Carbon Dioxide Separation from Flue Gas

By Phase Enhanced Absorption

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Final Report

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Principal Investigator: Dr. Liang Hu

DOE Project Manager: Tim Fout

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School of Engineering and Technology
Hampton University
Hampton, VA 23668

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ABSTRACT

A new process, phase enhanced absorption, was invented. The method is carried out in an absorber, where a liquid carrier (aqueous solution), an organic mixture (or organic compound), and a gas mixture containing a gas to be absorbed are introduced from an inlet. Since the organic mixture is immiscible or at least partially immiscible with the liquid carrier, the organic mixture forms a layer or small parcels between the liquid carrier and the gas mixture. The organic mixture in the absorber improves mass transfer efficiency of the system and increases the absorption rate of the gas. The organic mixture serves as a transportation media. The gas is finally accumulated in the liquid carrier as in a conventional gas-liquid absorption system.

The presence of the organic layer do not hinder the regeneration of the liquid carrier or recovery of the gas because the organic layer is removed by a settler after the absorption process is completed. In another aspect, the system exhibited increased gas-liquid separation efficiency, thereby reducing the costs of operation and maintenance.

Our study focused on the search of the organic layer or transportation layer to enhance the absorption rate of carbon dioxide. The following systems were studied, (1) CO_2-water system and CO_2-water-organic layer system; (2) CO_2-Potassium Carbonate aqueous solution system and CO_2-Potassium Carbonate aqueous solution-organic layer system. CO_2-water and CO_2-Potassium Carbonate systems are the traditional gas-liquid absorption processes. The CO_2-water-organic layer and CO_2-Potassium Carbonate-organic layer systems are the novel absorption processes, phase enhanced absorption. As we mentioned early, organic layer is used for the increase of absorption rate, and plays the role of transportation of CO_2. Our study showed that the absorption rate can be increased by adding the organic layer. However, the enhanced factor is highly depended on the liquid mass transfer coefficients for the CO_2-water-organic layer system. For the CO_2-Potassium Carbonate aqueous solution-organic layer system, the enhanced factor is not only depended on the liquid mass transfer coefficients, but also the chemical reaction rates.

Keywords: Absorption, Phase enhanced absorption, Separation

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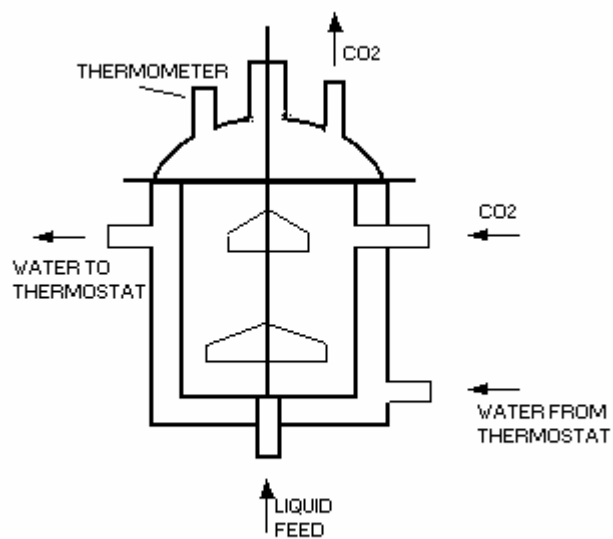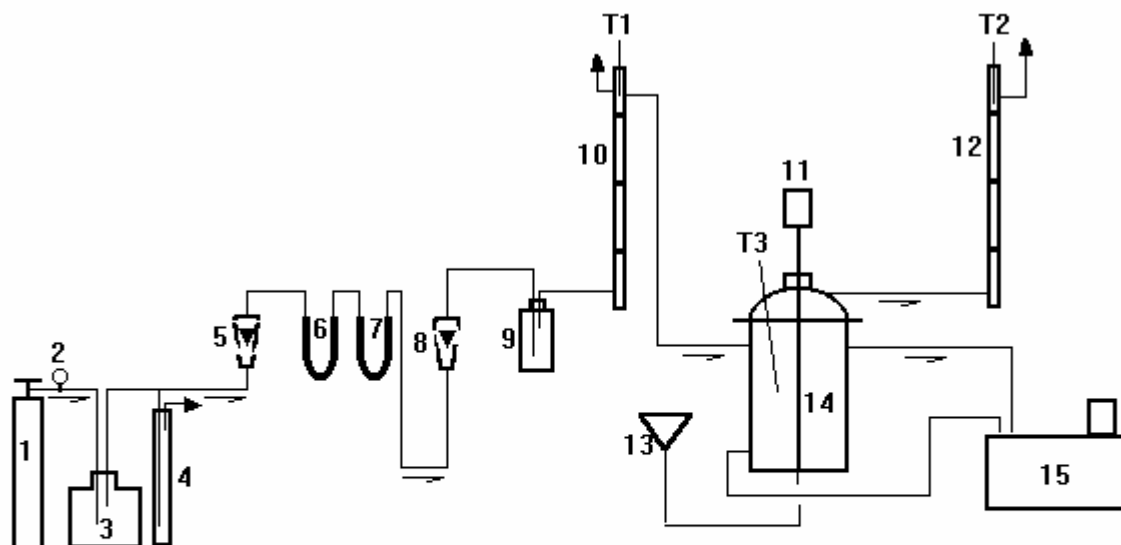
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5, 8 - ROTATING FLOW METER;   6 - SILICON GEL U TUBE;   7 - ACTIVE CARBON U TUBE;
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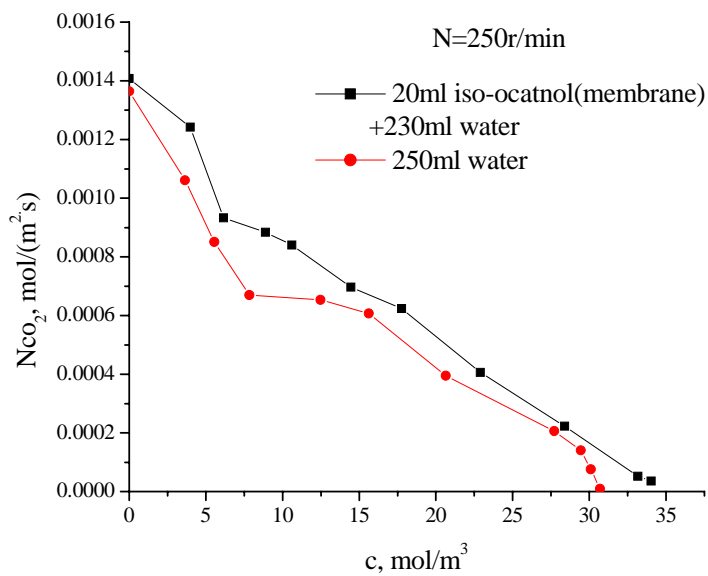
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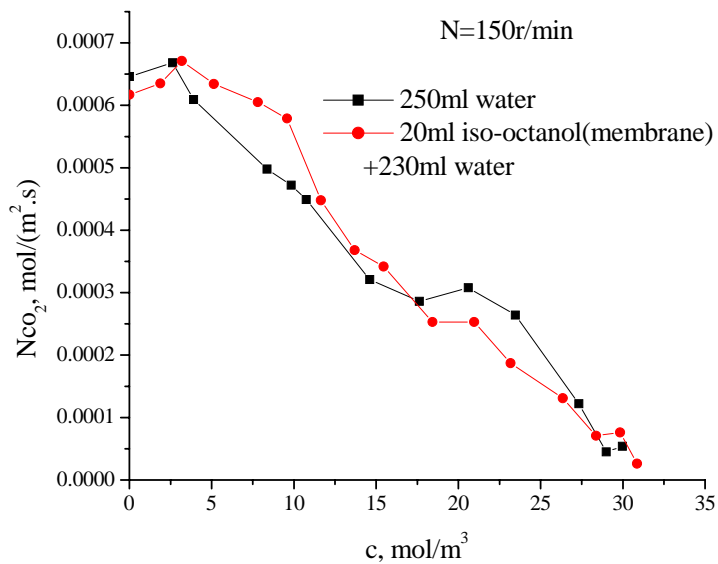
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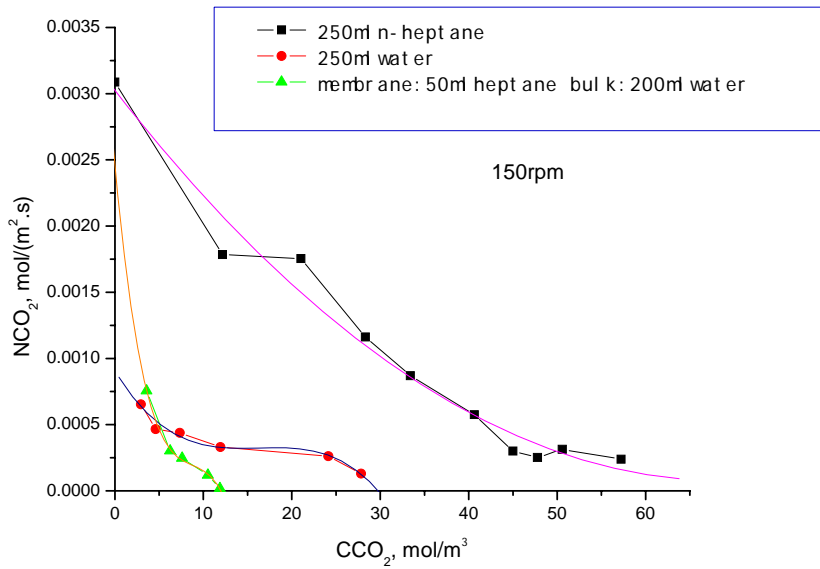
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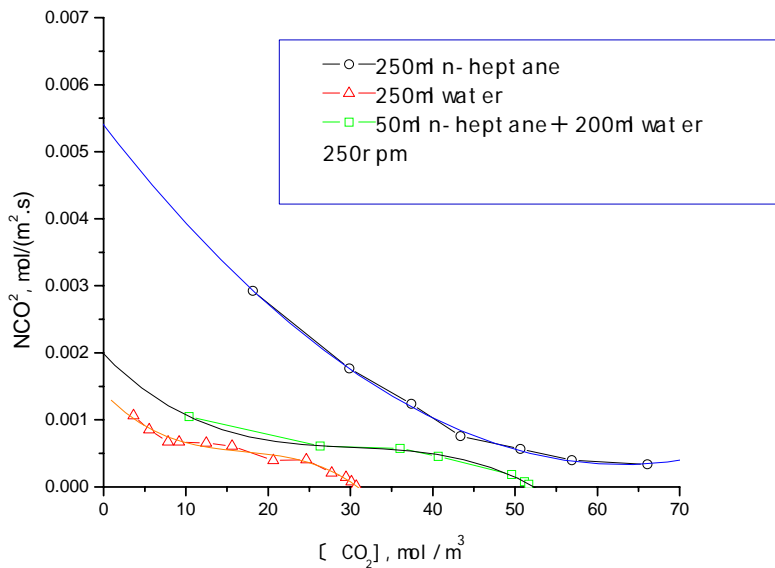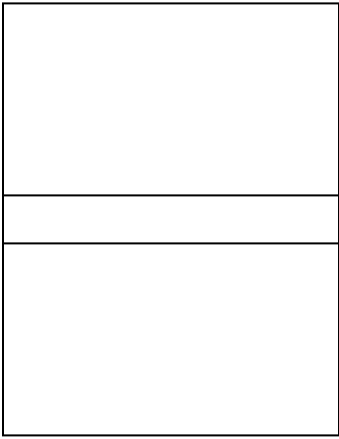

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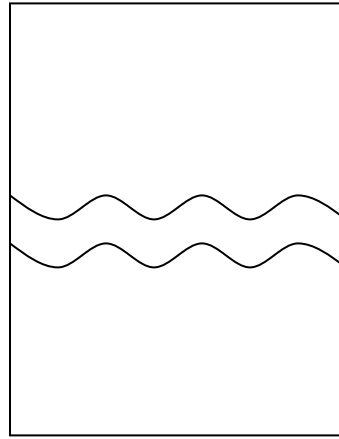
Flow Pattern I

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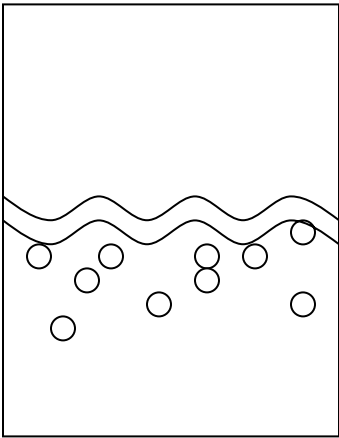
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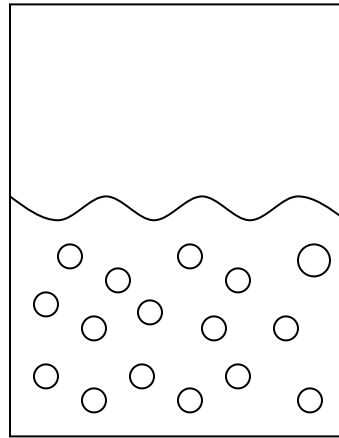
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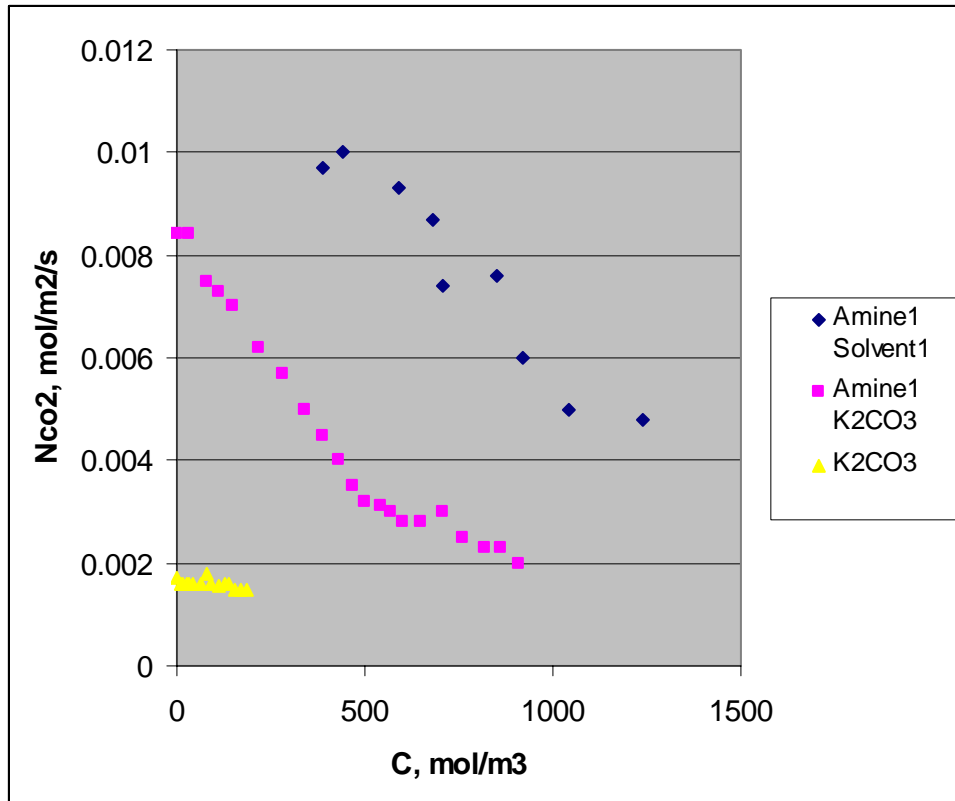
Figure 8   Comparison of absorption rates among amine1 in solvent1 (180 g/l), amine (180 g/l) in potassium carbonate aqueous solution, potassium carbonate aqueous solution (150 g/l);

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      Amine1 in solvent1 (180 g/l);
      Total absorbent volume 250 ml, Temperature: 25 oC, Pressure: 1 atm (pure CO2),
      Agitation speed: 150 rpm

  (2) Absorbent: (red dots)
      Amine1 (180 g/l) in potassium carbonate aqueous solution (150 g/l);
      Total absorbent volume 250 ml, Temperature: 25 oC, Pressure: 1 atm (pure CO2),
      Agitation speed: 150 rpm

  (3) Absorbent: (yellow dots)
      Potassium carbonate aqueous solution (150 g/l);
      Total absorbent volume 250 ml, Temperature: 25 oC, Pressure: 1 atm (pure CO2),
      Agitation speed: 150 rpm

Figure 9   Comparison of absorption rate enhanced by organic layer (Amine1 in Solvent1) with the absorption rate of potassium carbonate aqueous solution

(1)   Absorbent: (dark blue dots)
        Organic layer: Amine1 in solvent1 (180 g/l); volume 50 ml
        Balk: potassium carbonate aqueous solution (150 g/l); volume 200 ml
        Total absorbent volume 250 ml, Temperature: 25 oC, Pressure: 1 atm (pure CO_2),
        Agitation speed: 150 rpm
(2)   Absorbent (traditional absorption): (red dots)
        Potassium carbonate aqueous solution (150 g/l); volume 250 ml
        Total absorbent volume 250 ml, Temperature: 25 ^{o}C, Pressure: 1 atm (pure CO_2),
        Agitation speed: 150 rpm
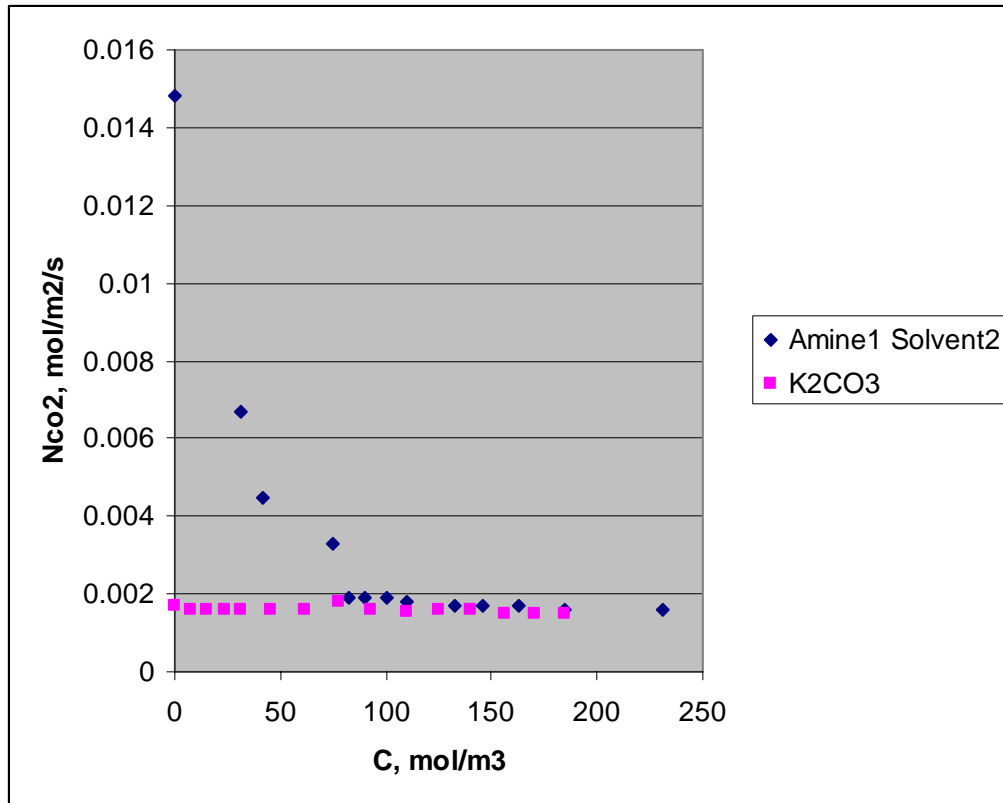
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     Organic layer: Amine1 in Solvent2 (180 g/l); volume 50 ml
     Balk: potassium carbonate aqueous solution (150 g/l); volume 200 ml
     Total absorbent volume 250 ml, Temperature: 25 ^{o}C, Pressure: 1 atm (pure CO_2),
     Agitation speed: 150 rpm
  (2) Absorbent (traditional absorption): (red dots)
     Potassium carbonate aqueous solution (150 g/l); volume 250 ml
     Total absorbent volume 250 ml, Temperature: 25 ^{o}C, Pressure: 1 atm (pure CO_2),
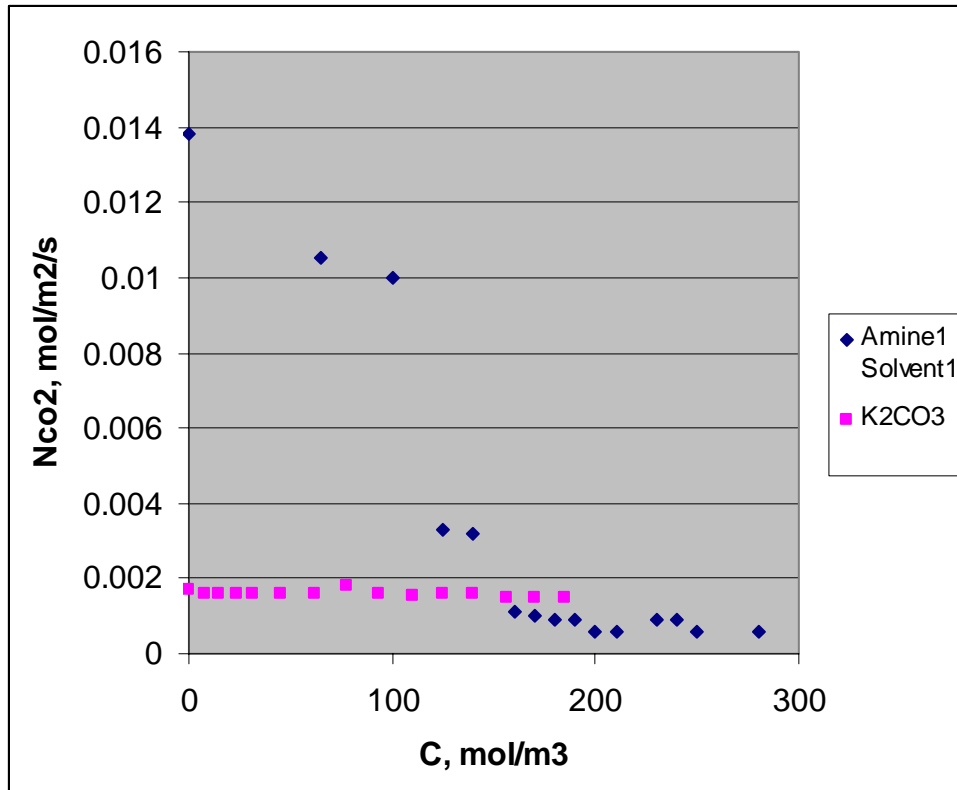   Agitation speed: 150 rpm
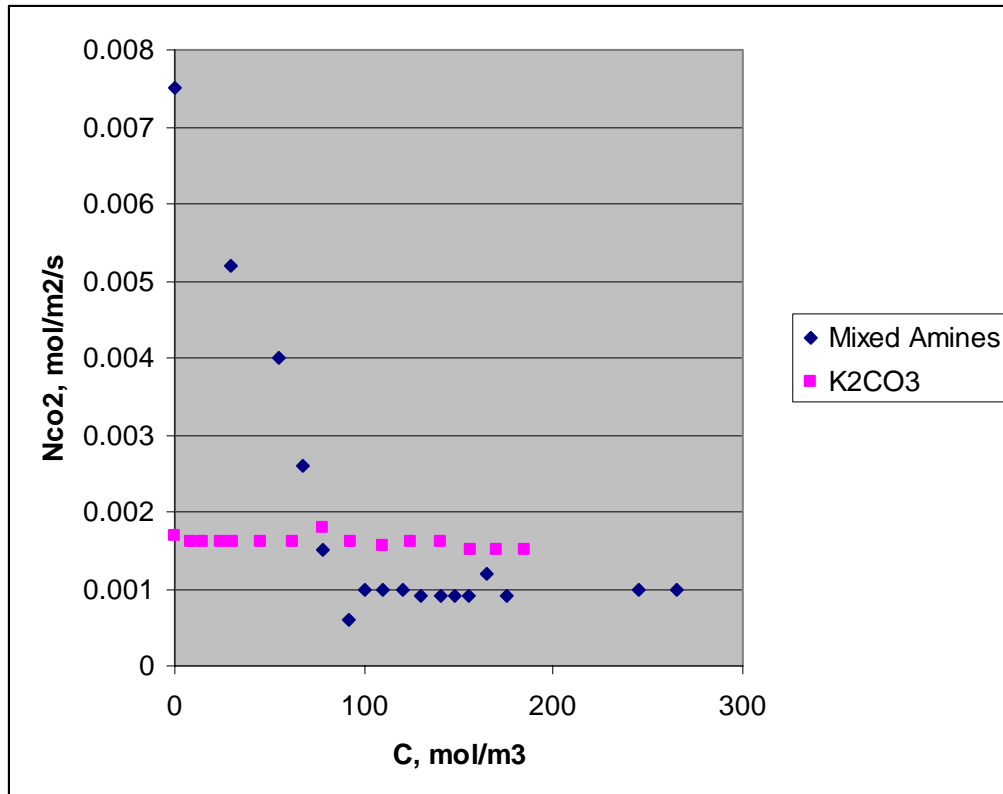
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    (1) Absorbent: (dark blue dots)
       Organic layer: Mixed amines; volume 50 ml
       Balk: potassium carbonate aqueous solution (150 g/l); volume 200 ml
       Total absorbent volume 250 ml, Temperature: 25 ^{o}C, Pressure: 1 atm (pure CO2),
       Agitation speed: 150 rpm
    (2) Absorbent (traditional absorption):   (red dots)
       Potassium carbonate aqueous solution (150 g/l); volume 250 ml
       Total absorbent volume 250 ml, Temperature: 25 ^{o}C, Pressure: 1 atm (pure CO2),
   Agitation speed: 150 rpm

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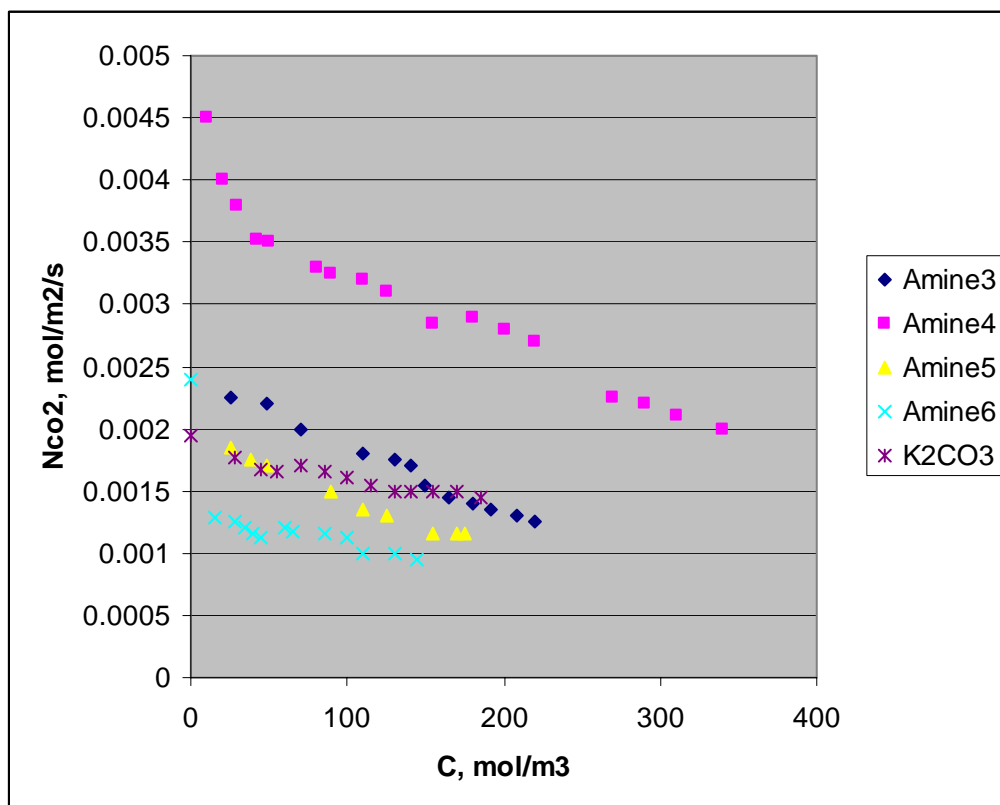
Figure 12   Phase Enhanced Absorption, Absorption Rate N (mol/m2/s) vs. CO_2 Concentration in liquid C (mol/m3)

The experimental conditions were as follows:

Temperature 25 ^{o}C,   Pressure (pure CO_2) 1 atm,

Liquid agitation speed 150 rpm,   Volume of organic phase 20 ml,

Volume of aqueous phase 230 ml.

The aqueous phase was 150 g/l of potassium carbonate solution.

The organic layer made from amine in organic solvent with the concentration of 20 % by volume,

INTRODUCTION

Among the methods used to separate and purify gases, the gas-liquid absorption method is one of the most powerful and efficient techniques. A conventional system designed to separate and purify gas consists of a gas phase (mixture of gas including the one to be isolated) and a liquid phase (solution that maximizes absorption).

In chemical absorption, the chemical compounds in the liquid solution react with the gas to form other compounds. This process serves two major purposes. First, chemical reaction with the gas can increase the carrying capacity of the absorbed gas. Second, it can reduce the mass transfer resistance or increase mass transfer coefficient. Both effects contribute to an increased absorption rate. However, such chemical reactions have setbacks: they hinder the release of the absorbed gas from the liquid solution.

Arthur L. Kohl and Fred C. Riesenfeld in their book "Gas Purification," Gulf Publishing Company (1985) at page 235, discussed the effects of promoters or activators on the carbon dioxide absorption rate and vapor-liquid equilibria. Compared with hot potassium carbonate solutions, diethanolamine (DEA) and sterically hindered amines were found to be very effective in increasing the absorption rate of carbon dioxide. However, the partial pressure of carbon dioxide at equilibrium decreases after an activator is added into the carbonated solution. This means that it is more difficult to recover carbon dioxide from the activated solution than from a solution containing no activator.

Although amine compounds are commonly added into the aqueous solution of alkaline salts in a conventional absorption system, these types of absorbents have

numerous setbacks. They increase the difficulty of carbon dioxide regeneration from the liquid carrier. The method discussed in this report, the phase enhanced absorption, significantly increased the absorption rate of carbon dioxide. At the same time, adding an organic layer to the conventional system does not further hinder regeneration.

Theory

Absorption is a process by which one or more components of a gas mixture are transferred to a liquid where it is soluble. There are two types of absorption: they differ by the nature of the interaction between absorbent and absorbate. In the process of a physical absorption, the gas component being absorbed is simply dissolved in the liquid absorbent. However, the solute does not react chemically with the absorbent. In the case of chemical absorption, there is a chemical reaction between the gas component being absorbed and a component in the liquid to form a compound. In a chemical absorption, the chemical reaction between the gas solute and some component in the liquid solution enhances the absorption rate of the gas.

The phase enhanced absorption features an organic compound in addition to the traditional gas and liquid components. Adding an organic compound or mixture into the absorption system increases the absorption rate of the gas significantly. In phase enhanced absorption, more than one liquid phase is involved in absorbing the gas. One of the liquids serves as an absorbing solution (carrying phase), where the gas is ultimately accumulated. The other liquid, the transportation layer (transportation phase), plays the role of transporting the gas from the gas mixture to the absorbing solution and increasing the absorption rate of the gas. This transportation layer is composed of an organic

compound and simply plays the role of accelerating the transport of the gas to be isolated (in the case carbon dioxide) from the gas phase to the carrying phase.

Due to the added organic layer, phase enhanced absorption has a unique mass transfer model. The gas to be isolated first separates from the bulk of the gas phase and comes in contact with the interface of the transportation phase. This liquid layers absorbs the gas. The absorption is either physical or chemical. In other words, while in the transportation phase, the gas solute may react with the components in transportation phase. In the next step, the gas solute dissolved in the transportation phase passes through the interface between the transportation phase and the carrying phase, and enters into carrying phase. Once the gas is in the carrying phase, the gas solute may exist in two forms: it may be physically dissolved or in a chemical compound resulting from a reaction between the gas and a component of the carrying phase.

The function of the transportation phase is to deliver gas solute from the gas phase to the carrying phase and to increase the absorption rate. Viewed with the film theory, the phase enhanced absorption mass transfer model can be summarized in the following sketch:

gas solute A

A

A

gas phase   transportation phase   carrying phase

MASS TRANSFER MODEL

This report examines the absorption rate of carbon dioxide with phase enhanced absorption and compares this rate to that of a conventional gas-liquid absorption method (without the transportation layer). In our experiments, carbon dioxide gas was ultimately absorbed by water and sodium carbonate aqueous solution (carrying phase). The experiments that follow are designed to demonstrate that adding a liquid phase consisting of an organic compound significantly improves the absorption rate of carbon dioxide.
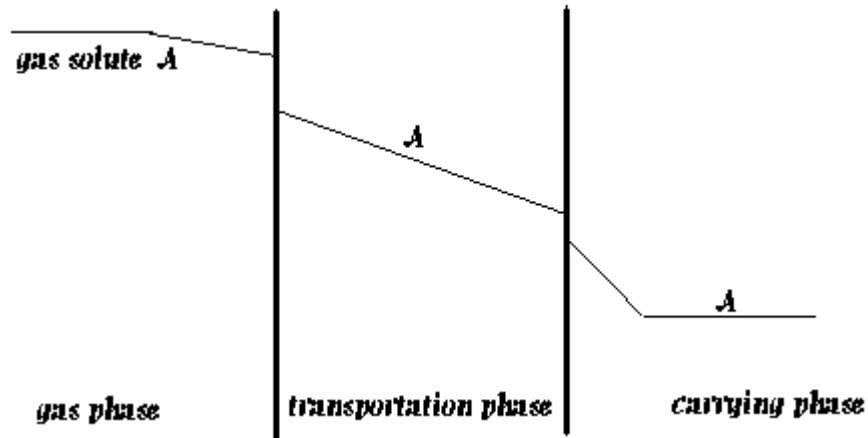
EXECUTIVE SUMMARY

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Our research was divided into two parts, the fundamental study of the phase enhanced absorption and the application study of the phase enhanced absorption. In the fundamental study, we investigated the feasibility of the phase enhanced absorption accompanied by both physical and chemical reaction, and the mechanism of the phase enhanced absorption. Our study showed that the absorption rate can be increased by adding the organic layer. However, for the absorption without chemical reactions, the enhanced factor is highly depended on the liquid mass transfer coefficients. For the absorption with chemical reactions, the enhanced factor is not only depended on the liquid mass transfer coefficients, but also the chemical reaction rates. In the application study, we used the organic layer to enhance the CO_2 absorption rate by potassium carbonate aqueous solution. Our results showed that the CO_2 absorption rate by potassium carbonate aqueous solution was doubled by adding the organic layer into the CO_2 – potassium carbonate aqueous solution system.

EXPERIMENTAL METHODS

Experimental Method and Apparatus

Apparatus:

Phase enhanced absorption can be demonstrated using a simple system consisting of a stirring cell and a series of connecting apparatuses, all sketched and explained below. Figure 1 is a sketch of a stirring cell, the most important component that includes the three phases unique to the phase enhanced absorption method. The remaining apparatus necessary to measure the absorption rate is sketched in Figure 2. The stirring cell described is also identified in Figure 2.

The stirring cell, made of glass, contains all three phases of a phase enhanced absorption system (gas phase, organic layer, and aqueous solution). The cell's inner diameter is 121 mm and its depth is 130 mm. Two agitating blades, one for the aqueous phase, one for the gas phase, are driven by a motor. The agitating speed is monitored. The rest of the experimental apparatus is shown in Figure 2. The function of each component of the experimental system is explained below.

Method:

To measure the absorption rate of carbon dioxide in the system maintained in the stirring cell, the gas originating from the initial cylinder must pass through the series of apparatus to flow out of the flow meter (12). First, the carbon dioxide cylinder (1) releases carbon dioxide, which passes through the buffer bottle (3) and the pressure stable tube (4). The gas flow rate is controlled and measured by the rotating flow meters (5 and 8). The gas clean system consists of two U tubes. The first U tube (6) is filled with silicon gel and the second U tube (7) is filled with active carbon. The gas is saturated

with moisture by the saturator (9). The solution in the saturator is the same solution that is in the stirring cell (14). Gas flow rate is measured by the foam film flow meters (10 and 12) before and after absorption in the stirring cell (14). The difference between two flow rates is the gas absorption rate. After the measurement, the carbon dioxide gas is released.

The absorption rate of gas, carbon dioxide, at time **t** was determined by the difference of two flow rates, in and out of stirring cell with two foam film flow meters. As the results of the measurement, the relationship of absorption rate r and elapsed time t would be obtained. Integration of absorption rate with elapsed time, r ~ t, the total amount of carbon dioxide absorbed into the liquid phase can be obtained.

Experimental steps:

(1) Measure the flow rate of gas in and out of the absorption cell at the same time (volume flow rate);

(2) Measure the temperature of each foam film flow meter **T1** and **T2**;

(3) Use idea gas equation to calculate the mass flow rates **r1** and **r2** [mol/s];

(4) Subtract the flow rate of gas in and out of the absorption cell, which is equal to the absorption rate **r**.

Calculation:

The idea gas equation: $PV = nRT$

Divide by time t: $PV/t = RTn/t$

The mass flow rate: $n/t = PV/(tRT)$

Subtract mass flow rate of in and out of absorption cell, which is the absorption rate r:

$$r = r1 - r2 = (n/t)_1 - (n/t)_2 = PV_1/(tRT_1) - PV_2/(tRT_2)$$

Where t (s) is the elapsed time.

The absorption rate per square area of gas-liquid interface N $[mol/(m^2 \cdot s)]$:

$$N = r/\text{area of gas-liquid interface}$$

CO_2 concentration in liquid **c**:

$$c = \int r \, dt \ \ (\text{from 0 to t})$$

RESULTS AND DISCUSSION

Part I.   Using organic phase to enhance CO_2 absorption rate by water

  1. CO_2-water system and CO_2-water-isooctanol system study

The CO_2-water system is a traditional absorption process. CO_2 is absorbed into water. This is a physical absorption. The CO_2-water-isooctanol system is a phase enhanced absorption process, where isooctanol forms an organic layer between CO_2 gas and water to increase the CO_2 absorption rate. CO_2 absorption rate by water and by water with isooctanol layer were measured individually under the same experimental condition: the temperature 25 ^{o}C, pressure (pure CO_2 gas used): 1 atm, agitation speed: 250 rpm and 150 rpm, and liquid volume: 250 ml. The experimental results are shown in Figures 3 & 4.

Figure 3 is the comparison of CO_2 absorption rate by water and by water + isooctanol layer at the <u>agitation speed 250 rpm</u>. In Figure 3, the line with square indicates the relationship between CO_2 absorption rate by water and CO_2 concentration in liquid. The line with diamond is the relationship between CO_2 absorption rate by water + isooctanol layer and CO_2 concentration in liquid. The liquid was agitated at the speed of 250 rpm

with the total liquid volume of 250 ml(230 ml water and 20 ml isooctanol). As seen in Figure 3, the absorption rate by water + isooctanol layer is higher than that by water.

Figure 4 is the comparison of CO_2 absorption rate by water and by water with isooctanol layer at the <u>agitation speed 150 rpm</u>. In Figure 4, the line with square indicates the relationship between CO_2 absorption rate by water and CO_2 concentration in liquid. The line with diamond is the relationship between CO_2 absorption rate by water + isooctanol layer and CO_2 concentration in liquid. The total volume of the liquid was 250 ml(230 ml water and 20 ml isooctanol). As seen in Figure 4, the absorption rate by water + isooctanol layer is close to the absorption rate by water.

By comparing Figures 3 and Figure 4, the absorption rate by water with isooctanol layer is highly depended on the agitation speed. The liquid mass transfer resistance between water and isooctanol layer caused the absorption rate depression at lower agitation speed.

2. CO_2-water system and CO_2-water-n-haptane layer system study

Figure 5 is the comparison of CO_2 absorption rates by water, by n-heptane and by water + n-heptane layer at the <u>agitation speed of 150 rpm</u>. CO_2 absorption rate by water + n-heptane layer was the slowest process. CO_2 absorption by n-heptane had the highest absorption rate. While at the <u>agitation speed of 250 rpm</u> (see Figure 6), CO_2 absorption rate by water + n-heptane layer was higher than that by water along. In both agitation speeds, CO_2 absorption by n-heptane had the highest rate. The experimental results showed that (1) introduction of n-heptane layer into CO_2 – water absorption system is able to enhance the absorption rate by water, however the absorption rate is highly depended on the agitation speed, and (2) because of the higher CO_2 absorption rate by n-

haptane or lower mass transfer resistant between the interface of gas and n-haptane, the transportation layer of n-haptane delivers CO_2 from a gas phase into water phase and enhances the absorption rate as long as there is the sufficient mass transfer (agitation) between the two liquid phases is provided.

3.   Mechanism of phase enhanced absorption for the system of CO_2-water-organic layer

To enhance absorption rate, the organic layer introduced into the system should meet the following conditions (for physical absorption):

(1)   The mass transfer resistance between organic layer-water is much less than the mass transfer resistance between gas-liquid at the same experimental conditions.

(2)   The mass transfer resistance between the CO_2-organic layer is less than the mass transfer resistance between CO_2-water.

(3)   The sufficient mass transfer from organic layer to water for the dissolved gas, CO_2, is provided.

Conditions (1) and (2) are dependent on the properties of the substances. Condition (3), in our case, is depended on the agitation speed.

Since the absorption rate is highly depended on the agitation speed, and the agitation speed is relative to the liquid flow pattern, the investigation of the liquid flow pattern will disclose the mechanism of the Phase Enhanced Absorption.

Four different flow patterns were observed in our experiments (see Figure 7). In flow pattern I, the organic layer was agitated very gently. The flow in the organic layer was laminar. No convective movement occurred. The transport of the dissolved gas from gas

to water was diffusion. In this case, the organic layer was the barrier for the transport of dissolved gas into water. Adding the organic layer on the water would decrease the absorption rate of the dissolved gas.

With the increase of the agitation speed, the wave on both gas-organic layer interface and organic layer-water interface was observed. This is flow pattern II. In this flow pattern, both diffusion and convective movement were played the role of the transport of the dissolved gas. In this case, dissolved gas was transported into water with the aid of convective movement. When the convective movement provided sufficient mass transfer rate for the dissolved gas, the transportation rate of dissolved gas from organic layer into water was much faster than that from gas into organic layer. Adding the organic layer on the water would enhance the absorption rate of dissolved gas.

In flow pattern III (by further increase of agitation speed), part of the organic layer dispersed its particles into water. At the same time, the dispersed particles coalesced. The dispersion and coalescence promoted the mass transfer of the dissolved gas into water. In flow pattern III, the diffusion, convective movement, dispersion and coalescence, and the increase of the organic layer-water interface area contributed to the transport of the dissolved gas. In this flow pattern, adding the organic layer on the water would significantly enhance the absorption rate of dissolved gas.

When the agitation speed reached the highest level, or in flow pattern IV, the organic layer completely dispersed its particles into water. In this flow pattern, the organic layer is not a continuous phase. The diffusion, convective movement, dispersion and coalescence, and the increase of the organic layer-water interface area contributed the transport of the dissolved gas.

In the case of flow pattern III and IV, the dissolved gas was transported into water with the aid of the convective movement, dispersion and coalescence, and the increase of the organic layer-water interface area beside diffusion. The transport rate of dissolved gas from organic layer into water was much faster than that from gas into organic layer. Adding the organic layer on the water would enhance the absorption rate of dissolved gas.

To explain the experimental results, we take an example of CO_2-water-n‒haptane system. Water had slow absorption rate for CO_2 by comparing with organic solvent, n‒haptane (see Figures 5 and 6). We knew that water and n‒haptane are immiscible. In order to increase the absorption rate of CO_2 into water, a layer of n‒haptane was added on water. Because of the lower mass transfer resistance between CO_2 and n‒haptane interface, CO_2 dissolved into n‒haptane organic layer at a rate 3-4 times faster than that into water (see Figures 5 and 6). At a low agitation speed, 150 rpm, CO_2 absorption rate by water- n‒haptane layer was higher than that by water initially. The absorption rate quickly dropped to below the absorption rate by water as the absorption progressed. The experimental phenomena can be explained as follows.

The initial fast absorption rate was contributed by n‒haptane layer. At a low agitation speed, the n‒haptane layer was agitated gently. The flow in organic layer and water was laminar. No convective movement occurred during the transport of the dissolved gas CO_2. As soon as the n‒haptane layer was saturated with CO_2, the absorption rate quickly dropped to below the absorption rate by water. However, at this moment, water contained very small amount of CO_2 (see Figure 5).

When the agitation speed was increased to 250 rpm, CO_2 absorption rate by water- n‒haptane layer was higher than that by water all the time (see Figure 6). It was

observed that the wave appeared on both CO_2- n–haptane interface and n–haptane-water interface at 250 rpm agitation speed. In this flow pattern (flow patent II), the convective movement was played a role in the transport of dissolved gas CO_2. The dissolved gas CO_2 was transported into water from n–haptane layer with the aid of convective movement. Since the convective movement provides sufficient mass transfer of the dissolved gas CO_2, the absorption rate of CO_2 was enhanced by the organic layer.

Part II.   Using organic phase to enhance CO$_2$ absorption rate by potassium carbonate aqueous solution

This part of the research is to enhance potassium carbonate aqueous solution by using phase enhanced absorption. An organic layer was added into the traditional absorption system, CO$_2$ - potassium carbonate aqueous solution, to enhance the absorption rate. More detail, amine was used as activated agents that existed in organic phase. The mechanism, in some way, was similar with the mechanism of amine activated potassium carbonate aqueous solution. CO$_2$ first reacted with amine in organic layer to form carbamate. Then, carbamate is transferred to organic-aqueous interface to react with hydroxyl ions in aqueous phase to form bicarbonate. Finally, CO$_2$ was delivered from gas phase to potassium carbonate aqueous solution. By selecting proper amine, the absorption rate was able to be enhanced.

1.   Mechanism discussion

1.1   Mechanism for CO$_2$ absorption by amine activated potassium carbonate aqueous solution:

The popular accepted basic reactions for potassium carbonate aqueous solution and CO$_2$ is

$$CO_2 + K_2CO_3 + H_2O = 2\ KHCO_3 \qquad\qquad (1)$$

Since the solution is strong electrolyte, it may be assumed that the metal is present only in the form of K$^+$ ions, reaction (1) may be described as the ionic terms as:

$$CO_2 + CO_3^{2-} + H_2O = 2HCO_3^- \qquad\qquad (2)$$

The above reaction is evidently consisted of a sequence of steps. The carbonate ion first reacts with water to generate hydroxyl ions. Then, hydroxyl ions react with CO_2 to form bicarbonate ions:

$$CO_3^{2-} + H_2O = HCO_3^- + OH^- \qquad (3)$$
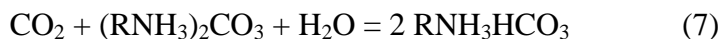
$$CO_2 + OH^- = HCO_3^- \qquad (4)$$

Since reaction (3) is instantaneous reaction, reaction (4) is the rate-controlling step.

When a small amount of amine is added into the solution, the absorption rate of carbon dioxide is enhanced greatly by following reactions:

$$CO_2 + 2\ RNH_2 = RNHCOONH_3R \qquad (5)$$

$$\text{(Amine)} \quad \text{(Carbamate)}$$

$$CO_2 + 2\ RNH_2 + H_2O = (RNH_3)_2CO_3 \qquad (6)$$

$$CO_2 + (RNH_3)_2CO_3 + H_2O = 2\ RNH_3HCO_3 \qquad (7)$$

$$RNHCOONH_3R + OH^- = HCO_3^- + RNH_2 \qquad (8)$$
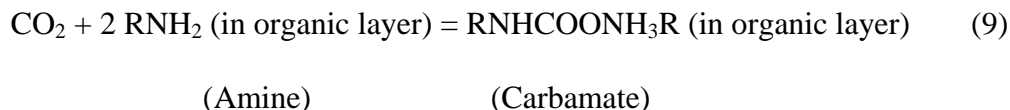
$$\text{(Carbamate)} \qquad\qquad \text{(Amine)}$$

Since reaction (5) is fast reaction, and reactions (6) and (7) are slow reactions, majority of CO_2 is reacted with amine to form carbamate. Produced carbamate is further reacted with hydroxyl ions OH^- to form HCO_3^- and RNH_2 through reaction (8). Finally, the absorption rate by potassium carbonate aqueous solution is enhanced by adding a small amount of amine into the solution.

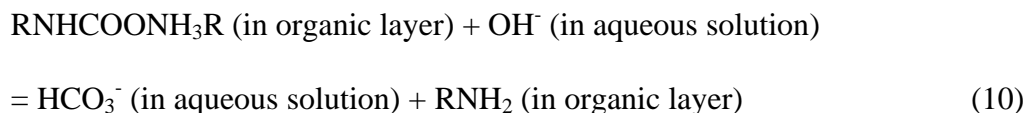## 1.2 The principle for using organic phase to enhance potassium carbonate aqueous solution for CO_2 absorption

The principle for using organic phase to enhance potassium carbonate aqueous solution for CO_2 absorption was based on following:

Amine in organic layer was immiscible or partial miscible with the potassium carbonate aqueous solution. The organic phase, only a layer, was added on the potassium carbonate aqueous solution for CO_2 absorption. Since the reaction between amine and CO_2 to form carbamate was a fast process, CO_2 reacts with amine in organic layer to form carbamate.

$$CO_2 + 2\ RNH_2 \text{ (in organic layer)} = RNHCOONH_3R \text{ (in organic layer)} \quad (9)$$

$$\text{(Amine)} \qquad\qquad \text{(Carbamate)}$$

Formed carbamate was transferred to the interface between organic phase and aqueous phase, and further reacted with hydroxyl (in aqueous solution) to form bicarbonate in aqueous phase and amine in organic phase:

$$RNHCOONH_3R \text{ (in organic layer)} + OH^- \text{ (in aqueous solution)}$$

$$= HCO_3^- \text{ (in aqueous solution)} + RNH_2 \text{ (in organic layer)} \quad (10)$$

As long as the mass transfer rate of all reactants and products between organic phase and aqueous phase and the reaction rate between $RNHCOONH_3R$ (in organic layer) and OH^- (in aqueous solution) were fast enough, the CO_2 absorption would be enhanced by the organic layer.

The challenge for this research was to find an organic layer to enhance the CO_2 absorption rate by potassium carbonate aqueous solution.

2. Experiments and results

By introducing an organic layer into CO_2-potassium carbonate aqueous solution to enhance CO_2 absorption rate was studied. The liquid carrier was potassium carbonate aqueous solution (150 g/l). We investigated the effects by different activated agents, different solvents in organic layer on the absorption rate. In order to learn the influence of

the chemical reactions on the absorption rate, the special experimental method was used to explain the possible mechanism. The experiments were conducted at 25 $^\circ$C, and 1 atm. 99.99% CO_2 was used in absorption process. Liquid was agitated to provide sufficient mass transfer. Our study showed that for the absorption with chemical reactions, the enhanced factor was not only depended on the liquid mass transfer coefficients, but also the chemical reaction rates. Since the chemical reactions also occurred in organic layer (CO_2 reacted with the components in organic layer), the components in organic layer played an important role in enhancing the absorption rate. Only the proper components would be able to enhance the absorption rate.

Many organic layers were investigated for enhancing CO_2 absorption rate by potassium carbonate aqueous solution. The detail of the study cases was described as follows.

Case study 1: Organic layer was made of Amine1 in solvent1 with the concentration of Amine1 (180 g/l).

The experiments was designed

(1) to compare the absorption rate among Amine1 in solvent1 (180 g/l) (same components as that in organic layer), Amine1 activated (180 g/l) potassium carbonate aqueous solution (150 g/l) and potassium carbonate aqueous solution (150 g/l);

(2) to compare the absorption rate between phase enhanced absorption with the organic layer of Amine1 in solvent1 (180 g/l) (phase enhanced absorption) and potassium carbonate aqueous solution (150 g/l) (traditional absorption);

In Figure 8, the absorption rate by Amine1 in solvent1 (180 g/l) was shown as dark blue dots, the absorption rate by Amine1 activated (180 g/l) potassium carbonate aqueous solution (150 g/l) was shown as red dots, and the absorption rate by potassium carbonate aqueous solution (150 g/l) was shown as yellow dots. The experimental results showed that the absorption rate by Amine1 in solvent1 (180 g/l) (dark blue dots) was much higher than the absorption rates by Amine1 activated (180 g/l) potassium carbonate aqueous solution (150 g/l) (red dots) and by potassium carbonate aqueous solution (150 g/l) (yellow dots).

This result indicated that the CO_2 absorption rate from gas into organic layer was much faster than that from gas into potassium carbonate aqueous solution.

In Figure 9, the absorption rate enhanced with the organic layer of Amine1 in solvent1 (180 g/l) (dark blue dots) was compared with the absorption rate by potassium carbonate aqueous solution (150 g/l) (red dots). The results showed that the absorption rate is sharply decreased initially and then maintained stable at the level that the absorption rate by potassium carbonate aqueous solution.

By comparing both absorption rates, the experimental results for the system with organic layer can be explained. The initial fast absorption rate was caused by the absorption of organic layer (see Figure 8). With the organic layer approaching to the saturation concentration, the absorption rate was sharply decreased. As soon as the organic layer was saturated by

CO_2, the absorption rate was at the point that was either controlled by the mass transfer rate between organic layer and aqueous solution or by the reaction rate of carbamate with hydroxyl ion (reaction 8). It was also possible the absorption rate was controlled by both steps. In these cases, the addition of organic layer was not able to enhance the absorption rate by potassium carbonate aqueous solution.

Case study 2: Organic layer was made of Amine1 in solvent2 with the concentration of 180 g/l.

The organic layer made of Amine1 in solvent2 with the concentration of 180 g/l was used to enhance the CO_2 absorption rate by potassium carbonate aqueous solution. The potassium carbonate aqueous solution (200 ml) with the concentration of 150 g/l was placed into the absorption cell. The organic layer (50 ml) was also placed into absorption cell. The potassium carbonate aqueous solution was covered by the organic layer. The liquids were agitated at the speed of 150 rpm. The CO_2 gas was introduced into agitation cell from the top of the cell. The contact of gas-liquid occurred only at the interface of gas-organic layer. The absorption was conducted at the experimental conditions: temperature 25 ^{o}C, pressure 1 atm with pure CO_2, liquid agitation speed 150 rpm. Figure 10 is the experimental result. From Figure 10, we found that the absorption rate was sharply decrease to about 0.0015 - 0.0018 mol/(m^2·s) range initially and then maintain stable at this level (dark blue dots).

To compare the absorption rate with potassium carbonate aqueous solution, another experiment was conducted as follows:

The potassium carbonate aqueous solution (250 ml) with the concentration of 150 g/l was placed into the absorption cell (no organic layer was placed into absorption cell). The liquid was agitated. The CO_2 gas was introduced into agitation cell from the top of the cell. The contact of gas-liquid occurred at the interface of gas- potassium carbonate aqueous solution. The absorption was conducted at the same experimental conditions as above: temperature 25 ^{o}C, pressure 1 atm with pure CO_2, liquid agitation speed 150 rpm. The experimental results are also shown in Figure 10 as red dots. As shown in Figure 10, the absorption rate of CO_2 was always in the range of 0.0015 – 0.0018.

Again, both experiments proved that the absorption rate was controlled either by the mass transfer rate between organic layer and aqueous solution or by the reaction rate binding potassium carbonate with CO_2. It was also possible that the absorption rate was controlled by both mass transfer rate between organic layer and aqueous solution and the reaction rate binding potassium carbonate with CO_2.

Case study 3: Organic layer was made of mixed amines

I consider the reaction as two aspects, one was the binding power of the amine with CO_2, another was the binding power of potassium carbonate with CO_2. The weaker the binding power of the amine with CO_2 was, the easier the

carbamate releases the CO_2, and the easier CO_2 transfers into aqueous phase from organic phase. The carbamate formed by mixed amines with CO_2 had much weaker binding power than that by amine 1 with CO_2. The carbamate formed by mixed amines with CO_2 was much easier to release CO_2. Figure 11 is the experimental result. From Figure 11, we found that the absorption rate had the similar curve sharp with figure 10. The results indicated that it was possible that the absorption rate was controlled by the mass transfer rate between organic layer and aqueous solution or by the reaction rate binding potassium carbonate with CO_2.

Case study 4:

Based on the above studies, the criteria for selection of amines for the organic layers that enhance the CO_2 absorption rate of potassium carbonate aqueous solution was made as follows:

(1) The CO_2 absorption rate by the organic layer should be higher than that by potassium carbonate aqueous solution. (2) The amine in organic layer has proper binding power. The amine should have sufficient power to bind CO_2 from gas and release CO_2 to potassium carbonate in aqueous solution. (3) The amine in organic layer should have the high (organic solvent)/(water) partition coefficient. The amine should stay in the organic layer during the CO_2 absorption.

Based on above criteria, four amines that met the criteria (3) were selected as follows.

Amine3 has the (organic solvent)/(water) partition coefficient 6200.

Amine4 has the (organic solvent)/(water) partition coefficient 1000.

Amine5 has the (organic solvent)/(water) partition coefficient 3190000.

Amine6 has the (organic solvent)/(water) partition coefficient 42160.

Tests of amines

Did these selected amines have sufficient power to capture CO_2 from gas and later to release CO_2 to potassium carbonate in aqueous solution? Is the organic layer made from amines has sufficient CO_2 absorption rate to enhance the absorption rate of potassium carbonate aqueous solution?

Four amines were further tested to screen out the proper amine(s) that meet the criteria (1) and (2). The further study was based on the experimental tests, phase enhanced absorption tests. The amine was mixed with organic solvent to form organic layer. The organic layer with potassium carbonate aqueous solution together absorbed CO_2 in the absorption cell. The detail absorption method had been described before. The experimental conditions were as follows:

Temperature 25 ^{o}C,   Pressure (pure CO_2) 1 atm,

Liquid agitation speed 150 rpm,   Volume of organic phase 20 ml,

Volume of aqueous phase 230 ml.

The aqueous phase was 150 g/l of potassium carbonate solution.

The organic layer made from amine in organic solvent with the concentration of 20 % by volume,

Figure 12 showed that the organic layer made from Amine3 had the best performance. The organic layer made from Amine3 was able to increase the CO_2 absorption rate of potassium carbonate aqueous solution with the concentration of 150

g/L by about 2 times. The organic layer made from Amine4 do not made significant increase of the CO_2 absorption rate of potassium carbonate aqueous solution with the concentration of 150 g/L, only about 10 % increase. However, the organic layers made from Amine5, and Amine6 had the worst performance. Both layers decreased the CO_2 absorption rate of potassium carbonate aqueous solution. As discussed in mechanism, the absorption rate of phase enhanced absorption was depended on CO_2 mass transfer rate between organic layer and potassium carbonate aqueous solution, the mass transfer rate between gas phase to organic layer, the reaction rate of CO_2 with amine and the reaction rate of releasing CO_2 from amine and further binding CO_2 with potassium carbonate.

In this study, four amines were tested at the same experimental conditions. Some of the amines like Amine3 and Amine4 were able to increase the absorption rate, and some were not. The effects from mass transfer on the absorption rate could be eliminated because of the same experimental conditions. The reasons that caused the differences on the absorption rate were the reaction rate of CO_2 with amines and the reaction rate of releasing CO_2 from amines and further binding CO_2 with potassium carbonate.

CONCLUTION

Our research compared the absorption rate of a conventional gas-liquid absorption system with that of a modified system using phase enhanced absorption. Our study showed that phase enhanced absorption exhibited a higher absorption rate as long as the sufficient mass transfer was provided for the system without chemical reaction. For the system with chemical reactions, the enhanced factor was not only depended on the liquid mass transfer coefficients, but also the chemical reaction rates.

The novel system consisted of a gas component (carbon dioxide), an organic layer, and an aqueous solution. The studied systems included (1) CO_2-water system and CO_2-water- isooctanol layer system; (2) CO_2-water system and CO_2-water-n-haptane layer system; (3) CO_2-Potassium Carbonate aqueous solution system and CO_2-Potassium Carbonate aqueous solution-organic layer system. The CO_2-water and CO_2-Potassium Carbonate systems were the traditional gas-liquid absorption processes. The CO_2-water-organic layer and CO_2-Potassium Carbonate-organic layer systems were the novel absorption processes, phase enhanced absorption. As we mentioned early, organic layer (transportation layer phase) was used for the increase of absorption rate. Our study showed that the absorption rate was able to be increased significantly by adding the organic layer. However, the enhanced factor was highly depended on the liquid mass transfer coefficient for the system without the chemical reactions. The mechanism was obvious because of the higher CO_2 absorption rate by organic layer or lower mass transfer resistant between the interface of gas and the organic layer, the transportation layer (organic layer) delivered CO_2 from the gas phase into water phase and enhanced the absorption rate as long as there was sufficient mass transfer (agitation) between two liquid phases were provided.

For the system with chemical reactions, such as CO_2-Potassium Carbonate aqueous solution-organic layer systems, the enhanced factor was not only depended on the liquid mass transfer coefficients, but also the chemical reaction rates. Since the chemical reactions also occurred in organic layer (CO_2 reacted with the components in organic layer), the components in organic layer played an important role in enhancing the

absorption rate. Only the proper components would be able to enhance the absorption rate.

The mechanism of phase enhanced absorption to activate potassium carbonate aqueous solution for CO_2 absorption was discussed. CO_2 first reacted with amine in organic layer to form carbamate. Then, carbamate was transferred to organic-aqueous interface to react with hydroxyl ions in aqueous phase to form bicarbonate. Finally, carbamate is converted into amine and CO_2 was delivered from gas phase to potassium carbonate aqueous solution.

Our study showed that the phase enhanced absorption was depended on (1) CO_2 mass transfer rate between gas phase and organic layer, (2) CO_2 mass transfer rate between organic layer and potassium carbonate aqueous solution, (3) the reaction rate of CO_2 with amine and (4) the reaction rate of releasing CO_2 from amine and further binding CO_2 with potassium carbonate.

Our results showed that the organic layer made from Amine3 was able to double the CO_2 absorption rate of potassium carbonate aqueous solution with the concentration of 150 g/L.

GLOSSARY

C: CO_2 concentration in liquid, [mol/m^3]

Nco$_2$: CO_2 absorption rate, [mol/m^2/s]

P: Pressure, [atm]

R: Gas constant, e.g. 8.314 [m^3·Pa/K/mol]

T: Temperature, [^{o}C]

V: Volume, [m^3]

n: Amount of substance, [mol]

r1, r2:   Mass flow rate, [mol/s]

t: Time [s]