1. INTRODUCTION

A key step of the refined sodium bicarbonate (BIR®) production by the Solvay process consists in the gas-liquid mass transfer of carbonic gas CO$_2$ from a gaseous mixture of CO$_2$ and air to a sodium carbonate Na$_2$CO$_3$ and bicarbonate NaHCO$_3$ brine. This transfer takes place in 20-m high and 2.5-m wide bubble columns (the BIR columns). This large size induces a large contact time between gas and liquid, in order to increase the amount of transferred CO$_2$. Nevertheless, the gas phase leaving the columns contains an important quantity of CO$_2$ (only half of the CO$_2$ is transferred). It causes a huge CO$_2$ emission to the atmosphere (the equivalent of 150 Smart® driving at 100 km/h, for a single column). More, the CO$_2$ is produced by lime calcination. This process requires a large amount of energy. It represents the major part of the energy consumption to produce BIR. In the past decades, several optimizations of the BIR process were performed by an empiric approach. There are today some limits to this approach for applications requiring high levels of purity and a well-defined granulometry. Moreover, the ecologic pressure becomes more and more constraining for the greenhouse effect gas emission.

Accordingly, Solvay is seeking for a more fundamental approach. Currently, several studies are realized in the chemical engineering department at the ULB. The final goal is to create a complete model of a BIR bubble column, taking into account all the phenomena taking place in it. This model will be used in order to optimize the CO$_2$ transfer rate in the column. As a direct consequence of this optimization, the CO$_2$ emission and the energy consumption of the BIR production will hopefully be reduced.

The objective of the work presented in this paper is to develop a model of the mean CO$_2$ flux density, expressed by unit of time and interfacial area, in a BIR bubble column, that will be integrated in the future complete model of a BIR column. No solid phase is considered in this paper.

The CO$_2$ transfer rate from a bubble of gas to the brine is controlled by the physico-chemical phenomena occurring in the thin layer of liquid near the interface. After the CO$_2$ absorption in this liquid layer, the CO$_2$ is transferred by diffusion and is involved in several chemical reactions. These reactions modify (accelerate) the gas-liquid mass transfer rate.

The liquid phase flow around the bubbles, rising up in the columns, influences the mass transfer rate too. The scale of this phenomenon is different from the physico-chemical phenomena. A multiscale approach is then followed.

A mathematical modelling of the coupling between mass transfer and chemical reaction is first developed. The equations of the model are solved numerically, using COMSOL Multiphysics. In order to validate experimentally this model, a Mach-Zehnder interferometer is set up.
The scale-up of this model to a bubble, in a second time, is carried out by completing the model of the coupling with a representation of the liquid phase flow around a bubble. It is called the bubble-liquid mass transfer model. A stirred tank reactor is proposed to verify the ability of the model to predict the gas-liquid transfer rate from gas bubble.

2. MODELLING

2.1 Modelling of the coupling between mass transfer and chemical reactions in a quiescent liquid

The modelled system is presented in figure 1. It can be considered like a one-dimensional transient problem, the gradients are only in the direction perpendicular to the gas-liquid interface, depicted by the $x$-axis. This axis points toward the liquid phase. The system is assumed to be infinite in other directions. Since it is considered that the gaseous phase is pure CO$_2$, there is no concentration gradient in the gaseous phase side. Therefore, all the mass transfer resistance lies in the liquid phase side. Chemical equilibrium is assumed to be reached at the interface (Harvey & Smith, 1959). Liquid is supposed to be quiescent. Hence, the molecular diffusion is the only mass transfer mechanism.

![Figure 1: System representation](image)

Far from the interface (bulk), it is assumed that the concentrations of all the species are in the chemical equilibrium state.

In the liquid phase, the CO$_2$ takes part to the following chemical reactions (Haut, 2004; Rhem et al., 1963):

\[
\begin{align*}
\text{CO}_2 + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- \\
\text{HCO}_3^- + \text{OH}^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}
\end{align*}
\]

(1)  (2)

Reaction kinetics are supposed to be first order relative to the concentrations, as written below (Vas Bhat et al., 2000; Cents et al., 2005):

\[
r_1 = k_{11}[\text{CO}_2][\text{OH}^-] - k_{12}[\text{HCO}_3^-]
\]

(3)
\[ r_2 = k_{21} [\text{HCO}_3^-][\text{OH}^-] - k_{22} [\text{CO}_3^{2-}] \]  \hspace{1cm} (4)

\( r_1 \) and \( r_2 \) are respectively the reaction rates of reaction (1) and reaction (2).

Reaction (1) consumes \( \text{CO}_2 \) provided by the gaseous phase and subsequently changes the chemical balance of the reaction (2). Reaction (1) is like a "\( \text{CO}_2 \) pump". The mass transfer rate is higher than without reactions. These reactions affect the \( \text{CO}_2 \) concentration gradient at the interface, and the altered reagent introduction rate affects backward the reaction rates.

The one-dimensional transport-reaction equations are obtained from mass balances on an infinitesimal element of the quiescent liquid. To find the concentrations of all species at all time, a four PDE (Partial Differential Equations) system has to be solved. These PDE have the following form (Danckwerts, 1970; Bird et al., 2002):

\[
\frac{\partial [A]}{\partial t} = \frac{\partial}{\partial x} \left( D_A \frac{\partial [A]}{\partial x} \right) - \sum_i \nu_{A,i} r_i \hspace{1cm} (5)
\]

with \( \nu_{A,i} \) the stoichiometric coefficient of the species \( A \) taking part to the \( i \)th reaction.

The system has four initial conditions (one by species):

\[
[A]_{x,t=0} = [A]_{\text{bulk}} \hspace{1cm} (6)
\]

At the interface, the \( \text{CO}_2 \) concentration is supposed to be in the equilibrium state with the gaseous phase. Therefore the following boundary condition is used:

\[
[\text{CO}_2]_{x=0,t} = [\text{CO}_2]_{\text{interface}} = h \frac{p_{\text{CO}_2}}{RT} \hspace{1cm} (7)
\]

where \( h \) is the \( \text{CO}_2 \) concentration ratio between liquid and gaseous phase, when the interface is in the chemical equilibrium state. It is assumed that other species do not diffuse throughout the interface:

\[
\frac{\partial [A]}{\partial x} \bigg|_{x=0,t} = 0 \hspace{1cm} (8)
\]

Far from the interface (bulk), homogeneity is reached:

\[
\lim_{x \to \infty} \frac{\partial [A]}{\partial x} \bigg|_{x,t} = 0 \hspace{1cm} (9)
\]

Such a system does not have an analytical solution. Therefore, it is solved numerically, by the finite element method, with the COMSOL Multiphysics software. This is a numerically stiff problem because of the differences between the order of magnitude of some parameters of the model, such as the bulk concentrations and the kinetic constants. \( \text{CO}_2 \) and \( \text{OH}^- \) bulk concentration are about four
order of magnitude lower than $\text{HCO}_3^-$ and $\text{CO}_2^{2-}$ bulk concentration and $k_{11}$ is five order of magnitude lower than $k_{21}$.

Numerical solving allows to find out the concentration profiles of all the species in the liquid near the interface. An example of dimensionless concentration profiles are given in figure 2. The concentration of each species is divided by a reference concentration. For the $\text{CO}_2$, the reference is the concentration at the interface. For the other species, the reference concentrations are those in the bulk. The conditions for this example are specified on the figure. If the system is solved from $t = 0$ until $t = t_c$, then the $x$-axis is discretized from $x = 0$ until $x = 4\sqrt{D_{\text{CO}_2}t_c}$. Indeed, it has been checked that the concentrations profiles do not change anymore after $x = 4\sqrt{D_{\text{CO}_2}t_c}$ and that the solution is independent of the space size when the upper-boundary is larger than $4\sqrt{D_{\text{CO}_2}t_c}$.

Figure 2: Dimensionless concentration profiles of $\text{CO}_2$, $\text{OH}^-$, $\text{HCO}_3^-$ and $\text{CO}_2^{2-}$

From the $\text{CO}_2$ concentration profile, the mass quantity crossing the interface can be deduced, by unit of time and interfacial area:

$$F_{\text{CO}_2}(t) = -D_{\text{CO}_2} \left. \frac{\partial [\text{CO}_2]}{\partial x} \right|_{0,t}$$

(10)

The physico-chemical parameters of the transport-reaction equations are not constant. The major part of them depends on the temperature. Some depend on the composition too. They are obtained from correlations found in the literature or provided by Solvay (see appendices). However, it has been checked that the variations of these parameters in the liquid during the transfer are negligible. They are calculated for the given initial conditions and they are supposed to remain constant.
2.2 Model of bubble-liquid mass transfer

In a BIR column, CO₂ is transferred from bubbles rising up to the top of the column. The gas to liquid relative velocity of a bubble in the BIR column, \( G \), is about 0.2 m/s (Haut & Cartage, 2005). The bubble diameter lies therefore between 1 mm and 1 cm.

The liquid phase in the vicinity of the interface of a bubble can be seen as a mosaic of liquid elements continuously renewed. Since the depth of the diffusion boundary layer is much smaller than the bubble diameter, the gas-element interface is supposed to be a plan.

For the mass transfer, these elements can be considered as being semi-infinite (Haut, 2004; Levich, 1962). During the bubbles rise, some elements reach the gas bubble interface and slip along the bubbles. They accumulate CO₂, afterward they come back into the bulk, as it is schematically represented in figure 3. The existence of velocity gradients within a fluid element is ignored (Coulson & Richardson, 1999). Therefore, the liquid flow rate in an element, for an observer attached to this element, is null, and the transport of CO₂ takes place only by diffusion in a direction normal to the interface.

![Figure 3: Schematic view of the liquid flow around a rising bubble](image)

It is assumed that each element stays in contact with the liquid a constant time \( t_c \). Therefore, elements around the bubble have an age distribution that is called the Higbie age distribution (Danckwerts, 1955; Coulson & Richardson, 1999). The age distribution function is:

\[
\xi(t) = \begin{cases} 
\frac{1}{t_c} & \text{for } t \leq t_c \\
0 & \text{for } t > t_c 
\end{cases} 
\]  

(11)

In the Higbie approach, \( t_c \) is commonly taken equal to \( \frac{d_b}{G} \), where \( d_b \) is the bubble diameter. Other correlations like the one presented in (Haut & Cartage, 2005).
2005) can be used to calculate \( t_c \) (see appendices). It is this last correlation which is used in this work.

At all time, the CO\(_2\) transfer rate from a bubble into a liquid element in contact with its interface is a function of the liquid side CO\(_2\) concentration gradient at the interface. The transport-reaction model in a quiescent liquid is thus completed by the Higbie age distribution of liquid elements. Consequently, the mean CO\(_2\) flux density, by unit of time and interfacial area, is expressed by:

\[
\overline{J}_{CO_2, Higbie} = -\frac{D_{CO_2}}{t_c} \int_0^{t_c} \frac{\partial [CO_2]}{\partial x} \bigg|_{x=0} \, dt
\]  

(12)

A numerical estimation is calculated by a MATLAB program coupled with the numerical solving of the transport-reaction model in a quiescent liquid with COMSOL Multiphysics.

In figure 4, the contours of \( \overline{J}_{CO_2, Higbie} \) as a function of the NaHCO\(_3\) and Na\(_2\)CO\(_3\) concentrations in the bulk (in g/(kg brine)) are presented. The bubble diameter is 5 mm (contact time \( t_c = 0.04 \) s). The considered temperature and CO\(_2\) pressure are respectively 338 K and 1.2 bar. These conditions are representative of the conditions in a BIR bubble column.

![Figure 4: Contours of \( \overline{J}_{CO_2, Higbie} \) (mol/m\(^2\) s) as a function of the brine bulk composition, for \( t_c = 0.04 \) s](image)

In extension of this work, a simplification of the bubble-liquid mass transfer model is investigated. Indeed, the equation system is complex and the equations of the model have to be solved numerically, using COMSOL Multiphysics and MATLAB softwares. This method of resolution is awkward to integrate in a BIR column complete model.
To simplify the model, the CO$_2$ is supposed taking part to only one first order reversible reaction and the OH$^-$ concentration is supposed to remain constant. The simplified reaction rate $r^*$ is written:

$$r^* = k^* [\text{OH}^-]_{\text{bulk}} ([\text{CO}_2]^* - [\text{CO}_2]_{\text{bulk}})$$  \hspace{1cm} (13)

where $k^*$ is a pseudo kinetic constant. It is an adjustable parameter to be identified for each couple of NaHCO$_3$/Na$_2$CO$_3$ concentrations.

In the frame of this simplified model, there is only one diffusion-reaction equation to be solved. This equation has the following form:

$$\frac{\partial [\text{CO}_2]^*}{\partial t} = D_{\text{CO}_2} \frac{\partial^2 [\text{CO}_2]^*}{\partial x^2} - k^* [\text{OH}^-]_{\text{bulk}} ([\text{CO}_2]^* - [\text{CO}_2]_{\text{bulk}})$$  \hspace{1cm} (14)

Again, the Higbie age distribution is used to model the liquid flow around a bubble, and the mean CO$_2$ flux density, by unit of time and interfacial area, is expressed by:

$$\overline{F}_{\text{CO}_2, \text{Higbie}}^* = -\frac{D_{\text{CO}_2}}{t_c} \int_0^{t_c} \frac{\partial [\text{CO}_2]^*}{\partial x} \bigg|_{x=0,t} dt$$  \hspace{1cm} (15)

This equation has an analytical solution. Using initial condition (6), and boundary conditions (7) and (9), the solution of (15) is:

$$\overline{F}_{\text{CO}_2, \text{Higbie}}^* = ([\text{CO}_2]_{\text{int}} - [\text{CO}_2]_{\text{bulk}}) \sqrt{\frac{D_{\text{CO}_2}}{k^* [\text{OH}^-]_{\text{bulk}}}} \left( k^* [\text{OH}^-]_{\text{bulk}} + \frac{1}{2t_c} \right) \text{erf} \left( \sqrt{k^* [\text{OH}^-]_{\text{bulk}} t_c} \right)$$

$$+ \frac{k^* [\text{OH}^-]_{\text{bulk}}}{\pi t_c} \exp \left( -k^* [\text{OH}^-]_{\text{bulk}} t_c \right)$$

(16)

This solution is obtained using Laplace transforms. This analytical expression is well-suited for an integration in a complete model of a BIR column.

$k^*$ is calculated to satisfy $\overline{F}_{\text{CO}_2, \text{Higbie}}^* = \overline{F}_{\text{CO}_2, \text{Higbie}}$. It has the same dimension than $k_{11}$ in the non-simplified model. In order to quantify the difference between $k_{11}$ et $k^*$, the $k^*/k_{11}$ ratio is computed as a function of the NaHCO$_3$ and Na$_2$CO$_3$ concentrations in the bulk. The contours of the $k^*/k_{11}$ are presented in figure 5, for the pressure, temperature and contact time conditions of the BIR columns. It is observed that this ratio changes with the brine bulk composition.

In figure 6, the concentration profiles for two different couples of brine composition are presented. On the left side, the considered brine composition is
Figure 5: Contours of the $k^*/k_{11}$ ratio as a function of the NaHCO$_3$ and Na$_2$CO$_3$ concentrations in the bulk, when T=338K - $p_{CO_2}$=1.2bar - $t_c$=0.04s

$[\text{NaHCO}_3]$=100g/kg - $[\text{Na}_2\text{CO}_3]$=100 g/kg. The corresponding $k^*/k_{11}$ ratio is about 0.97 (close to 1). It can be noted that the OH$^-$ concentration at the interface is very close to the OH$^-$ bulk concentration. On the right side, the brine composition is $[\text{NaHCO}_3]$=20 g/kg - $[\text{Na}_2\text{CO}_3]$=100 g/kg. This time, the ratio is about 0.75. The OH$^-$ concentration at the interface differs from the OH$^-$ bulk concentration: $[\text{OH}^-]_{int} \approx 0.7 [\text{OH}^-]_{bulk}$.

Figure 6: Dimensionless concentration profiles for two different brine composition, when T=338K - $p_{CO_2}$=1.2bar - $t_c$=0.04s
Therefore, these discrepancies between $k_{11}$ and $k^*$ are observed when the hypothesis $[OH^-] = [OH^-]_{bulk}$ is not reached at the interface during the entire contact time. If the ratio is close to 1, it is correct to use $k^* = k_{11}$ in the simplified model to compute the average bubble-liquid $CO_2$ transfer rate. Otherwise, it is preferable to use a fitted value of $k^*$ to calculate $\overline{F}_{CO_2, Higbie}$.

The brine composition in the BIR columns is such that the $k^*/k_{11}$ ratio is very close to 1. This simplified model for the mean $CO_2$ flux density calculation is then well-suited to be integrated in a future complete model of BIR column with $k^* = k_{11}$.

3. EXPERIMENTAL VALIDATION PROSPECTS

Since the multiscale approach is followed for the modelling, two different experimental devices are proposed, one for each scale of modelling.

First, an original experimental device is set up. A NaHCO$_3$-Na$_2$CO$_3$ brine is put in contact with gaseous $CO_2$ in a Hele-Shaw cell (small gap between two transparent plates). The time evolution of the $CO_2$ concentration profile is proposed to be determined from the liquid phase refractive index profile, followed using a Mach-Zehnder interferometer.

On the other hand, a stirred tank reactor is filled with a NaHCO$_3$-Na$_2$CO$_3$ brine and pure $CO_2$ bubbles are dispersed through the liquid. The dissolved $CO_2$ concentration and pH are measured against time. The bubble-liquid mass transfer model is incorporated into a model of the stirred tank reactor, developed with MATLAB. Experimental results are compared to the simulations performed with this model.

3.1 Validation of the model of coupling between mass transfer and chemical reaction in a quiescent liquid

A pure $CO_2$ gas flow is put in contact with an aqueous NaHCO$_3$ and Na$_2$CO$_3$ solution in a Hele-Shaw cell. The liquid is confined between two glass plates (5cm x 10cm). The gap between the two plates is 1 mm. This cell is set in a Mach-Zehnder interferometer (Hecht, 1987). A block diagram is given in figure 7. This experimental device allows to follow the time evolution of the refractive index profile in the liquid phase near the gas-liquid interface, caused by the $CO_2$ transfer.

A source emits a laser beam (wavelength $\lambda$=632.8 nm) towards a beam-splitter. The beam is split into two identical beams : a reference beam and an object beam. The reference beam passes through the air while the object beam passes through the cell and the content of the cell. The two beams are combined by a
beam-combiner and they are directed through a photo objective towards a CCD camera. The optical paths of the two beams are different, so the combined beam presents interference fringes.

During the transfer, the CO$_2$, the OH$^-$, the HCO$_3^-$ and the CO$_3^{2-}$ concentrations change near the interface, which affects the refractive index of the liquid. Consequently, the optical path of the object beam changes as well. A bending of the interference fringes is therefore observed in the liquid phase near the interface during the transfer.

It has been checked by a theoretical estimation, with COMSOL Multiphysics software, that the heat of reactions and absorption do not produce significant refractive index gradients in the vicinity of the interface. The temperature in the liquid remains homogeneous. Consequently, the temperature variations do not affect the refractive index.

It can be demonstrated that the fringe bending between the bulk of the liquid and the interface is proportional to the refractive index variation $\Delta n_{int-bulk}$. It is the difference between the interface refractive index and the bulk refractive index, following this relation:

$$\Delta n_{int-bulk} = n_{int} - n_{bulk}$$

(17)

An image, acquired with the interferometer, is presented in figure 8. The temperature is 293K. The initial NaHCO$_3$ and Na$_2$CO$_3$ concentrations are 60 g/kg. The CO$_2$ pressure is 1 bar. The interference fringe bending is clearly visible. This interferogram can be processed to extract the object beam phase variations, that are directly correlated to the refractive index variations in the experimental cell. The method is described by (Kreis, 1986). This processing allows determining the refractive index profile near the interface.

An example of the refractive index variations profiles at different times are presented in figure 9. $x$ is the depth in the liquid from the interface. $x = 0$ is the
approximate position of the interface since it is not-well defined because of the low quality of the images. These profiles are deduced from the interferograms observed during the same experiment to which figure 8 corresponds.

The refractive index variations are caused by the CO$_2$ transfer. To validate experimentally the model of the coupling between mass transfer and chemical reactions in a quiescent liquid, a calibration curve is preliminarily required. A model correlating the refractive index variations in function of the transferred CO$_2$ is currently in development. Moreover, before more experiments will be run, some revision of the device are needed in order to improve the quality of the interferograms and the refractive index variations profiles.

Nevertheless, the results obtained with the interferometer and the proposed interferogram processing method are promising and the validation of the model of the coupling between mass transfer and chemical reactions in a quiescent liquid will be presented in a future work.

### 3.2 Validation of the bubble-liquid mass transfer model

In order to validate the model to predict the mean CO$_2$ flux density, by unit of time and interfacial area, measurements in an isothermal stirred tank reactor are performed. This reactor is cylindrical and it is filled with a NaHCO$_3$ and Na$_2$CO$_3$ aqueous solution of given composition. The solution volume is 8 dm$^3$ and the temperature is 298 K. A constant bubble gas flow passes through the liquid. The gas flow rate is set to 1 dm$^3$/min and the CO$_2$ pressure is 1 bar. The diameter of the generated bubble is 1.5 mm. The rotating speed of the stirrer is constant (set to 180 rpm) and the liquid is assumed perfectly mixed. The mass transfer modifies gradually the liquid concentrations.
The concentration evolution rate is a function of $F_{CO_2,Higbie}$. pH and dissolved CO$_2$ concentration are followed against time. With these informations, the concentrations of all species can be determined. Indeed, the chemical equilibrium state is assumed to be reached far from the bubble-liquid interface at all time. Let $K_1$ and $K_2$ be the equilibrium constants of reactions (1) and (2). The following equations can be written:

$$K_1 = \frac{[HCO_3^-]}{[CO_2][OH^-]}$$ \hspace{1cm} (18)

$$K_2 = \frac{[CO_3^{2-}]}{[HCO_3^-][OH^-]}$$ \hspace{1cm} (19)

Let $S_e$ be the total gas-liquid interfacial area. The transferred CO$_2$ mole number, $m_{CO_2}$, during a time interval between $t$ and $t + \Delta t$, is a function of $S_e$ and $F_{CO_2,Higbie}$. Let $[CO_2](t), [OH^-](t), [HCO_3^-](t)$ and $[CO_3^{2-}](t)$ be the species concentrations in the brine at the time $t$. $m_{CO_2}(t)$ is expressed by:

$$m_{CO_2}(t) = S_e F_{CO_2,Higbie} (t_c, [CO_2](t), [OH^-](t), [HCO_3^-](t), [CO_3^{2-}](t)) \Delta t \hspace{1cm} (20)$$

This CO$_2$ inflow causes a displacement of the equilibria. Let $\alpha$ and $\beta$ be the quantities of which the equilibria of the reaction (1) and (2) are displaced respectively. The brine composition at the time $t + \Delta t$ is then given by:

$$[CO_2](t + \Delta t) = [CO_2](t) + \frac{m_{CO_2}(t)}{V_{brine}} - \alpha(t)$$ \hspace{1cm} (21)
\[
\begin{align*}
&\left[\text{OH}^-\right] (t + \Delta t) = \left[\text{OH}^-\right] (t) - \alpha(t) - \beta(t) \\
&\left[\text{HCO}_3^-\right] (t + \Delta t) = \left[\text{HCO}_3^-\right] (t) + \alpha(t) - \beta(t) \\
&\left[\text{CO}_3^{2-}\right] (t + \Delta t) = \left[\text{CO}_3^{2-}\right] (t) + \beta(t)
\end{align*}
\] (22) (23) (24)

Using equilibrium equations (18) and (19), \( \alpha(t) \) and \( \beta(t) \) are computed and concentrations at the time \( t + \Delta t \) can be calculated. So, the bubble-liquid mass transfer model, coupled with balance equations in the perfectly mixed liquid bulk, is applied to predict the pH and dissolved CO\(_2\) concentration against time, in an iterative manner. This model contains two adjustable parameters: the contact time \( t_c \) and the total exchange interfacial area \( S_e \).

Comparison between experimental and theoretical results are presented in figures 10 and 11. The contact time is \( t_c = 0.02s \). It is deduced from the correlation of (Haut & Cartage, 2005) for a bubble diameter \( d_b = 1.5\text{mm} \). \( S_e \) is adjusted to \( S_e = 0.031\text{m}^2 \), in order to minimize the difference between experimental and theoretical curves.

In figure 10, the pH evolution against time is presented. A good agreement between experimental results and the simulation is observed. In figure 11, the experimental and theoretical time evolutions of the total amount of CO\(_2\) transferred in the liquid phase are presented.

Figure 10: Experimental and theoretical pH evolutions against time (\( T = 293K \) - initial NaHCO\(_3\) concentration=10 g/kg - initial Na\(_2\)CO\(_3\) concentration=30 g/kg - \( p_{CO_2} = 1\text{bar} \) - gas flow=1dm\(^3\)/min - stirring speed=180rpm)
Figure 11: Experimental and theoretical evolutions of the total amount of CO\textsubscript{2} transferred in the liquid phase (T=293K - initial NaHCO\textsubscript{3} concentration=10 g/kg - initial Na\textsubscript{2}CO\textsubscript{3} concentration=30 g/kg - $p_{\text{CO}_2}=1$bar - gas flow=1dm\textsuperscript{3}/min - stirring speed=180rpm)

From this result, it is showed that the bubble-liquid mass transfer model for the perfectly mixed stirred tank reactor is able to reproduce the evolution of pH and cumulated transferred CO\textsubscript{2}. A similar comparison is observed for other couple of NaHCO\textsubscript{3}-Na\textsubscript{2}CO\textsubscript{3} initial brine composition.

4. CONCLUSION AND PERSPECTIVES

A multiscale approach is followed to develop a model to calculate the mean CO\textsubscript{2} flux density, by unit of time and interfacial area, from bubbles in a BIR column.

A mathematical model of the coupling between mass transfer and chemical reactions in a quiescent liquid has been first developed. Equations of the model are solved numerically by the finite element method, with COMSOL Multiphysics software. Solving allows to determine the concentration profiles developing near the gas-liquid interface. From the CO\textsubscript{2} concentration profile, the CO\textsubscript{2} transfer rate passing through the interface can be deduced.

This model is completed by a representation of the liquid flow around a gas bubble, using a Higbie age distribution. This model of the bubble-liquid mass transfer is applied to calculate the mean CO\textsubscript{2} flux density, by unit of time and interfacial area, from bubble into liquid in the case of absorption into a NaHCO\textsubscript{3} and Na\textsubscript{2}CO\textsubscript{3} brine. This operation is performed in the BIR bubble columns.
Moreover, a simplification of this last model is investigated. The proposed simplified model has an analytical solution for the mean CO\textsubscript{2} flux density calculation, well-suited to be integrated in a future complete model of BIR column, with \( k^* = k_{11} \).

To validate the models, an experimental device is proposed for each scale of modelling. First, a Mach-Zehnder interferometer is proposed to study the CO\textsubscript{2} transfer by following the time evolution of the refractive index variation profile developing near the interface of quiescent NaHCO\textsubscript{3} and Na\textsubscript{2}CO\textsubscript{3} brine during the CO\textsubscript{2} absorption. The device is now finalized but some improvements of the interferogram quality are desirable. A model to create a calibration curve is in development. Soon, this device will allow the validation of the model of the coupling between mass transfer and chemical reaction in a quiescent liquid.

On the other hand, a stirred tank reactor is proposed in order to validate the bubble-liquid mass transfer model. The device is finalized and many experiments were performed. Experiments showed that this model, coupled with mass balances in the perfectly mixed stirred tank reactor, is able to reproduce the evolution of pH and cumulated transferred CO\textsubscript{2}. The identification of the adjustable parameter \( S_e \) of this model for different brine composition has to be run. A cross validation of the bubble-liquid mass transfer model will be performed after the identification of these parameters.

**NOTATION**

\[
\begin{align*}
[A] & \quad \text{concentration of A} & \text{mol m}^{-3} \\
\bar{d}_b & \quad \text{bubble diameter} & \text{m} \\
D_A & \quad \text{diffusion coefficient of A} & \text{m}^2 \text{s}^{-1} \\
E_o & \quad \text{Eotvos number} & - \\
F & \quad \text{Faraday constant} & \text{C mol}^{-1} \\
F_{\text{CO}_2} & \quad \text{instantaneous interfacial CO}_2 \text{ transfer rate} & \text{mol m}^{-2} \text{s}^{-1} \\
\bar{F}_{\text{CO}_2} & \quad \text{mean CO}_2 \text{ flux density from bubble into liquid} & \text{mol m}^{-2} \text{s}^{-1} \\
G & \quad \text{gas to liquid relative velocity of a bubble} & \text{m s}^{-1} \\
h & \quad \text{liquid-gas concentration ratio of CO}_2 \text{ at the interface} & - \\
k^* & \quad \text{pseudo kinetic constant} & \text{mol m}^3 \text{s}^{-1} \\
k_{11} & \quad \text{kinetic constant of forward reaction (1)} & \text{mol}^3 \text{mol}^{-1} \text{s}^{-1} \\
k_{12} & \quad \text{kinetic constant of backward reaction (1)} & \text{s}^{-1} \\
k_{21} & \quad \text{kinetic constant of forward reaction (2)} & \text{mol}^3 \text{mol}^{-1} \text{s}^{-1} \\
k_{22} & \quad \text{kinetic constant of backward reaction (2)} & \text{s}^{-1} \\
K_1 & \quad \text{equilibrium constant of reaction (1)} & \text{mol}^3 \text{mol}^{-1}
\end{align*}
\]
$K_2$ equilibrium constant of reaction (2) m$^3$ mol$^{-1}$

$K_w$ ionic product of water mol$^2$ m$^{-6}$

$m_{CO_2}$ transferred CO$_2$ mole number mol

$n$ refractive index 

$p_{CO_2}$ CO$_2$ pressure in gaseous phase bar

$r_1$ reaction rate of reaction (1) mol m$^{-3}$ s$^{-1}$

$r_2$ reaction rate of reaction (2) mol m$^{-3}$ s$^{-1}$

$R$ perfect gas constant J mol$^{-1}$ K$^{-1}$

$S_e$ interfacial exchange area between gas and liquid m$^2$

$t$ time s

$t_c$ contact time of a liquid element with gas s

$T$ absolute temperature K

$V_{brine}$ brine volume in the stirred tank reactor m$^3$

$W$ ratio small/great axis of an ellipsoidal bubble 

$x$ distance on a normal direction of the interface and pointing toward the liquid phase m

Greek letters

$\alpha$ quantity of which the reaction 1 equilibrium is displaced mol m$^{-3}$

$\beta$ quantity of which the reaction 2 equilibrium is displaced mol m$^{-3}$

$\lambda$ wavelength of the laser beam m

$\mu$ viscosity Pa s

$\nu$ stoichiometric coefficient -

$\xi$ age distribution function s$^{-1}$

$\rho$ density kg m$^{-3}$

$\sigma$ surface tension of the gas liquid interface of a bubble N m

Subscripts

$bulk$ far from the interface ($x \rightarrow \infty$)

$Higbie$ relative to the Higbie age distribution

$int$ at the interface

$w$ pure water

Superscripts

* simplified model
APPENDICES

CO₂ solubility

The CO₂ solubility in the solution is represented by $h$. It is the CO₂ concentration ratio between liquid and gaseous phase, when the interface is in the chemical equilibrium state:

$$h = \frac{[\text{CO}_2]_{\text{int}}}{p_{\text{CO}_2,\text{int}} RT}$$

with $[\text{CO}_2]_{\text{int}}$ the CO₂ concentration at the interface in the liquid phase and $p_{\text{CO}_2,\text{int}}$ the pressure of CO₂ at the interface in the gaseous phase.

In pure water, $h = h_w$, and it is estimated by the following expression (Vas Bhat et al., 2000):

$$h_w = 3.59 \times 10^{-7} RT \exp \left( \frac{2044}{T} \right)$$

The CO₂ solubility is affected by the presence of ions. The solubility decreases if the ion concentration increases. In the presence of ions, $h$ is calculated by (Vas Bhat et al., 2000; Schumpe, 1993; Pohorecki & Moniuk, 1988; Taghizadeh et al., 2001):

$$h = h_w 10^{-\left(9.88 \times 10^{-5} [\text{Na}^+] + 5.73 \times 10^{-5} [\text{OH}^-] + 1.189 \times 10^{-4} [\text{HCO}_3^-] + 1.483 \times 10^{-4} [\text{CO}_3^{2-}]\right)}$$

Diffusion coefficients

The diffusion coefficient of CO₂ is obtained from (Pohorecki & Moniuk, 1988):

$$D_{\text{CO}_2} = D_{\text{CO}_2,w} \frac{\mu_w}{\mu}$$

with the CO₂ diffusion coefficient in pure water, $D_{\text{CO}_2,w}$, calculated by:

$$D_{\text{CO}_2,w} = 10^{-8.1764 + 712.52/T - 259070/T^2}$$

The diffusion coefficients of the other species are estimated using the following correlations (Vas Bhat et al., 2000):

$$D_{\text{OH}^-} = \left(-0.1925 + 1.2291 \sqrt{T}\right) 10^{-3} \frac{RT}{T^2}$$

$$D_{\text{HCO}_3^-} = 4.45 \times 10^{-3} \frac{RT}{T^2}$$

$$D_{\text{CO}_3^{2-}} = \left(3.11 \times 10^{-5} + 2.63 \times 10^{-10} (T)^3\right) \frac{RT}{2T^2}$$
Equilibrium constants

The equilibrium constant of the reaction (1), $K_1$, is a function of the temperature and the density of the solution. It is calculated using (Edwards et al., 1978):

$$K_1 = \frac{1}{K_w} \exp \left( \frac{-12092.1}{T} - 36.786 \ln(T) + 235.482 \right) \rho_w$$ (33)

with $K_w$, the ionic product of water, given by (Vas Bhat et al., 2000):

$$K_w = 10^{(-5839.5\frac{T}{T} + 22.4773 \log(T) - 61.2062)} \rho_w^2$$ (34)

The equilibrium constant of the reaction (2), $K_2$, is a function of the temperature, the density and the ionic strength of the solution. A correlation taking into account the ionic strength is available in the literature (Vas Bhat et al., 2000). However, other works have shown that it leads to an underestimation of $K_2$ (Cents et al., 2005). In this work, the value of $K_2$ at infinite dilution is used:

$$K_2 = 10^{\left(\frac{1568.924}{T} - 2.5865 - 6.737 \times 10^{-3} T\right)}$$ (35)

Kinetic constants

The kinetic constant of the forward reaction (1), $k_{11}$, is calculated with the following expression (Pohorecki & Moniuk, 1988; Taghizadeh et al., 2001; Aroonwilas et al., 2003):

$$k_{11} = 10^{\left(8.916 - \frac{2383}{T}\right)} 10^{\left(6 \times 10^{-5} [\text{Na}^+] + 1.1 \times 10^{-4} [\text{OH}^-] + 1.7 \times 10^{-4} [\text{CO}_3^{2-}]\right)}$$ (36)

The kinetic constant of the backward reaction (1), $k_{12}$, is calculated from $k_{11}$ and the equilibrium constant $K_1$:

$$k_{12} = \frac{k_{11}}{K_1}$$ (37)

Since reaction (2) involves proton transfer, it is extremely faster than reaction (1). The value of the kinetic constant of the forward reaction (2), $k_{21}$, is not known accurately. In this work, a value of $10^7$ m$^3$mol$^{-1}$s$^{-1}$ (Vas Bhat et al., 2000) is used.

The kinetic constant of the backward reaction (2), $k_{22}$, is calculated from $k_{21}$ and the equilibrium constant $K_2$:

$$k_{22} = \frac{k_{21}}{K_2}$$ (38)
Density and viscosity

The density of the solution, $\rho$, and the viscosity, $\mu$, are function of the brine composition. They are calculated from correlations provided by Solvay.

Contact time

For bubble of diameter between 1 mm and 1 cm, the contact time $t_c$ is calculated with the correlation of (Haut & Cartage, 2005). For this diameter range, the bubbles have an ellipsoidal shape. The ratio between small axis and great axis is given by the correlation of Welleck:

$$W(d_b) = \frac{1}{1 + 0.163E_o^{0.757}}$$

(39)

where $E_o = \frac{g_d d_b}{\sigma}$ is the Eotvos number of the bubble. The contact time $t_c$ is computed from:

$$t_c = \frac{2d_b}{3} \frac{1 + W(d_b)^2}{G^{2/3} W(d_b)^{4/3} (3 + W(d_b)^2)^{1/3}} \arccos \left( \frac{1-W(d_b)^2}{1+W(d_b)^2} \right)^2$$

(40)

REFERENCES


