A Mass Transfer Model of Absorption of Carbon Dioxide in a Bubble Column Reactor by Using Magnesium Hydroxide Slurry

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Introduction

A novel CO₂ scrubbing process, using Mg(OH)₂ slurry as the removal agent, has been proposed and investigated at the University of Cincinnati. The proposed Flue Gas Decarbonation system (FGDC) consists of a bubble column reactor, where the magnesium hydroxide slurry is injected at the top of the reactor to encounter the fine flue gas bubbles which are introduced through a fine fritted glass bubbler at the bottom of the reactor. The FGDC system also has a desorption reactor in order to increase the magnesium utilization, where the rich slurry is regenerated by applying the means of thermal-pressure swing. In the meantime, concentrated CO₂ in the gas stream is collected. The absorption of CO₂ from the flue gas is accomplished at 52 °C which falls into the typical range of Flue Gas Desulfurization (FGD) outlet temperature. Therefore, the unit may be retrofitted or attached to FGD system without modification of the existing boiler-heat transfer configuration. In addition, compared to the most widely used solvents, such as MEA, ammonia, ionic solution, and PZ-K₂CO₃ solution, magnesium hydroxide slurry is non-toxic, non-flammable, non-corrosive and odorless milky solution and can be reclaimed (Lani, 1998) from any limestone based FGD sorbents or obtained from commercial sources at a reasonable price. Bubble column is selected as the gas-liquid contacting device for this study due to the simple internal design, good mass transfer performance and great ability of handing solid containing solution or slurry for the magnesium slurry test. The tests using magnesium hydroxide demonstrate comparable CO₂ removal efficiencies to the MEA, NaOH, ammonia, ionic solution these solvents. The purpose of this study is to investigate the chemical reaction mechanisms and the mass transfer phenomena in the absorption process, and to develop a bubble column absorber model to assist in the understanding of the mass transportation of CO₂ removal within a gas-liquid-solid system.

Model development

The whole scrubbing process may be characterized as physical absorption of CO₂ in water coupled with 1). Ionic reactions between dissolved CO₂ and magnesium ions; and 2). Solid dissolution of magnesium particles. Therefore, this paper will first present physical absorption case of CO₂-H₂O and then absorption with chemical reactions case of CO₂-Mg(OH)₂ as following.
Physical absorption of CO₂-H₂O

Bubble column is preferred to operating under homogeneous conditions which the flow motion falls into the laminar flow regime (Shah et al., 1982; Treybal, 1967). This bubbly flow may give more uniform and smaller bubbles resulting larger surface area and longer retention time. Under such flow regime, liquid phase and bubble phase coexists. Therefore, the system may be described by the two film theory model. The model is based on the main assumptions: the liquid phase is well mixed and the gas phase is in plug flow. Absorption rate, $\frac{dC_l}{dt}$, can be expressed in terms of gas or liquid side mass transfer coefficient based on the film theory:

$$ \frac{dC_l}{dt} = \frac{C_g - C_l}{h_{fl}} $$

and $C_g$ are CO₂ concentrations at the gas-liquid interface following the Henry’s Law.

The interfacial compositions cannot be determined. Instead, the bulk driving force which may be characterized as overall mass transfer coefficient can be applied. Therefore, the absorption rate can be written as:

$$ \frac{dC_l}{dt} = \frac{C_g - C_l}{h_{bl}} $$

The CO₂ partial pressure in the bubble will change with the position in the column. Here, it is assumed that a pseudo-steady state condition exists between the CO₂ partial pressure of the bubble and the CO₂ concentration in the liquid. Therefore, the Equation (4) can be rewrite as:

$$ \frac{dC_l}{dt} = \frac{C_g - C_l}{h_{bl}} $$

Perform a mass balance on CO₂ in the bubble as it rises up the column in the x direction assuming a pseudo-steady state condition.

Letting $-\frac{d}{dt}$, $C_l$, then:

$$ \int_{z=0}^{z=1} \frac{dC_l}{dt} \, dz = \frac{C_g - C_l}{h_{bl}} $$

This is the governing equation for bubble column absorption. It expresses the change of concentration of CO₂ in the liquid in terms of the bubble CO₂ partial pressure which is changing with respect to the position in the liquid column, z. Therefore, the average CO₂ concentration in the bubble can be found by integrate Equation (7) between the limits of $z=0$, $p_A=p_0$ and $z=1$:
Substitute the average bubble CO₂ concentration into the Equation (5), integrated with respect to the time:

(9)

Where:

Then, solve for overall mass transfer coefficient as:

(10)

This equation revealed that the overall mass transfer rate is depend on the hydrodynamic parameters, equilibrium constant, CO₂ partial pressure in the gas phase and the temperature. In addition, it is necessary to calculate the total dissolved carbon and pH when system reaches the equilibrium. These numbers provide the quality assurance when we perform the experiment data analysis.

**Absorption with reaction of CO₂-Mg(OH)₂ system**

The major reactions in the system are: gas absorption and diffusion, ionic ions reactions at liquid phase, solid dissolution and diffusion. It is assumed that the reaction between dissolved CO₂ and the magnesium ions is instantaneous with respect to the mass transfer. Therefore, the chemical reaction is viewed as an enhancement factor for the process; while the gas side mass transfer and the dissolution of solid magnesium hydroxide particles are viewed as rate limiting steps. According to the film theory, in order to make CO₂ gas reacts with the magnesium hydroxide slurry, the CO₂ in the gas phase needs to be dissolved and disassociated to form carbonate ions and transferred into the liquid phase; on the other hand, the magnesium hydroxide solid particles need to be dissolved and disassociated as magnesium and hydroxyl ions and transferred into the liquid phase. The reaction will occur at a plane in the liquid at a position close to the gas/liquid interface as these ions reach the reaction zone. The rate will be determined by the mass transfer rate of diffusion of CO₂ and magnesium ions.

The rate of CO₂ absorption in the liquid may be expressed as:

(11)

(12)
The interfacial concentrations are assumed to be at equilibrium and may be related through Henry’s Law. The mass transfer of CO$_2$ and magnesium ions within the film may be explained by the diffusion, therefore, the transfer coefficient for CO$_2$ (A) and magnesium ions (B) in the liquid are related by:

\[ \text{Where } D_A \text{ and } D_B \text{ are the liquid diffusivities of dissolved CO}_2 \text{ and magnesium ions, respectively.} \]

Also, the dissolution rate $r$ may be explained by the diffusivity of magnesium ions in the solution and the film thickness around the solid particle:

Equations listed above can be solved to obtain a rate expression for Mg(OH)$_2$ slurry scrubbing CO$_2$:

Letting $\phi$, the equation becomes

\[ \text{Where } \phi \text{ is the chemical enhancement factor; and } \alpha \text{ is the overall mass transfer coefficient, and the unit is mol/cm}^2\text{-atm-sec:} \]

This is the definition term of the overall mass transfer coefficient. It clearly revealed that physical absorption and diffusion are rate limiting steps; but chemical reactions serve as rate enhancement factor. In order to quantify this coefficient, the rate expression may need to be rewritten as:
Repeat the steps from Equation (7) to (10) to solve for the overall mass transfer coefficient, :  

\[ \text{(20)} \]

This equation allows us to calculate the overall mass transfer coefficient once the amount of carbon removal with respect to time is known.

**Experimental**

The absorption experimental setup consists of six major sections: (1) simulated flue gas generation; (2) flow control; (3) bubble column reactor; (4) gas sampling and analysis; (5) pH, temperature measurement; (6) data acquisition. The experimental setup is shown schematically in Figure 1.

A 130 cm tall, diameter of 10 cm column made of plastic glass with a heating jacket and thermo insulation was used as the main body of the bubble column reactor. 3 sampling ports are respectively located near the top, middle and bottom of the reactor to obtain complete temperature and pH profile of the reactor. Fritted glass size C (porosity 25-50 micron, ACE glass Inc.) was installed at the bottom of the reactor as the gas bubbler. The column was sat on the magnetic stirrer plate which allows magnetic mixing to be applied to the fluid inside the column.

The simulated flue gas is produced by mixing pure CO\textsubscript{2} gas with pure N\textsubscript{2} gas (high purity >99%, Wright Brothers Inc.). Both gas streams are controlled by mass flow controllers (Thermal gas mass flow controller, Cole Parmer Inc.) in order to have desirable CO\textsubscript{2} concentration. The mixed gas stream is heated and maintained at 52 °C which is close to the typical temperature at FGD outlet.

The gas sampling system consists of an in-line flue gas conditioning unit (IMR 400 flue-gas conditioning system, Environmental Equipment Inc.) where the particles in the sample are removed by the filter, and water vapor is removed by passing through the nafion dryer. The pretreated gas sample is then analyzed for CO\textsubscript{2} concentration by an infrared CO\textsubscript{2} gas analyzer (Model ZRH infrared analyzer, California Analytical Instruments Inc.) The CO\textsubscript{2} gas analyzer is periodically calibrated by using pure N\textsubscript{2} (high purity >99%, Wright Brothers Inc), 5% CO\textsubscript{2} and 16% CO\textsubscript{2} (certified grade, CO\textsubscript{2} in N\textsubscript{2}, Purity Plus Gas Inc) standard gases.

Magnesium hydroxide solution is prepared by dissolving magnesium hydroxide powder (industry grade, 81% purity, Garrison Minerals LLC.) into deionized water.

Table 1. Experiment conditions.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet gas temperature</td>
<td>~52 °C</td>
</tr>
<tr>
<td>Liquid temperature</td>
<td>25 to 54 °C</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>0.5 L/min</td>
</tr>
<tr>
<td>Inlet CO₂ concentration</td>
<td>~12 % vol.</td>
</tr>
<tr>
<td>Mg(OH)₂ concentration</td>
<td>0.01 to 1 M</td>
</tr>
<tr>
<td>Liquid volume</td>
<td>2.1 L</td>
</tr>
<tr>
<td>Mixing rate</td>
<td>1200 RPM</td>
</tr>
<tr>
<td>Porosity of gas bubbler</td>
<td>25-50 micron</td>
</tr>
</tbody>
</table>

- \[22\]

*Figure 1. Schematic of the experimental setup.*

**Results and discussion**

**CO₂-H₂O system**

25, 39, 47 and 54°C temperatures have been tested for pure water absorption. The average overall mass transfer coefficient is found from 2.75E-7 to 4.1E-7 mol/cm³-atm-sec. As showed in Figure 2, it was found that the overall mass transfer rate decreases as the temperature increases. This is because that as temperature increases, both diffusivities of CO₂ in air and in water increase leading the individual mass transfer coefficient on gas \(k_g\) and liquid side \(k_l\) to increase; however, the physical absorption governing factor-Henry’s constant decreases as temperature increases. The change of Henry’s constant is greater than the change of individual mass transfer rates; therefore, the overall mass transfer rate is calculated to follow the same trend as Henry’s constant.

\[22\]

Where: ;
If we assume that gas film thickness equals liquid film thickness and they do not change with respect to the temperature. It is found that 0.024 cm is the film thickness.

The increase of temperature also decreased the water absorption capacity on CO₂. It is found that the dissolved carbon concentration at equilibrium decreased from 0.004 mol/L to 0.002 mol/L when temperature increased from 25 to 54 °C.

Figure 3 shows that our model can adequately predict the total carbon concentration in the liquid for CO₂-water absorption process in the bubble column.

![Figure 2 (left graph). Overall mass transfer rate at different temperatures for water absorption.](image1.png)

![Figure 3 (right graph). Comparison of measured value and predicted value of total carbon concentration in the liquid.](image2.png)

Figure 4 shows the relationship of overall mass transfer rate and the concentration of Mg(OH)₂ solutions under the temperature of 25 and 52°C. It is found that higher the concentration of magnesium solutions and higher the temperature, higher the overall mass transfer coefficient. But 0.1M solution only has slightly higher mass transfer rate than 0.05 M solution at both tested temperatures.
Figure 4 (left graph). Overall mass transfer coefficient comparison at temperatures of 25 and 52 °C.

Figure 5 (right graph). Comparison of measured and predicted values of total dissolved carbon.

Figure 5 shows that the predicted and measured values of total dissolved carbon in the liquid for CO$_2$-Mg(OH)$_2$ batch mode operations are close to each other. In addition, a serial of continuous tests for each concentration are conducted. It is confirmed that the model can accurately predict the concentration of dissolved carbon with respect to the time. Therefore, the overall mass transfer coefficient found from batch tests can be used for designing the continuous system in the future.

Table 2 summaries the literature findings on mass transfer coefficients. It is revealed that our system has comparable mass transfer rate as MEA and NaOH’s.

Table 2. Comparison of mass transfer coefficients.

<table>
<thead>
<tr>
<th>Scrubbing agent</th>
<th>Contacting device</th>
<th>Experiment conditions</th>
<th>Mass transfer coefficient, gmol/cm$^3$-atm-second</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA-MDEA(Sema et al., 2012)</td>
<td>Structured DX packed column</td>
<td>T=25-60 °C; C$_{MDEA/MEA}$ = 1.95/1.16, 2.1/0.8, 2.3/0.5 M</td>
<td>2.8E-6 to 2.5E-5</td>
</tr>
<tr>
<td>MEA(Kuntz and Aroonwilas, 2009)</td>
<td>Spray tower and packed tower</td>
<td>T=25 °C; C$<em>{MEA}$ = 3-7 M; P$</em>{CO_2}$ = 0.05-0.15 atm</td>
<td>2.2E-6 to 1.25E-4; 2E-6 to 4.2E-6</td>
</tr>
<tr>
<td>MEA(Luo et al., 2011)</td>
<td>String of discs contactor</td>
<td>T=50 °C; C$_{MEA}$ = 5 M</td>
<td>8.3E-7</td>
</tr>
<tr>
<td>MEA(Chen, 2012; Chen et al., 2008)</td>
<td>Bubble column</td>
<td>T=25-45 °C; P$<em>{CO_2}$ = 0.1-0.3 atm; C$</em>{MEA}$ = 4 M</td>
<td>6.6E-7 to 9.1E-6</td>
</tr>
<tr>
<td>NaOH(Chen et al., 2008)</td>
<td>Packed column</td>
<td>P$<em>{CO_2}$ = 0.1-0.3 atm; C$</em>{NaOH}$ = 2 M</td>
<td>5.4E-7 to 7.7E-6</td>
</tr>
<tr>
<td>NH$_3$(Chen, 2012)</td>
<td>Bubble column</td>
<td>T=25-60°C; P$<em>{CO_2}$ = 0.15-0.6 atm; C$</em>{NH_3}$ = 7.7 M</td>
<td>4.9E-7 to 2.1E-5</td>
</tr>
</tbody>
</table>
Conclusions

A bubble column reactor model, based on the assumptions of 1). Liquid is well mixed and under laminar flow region; 2). Gas is plug flow, was developed for CO₂ removal data analysis. The model incorporated physical absorption between CO₂ and water, dissolution of Mg(OH)₂ solid particles, diffusion within the gas and liquid phases, and chemical reactions of the ions. The film theory was used to understand the transport phenomenon. It is found that 0.024 cm is the film thickness which explains the change of the overall mass transfer rates caused by the change of temperatures. The overall mass transfer coefficient, a key designing parameter, is found to be a function of the hydrodynamic parameters, Henry’s constant, CO₂ partial pressure in the gas phase, diffusivities, solid dissolution constant and temperature. The overall mass transfer coefficients found from this study are comparable to the other widely studied scrubbing chemicals, such as MEA and ammonia solutions.

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References
