Carbon Dioxide Transfer with Chemical Equilibrium Reactions:  
An Alternative Mathematical Approach  

A. Shanableh  
Department of Civil and Environmental Engineering,  
University of Sharjah, P.O. Box 27272, Sharjah, United Arab Emirates

Abstract: Problem statement: Despite intensive research efforts on CO\textsubscript{2} transfer, mathematical models that describe the dependence of the CO\textsubscript{2} transfer rate on the pH and the degree of rate enhancement due to CO\textsubscript{2} chemical reactions remain unavailable. Approach: Such models are essential for assessing and accurately describing the progress of the CO\textsubscript{2} transfer process. Results: In this study, an alternative view of CO\textsubscript{2} transfer with chemical reactions was used to develop simple mathematical models to describe the pH dependence and degree of enhancement of the CO\textsubscript{2} transfer rate. In the alternative view, the driving force for CO\textsubscript{2} transfer was described in terms of the differences in the concentrations of the various carbonic species in the bulk liquid (i.e., \(\Delta C_{\text{H}_2\text{CO}_3}^+\), \(\Delta C_{\text{HCO}_3}^-\), and \(\Delta C_{\text{CO}_3}^{2-}\)) in time (i.e., between time, \(t\), and the time when equilibrium is achieved, \(t_{eq}\)) rather than in terms of the concentrations gradients across the liquid film. Using the concentration differences in time, simple mathematical models describing the pH dependence of the CO\textsubscript{2} transfer rate and the contributions of the various carbonic species to the rate were formulated. Furthermore, the degree of CO\textsubscript{2} transfer rate enhancement due to CO\textsubscript{2} reactions in water was considered proportional to the sum of the rates of HCO\textsubscript{3}\(^-\) and CO\textsubscript{3}\(^{2-}\) transfer. Conclusion/Recommendations: The mathematical models were tested using data from batch and continuous-flow CO\textsubscript{2} transfer experiments, and the results revealed that the mathematical models explained the experimental data in an excellent manner.

Key words: CO\textsubscript{2} transfer, transfer rate, mathematical models, pH-dependant transfer rate, contributions of carbonic species to the transfer rate, enhancement of CO\textsubscript{2} transfer

INTRODUCTION

Carbon dioxide exchange across the gas/liquid interface is related to numerous natural and engineered processes and as such, the topic is of multidisciplinary interest in the scientific community\cite{1-6}. The theory and mathematics describing CO\textsubscript{2} transfer have generally evolved in agreement with earlier concepts describing the process in natural and engineered systems\cite{7-10}. The current CO\textsubscript{2} transfer theory relies on steady-state chemical equilibrium models to describe the impact of CO\textsubscript{2} transfer on the pH of aqueous solutions. However, the dependence of the CO\textsubscript{2} transfer rate on the pH and the variations of pH during CO\textsubscript{2} transfer are typically ignored. Furthermore, there are no mathematical models that explicitly and accurately describe the dependence of the CO\textsubscript{2} transfer rate on the pH. Similarly, there are no mathematical models to describe the degree of enhancement of the CO\textsubscript{2} transfer rate as a function of pH due to chemical reactions involving hydration (de-hydration) of CO\textsubscript{2} and acid-base ionization reactions leading to the formation (or removal) of HCO\textsubscript{3}\(^-\) and CO\textsubscript{3}\(^{2-}\). As such, the main objective of the study was to develop simple mathematical models to describe the dependence of the CO\textsubscript{2} transfer rate on the pH and the degree of rate enhancement due to chemical reactions.

In the current theory, the CO\textsubscript{2} transfer rate is mathematically described through comparing the relative rates of CO\textsubscript{2} diffusion and chemical reactions across the Liquid Layer (LL) with thickness equal to \(\delta_{LL}\) with the rate of CO\textsubscript{2} transfer being controlled by the slower of the two processes. For example, Emerson\cite{8} and Stumm and Morgan\cite{10} described the concentration gradient (\(\Delta C\)) across the liquid layer that drives CO\textsubscript{2} flux (\(F = \frac{D}{\delta_{LL}} \Delta C\), where D is the diffusion coefficient) based on which of the two processes is faster, as follows:

- In the case where diffusion of CO\textsubscript{2} through the liquid layer is slow compared to the rates of reactions (i.e., diffusion controlled transfer), then
HCO$_3^-$ and CO$_3^{2-}$ form within the liquid layer and thus concentration gradients develop for each of the carbonic species within the layer. In this case, $\Delta C$ is that for total carbonic species with the contributions of HCO$_3^-$ and CO$_3^{2-}$ enhancing the overall CO$_2$ transfer rate, as in Eq. 1:

$$F = F_{CO_2} + F_{HCO_3} + F_{CO_3}$$

(1)

- In the case where CO$_2$ diffusion through the liquid film is fast compared to the rates of chemical reactions (i.e., chemically controlled transfer), then HCO$_3^-$ and CO$_3^{2-}$ are not formed or consumed within the diffusion zone due to chemical reactions and the diffusion of CO$_2$ alone accounts for transport with the concentration gradient, $\Delta C$, being that in CO$_2$ alone

In the chemically controlled transfer process, equilibrium is not achieved within the LL during CO$_2$ transfer, but beyond in the bulk liquid. In the diffusion controlled CO$_2$ transfer process, chemical equilibrium may or may not develop within the LL, depending on the rates of chemical reactions compared to slow diffusion. If chemical reactions are assumed to be instantaneous, which is unlikely, then equilibrium is achieved everywhere within the LL. Stumm and Morgan$^{[10]}$ and Morel and Hering$^{[11]}$ suggested that enhancement of CO$_2$ transfer is not considered significant except in alkaline waters or very quiescent water bodies.

Livansky$^{[12]}$ studied the rate of absorption of carbon dioxide as a function of pH in different buffers and concluded that the absorption rate increased for all buffers tested with increasing pH. Howe and Lawler$^{[11]}$ presented a mathematical model, Eq. 2, to describe the relationship between the CO$_2$ transfer rate and pH over a wide range of pH, as in Eq. 2:

$$r_t = \alpha_e K_i a (C_{T_{eq}} - C_T)$$

(2)

Where:
- $C_T$ = The concentration of total carbonic species in the bulk liquid
- $C_{T_{eq}}$ = The equilibrium concentration in the bulk liquid as determined by Henry's law
- $\alpha_e$ = $[H_2CO_3]/[C_T]$, which is pH dependent
- $K_i a$ = Mass transfer coefficient

Howe and Lawler$^{[13]}$ described the model in Eq. 2 as being suitable for use whether the pH changes or not as a result of pH transfer. However, due to the change in pH as a result of CO$_2$ transfer, the use of $\alpha_e$ as a common factor that applies to both $C_T$ and $C_{T_{eq}}$ may not be appropriate. As such, the model is not suitable for use except in the special and unlikely case in which the pH does not change or is not allowed to change due to CO$_2$ transfer.

In this study, an alternative view of CO$_2$ transfer with chemical reactions was used to facilitate the development of simple mathematical models to describe the pH dependence and degree of enhancement of the CO$_2$ transfer rate. The alternative view was based on describing CO$_2$ transfer rate in terms of the ultimate driving force represented by the difference in time between the concentration of aqueous CO$_2$ in the bulk liquid at any time ($t$) and the ultimate concentration of aqueous CO$_2$ at the time of equilibrium ($t_{eq}$). Using the mathematical description of the ultimate driving force, as described in the following sections, the degree of CO$_2$ transfer rate enhancement was estimated based on the contributions of the various carbonic species to the transfer rate, which were considered proportional to their concentration gradients in time. The development of the mathematical models is described in details in the following section.

**Theoretical considerations:** Stumm and Morgan$^{[10]}$ accounted for the enhancement of the CO$_2$ transfer rate through expressing the concentration gradient in aqueous CO$_2$ alone (chemically controlled transfer without enhancement) or in the total carbonic species (diffusion controlled transfer with rate enhancement). In the case where diffusion is fast compared to chemical reactions, HCO$_3^-$ and CO$_3^{2-}$ are not formed (or consumed to release CO$_2$) nor chemical equilibrium among the carbonic species is achieved within the LL. In this case, formation (or consumption) of HCO$_3^-$ and CO$_3^{2-}$ and establishment of chemical equilibrium require more time than available within the LL. As such, rapid diffusion results in excess or deficiency in CO$_2$ concentration in the bulk liquid that is not in equilibrium with the other carbonic species but requires additional time or space to achieve equilibrium. Current theory however does not account for the extra time or space needed to achieve chemical equilibrium in the bulk liquid. In fact, chemical reactions work on bringing the carbonic species in chemical equilibrium with each other, whether such reactions take place in the traditionally defined LL or in the bulk liquid and as such the influence of chemical reactions on the transfer rate cannot be separated from the mass transfer process.

In the case where diffusion is slow compared to the rates of chemical reactions, HCO$_3^-$ and CO$_3^{2-}$ form
within the LL. Slow diffusion may also allow enough time for chemical equilibrium to be established within the LL. Theoretically, if the chemical reactions were considered to be instantaneous, which is unlikely, then chemical equilibrium among the carbonic species is achieved everywhere within the LL and the bulk liquid.

The target of both diffusion and chemical reactions is to achieve equilibrium between the concentrations of CO$_2$ in the gas and bulk liquid and also chemical equilibrium among the various carbonic species (CO$_2$, H$_2$CO$_3$, HCO$^-$ and CO$_3^{2-}$). When equilibrium is disturbed, both processes proceed to reestablish a new state of equilibrium in which net diffusion ceases when equilibrium among the carbonic species is reestablished. As such, the ultimate driving force for CO$_2$ transfer must be the concentration difference between two equilibrium states separated by the time required to reestablish equilibrium in terms of diffusion and chemical reactions. Using the ultimate driving force accounts for the time required to establish chemical equilibrium among the carbonic species.

Using H$_2$CO$_3^-$ to represent aqueous CO$_2$, which includes both dissolved CO$_2$ and H$_2$CO$_3$, the ultimate driving force can be mathematically described as the difference in time between the concentration of H$_2$CO$_3^-$ in the bulk liquid at any time, or \([H_2CO_3^-]_{b(t)}\), and the ultimate concentration of H$_2$CO$_3^-$ at the time of equilibrium, or \([H_2CO_3^-]_{b(e)}\). Mathematically, the ultimate driving force can be described as \(\Delta C_{H_2CO_3^-} = [H_2CO_3^-]_{b(e)} - [H_2CO_3^-]_{b(t)}\). The current CO$_2$ transfer theory is based on describing the driving force using the concentration gradient in space (i.e., across the liquid layer with thickness equal to \(\delta_L\)). The ultimate concentration difference in time \(\Delta C_{H_2CO_3^-} = [H_2CO_3^-]_{b(e)} - [H_2CO_3^-]_{b(t)}\) can be considered equivalent to the ultimate concentration gradient in space across the liquid layer, or \(\Delta C_{H_2CO_3^-} = [H_2CO_3^-]_{b(e)} - [H_2CO_3^-]_{b(t)}\). The equivalency between the concentration difference in time and space assumes that \([H_2CO_3^-]_{b(e)} = [H_2CO_3^-]_{b(t)}\) and \([H_2CO_3^-]_{b(e)} = [H_2CO_3^-]_{b(t)}\). A view of the ultimate concentration difference in time and space is presented in Fig. 1. The equivalency between the driving force in time and space provides important insight into the progress of diffusion and reaction across the LL. For example, the equivalent concentration profiles for the various carbonic species and the pH across the LL at any time can be considered equivalent to the variations of the carbonic species concentrations and the pH with time leading to equilibrium as described by Henry's law.

**Mathematical considerations:** According to the two films gas transfer theory, CO$_2$ flux in the liquid and gas films is driven by the corresponding concentration gradients, as expressed in Eq. 3 and 4:

\[
F_{LL} = K_f([H_2CO_3^-]_{int} - [H_2CO_3^-]_{b(t)}) \tag{3}
\]

\[
F_{GL} = K_g([CO_2g] - [CO_2g,int]) \tag{4}
\]

Where:

- \(F_{LL}\) = Flux across the liquid layer
- \(F_{GL}\) = Flux across the gas layer
- \([H_2CO_3^-]_{int}\) = Concentration of aqueous CO$_2$ in the liquid at the gas/liquid interface
- \([H_2CO_3^-]_{b(t)}\) = Concentration of aqueous CO$_2$ in the bulk liquid at time \(t\)
- \([CO_2g]\) = Concentration of gaseous CO$_2$ in the gas phase at the interface
- \([CO_2g,int]\) = Concentration of gaseous CO$_2$ in the bulk gas phase
- \(K_f\) and \(K_g\) = Liquid and gas phase transfer coefficients, respectively

Equating flux across the liquid film with flux across the gas film (Eq. 5), then substituting for \([CO_2g,int]\) and \([CO_2g]\) from Henry's law (Eq. 6 and 7) into Eq. 5 and solving for \([CO_2g,int]\) results in Eq. 8. Substituting from Eq. 8 into Eq. 3 results in Eq. 9-11:

\[
K_f([H_2CO_3^-]_{int} - [H_2CO_3^-]_{b(t)}) = K_g([CO_2g] - [CO_2g,int]) \tag{5}
\]

\[
[CO_2g] = H_k [H_2CO_3^-]_{int} \tag{6}
\]

Fig. 1: A simplified view of CO$_2$ transfer with the concentration gradient across the LL (i.e., gradient in space) is equivalent to the concentration difference in the bulk liquid in time (i.e., between any time during CO$_2$ transfer and the time when equilibrium as defined by Henry's law is achieved)
CO\textsubscript{2,lin} = H\textsubscript{2}HCO\textsubscript{3,lin} \tag{7}

H\textsubscript{2}CO\textsubscript{3,lin} = \frac{K\textsubscript{H}H\textsubscript{2}CO\textsubscript{3},(\text{eq}) + H\textsubscript{2}K\textsubscript{H}H\textsubscript{2}CO\textsubscript{3},(\text{lin})}{K\textsubscript{H} + H\textsubscript{2}K\textsubscript{H}} \tag{8}

F\textsubscript{LL} = \frac{H\textsubscript{2}K\textsubscript{H}K\textsubscript{H}}{K\textsubscript{H} + H\textsubscript{2}K\textsubscript{H}}(H\textsubscript{2}CO\textsubscript{3},(\text{lin}) - H\textsubscript{2}CO\textsubscript{3},(\text{eq})) \tag{9}

F\textsubscript{LL} = K\textsubscript{L}(H\textsubscript{2}CO\textsubscript{3},(\text{lin}) - H\textsubscript{2}CO\textsubscript{3},(\text{eq})) \tag{10}

K\textsubscript{L} = \frac{H\textsubscript{2}K\textsubscript{H}K\textsubscript{H}}{K\textsubscript{H} + H\textsubscript{2}K\textsubscript{H}} \tag{11}

Where:

H\textsubscript{2}CO\textsubscript{3,lin} = Concentration of aqueous CO\textsubscript{2} in the bulk liquid at the time when equilibrium according to Henry's law is achieved

H\textsubscript{H} = Henry's law constant

The gas transfer rate (r\textsubscript{c}) can be obtained by multiplying the flux in Eq. 10 by the specific surface area (a) of contact between the gas and liquid phases at the interface, as in Eq. 12:

r\textsubscript{c} = K\textsubscript{L}a(H\textsubscript{2}CO\textsubscript{3},(\text{lin}) - H\textsubscript{2}CO\textsubscript{3},(\text{eq})) \tag{12}

Using molar concentrations, the transfer rate can be expressed as in Eq. 13:

r\textsubscript{c} = K\textsubscript{L}a \left( [H\textsubscript{2}CO\textsubscript{3},(\text{lin})] - [H\textsubscript{2}CO\textsubscript{3},(\text{eq})] \right) \tag{13}

Noting that the pH in the bulk liquid changes as a result of mass transfer from pH\textsubscript{lin} to pH\textsubscript{eq} and with chemical equilibrium established among the carbonic species in the bulk liquid, the transfer rate in Eq. 13 can be expressed in terms of the total and other carbonic species according to their relative abundance, as follows:

r\textsubscript{c} = K\textsubscript{L}a \left( \alpha_{\text{eq}}[TC,\text{lin}] - \alpha_{\text{eq}}[TC,\text{eq}] \right) \tag{14}

r\textsubscript{c} = K\textsubscript{L}a \left( \frac{[H\textsubscript{2}CO\textsubscript{3},(\text{lin})]}{\alpha_{\text{eq}}} - \frac{[H\textsubscript{2}CO\textsubscript{3},(\text{lin})]}{\alpha_{\text{eq}}} \right) \tag{15}

r\textsubscript{c} = K\textsubscript{L}a \left( \frac{[CO\textsubscript{3}^{2-},(\text{lin})]}{\alpha_{\text{eq}}} - \frac{[CO\textsubscript{3}^{2-},(\text{lin})]}{\alpha_{\text{eq}}} \right) \tag{16}

Where:

[TC]\textsubscript{lin} = The concentration of total carbonic species in the bulk liquid at any time

[TC]\textsubscript{eq} = The equilibrium concentration in the bulk liquid as determined by Henry's law

\alpha = The different (\alpha) values represent the relative abundance of the carbonate species in solution as defined in Table 1, with [H\textsuperscript{+}][HCO\textsubscript{3}]/[H\textsubscript{2}CO\textsubscript{3}] = k\textsubscript{1} and [H\textsuperscript{+}][CO\textsubscript{3}^{2-}]/[HCO\textsubscript{3}] = k\textsubscript{2}

**Practical considerations:** In practical CO\textsubscript{2} absorption and desorption applications, the CO\textsubscript{2} transfer rate is assessed through measuring the concentration of the total carbonic species TC in the aqueous phase or the concentration of CO\textsubscript{2} in the gas phase, or both. In such applications, it is convenient to express the transfer rate using the concentration of the total carbonic species, as presented in Eq. 17, below:

r\textsubscript{c} = K\textsubscript{L,a(Apparent)} \left( [TC]\textsubscript{lin} - [TC]\textsubscript{eq} \right) \tag{17}

where, K\textsubscript{L,a(Apparent)} is apparent mass transfer coefficient.

By comparing Eq. 14 and 17, the relationship between K\textsubscript{L,a(Apparent)} and K\textsubscript{L,a} can be expressed as in Eq. 18:

\frac{K\textsubscript{L,a(Apparent)}}{K\textsubscript{L,a}} = \frac{\alpha_{\text{eq}}[TC,\text{lin}] - \alpha_{\text{eq}}[TC,\text{eq}]}{[TC]\textsubscript{lin} - [TC]\textsubscript{eq}} \tag{18}

**Transfer rate enhancement due to chemical reactions:** Equation 14 and 17, expressed in terms of the concentration gradient in total carbonic species account for enhanced CO\textsubscript{2} transfer, with its various components, as follows:

r\textsubscript{c} = r_{H\textsubscript{2}CO\textsubscript{3}} + r_{CO\textsubscript{3}^{2-}} \tag{19}

As such, the contributions of the various carbonic species to the overall transfer rate can be expressed in terms of their relative abundance as follows:

r_{H\textsubscript{2}CO\textsubscript{3}} = K\textsubscript{L,a} \left( \alpha_{\text{eq}}[TC,\text{lin}] - \alpha_{\text{eq}}[TC,\text{eq}] \right) \tag{20}

r_{CO\textsubscript{3}^{2-}} = K\textsubscript{L,a} \left( \alpha_{\text{eq}}[TC,\text{lin}] - \alpha_{\text{eq}}[TC,\text{eq}] \right) \tag{21}

r_{H\textsubscript{2}CO\textsubscript{3}} = K\textsubscript{L,a} \left( \alpha_{\text{eq}}[TC,\text{lin}] - \alpha_{\text{eq}}[TC,\text{eq}] \right) \tag{22}


Based on the above equations, CO₂ transfer without enhancement can be represented by \( r_{\text{H,CO}_2} \) as expressed in Eq. 20. The Enhancement Factor (EF) thus can be defined as in Eq. 23, below:

\[
\text{EF}(\%) = \frac{r_{\text{H,CO}_2} + r_{\text{CO}_2}}{r_{\text{C}}} \times 100
\]  

(23)

MATERIALS AND METHODS

Experimental evaluation: Because the behavior of CO₂ absorption and desorption is well known and predictable, a detailed CO₂ experimental program was not deemed necessary. Instead, available experimental data, conducted under the conditions described below, were used to clarify various aspects and applications of the theory.

Two sets of batch experiments were conducted at different initial pH values in a 15 cm diameter \( \times \) 40 cm height cylinder filled with five liters carbonate solution. In the first set, a phosphate buffer (0.05 M) was added to reduce pH increase due to CO₂ removal. In the second set, no phosphate buffer was added. The initial total inorganic carbon in each solution was designed to be approximately 100 mg L\(^{-1}\). During each experiment, Helium was bubbled at the bottom of the cylinder for 30 min and the total inorganic carbon concentration and pH were measured with time.

The continuous-flow, packed column experiments were conducted in a 15 cm diameter \( \times \) 100 cm height cylinder (Fig. 2) filled with plastic media to a depth of 82 cm. The experiments were conducted using a solution containing 0.05 M phosphate pumped separately from the solution containing the inorganic carbonates. The liquid stream was introduced at the top of the column. Air was introduced at the bottom of the column. The experiments were conducted at different initial pH values and the pH and inorganic carbon concentration in samples collected from the column influent and effluent were measured over a period of time until steady-state removal results were attained.

RESULTS

With the desorption gas CO₂-free and with \( [\text{TC}]_{(i)} = 0 \), the general transfer rate presented in Eq. 17 reduces to the form expressed in Eq. 24. Assuming that the pH remains unchanged in the PO₄ buffered solution, then \( K_{L,a(\text{Apparent})} \) remains constant and the integrated form of Eq. 24 is expressed in Eq. 25:

\[
\frac{d[\text{TC}]_{(i)}}{dt} = -K_{L,a(\text{Apparent})}[\text{TC}]_{(i)} = -\alpha_{(i)} \times K_{L,a} [\text{TC}]_{(i)}
\]  

(24)

\[
\ln[\text{TC}] = \ln[\text{TC}]_{(i)} - K_{L,a(\text{Apparent})} t
\]  

(25)

Based on Eq. 25, the \( K_{L,a(\text{Apparent})} \) values were determined from the slopes of the lines of best-fit expressing the linear relationships between \( \ln[\text{TC}] \) versus time for each of the desorption experiments conducted at different initial pH values. The relationship between the resulting \( K_{L,a(\text{Apparent})} \) values and removals achieved are presented in Fig. 3. The results matched the expected relationship between \( K_{L,a(\text{Apparent})} \) and \( K_L,a \) as predicted from Eq. 18 and expressed in Eq. 26:

\[
K_{L,a(\text{Apparent})} = \alpha_{o,h} \times K_L,a
\]  

(26)
The theoretical pH change due to CO$_2$ desorption can be estimated using the alkalinity Eq. 27. Equation 27 is expressed in terms of the relevant abundance of the negatively charged carbonate species (i.e., using $\alpha_{1(t)}$ and $\alpha_{2(t)}$) and the negatively charged phosphates species (i.e., using $\alpha_{1P(t)} = [HPO_4^{2-}] / [TP]$ and $\alpha_{2P(t)} = [PO_4^{3-}] / [TP]$), with [TP] being the total phosphates concentration). In Eq. 27, the Alk$_{Initial}$ and [TP] do not change due to CO$_2$ desorption but the pH does. In this case, the pH change due to CO$_2$ removal reached a maximum of approximately 0.3 units:

$$\text{Alk}_{Initial} = \frac{k_u}{[H^+]_{(t)}} + (\alpha_{1(t)} + 2\alpha_{2(t)})[TC]_{(t)}$$

$$+ (\alpha_{1P(t)} + 2\alpha_{2P(t)} + 3\alpha_{3P(t)})[TP] - [H^+]_{(t)}$$

Without the phosphate buffer, the pH was allowed to increase more freely as a result of CO$_2$ removal using the batch system. In this case, both $K_{L_a(Apparent)}$ and [TC]$_{(t)}$ in Eq. 24 change with time as CO$_2$ is removed, but the initial alkalinity (Eq. 28) does not change. Solving Eq. 28 for [TC]$_{(t)}$ then substituting into Eq. 24 results in the CO$_2$ removal rate (Eq. 29). Using numerical integration, the model parameters (i.e., $K_{L_a(Apparent)}$ and final pH$_{(t)}$) were determined and compared with the measured values, as shown in Fig. 3. The pH change due to CO$_2$ desorption reached approximately 0.45 units:

$$\text{Alk}_{Initial} = \frac{k_u}{[H^+]_{(t)}} + (\alpha_{1(t)} + 2\alpha_{2(t)})[TC]_{(t)} - [H^+]_{(t)}$$

$$\frac{d[TC]_{(t)}}{dt} = -K_{L_a(Apparent)} \left( \frac{[H^+]_{(t)}}{[H^+]_{(t)} (\alpha_{1(t)} + 2\alpha_{2(t)})} \right)$$

The CO$_2$ removal results obtained using the continuous flow system exhibited the same trends as the results obtained using the batch system. The CO$_2$ reaction rate equation that describes the removal of CO$_2$ from any section of the counter-current desorption column is expressed in Eq. 31, with:

$$\frac{d[TC]_{(h)}}{dt} = \frac{-A}{Q_L} \frac{[TC]_{(h)}}{dh}$$

$$\frac{A}{Q_L} \alpha_{1P(h)} [TC]_{(h)} = \alpha_{1P(h)} [TC]_{(h)}$$

$$\frac{\alpha_{1P(h)} [TC]_{(h)} - \alpha_{1P(h)} [TC]_{(h)}}{dh}$$

Where:

- $A$ = Column cross sectional area
- $Q_L$ = Volumetric liquid flow rate
- $dh$ = Section thickness along the column height

As the concentration of CO$_2$ in the gas phase increases as the gas travels up the column, the equilibrium concentration at any height can be described using Henry’s law as CO$_2$$_{(h)} = \alpha_{1P(h)} [TC]_{(h)}$. A value for $\alpha_{1P(h)}$ in Eq. 32 can be determined from a mass balance on the bottom section of the column with CO$_2$$_{(h)} = \alpha_{1P(h)} [TC]_{(h)}$. The result is the general mass transfer rate expression, Eq. 33. Assuming that the pH does not significantly change as a result of CO$_2$ removal, the integrated from of Eq. 33 is presented in Eq. 34:

$$\frac{d[TC]_{(h)}}{dh} = \frac{-1}{R} \frac{[TC]_{(h)}}{[TC]_{(h)} - [TC]_{(Effluent)}}$$

$$\frac{CO_2}{H_u}$$

Where:

- $Q_L$ = Volumetric gas flow rate
- CO$_2$$_{(h)}$ = Initial concentration of CO$_2$ in the desorption gas
- CO$_2$$_{(h)}$ = Concentration of CO$_2$ in the desorption gas at height h
Fig. 4: Dependence of the mass transfer coefficient (K_{L,a(Apparent)}) and [TC] removal on the pH in the buffered column desorption experiments

\[ [TC]_{\text{in}} = \text{Total carbonates concentration at height } h \]
\[ [TC]_{\text{Effluent}} = \text{Total carbonates concentration in the final effluent} \]
\[ R = \frac{H_nQ_G}{Q_L} \text{ is the desorption factor} \]
\[ h = \text{Column height:} \]
\[ K_{L,a} = -\frac{Q_R}{Ah(1-\alpha_{\text{in}}(R))} \ln \left( \frac{1-\alpha_{\text{in}}(R)}{R} \right) \left( \frac{[TC]_{\text{Effluent}}}{R} \right) - \frac{1}{R} \left( \frac{[TC]_{\text{Effluent}} - CO_{2(\text{in})}}{H_n} \right) \]

The data in Fig. 4 represent a direct application of Eq. 34, with the results providing good representation of the expected relationships for K_{L,a} and [TC] removals.

**DISCUSSION**

The enhancement of the CO_2 transfer rate due to chemical reactions is contributed by HCO_3^- and CO_3^{2-}, with the transfer rate of H_2CO_3 alone representing the case without enhancement. To illustrate the contributions of HCO_3^- and CO_3^{2-}, the transfer rate models used in the analysis of the batch experimental results without phosphate buffer and with [TC]_{\text{in}} = 0 are used. For example, the contributions of the various carbonic species to the CO_2 removal rate, according to Eq. 35-37 which are based on Eq. 20-22, are depicted in Fig. 5 and 6. In Fig. 5, the contributions of the various carbonic species to the total CO_2 transfer rate and the degree of chemical enhancement, according to Eq. 23, are presented. In Fig. 6, four examples showing the variations of the contributions of the carbonic species to the transfer rate together with the increase in the pH during 180 min of CO_2 desorption at four different initial pH values are presented. The data in Fig. 5 and 6 show that the transfer rate declines as the pH increases with enhancement occurring in the range of pk_1-2<pH< pk_1+2 due to the contribution of HCO_3^- . At pH = pk_1, the rate components contributed by H_2CO_3 and HCO_3^- become equal, with each accounting for approximately 50 percent of the total rate. In the pH range between pk_1 and pk_2, the rate component contributed by HCO_3^- has the largest value. Above pH = pk_2, the transfer rate becomes negligible but dominated by CO_3^{2-} contribution.
These results clearly suggest that the contributions of the various carbonic species to the transfer rate are consistent with their relative abundance in the bulk liquid.

\[
\begin{align*}
    r_{HCO_3^-} &= \alpha_{HCO_3^-}(t) \alpha_{TC}(t) K_{TC} \Delta C_{HCO_3^-} \\
    r_{CO_3^{2-}} &= \alpha_{CO_3^{2-}}(t) \alpha_{TC}(t) K_{TC} \Delta C_{CO_3^{2-}} \\
    r_{H_2CO_3} &= \alpha_{H_2CO_3}(t) \alpha_{TC}(t) K_{TC} \Delta C_{H_2CO_3}
\end{align*}
\]

CONCLUSION

The alternative view of CO₂ transfer with chemical reactions presented in this study was based on describing CO₂ transfer in terms of the ultimate driving force, \(\Delta C_{\text{eq}} = \Delta [H_2CO_3(t)]_{eq} - \Delta [HCO_3^-(t)]_{eq} \), or \(\Delta C_{\text{eq}} = \alpha_{HCO_3^-}(t)[TC]_{eq} - \alpha_{H_2CO_3}(t)[TC]_{eq} \). The use of the ultimate driving force concept allowed describing the pH dependence of the transfer rate and the degree of rate enhancement due to chemical reactions using simple and straightforward mathematical models. Furthermore, the use of the ultimate driving force allowed estimating the contribution of each of the carbonic species to the total transfer rate according to their relative abundance. The approach presented in this study simplifies the analysis of gas transfer with chemical reactions and can easily be extended to describe the transfer of other gases that undergo similar reactions leading to ultimate equilibrium in the aqueous phase.

REFERENCES