript{2} capture process. Amines, and mixtures containing amines, are the most used solvents as these compounds react quickly with CO\textsubscript{2}, maintaining high mass transfer-driving forces [2]. Industrially important amines are monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), and the tertiary amine N-methyldiethanolamine (MDEA). Most industrial processes are operated with aqueous amine solutions, but solvents consisting of a mixture of water and a nonaqueous solvent, for example, sulfolane in the Shell-Sulfinol process [3], are also frequently used [4]. Blending of different amines is considered to be attractive because in this way the high absorption capacity of tertiary amines can be combined with the high absorption rates of primary or secondary amines [5]. Blends are also more flexible than singular amines because the relative concentration of the amines can be varied [6]. Other combinations have been considered, such as MEA and 2-amino-2-methyl-1-propanol (AMP). The latter amine is an attractive alternative since it offers higher absorption capacity and lower regeneration energy. Blending MEA with AMP is considered to combine all favorable characteristics of both amines and overcome the unfavorable characteristics [7]. Some studies have been carried out considering the influence of the solvent mixed with the alkanolamines. For example, Usbharatana and Tontiwachwuthikul [8] studied the kinetics of CO\textsubscript{2} capture using methanol mixed into solutions of MEA.

The goal of this work is to develop a theoretical model for dynamic simulations of CO\textsubscript{2} absorption using a generic
blend of amines and/or other solvents. The proposed model can be used to simulate chemical absorption using a wide range of CO₂ input stream concentrations. Through computational implementation, the derived model can be used for design, optimization, and control applications.

1.2. Model Organization. In this work, we will follow an approach similar to the one used by Greer et al. [9] in the dynamic simulation of the absorption/desorption of carbon dioxide from monoethanolamine (MEA). A dynamic model of the absorption process will be developed using a generic mixture of solvents to increase the absorption rate.

Mass transfer rates are calculated using the thin film model with chemical reactions confined to the liquid thin film. Henry’s law is used for modeling the vapor-phase equilibrium of CO₂. Henry’s constant values for the different gas-phase species are calculated using fugacity ratios obtained by the Peng–Robinson equation of state (EOS). A kinetic scheme is proposed to represent the complex chemical reactions between CO₂ and the solvents. Liquid and vapor energy balances are developed to calculate the liquid and vapor temperature, respectively. A schematic of the column is shown in Figure 1. The model of the absorption tower is developed by taking a small slice of the tower of height \( dz \). The height of the packing goes from \( z = 0 \) to \( z = H \), where \( H \) is the packing height.

1.3. Kinetic Studies. The most important part of the proposed model is the simulation of the complex chemical reactions involving the solvents and CO₂. In the case of primary and secondary amines, the reaction mechanism is well understood as was originally proposed by Caplow [10] and reintroduced by Danckwerts [11]. CO₂ reacts with the amine through a two-step process. The first step proceeds through the formation of a zwitterion intermediate:

\[
\text{RNH}_2 + \text{CO}_2 \stackrel{k_1}{\leftrightarrow} \text{RNH}^+\text{COO}^- \tag{1}
\]

This step is slow and considered to be the rate-controlling step; it is followed by a very fast removal of a proton by a base:

\[
\text{RNH}^+\text{COO}^- + B_i \stackrel{k_{1i}}{\leftrightarrow} \text{RNCOO}^- + B_i\text{H}^+ \tag{2}
\]

It is important to notice that all bases present in the liquid phase will participate in reaction (2); therefore, \( B_i \) represents a generic base participating in the reaction with the zwitterion. In this mechanism, the overall forward reaction rate equation can be derived using the quasi-steady-state assumption for the zwitterion intermediate [12]:

\[
r_1 = \frac{k_1[\text{CO}_2][\text{RNH}_2]}{1 + (k_{-1} + \sum k_{bi}[B_i])}, \tag{3}
\]

where \( k_1, k_{-1}, \) and \( k_{bi} \) are the respective specific constants and \( \sum k_{bi}[B_i] \) represents the summation over the reaction rates of all the bases reacting with the zwitterion present in the solution. In dilute aqueous solutions, for example, the amine, \( \text{OH}^- \), and water act as a base, while in nonaqueous solvents, only the amine can be considered a base [12].

In the case of high amine concentration in the solvent, Equation (3) is simplified to

\[
r_1 = k_1[\text{CO}_2][\text{RNH}_2]. \tag{4}
\]

For aqueous MEA solutions, the overall reaction rate is of second order, and is of first order with respect to the amine. This finding indicates that the deprotonation of the zwitterion by the bases present in the solution is very fast compared to the reverse reaction. Therefore, Equation (4) is considered the main reaction in the absorption of CO₂ in high-concentration aqueous alkanolamine solutions. In the case of low-concentration solutions, more complex rate equations hold [2, 13]. Alvarez-Fuster et al. [14] and Sada et al. [15] showed that changes in the solvent lead also to changes in the order of reaction.

A different mechanism applies to the reaction of CO₂ with ternary amines. According to Littel et al. [16], the reaction of CO₂ with tertiary amines can be described satisfactorily using the base-catalysis reaction mechanism proposed by Donaldson and Nguyen [17]:

\[
\text{R}_1\text{R}_2\text{R}_3\text{N} + \text{CO}_2 + \text{H}_2\text{O} \stackrel{k_1}{\leftrightarrow} \text{R}_1\text{R}_2\text{R}_3\text{NH}^+ + \text{HCO}_3^- \tag{5}
\]

This mechanism is essentially a base-catalyzed hydration of CO₂; thus, tertiary amines cannot react directly with CO₂. This finding was confirmed by Versteeg and Van Swaaij [18], who studied the absorption of CO₂ into a solution of MDEA and ethanol without water.

In all the cases discussed above, the following CO₂ reactions are also present:

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \tag{6}
\]

\[
\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^- \tag{7}
\]

Reaction (6) is very slow and can be neglected in most circumstances. Reaction (7), however, is fast and can enhance
mass transfer even when the concentration of the hydroxyl ion is low [19].

1.4. Reaction Scheme

1.4.1. Introduction. The components in the gas phase are RNH₂, R₁R₂R₃N, CO₂, H₂O, N₂, and O₂, while the species considered in the liquid phase are RNH₃⁺, RNCOO⁻, RNH₂, R₁R₂R₃NH⁺, CO₂, H₂O, N₂, O₂, HCO₃⁻, OH⁻, and H₂O⁺. The ionic species remain in the liquid phase, while the others are transferred from one phase to the other according to the scheme shown in Figure 2.

Only gas-phase mass transfer resistance is considered for liquid solvents (H₂O, R₁R₂R₃N, and RNH₂), while liquid-only mass transfer resistance for the gas species has been considered: CO₂, N₂, and O₂ ([2], among others). Under certain conditions, however, both resistances have to be considered for the reacting species CO₂. In our computer code, we consider these situations by using a global mass transfer coefficient given by

\[
\frac{1}{K_{l,CO₂}^{g}} = \frac{1}{K_{g,CO₂}^{l}} + \frac{H_{cg}^{l}}{K_{l,CO₂}^{g}}
\]

(8)

where \(K_{l,CO₂}^{g}\) is the overall mass transfer coefficient based upon liquid-phase concentrations; \(K_{g,CO₂}^{l}\) is the liquid-phase mass transfer coefficient; \(H_{cg}^{l}\) is the gas-phase mass transfer coefficient; \(H_{cg} = C_{i}^{l}/C_{i}^{g}\) is the concentration-based Henry’s constant, in which \(C_{i}^{l}\) and \(C_{i}^{g}\) are the liquid- and gas-phase i-species concentrations, respectively; and \(E\) is the enhancement factor defined in the subsection below. Typical values of these coefficients are given in Table 1. In Table 2, all the chemical species considered in the model are included.

1.4.2. Reactions. Mandal et al. [20] and Benamor and Aroua [21] proposed the following set of reactions occurring in the aqueous primary amine solution. A gas-liquid equilibrium equation and six chemical equilibria equations are introduced to describe the chemistry involved in CO₂ absorption:

\[
2RNH₂ + CO₂ \rightleftharpoons RNHCOO⁻ + RNH₃⁺ (9)
\]

\[
CO₂ + H₂O \rightleftharpoons HCO₃⁻ + H⁺ (10)
\]

\[
CO₂ + OH⁻ \rightleftharpoons HO₂⁻ + H⁺ (11)
\]

\[
H₂O \rightleftharpoons OH⁻ + H⁺ (12)
\]

\[
RNH₃⁺ \rightleftharpoons RNH₂ + H⁺ (13)
\]

\[
RNHCOO⁻ + H₂O \rightleftharpoons RNH₂ + HCO₃⁻ (14)
\]

\[
CO₂ (g) \rightleftharpoons CO₂ (l) (15)
\]

Following Bosch et al. [6] who studied blends of alkanol amines, we add reaction (5) catalyzed by ternary amines and

\[
R₁R₂R₃NH⁺ \rightleftharpoons R₁R₂R₃N + H⁺ (16)
\]

Reactions (5), (9), and (11) are the main reactions in CO₂ absorption by amines. The other reactions are required to complete the total reaction mechanism [6]. The CO₂ loading rate, defined as the ratio of CO₂ to alkanolamines, determines the relative weight of all reactions. For CO₂ loading rates below 0.5, Equation (9) is the main reaction. In the case of loading rates above 0.5, reaction (11) predominates, while reaction (5) will be important only for large amounts of ternary amine in the feed. In this work, we are interested in small loading rates and significant amounts of ternary amine present; therefore, the reactions with the amines will be the most important ones. A list of all

![Figure 2: Concentration gradients at the vapor-liquid interphase.](image)
reactions used in the model is included in Appendix. Equation (15) is considered by using the corresponding Henry’s law constant for CO₂.

1.4.3. Kinetic Parameters. Kinetic data were collected using a general primary-secondary amine that follows the zwiterion mechanism represented by Caplow [10] and Danckwerts [11]. The forward reaction (9) is thought to occur through a two-step mechanism. Initially, a CO₂ molecule and an alkanolamine molecule form a zwiterion intermediate which, in a second step, reacts with another alkanolamine molecule. The second step is much faster than the first step; hence, the first step is rate limiting and of second order. The forward rate for the formation of bicarbonate is calculated using

\[ -r_1 = k_{1f}[\text{CO}_2][\text{RNH}_2](\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-3}). \]  

(17)

The specific forward rate constant \( k_{1f} \) is calculated using the method in [22]:

\[ k_{1f} = \exp\left[\frac{24.4 - 6864}{T_1}\right](\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}). \]  

(18)

The bicarbonate ion formation, reaction (11), is the most important reaction for CO₂/alkanolamine loadings above 0.5. It is of second order, given by

\[ -r_3 = k_{3f}[\text{CO}_2][\text{OH}^-](\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-3}). \]  

(19)

The forward rate for the formation of carbonate is significantly fast, but the overall rate is usually quite small due to the low concentration of OH⁻ ions used. At loadings of CO₂/alkanolamines above 0.5, this becomes the dominant reaction for CO₂ removal. The forward rate is calculated from [23]:

\[ k_{3f} = \exp\left[\frac{31.396 - 66580.0/T_1}{1000}\right](\text{mol}^2\cdot\text{mol}^{-1}\cdot\text{s}^{-1}). \]  

(20)

In order to complete the rate calculations, we collected literature data corresponding to the equilibrium rate constants of reactions (9)–(14) from Bedelbayev et al. [24] and Greer [2]. In order to deal with reactions (5) and (16) for ternary alkanolamines, we followed many investigators including Haimour et al. [25], Critchfield [26], Littel et al. [16], and Rangwala et al. [27] who fit the rate constant of the reaction as a function of temperature using

\[ k_i = k_i^0 \exp\left[\frac{-E_a}{RT}\right]. \]  

(21)

All values of kinetic parameters used are listed in Table 3. A full description of all the rate equations and calculation of generation terms is also included in Appendix.

1.4.4. Enhancement Factor. The carbon dioxide absorption is accompanied by strong chemical reactions. Therefore, the calculation of the CO₂ flux term requires the use of an enhancement factor (E) to account for the enhanced mass transfer. The enhancement factor is defined as the mass transfer rate under reactive absorption divided by the mass transfer rate under nonreactive absorption conditions [31]. The CO₂ molar flow term (\( N_{\text{CO}_2,\text{diff}} \)) is given as follows [2, 9, 24]:

\[ N_{\text{CO}_2,\text{diff}} = -k_{1f}^1\text{a}_wH^\text{cc}C_{\text{CO}_2}^\text{g} \]  

(22)

where \( a_w \) is the interphase area per unit volume. The enhancement factor (E) is a function of the Hatta number (Ha) defined as

\[ Ha = \sqrt{D_{\text{CO}_2}(k_{1f}C_{\text{RNH}_2} + k_{3f}C_{\text{OH}^-} + k_{5f}C_{\text{R}_1\text{R}_2\text{R}_3N})/k_{\text{i}}} \]  

(23)

where \( D_{\text{CO}_2} \) is the diffusion coefficient and \( k_{1f} \) are the forward specific reaction rate constants. The influence of the different reactions on the total rate of CO₂ absorption is considered by the enhancement factor E. The Hatta number is the ratio of the rate of homogeneous reaction relative to the rate of gas dissolution. Ha is also a measure of the amount of dissolved gas that reacts inside the diffusion film near the gas-liquid interface compared to the amount that reaches the bulk of the solution without reacting. When Ha = 0, we have purely physical absorption. The higher the value of the Hatta number, the stronger the effect of chemical reactions on mass transfer. In the case of Ha > 2, the enhancement factor E is directly equal to Ha [31].

Versteeg et al. [32] recommended a different definition of the Hatta number including \( C_{\text{CO}_2}^\text{g} \) instead of \( C_{\text{CO}_2}^\text{g} \) in Equation (23) to calculate the enhancement factor when all RNH₂ is consumed, and reaction (3) is the dominant CO₂ removal reaction. Other authors have used both formulations with similar results [24, 33, 34]. In this work, however, we preferred to use the general definition of the Hatta number, Equation (23).

1.5. Mass Transfer Model

1.5.1. Mass Balances. The mass balance of component \( i \) in the liquid phase was calculated using the following equation [2, 35]

\[ \frac{\partial C_i^l}{\partial t} = u_l \frac{\partial C_i^l}{\partial z} - N_{i,\text{diff}} + R_{\text{gen},i}, \]  

(24)

where \( u_l \) is the superficial liquid-phase velocity, \( R_{\text{gen},i} \) represents moles of species \( i \) generated/consumed by interphase reaction per unit volume, and \( N_{i,\text{diff}} \) is the mass flow of component \( i \) from the liquid phase into the gas phase. In the model presented in this work, the effect of reaction on the CO₂ absorption is considered through the use of the enhancement factor. In the cases of ionic species, there is no interphase mass transfer; therefore, for these reactions, Equation (24) becomes

\[ \frac{\partial C_i^l}{\partial t} = u_l \frac{\partial C_i^l}{\partial z} + R_{\text{gen},i}. \]  

(25)

The generic amines (RNH₂ and R₁R₂R₃N) are the only chemical species for which we have to calculate a generation term plus an interfacial mass transfer term (\( N_{\text{RNH}_2,\text{diff}} \) and \( N_{\text{R}_1\text{R}_2\text{R}_3,\text{diff}} \)).
1.6. Energy Balances. The reactions given by Equations (8) and (11) are highly exothermic; therefore, an energy balance has to be solved in order to consider temperature changes. The heat of reactions for Equations (9) and (11) used was 65 kJ/molCO₂ and 20 kJ/molCO₂, respectively. The first value was taken from Greer [2] and the second from Pinsent et al. [28].

A two-equation model for the transient energy balance in the control volume depicted in Figure 1 leads to the following equations for all the components shown in the figure [9, 36]:

$$\frac{\partial T_i}{\partial t} = -u_i \frac{\partial T_i}{\partial t} - \frac{\Delta H_R}{\sum C_i^p C_i^l} - \frac{U_T a_w}{\sum C_i^p C_i^l} (T_i - T^*)$$

$$\frac{\partial T^*}{\partial t} = -u_i \frac{\partial T^*}{\partial t} - \frac{U_T a_w}{\sum C_i^p C_i^l} (T^* - T)$$

where $C_i^p$ and $C_i^l$ are the heat capacities of component $i$ in the mixture, $U_T$ is the global heat transfer coefficient, $u_i$ is the superficial velocity inside the gas phase, and $\Delta H_R$ is the heat released by the chemical reaction. The CO₂ molar flow term ($N_{CO_2, diff}$) is given by Equation (22), while the enhancement factor ($E$) is given by the Hatta number defined by Equation (23).

1.7. Thermodynamics. The molar flow of component $i$ from the gas phase into the liquid phase ($N_{i, diff}^g$) is calculated using

$$N_{i, diff}^g = -k_i a_w (C_i^l - C_i^g).$$

where $C_i^l$ is the interfacial liquid equilibrium concentration. In order to evaluate $C_i^l$, we use a formulation based upon the calculation of gas and liquid fugacity values [2]. This formulation avoids the use of an iterative procedure as the fugacity values can be calculated directly as

$$N_{i, diff}^g = \frac{k_i^* a_w}{\phi_i^* Z_i^* R T^*} (f_i^g - f_i^l).$$

This expression for the diffusion molar flow is valid for the RNH₂, R₃R₄R₅N, and H₂O components when the resistance is assumed to be in the gas-liquid film [2]. A similar expression for CO₂, O₂, and N₂ can also be derived by

2. Results and Discussion

2.1. Model Validation. A FORTRAN computer code was developed based upon a previous one prepared for simulating CO₂ absorption using primary/binary amine solvents [30]. An explicit finite-difference scheme was used to solve the relevant hyperbolic partial differential equations. For convenience, in our equations, all variables were made dimensionless, but the species concentrations were calculated in dimensional values (mM and mol/m³). The residence time of the liquid phase ($t_r = H/u$) was used to define a dimensionless time ($t^* = t/t_r$). In all our simulation runs, we used geometric parameters and operating conditions taken from the literature. A list of our input data is shown in Table 4. This list includes information about the packing, the ranges of all values, and the standard set used in most of our calculations.

Validation of the computer code was achieved by comparing calculated parameters with data from the literature, especially with the work of Greer [2]. The validation process included checking against literature values [2, 5, 6, 23, 26, 39] the values of our calculated geometric parameters ($d_s$, $a_T$, and $a_w$), transfer coefficients ($k_i$ and $k_i^*$), kinetic parameters ($k_{diff}$, $k_{init}$, $K_i$, and $E$), and equilibrium parameters ($H_{cc}^{eq}$, $f_i^c$, $f_i^g$, $\phi_i^c$, and $\phi_i^g$). It also included a comparison of calculated mass species concentration profiles against literature values [2, 5, 23, 26, 30].

In Figure 3, we show a comparison of calculated CO₂ axial concentration profiles against those values reported by Greer [2] for dimensionless time ($t^*$) equal to 0.328 (2000 s) and steady-state condition. The basic set of parameters and operating conditions reported by Greer ([2] Table 4.2 in page 90) was used in these calculations. It can be seen in the
figure that there is good agreement between our calculated data and those from Greer [2] for the CO$_2$ axial concentration profiles; our calculated values, however, were always slightly lower than those reported by Greer [2]. Similar agreement, not shown in this work, was achieved when calculating the other chemical compounds’ axial profiles.

The accuracy of the reaction model was validated by carrying out a mass balance for the amine chemical species. A global mass balance for the amines and their reaction products at equilibrium gives

\[ u_t A_{sec} [RNH_2]_{IN} = u_t A_{sec} \left( [RNH_2]_{OUT} + [RNH_3^+]_{OUT} + [RNHCOO^-]_{OUT} \right), \]  
\[ u_t A_{sec} [R_1R_2R_3N]_{IN} = u_t A_{sec} \left( [R_1R_2R_3N]_{OUT} + [R_1R_2R_3N^+]_{OUT} \right). \]  

Equations (31) and (32) was used as a way of estimating the accuracy of the reaction scheme. In all our calculations, the error between the calculated concentrations was on the order of the code precision ($10^{-6}$). A global mass balance for CO$_2$ was used as another way of estimating the global accuracy of the proposed model. The biggest relative error in all our calculations was 0.01%.

### Table 4: Typical values of column geometric parameters and operating variables.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Default value</th>
<th>Range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>M</td>
<td>5</td>
<td>1–10</td>
<td>Richardson et al. [37]</td>
</tr>
<tr>
<td>Tower diameter</td>
<td>M</td>
<td>1</td>
<td>0.5–2</td>
<td>Richardson et al. [37]</td>
</tr>
<tr>
<td>Dry specific area ($\sigma_T$)</td>
<td>m$^2$/m$^3$</td>
<td>200</td>
<td>200–500</td>
<td>Billet and Schultes [38]</td>
</tr>
<tr>
<td>Void fraction ($\varepsilon$)</td>
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<td>0.979</td>
<td>Billet and Schultes [38]</td>
</tr>
<tr>
<td>Packing equivalent diameter</td>
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<td>0.005–0.02</td>
<td>Billet and Schultes [38]</td>
</tr>
<tr>
<td>Packing coefficient ($C_n$)</td>
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<td>0.971</td>
<td>Billet and Schultes [38]</td>
</tr>
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<td>Packing coefficient ($C_h$)</td>
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<td>0.547</td>
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<tr>
<td>Packing coefficient ($C_v$)</td>
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<td>0.390</td>
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<tr>
<td>Liquid-phase superficial velocity ($u_l$)</td>
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<td>0.01</td>
<td>0.001–0.1</td>
<td>Greer [2]</td>
</tr>
<tr>
<td>Gas-phase superficial velocity ($u_g$)</td>
<td>m/s</td>
<td>1</td>
<td>0.5–5</td>
<td>Greer [2]</td>
</tr>
<tr>
<td>Input temperature</td>
<td>K</td>
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<td>293–323</td>
<td>Greer [2]</td>
</tr>
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<td>CO$_2$ concentration</td>
<td>mol/m$^3$</td>
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<td>0.017–17.0</td>
<td>This work</td>
</tr>
<tr>
<td>RNH$_2$ molar fraction</td>
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<td>0.01–0.5</td>
<td>Greer [2]</td>
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<tr>
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<td>0.1</td>
<td>0.01–0.2</td>
<td>This work</td>
</tr>
</tbody>
</table>

2.2. Simulation Results. The time change of the CO$_2$ concentration is depicted in Figure 4, where typical axial concentration profiles are presented. At dimensionless time equal to 0, a gas mixture containing CO$_2$ is injected. The CO$_2$ concentration is highest at the base of the column, $Z = 0$, and drops as we approach the top, $Z = 1$. The results in Figure 4 show that as time increases, the concentration of CO$_2$ increases as we approach the top. We can also see that, at long times, the steady state is achieved.

In order to study the time evolution of the concentration of the generic amine, we chose to use monoethanolamine (MEA) due to the high amount of data available for this particular chemical compound. MEA reacts with CO$_2$ following reaction (9). Two amine ions, the ammonium-like ion

![Figure 3: Comparison of carbon dioxide axial concentration profiles with literature data.](image)

![Figure 4: Carbon dioxide axial concentration profiles at different times.](image)
The results are shown in Figure 8 where the CO2 gas-phase concentration profile is depicted for the same CO2 input concentration as in Figure 4. This is the starting time for the simulation (t=0). At t=0, the CO2 input concentration is set to its original value (1.7 mol/m^3), and the CO2 concentration starts decreasing throughout the column. There is a continuous increase in CO2 concentration until the new steady-state values are reached. The area between both curves is proportional to the amount of extra mass added.

The simulation results for a discrete pulse are shown in Figure 9. We start from the final equilibrium concentration profile shown in Figure 8 (t=0). At t=0, the CO2 input concentration is set to its original value (1.7 mol/m^3), and the CO2 concentration starts decreasing throughout the column. There is a continuous increase in CO2 concentration until the new steady-state values are reached. The area between both curves is proportional to the amount of extra mass added.

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The results presented in Figures 8 and 9 show that the proposed model can be successfully used to analyze the response of the absorption column to sudden changes in CO$_2$ input concentrations.

3. Conclusions

A model for the dynamic behavior of reactive CO$_2$ absorption using mixtures of alkanolamine solvents has been successfully developed. The model is based upon transient mass and energy balances for several different chemical species commonly present in CO$_2$ gas-liquid absorption. The phase equilibrium has been considered using a thermodynamic model and through the use of experimentally based Henry’s law values. Typical values for the geometric parameters of the absorber and the packing characteristics have been collected. A reaction scheme that takes into account the different reactions between CO$_2$ and blends of amines in an alkaline environment has been proposed. A computer code has been written to implement the proposed model. The computer code has been validated by checking the values of parameters calculated and comparing results to those reported in the literature. The mass balances for CO$_2$ have been close within a 0.01% relative error, while the alkanolamine solvents’ mass balances have been close within the computer code precision ($10^{-6}$). The results have been collected, and they are logical and agree with equivalent literature results. The computer code developed in this work can describe adequately the dynamic processes occurring due to sudden changes in operating conditions. Therefore, it is a valuable tool to design, optimize, and control absorption processes in the nuclear industries.

Appendix

A. Overall CO$_2$ Mass Transfer Coefficient

The computer code developed to implement our model calculates an overall mass transfer coefficient based upon liquid-phase concentrations ($K_{l,CO_2}^i$) and compares its value with the liquid-layer mass transfer coefficient ($k_{l,CO_2}^i$) value to decide which one should be used at each step of the calculations. Typical results are presented in Table 2. Equation (8) was used to calculate $K_{l,CO_2}^i$. We can see that, in most of the calculations presented in this work, the relative error between using $k_{l,CO_2}^i$ and $K_{l,CO_2}^i$ is around 10%; therefore, the overall mass transfer coefficient is used.

B. Reaction List

The 8 reactions used in the kinetic model are listed below:

\[
\text{CO}_2 + 2\text{RNH}_2 \leftrightarrow \text{RNH}_3^+ + \text{RNHCOO}^- \quad \text{(B.1)}
\]

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \quad \text{(B.2)}
\]
\[ CO_2 + OH^- \leftrightarrow HCO_3^- \quad (B.3) \]
\[ H_2O \leftrightarrow OH^- + H^+ \quad (B.4) \]
\[ RNH_3^+ \leftrightarrow H^+ + RNH_2 \quad (B.5) \]
\[ RNHCOO^- \leftrightarrow HCO_3^- + RNH_2 \quad (B.6) \]
\[ CO_2 + R_1R_2R_3N + H_2O \leftrightarrow HCO_3^- + R_1R_2R_3NH^+ \quad (B.7) \]
\[ R_1R_2R_3NH^+ \leftrightarrow R_1R_2R_3N + H^+ \quad (B.8) \]

**C. Reaction Rates**

The equations used to calculate the forward and reverse reactions are

\[ -r_{1f} = k_{1f} [CO_2][RNH_2]^2 \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.1) \]
\[ -r_{2f} = k_{2f} [CO_2]x_{H_2O} \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.2) \]
\[ -r_{3f} = k_{3f} [CO_2][OH^-] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.3) \]
\[ -r_{4f} = k_{4f} \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.4) \]
\[ -r_{5f} = k_{5f} [RNH_3^+] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.5) \]
\[ -r_{6f} = k_{6f} [RNHCOO^-] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.6) \]
\[ -r_{7f} = k_{7f} [CO_2] [R_1R_2R_3N]x_{H_2O} \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.7) \]
\[ -r_{8f} = k_{8f} [R_1R_2R_3NH^+] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.8) \]
\[ -r_{1r} = k_{1r} [RNH_3^+] [RNHCOO^-] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.9) \]
\[ -r_{2r} = k_{2r} [HCO_3^-] [H^+] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.10) \]
\[ -r_{3r} = k_{3r} [HCO_3^-] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.11) \]
\[ -r_{4r} = k_{4r} [OH^-] [H^+] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.12) \]
\[ -r_{5r} = k_{5r} [H^+] [RNH_2] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.13) \]
\[ -r_{6r} = k_{6r} [HCO_3^-] [RNH_2] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.14) \]
\[ -r_{7r} = k_{7r} [HCO_3^-] [R_1R_2R_3NH^+] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right), \quad (C.15) \]
\[ -r_{8r} = k_{8r} [R_1R_2R_3N] [H^+] \left( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \right). \quad (C.16) \]

Here, \( x_{H_2O} \) is the water molar fraction in the feed solvent phase.

**D. Kinetic Data**

Table 3 summarizes all the rate equations used in the model. The first number in the first column is the equation number used in Appendix. The second number refers to the original equation number used in the article.

**E. Simulation Parameters**

In our simulation runs, we used a Montz B 200 metal structured packing [2] as typical packing. Table 4 shows typical geometric parameters and operating variables used in the simulation runs.

**F. Generation Terms**

Assuming the pseudo-steady state for every chemical species, we can calculate the generation terms that enter into the chemical species mass balances. In order to simplify the calculations, we determined an overall rate per reaction according to

\[ R_{\text{gen}} = R_{\text{st}} - R_{\text{fr}}. \quad (F.1) \]

Every generation term (\( R_{\text{gen}} \)) is calculated by a molar balance using

\[ R_{\text{gen}1} = R_{a_1} - R_{a_6}, \quad (F.2) \]
\[ R_{\text{gen}2} = R_{a_1} - R_{a_5}, \quad (F.3) \]
\[ R_{\text{gen}3} = R_{a_2} + R_{a_3} + R_{a_6}, \quad (F.4) \]
\[ R_{\text{gen}4} = R_{a_4} - R_{a_3}, \quad (F.5) \]
\[ R_{\text{gen}5} = R_{a_5} + R_{a_6} - 2R_{a_1}, \quad (F.6) \]
\[ R_{\text{gen}6} = R_{a_2} - R_{a_4} - R_{a_5}, \quad (F.7) \]
\[ R_{\text{gen}7} = -R_{a_1} - R_{a_2} - R_{a_3} - R_{a_5} - R_{a_7}, \quad (F.7) \]
\[ R_{\text{gen}8} = R_{a_2} + R_{a_4} + R_{a_5}, \quad (F.8) \]
\[ R_{\text{gen}9} = R_{a_4} + R_{a_5} + R_{a_8}, \quad (F.9) \]
\[ R_{\text{gen}10} = R_{a_7} - R_{a_8}. \quad (F.10) \]

**Nomenclature**

\( \alpha_f \): Mass transfer specific area (m\(^2\)-m\(^{-3}\))
\( \alpha_w \): Packing specific area (m\(^2\)-m\(^{-3}\))
Data Availability

The data collected during the submitted research project are stored in the authors’ servers. The data and metadata collected are stored in Excel spreadsheets and comprise less than 1 GB. They can be made public as required.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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