CO$_2$ Capture from Flue Gas by Phase Transitional Absorption (2005.7 – 2009.6)

Final Report

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ABSTRACT

A novel absorption process called **Phase Transitional Absorption** was invented. What is the Phase Transitional Absorption? Phase Transitional Absorption is a two or multi phase absorption system, CO\textsubscript{2} rich phase and CO\textsubscript{2} lean phase. During Absorption, CO\textsubscript{2} is accumulated in CO\textsubscript{2} rich phase. After separating the two phases, CO\textsubscript{2} rich phase is forward to regeneration. After regeneration, the regenerated CO\textsubscript{2} rich phase combines CO\textsubscript{2} lean phase to form absorbent again to complete the cycle.

The advantage for Phase Transitional Absorption is obvious, significantly saving on regeneration energy. Because CO\textsubscript{2} lean phase was separated before regeneration, only CO\textsubscript{2} rich phase was forward to regeneration.

The absorption system we developed has the features of high absorption rate, high loading and working capacity, low corrosion, low regeneration heat, no toxic to environment, etc.

The process evaluation shows that our process is able to save 80 \% energy cost by comparing with MEA process.

Keywords: Carbon Dioxide, Separation, Absorption, Phase Transitional Absorption
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INTRODUCTION

Lack of a cost-effective CO₂ capture technology is a major impediment to using coal for generating electric power. Coal fired power plants are the largest source of Green House Gas (GHG) emission. Increased concern to the damaging impact of GHG and the increase in the concentration of CO₂ in the atmosphere are the drivers for the search for low cost and efficient technology to capture and sequester the CO₂. Available commercial technologies for CO₂ capture are energy intensive and expensive. If applied, they would impose a heavy toll on the cost of power generation from coal-fired power plants.

Following are the brief summary [DOE NETL CO₂ Sequestration Roadmap (2006)] of the present CO₂ capture technologies in development.

(1) Amines

Using amines as absorbent currently is commercially available. Major suppliers include Fluor, Mitsubishi, Kerr/ McGee etc. Amines undergo a chemical reaction with CO₂ forming water soluble salts. In a conventional amine process an aqueous solution containing 25-30wt% amine is contacted with flue gas or other CO₂ -containing stream. CO₂ in the vapor phase dissolves in solution and reacts with the amine to form a salt. The “rich” solution from the contactor is heated, causing the salts to disassociate. Stripping steam is used to pull CO₂ from solution and recover it as a gas. The advantage for amine process is that the amine/ CO₂ reaction is fast and enables aqueous amines to effectively scrub CO₂ from post combustion flue gas where CO₂ is diluted and at low pressure. However, we are facing some of the challenges. Because amine sorption involves a chemical reaction, a significant amount of heat must be applied to recover the absorbed CO₂ (MEA, monoethanolamine, ∆Hᵣ 825 Btu/lb CO₂ captured)
-Amine solution that is too concentrated, rich, or lean is corrosive to carbon steel. This effect is exacerbated by oxygen in flue gas which degrades corrosion inhibitors. Typical conditions (30 wt% amine, 0.45 mole CO₂/mole amine rich, 0.20 moles CO₂/mole amine lean) require 20kg of water heated & cooled per kg of CO₂ absorbed.

-SOx in the flue gas reacts w/ amines in solution to form heat stable salts. This causes amine attrition & fouls heat transfer equipment.

(2) Aqueous Ammonia

This technology is developed by Powerspan and NETL and still in Laboratory scale. Ammonia reacts with CO₂ to form ammonium carbonate disassociates releasing a pure stream of CO₂. The advantage of this process is reduced heat of reaction compared to amines and potential for SOx and NOx capture with fertilizer by-product (ammonium sulfate and ammonium nitrate). Several disadvantage is that (1) Need to cool down flue gas to 80°F for ammonia carbonate to be stable, (2) Reaction cycles involving ammonia reacting with CO₂ do not offer energy savings compared to amines, (3) Degradation of carbonate in the CO₂ absorber causes ammonia slip in the flue gas exhaust. The process can be improved by (1) process optimization to increase CO₂ loading, (2) additives to raise process temperature above 70°F, (3) increase percent conversion of SOx and NOx to fertilizer by-products.

(3) Membrane/Liquid Sorbent Hybrids

Kvaerner/ MHI is developing the technology of membrane/liquid sorbent hybrids. Flue gas is contacted with a membrane, and a sorbent solution on the permeate side
absorbs CO₂ and creates a partial pressure differential to draw CO₂ across the membrane. The advantage of this technology is that the membrane shields the amine from the contaminants in flue gas, reducing attrition and allowing higher loading differentials between lean and rich amine. However, two issues should be addressed: (1) Capital cost associated with the membrane, (2) Membranes may not keep out all unwanted contaminants.

(4) Ionic Liquids

Ionic liquids are a broad category of organic chemical compounds consisting of anionic and cationic components. They can dissolve gaseous CO₂ and are stable at temperatures up to several hundred degrees C. Ionic liquids can avoid cooling down syngas and heating it back up in a gasification application. Ionic liquids require little heat for CO₂ recovery. The disadvantage is high cost and high viscosity.

(5) Amine-enriched adsorbents

A carbon material with amine compounds fixed upon it exposed to a CO₂ rich process stream. The amine sites absorb the CO₂. The temperature of the material is raised to release the CO₂. The advantage is high storage capacity and use of tertiary amines allows potential for lower energy required per CO₂ captured. However, it is difficult to lower and raise the temperature of a solid material. Also, small diameter particles can cause high pressure drop across absorber.

(6) Enzymatic CO₂ sorbents
Enzyme-based system achieves CO$_2$ capture and release by mimicking mammalian respiratory mechanism. The features include fast kinetic, resistance to SOx and NOx, and pH swing based operation offers potential to produce CO$_2$ above atmospheric pressure. The disadvantage includes 100$^\circ$ F operating limit and exothermic CO$_2$ sorption reaction requiring cooling of flue gas, entrained solids in flue gas from coal boilers may block membrane channels, and possible sensitivity to acid gases.

(7) Chilled ammonia CO$_2$ capture

ALSTOM’s unique system, based on chilled ammonia, captures CO$_2$ by isolating the gas from the power plant’s other flue gases and can significantly increase the efficiency of the CO$_2$ capture process. The system uses a CO$_2$ absorber similar to SO$_2$ absorbers and is designed to operate with slurry. The cooled flue gas flows upwards in counter current to the slurry containing a mix of dissolved and suspended ammonium carbonate and ammonium bicarbonate. More than 90% of the CO$_2$ from the flue gas is captured in the absorber. The remaining low concentration of ammonia in the clean flue gas is captured by cold-water wash and returned to the absorber. The clean flue gas, which now contains mainly nitrogen, excess oxygen and low concentration of CO$_2$, flows to the stack.

The process has the potential to be applied to capture CO$_2$ from flue gases exhausted from coal-fired boilers and natural gas combined cycle (NGCC) systems, as well as a wide variety of industrial applications. ALSTOM is today engaged in an extensive development and commercialization program with the objective of offering a commercial product for selected market segments before the end of 2011.
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).

It should been mentioned that SaskPower Boundary Dam Integrated Carbon Capture and Sequestration Demonstration project recently selected three technologies all absorption processes. These are Cansolv’s amine process, Fluor’s MEA process and Powerspan’s aqueous ammonia process.

In this report, we present a novel absorption and capture method titled, “Phase Transitional Absorption” process. The process has the capability to overcome the shortcomings of conventional MEA absorption. The phase transitional absorbent is stable in the flue gas environment. Its other attributes include high absorption rate, high CO₂ loading and working capacity, low regeneration temperature and heat requirement, low heat of reaction with CO₂, low corrosion on steel, and low amine loss and degradation.
EXECUTIVE SUMMARY

Cost of the amine process and system is very high and the net power output of a power plant with MEA process is 25%-30% lower than for comparable power plant without CO₂ capture. A better CO₂ absorbent and an absorption process are needed to reduce the cost of CO₂ capture to within acceptable range. An ideal absorbent and process for CO₂ capture should have the following characteristics:

- Low-cost and non-degradable
- High capacity and affinity for CO₂
- Low corrosion rates
- Low heat of reaction with CO₂
- Low temperature of regeneration
- Stable under absorption operating conditions.

A novel absorption and capture method titled, “Phase Transitional Absorption” process was invented by Dr. Liang Hu. The process has the capability to overcome the shortcomings of conventional MEA absorbent. The absorbent is stable in the flue gas environment. Its other attributes include high absorption rate, high CO₂ loading and working capacity, low regeneration temperature and heat requirement, low heat of reaction with CO₂, low corrosion on steel, and low amine loss and degradation.

Our initial bench scale work has shown that the proposed process in conjunction with the special absorbent is able to reduce cost of energy consumption by 80 percent. In addition, the absorbent is able to significantly reduce corrosion of carbon steel, and amine degradation and loss. In this respect, the proposed technology represents a significant advancement toward achieving the goal of capturing CO₂ without exceeding incremental cost of energy consumption by 20 percent. The technology can also be used in other industries representing large point source of CO₂ release such as petroleum, chemical, steel, food, etc. industries for CO₂ capture or separation.
EXPERIMENTAL METHODS

Experimental Method and Apparatus for Absorption

Apparatus:

Phase transitional absorption was studied 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 transitional 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 transitional absorption system (gas phase, and two liquid phases). The cell’s inner diameter is 100 mm and its depth is 100 mm. Two agitating blades, one for the liquid 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, $r \sim t$, 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 $T_1$ and $T_2$;

(3) Use idea gas equation to calculate the mass flow rates $r_1$ and $r_2$ [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 $t$: $\frac{PV}{t} = \frac{RTn}{t}$
The mass flow rate: \( n/t = \frac{PV}{(tRT)} \)

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

\[
r = r_1 - r_2 = (n/t)_1 - (n/t)_2 = \frac{PV_1}{(tRT_1)} - \frac{PV_2}{(tRT_2)}
\]

Where \( t \) (s) is the elapsed time.

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

\[
N = \frac{r}{\text{area of gas-liquid interface}}
\]

CO\(_2\) concentration in liquid \( c \):

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

**Experimental Method and Apparatus for Desorption**

![Experimental Apparatus for Regeneration Study](image)

**Figure 3**   Experimental Apparatus for Regeneration Study
Phase Transitional Absorbent was placed into the stirring cell to absorb CO$_2$. The detailed absorption procedure has been described in above section. After absorption, two liquid phases, CO$_2$ rich phase and CO$_2$ lean phase, were separated. The CO$_2$ rich phase, 80 ml, was placed into a three neck glass flask for regeneration. The regeneration temperature was controlled by oil bath that the glass flask was immersed into. A thermometer was inserted into the glass flask to measure the temperature of the CO$_2$ rich phase. The samples were taken from the CO$_2$ rich phase to determine the CO$_2$ concentration in the liquid.

**Experimental Method and Apparatus for Corrosion Study**

The NACE standard TM-01-69 (1976) and ASTM standard G1-88 (1989) are used as guideline in our corrosion testing procedures.

**Specimen**

Specimen description: ACT 1008 COLD ROLL STEEL 01X02X.125 CUT ONLY UNPOLISH CENTER HOLE 1/4” ALPHA NUMERIC I.D. STAMP

Specimen chemical composition: 0.07 C, 0.39 Mn, 0.008 P, 0.013 S.

Size of the specimen: 1 in. x 2 in. x 0.125 in. with ¼” diameter center hole

Manufacturer: ACT Test Panels, LLC. 273 Industrial Dr. Hillsdale, MI 49242

**Testing Procedure at Low Temperature**

The corrosion testing procedures are divided into two steps, the first step is the preparation of the liquid sample, and the second step is the weight loss test.

**Step 1. Preparation of liquid sample**
For MEA aqueous solution: The absorbent was made of 25 % MEA (by volume) and 75 % water. The absorbent was filled into the absorber. In the absorber, the CO₂ gas was absorbed into the absorbent to saturation. The CO₂ saturated absorbent was transferred into the glass bottle and sealed for further use.

For the absorbent of Phase Transitional Absorption: The absorbent was made of 25 % Activated agent (by volume) and 75 % solvent. The absorbent was filled into the absorber. In the absorber, the CO₂ gas was absorbed into the absorbent to saturation. The absorbent was split into two phases, CO₂ rich phase and CO₂ lean phase. Both phases were transferred into the glass bottle and sealed for further use.

Step 2. Weight loss test

For MEA aqueous solution: Tests were carried out at 30 °C. 120 ml CO₂ saturated absorbent was placed into an Erlenmeyers flask. The flask was set into a water bath where temperature was controlled at 30 °C. The mouth of Erlenmeyers flask was open to air that allows oxygen to contact the absorbent. The specimen was weighed after rinsing by both water and alcohol. The specimen was placed into Erlenmeyers flask and completely immersed into the absorbent. The liquid in Erlenmeyers flask was gently agitated every 6 hours. The specimen was soaked in the absorbent for 6 days. After taking out from Erlenmeyers flask, the specimen was rinsed by water and alcohol, and dried. The weight of the specimen was recorded. After subtraction of the initial and final weight of the specimen, the weight loss during 6 days was obtained.

For the absorbent of Phase Transitional Absorption: Tests were carried out at the different experimental conditions: temperature 30, 45 °C, CO₂ lean phase, CO₂ rich
phase without water, CO$_2$ rich phase with water (ratio CO$_2$/H$_2$O = 1). 120 ml CO$_2$

saturated absorbent was placed into an Erlenmeyers flask. The flask was set into a water
bath where temperature was controlled at 30 °C. The mouth of Erlenmeyers flask was
open to air that allows oxygen to contact the absorbent. The specimen was weighed after
cleaned by both water and alcohol. The specimen was placed into Erlenmeyers flask and
completely immersed into the absorbent. The liquid in Erlenmeyers flask was gently
agitated every 6 hours. The specimen was soaked in the absorbent for 6 days. After
taking out from Erlenmeyers flask, the specimen was rinsed by water and alcohol, and
dried. The weight of the specimen was recorded. After subtraction of the initial and final
weight of the specimen, the weight loss during 6 days was obtained.
RESULTS AND DISCUSSION

PART I STUDY OF ABSORPTION KINETICS AND MECHANISM

1. Effect of Temperature

Our experimental results showed that the change of temperature did not cause much absorption rate change for the absorbent we used. The small effect on the absorption rate by temperature should be contributed to the much smaller reaction heat.
2. Effect of Activated Agent Concentration

The experimental results showed that for the absorbent we used the highest absorption rate is in the range of activated agent between 30 to 40 % by volume. The range of activated agent may change if the different activated agents and solvents are used. The range of activated agent with highest absorption rate is highly related to the physical and chemical properties of the absorbent, ie. activated agents and solvents, and also the combination.

Figure 4  Absorption rate vs. Activated Agent Concentration

\[ T = 25 \, ^\circ C \quad P_{\text{CO}_2} = 1 \, \text{atm;} \quad N=250 \, \text{rpm;} \quad V_L=405\text{ml} \]

Phase Transitional Absorbent: activated agent: AD; solvent: B.
3. Effect of Agitation Speed

Our experimental results showed that the absorption rate was increased with the increase of liquid agitation speed. When the liquid agitation speed is less than 140 rpm, the effect of the liquid agitation speed on the absorption rate was significant. However, the effect of the liquid agitation speed on the absorption rate was much less sensitive. The experimental results well match the characteristics of the liquid side mass transfer control model. So, the mechanism of the absorption is the absorption with fast chemical reaction controlled by the liquid side mass transfer.

Figure 4  Absorption rates vs. liquid agitation speed

$P_{\text{CO}_2} = 1 \text{ atm}; \hspace{1em} N=250 \text{ rpm};$

Ratio (activated agent AMD/solvent B (by volume)) = 20/80; \hspace{1em} V_L=200\text{ml}

Phase Transitional Absorbent: activated agent: AMD; solvent: B.
4. Comparison of the absorption rate with MEA aqueous solution

Figure 5 Absorption rate comparison (Phase Transitional Absorption vs. MEA Technology)

\[ T = 25^\circ C \quad P_{CO_2} = 1 \text{ atm} \quad N = 60 \text{ rpm} \quad V_L = 900 \text{ ml} \]

Phase Transitional Absorption: activated agent: AM 20% by volume; solvent: B 80%.
MEA technology: 20% (by volume) MEA aqueous solution

The experiments were designed to verify the characteristics of the absorption. Based on the chemical engineering principle, the absorption rate is determined by the rate of chemical reaction and mass transfer. If the same experimental conditions, or similar mass transfer, are provided, the absorption rate is directly related to the chemical reaction rate. Two experiments, MEA aqueous solution and Phase Transitional Absorbent, were
conducted at the same experimental conditions, we believed at the very close mass transfer conditions. Phase Transitional Absorbent showed higher absorption rate than MEA aqueous solution. As we knew, CO₂ absorption by MEA aqueous solution has the mechanism of the absorption accompanied by the fast chemical reaction. So, we can predict that Phase Transitional Absorbent is also the absorption accompanied by the fast chemical reaction.

**ABSORPTION MECHANISM AND SUITABLE ABSORPTION COLUMN**

Based on the above investigation, we can determine that the mechanism of the Phase Transitional Absorbent is the absorption accompanied by fast chemical reaction, So, we are not going to further study the tasks that the purpose is to determine the mechanism: Task 1.4: “Effect of Carbon Dioxide Partial Pressure”, Task 1.5: “Effect of Liquid Holdup Task”, and Task 1.6: “Effect of Gas Liquid Interface”

Since Phase Transitional Absorbent has the clear characteristics of the mechanism of absorption accompanied by fast chemical reaction, an absorber with large gas-liquid interface and sufficient liquid turbulence are recommended in order to have higher absorption rate. So the packed column is suitable for Phase Transitional Absorbent.
Phase Transitional Absorbent was placed into the stirring cell to absorb CO₂. The detailed absorption procedure has been described in previous section. After absorption, two liquid phases, CO₂ rich phase and CO₂ lean phase, were separated. The CO₂ rich phase, 80 ml, was placed into a three neck glass flask for regeneration. The regeneration temperature was controlled by oil bath that the glass flask was immersed into. A thermometer was inserted into the glass flask to measure the temperature of the CO₂ rich phase. The samples were taken from the CO₂ rich phase to determine the CO₂ concentration in the liquid. The relationship of CO₂ concentration in CO₂ rich phase vs. elapsed time was shown in Figure 3. The experimental results showed that the desorption rate increases sharply with increase of the regeneration temperature.
PART III  COMPARISON OF PHASE TRANSITIONAL ABSORPTION WITH 30% MONOETHANOL AQUEOUS SOLUTION

The results of a comparison study conducted by Nexant, Inc. are presented in Table 1. The results, which are indicative at this stage of development, show that regeneration energy requirement for the Phase Transitional Absorption process is about 15 percent of that of the benchmark MEA-based process. Similarly, capital cost requirement is somewhat less than 80 percent of the conventional case.

**Table 1 Comparison of Phase Transitional Absorption with 30% MEA on 400 MW CCGT Power Plant**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Base Case Benchmark 30% MEA</th>
<th>Phase Transitional Absorption 20 vol% Activated Agent</th>
</tr>
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<tbody>
<tr>
<td>Flue Gas Feed, MMSCFD</td>
<td>1,585</td>
<td>1,585</td>
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<tr>
<td>CO₂ Concentration</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>CO₂ Recovered</td>
<td>86%</td>
<td>86%</td>
</tr>
<tr>
<td>CO₂ Recovered, Tons/day</td>
<td>1,572</td>
<td>1,572</td>
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<td><strong>Capital Costs</strong></td>
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<td>Exchangers</td>
<td>$23.2</td>
<td>$18.3</td>
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<tr>
<td>Vessels</td>
<td>23.6</td>
<td>18.1</td>
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<tr>
<td>Subtotal</td>
<td>46.8</td>
<td>36.4</td>
</tr>
<tr>
<td><strong>Utility Consumptions</strong></td>
<td></td>
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<tr>
<td>Reboil Duty, MMBtu/Hr</td>
<td>506</td>
<td>76.8</td>
</tr>
<tr>
<td>Cooling Water Duty, MMBtu/Hr</td>
<td>464</td>
<td>43.7</td>
</tr>
<tr>
<td>Heat input BTU/lb mol CO₂</td>
<td>85,000</td>
<td>12,902</td>
</tr>
<tr>
<td>6. Absorption solution</td>
<td>30wt% MEA + water</td>
<td>20 vol% Activated Agent</td>
</tr>
</tbody>
</table>
PART IV   CORROSION STUDY

Introduction

Corrosion has long been one of the most serious operational difficulties in the alkanolamine gas treatment plant. The corrosion occurs everywhere especially in regenerators, reboilers, and heat exchangers (Blanc et al., 1982; McDonald, 1983).

Corrosion mechanisms of carbon steel in the alkanolamine gas treatment plants are very complicated, and it is believed that a number of corrosion mechanisms are involved (Kohl and Riesenfeld, 1985). Most people thought the major parameters contributing to the corrosion process are dissolved carbon dioxide (CO₂), dissolved oxygen (O₂), alkanolamines, degradation products, temperature, and solution turbulence.

Lang and Mason (1958), Treseder (1984), and Kohl and Riesenfeld (1985) reported that the dissolved CO₂ was a primary corroding agent in alkanolamine gas treatment plants. Several iron corrosion mechanisms in aqueous CO₂ solutions have also been reported. One example is the reaction scheme of iron dissolution in bicarbonate solution proposed by Burstein and Davies (1980).

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

Dissolved O₂ is another corroding agent which plays an important role in corrosion. Dissolved O₂ can aggravate the corrosiveness of a system by oxidizing the metal surface of the container to form an oxide film as shown (Fontana, 1986):
2 Fe + 2H₂O + O₂  ===  2 Fe(OH)₂
2 Fe(OH)₂ + 2H₂O + 1/2O₂  ===  2Fe(OH)₂

Lang and Mason (1958), Kohl and Riesenfeld (1985), and DuPart et al. (1993) reported that alkanolamines themselves were not corrosive to carbon steel, regardless of temperature. They did indirectly influence corrosion rate by absorbing CO₂.

Alkanolamine degradation is claimed to be precursor for the formation of a corrosive environment. Alkanolamine solutions can be degraded by both carbon dioxide and oxygen. Gregory and Scharman (1937) reported a degree of iron corrosion caused by MEA degradation products in the presence of oxygen in MEA plants. The corrosiveness of DEA degradation products is still controversial. Blanc et al. (1982) stated that such degradation products had little or no effect on the corrosion of carbon steel equipment, while Polderman and Steele (1956), Moore (1960), and Chakam and Meisen (1986) were able to trace the corrosivity of such degradation products.

Temperature also affects corrosion rate. Generally, corrosion rates increase with temperature in a closed system.

Liquid turbulence can cause severe corrosion, in the form of erosion, particularly in the presence of solid contaminants. For systems without a film of corrosion products, corrosion rates are fully controlled by mass transfer and can be accelerated by flow rates (Videm and Dugstad, 1989). In inhibited systems, a protective film is developed to cover metal surfaces. Liquid turbulence can break the film and further cause the erosion.

Few researchers discussed the corrosion caused by water. Based on our research, water may be one of the parameters contributing to the corrosion process.
Research Objective

The research objective is to evaluate the corrosiveness of the absorbent of Phase Transitional Absorbent to the carbon steel. Also, the objective is to make comparison between Benchmark Process MEA aqueous solution with Phase Transitional Absorption on the corrosion to the carbon steel.

Following are the list of the experimental conditions and results of each corrosion test.

Experiment 1:

Phase Transitional Absorption (Activated Agent D)

Liquid: 25 % Activated Agent D (by volume), 75 % solvent, CO₂ rich phase

Temperature: 30 °C

Soaking duration: 6 days

Weight loss: 0.0000 (± 0.0005) g

Experiment 2:

Phase Transitional Absorption (Activated Agent D)

Liquid: 25 % Activated Agent D (by volume), 75 % solvent, CO₂ rich phase

Temperature: 45 °C

Soaking duration: 6 days

Weight loss: 0.0000 (± 0.0005) g

Experiment 3:

Industrial Benchmark MEA aqueous solution
Liquid: 25 % MEA (by volume) aqueous solution

Temperature: 30 °C

Soaking duration: 6 days

Weight loss: 0.0059 (± 0.0005) g

Experiment 4:

Phase Transitional Absorption (Activated Agent M)

Liquid: 25 % Activated Agent M (by volume), 75 % solvent, CO₂ rich phase

Temperature: 30 °C

Soaking duration: 6 days

Weight loss: 0.0000 (± 0.0005) g

Experiment 5:

Phase Transitional Absorption

Liquid: 25 % Activated Agent M (by volume), 75 % solvent, CO₂ lean phase

Temperature: 30 °C

Soaking duration: 6 days

Weight loss: 0.0000 (± 0.0005) g

Experiment 6:

Phase Transitional Absorption (Activated Agent M)

Liquid: 25 % Activated Agent M (by volume), 75 % solvent, CO₂ rich phase

Temperature: 45 °C
Soaking duration: 6 days
Weight loss: 0.0000 (+ 0.0005) g

Experiment 7:
Phase Transitional Absorption (Activated Agent M)
Liquid: 25 % Activated Agent M (by volume), 75 % solvent,
\[ \text{CO}_2 \text{ rich phase with water (ratio CO}_2/\text{H}_2\text{O} = 1) \]
Temperature: 45 °C
Soaking duration: 6 days
Weight loss: 0.0000 (+ 0.0005) g

As discussed above, the major parameters contributing to the corrosion process are dissolved carbon dioxide (CO\(_2\)), dissolved oxygen (O\(_2\)), alkanolamines, degradation products, temperature, and solution turbulence. In our experiments, we limited the corrosion caused by liquid turbulence because of the gentle liquid agitation. The corrosion to carbon steel was caused by only chemicals (dissolved carbon dioxide (CO\(_2\)), dissolved oxygen (O\(_2\)), amines, degradation products) and temperature.

The temperature range for corrosion tests is in the absorption temperature range. Our experimental results showed that the absorbent of Phase Transitional Absorption has very little corrosion to carbon steel by comparing with the Benchmark MEA Process at the absorption temperature range.
CONCLUSION

1. MEA aqueous solution and Phase Transitional Absorbent were conducted at the same experimental conditions for CO₂ absorption. Phase Transitional Absorbent showed higher absorption rate than MEA aqueous solution.

   Our experimental results also showed that the best concentration of activated agent is in the range of 30 – 40 % (by volume). The absorption temperature did not cause much change on the absorption rate.

   The mechanism study showed that the CO₂ absorption by Phase Transitional Absorption has the characteristics of the absorption accompanied by fast reaction.

2. Regeneration study showed that the desorption rate increases sharply with the increase of the regeneration temperature. Absorbent can be regenerated at 95°C. At 125°C, the CO₂ was released from the absorbent vigorously.

3. The results of a comparison study showed that regeneration energy requirement for the Phase Transitional Absorption process is about 15 percent of that of the benchmark MEA-based process. The capital costs of this case are 80% less than the conventional case.

4. Our experimental results showed that the absorbent of Phase Transitional Absorption has very little corrosion to carbon steel by comparing with the Benchmark MEA Process at the absorption temperature range.
GLOSSARY

C: CO₂ concentration in liquid, [mol/m³]

Nco₂: CO₂ absorption rate, [mol/m²/s]

P: Pressure, [atm]

R: Gas constant, e.g. 8.314 [m³·Pa/K/mol]

T: Temperature, [°C]

V: Volume, [m³]

n: Amount of substance, [mol]

r₁, r₂: Mass flow rate, [mol/s]

t: Time [s]
REFERENCE


McDonald, M.F. Corrosion Causes and Mitigation in Amine Sweetening Plants. NACE Western Canadian Reginonal Conference, Calgary, Alberta, Canada, Feb 1983.


