**CO₂ Capturing from Industrial Flue Gases**

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**Abstract**

Due to the ever-increasing cost of energy and more stringent pollution standards for atmospheric emissions, it is desirable to improve absorption processes for the removal of carbon dioxide from flue gas. The research needs have been reviewed for CO₂ capture from flue gas by aqueous absorption/stripping. A close-looped absorption/stripping pilot plant with 15 cm ID columns was used to capture CO₂ using a new blended amine (AIT 600) solution. Both the absorber and stripper contained 1.5 m of packing. The pilot plant campaign consisted of 27 runs at 9 operating conditions over the period of study. Various absorber temperature, gas and liquid rates and lean CO₂ loadings were tested. In this work by using Taguchi statistical method we studied the effect of operating conditions on the CO₂ capture efficiency. The operating parameter used in this study consisted of the following: gas flow rate, CO₂ mole fraction in feed gas, liquid flow rate and absorber temperature.

**Kew words:** absorption, stripper, CO₂, Global warming, Taguchi

**1. Introduction**

Global warming, believed to be caused by the greenhouse effect, has received increasing attention in recent years. When solar energy is transmitted through the atmosphere, greenhouse gases trap heat radiating from the earth to cause increasing global surface temperature, which is the greenhouse effect. Researchers estimate that the global average surface temperature has increased between 0.6 and 1.0 °C during the last 150 years and will increase by 1.4 to 5.8 °C from 1990 to 2100 [1].

The warmest year during the last 1200 years was 1998 and the warmest century over the last 1000 years was the twentieth century [1]. Global warming can melt icebergs and expand oceans. The Intergovernmental Panel on Climate Change (IPCC) predicts that the sea level will raise by 0.09 to 0.88 meters from 1990 to 2100, which will result in 25 percent of the world’s population living less than 1.1 meters above sea level [2]. Other probable consequences of global warming include droughts, expanding deserts, heat waves, ecosystem disruption, increasingly severe weather, and loss of agriculture productivity [3].

Greenhouse gases include carbon dioxide (CO₂), water vapor (H₂O), ozone (O₃), methane (CH₄), nitrous oxide (N₂O), and chlorofluorocarbons (CFCs) [4]. Since the beginning of the industrial period, the concentrations of the anthropogenic greenhouse gases (CO₂, CH₄, N₂O, CFC-11 (CCl₃F) and CFC-12 (CCl₂F₂)), have increased. Of those gases, CO₂ is considered to be the major greenhouse gas (GHG) contributing to global warming. Since the beginning of the industrial revolution in about 1850, the average atmospheric concentration of CO₂ has increased from 280 ppm to 370 ppm and as a result, the average global temperature has increased between 0.6 °C and 1°C in the same time period [4]. The International Panel on Climate Change (IPCC) predicts that, by the year 2100, the atmosphere may contain up to 570 ppm CO₂, causing a rise in the mean global temperature of around 1.9 °C [5]. Continued uncontrolled greenhouse gas emissions may contribute to sea level increases and species extinction. However, human activity, mainly burning fossil fuels, produces about 24 billion tons of CO₂ per year and only half of that is being absorbed by natural processes [5].
1.1. Efforts to Reduce GHG Emissions

Improving energy efficiency and using non-carbon energy sources are the most effective in the short term (next 20 years) to reduce GHG emissions. Four important areas are involved: improvement of thermo-electric energy conversion efficiency of power generation plants, using technology such as natural gas combined cycle systems (NGCC); better fuel efficiency in transportation, particularly automobiles, such as the introduction of hybrid cars, fuel cell vehicles (FCV), and electric vehicles; more efficient heating and hot water supplies in buildings and houses; and development of small scale power sources like fuel cells [6].

1.2. CO₂ Capture and Sequestration (CCS)

Over time, these methods may be effective in reducing CO₂ emissions, but generally they are not applicable to the large number of existing fossil fuel fired power plants. Therefore, CO₂ capture and sequestration (CCS) to reduce the CO₂ concentration in the atmosphere are needed during the next several decades [9]. Theoretically we can remove CO₂ from the air by enhancing natural sinks, such as growing more algae by ocean fertilization, planting trees, and greening the desert [6]. These ideas have long-term significance, but are not practicable at present; therefore to mitigate the global warming problem, removal of CO₂ from the industrial flue gases is necessary. Different technologies had been developed for CO₂ removal by various investigators in the past [6]. These include absorption by chemical solvents, physical absorption, cryogenic separation, membrane separation, CO₂ fixation by biological or chemical methods and O₂/CO₂ combustion. Among those methods, CO₂ absorption by chemical solvents appears to offer an interesting and practical alternative. In fact, CO₂ absorption by alkanolamines has been a popular and effective one. Many previous investigators looked in to the chemical reaction mechanism, mass transfer, gas/liquid equilibrium, and other related aspects of CO₂ absorption. Those studies focused primarily on determination of the reaction mechanism, rate of absorption and reaction, and efficiency of CO₂ absorption system by conducting experimental tests in pressure vessel or column absorber. In contrast, relatively little work was done on CO₂ absorption in a packed column. In fact, gas absorption in a packed column is deemed as a more efficient system than other alternatives.

Previously it was mentioned that we are going to be dependent on fossil fuels for the upcoming decades, as described in the IPCC report. This means that CO₂ emissions will continue to rise and with them, their interference with the climate. These emissions from different sources have increased its concentration in the atmosphere. It has to be stabilized so that anthropogenic disturbance in the climate system can be prevented. To reduce the emissions of CO₂, it can be captured with different technologies and sequestered in number of ways (see Figure 1). It can be disposed deep under the see using a long pipe line or with the help of ships. It can be stored geologically deep under the ground. This kind of storage is also used commercially to enhance the flow of crude oil from its sources and is therefore not restrained from the atmosphere. Captured CO₂ can also be used for some industrial purposes. It is used in gaseous or liquefied state as feedstock in chemical processes that produce valuable carbon containing products. However the potential for such use is limited by around 1% of anthropogenic CO₂ [7,8].

2. Existing capture technologies

Several technologies are available to capture CO₂ from fossil fuel industry. These include mainly

- Adsorption.
- Cryogenics separation (Low temperature distillation).
- Membranes
- Physical and chemical absorption.

Figure 1 shows classification of various separation technologies available for post combustion capture. A brief introduction of these technologies will set the background of this Literature Review.
3. Theoretical consideration

At this moment the most successful and well known acid gas treating processes are amine based. Alkanolamines remove CO$_2$ from the gas stream by the exothermic reaction of CO$_2$ with the amine functionality of the alkanolamine, with the following reactions taking place in the solvent.

\[
\begin{align*}
2\text{H}_2\text{O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \\
\text{CO}_2 + 2\text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \\
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \\
\text{R}_1\text{R}_2\text{R}_3\text{N}^- + \text{H}_2\text{O} & \leftrightarrow \text{R}_1\text{R}_2\text{R}_3\text{NH}^+ + \text{OH}^- 
\end{align*}
\]

(water ionization)

(bicarbonate formation)

(carbonate formation)

(amine protonation)

While for amines containing at least one hydrogen atom at the amino group (primary and secondary amines) a second, additional reaction can take place, a carbamate can be formed.

\[
2\text{R}_1\text{R}_2\text{R}_3\text{N}^- + \text{CO}_2 \leftrightarrow \text{R}_1\text{R}_2\text{R}_3\text{NCOO}^- + \text{R}_1\text{R}_2\text{R}_3\text{NH}^+ 
\]

This carbamate formation reaction is usually fast and the reason why primary and secondary amines are more reactive that tertiary amines.

Different amines have different reaction rates with respect to the various acid gases. In addition, different amines vary in equilibrium absorption characteristics for the various acid gases and have different sensitivities with respect to solvent stability and corrosion factors.

4. Experimental Designs

Several experimental designs exist that are practically used in the industry, which are subject to the objective of the experiment or the process of the experiment. The major classes of experimental designs typically used in the industries include: Two-level design,
multi-factor design, screening design for large numbers of factors, three-level, multi-factor designs (mixed designs with 2 and 3 level factors inclusive), central composite designs, Latin square design, Taguchi robust design analysis, and mixture designs. The choice of experimental design is subject to the objective and the number of factors to the investigated. However, many industrial experimental situation calls for standard and advance experimental design for the purpose of precision and optimal properties. In relation to this, Taguchi experimental method is one of the common advanced methods used today in the industry and has been adopted for this research work.

4.1. Design of experiments using Taguchi methodology

Design of experiments is an invaluable tool for identifying critical parameters, optimizing chemical processes and identifying operating regions for the process. The Taguchi method is a powerful problem solving technique for improving process performance. It reduces scrap rates, rework costs and manufacturing costs due to excessive variability in processes [11]. Taguchi method is capable of establishing an optimal design configuration, even when significant interaction exists between and among the control variables. It utilizes sets of orthogonal arrays (OA) which accommodates many experimental situations that are subject to the level of factors which could run from two to four levels. However, the number of parameters could vary from three to fifty. Hence, the experimental design will be selected (L4 to L50) which requisite the experimental phase. Noise factors are also considered in this phase which is the factors that that influence the response of a process. Taguchi’s orthogonal arrays provide an alternative to standard factorial designs. Using the orthogonal array the optimum experimental conditions can be easily determined [11]. This study considers four controllable factors, and each factor has three levels (Table 1). Therefore, an L₉(3⁴) orthogonal array is chosen from the array selector and the experimental conditions (Table 2) can be obtained by combining Table 1 and the L₉(3⁴) orthogonal array. Accordingly, an analysis of the signal-to-noise (S/N) ratio is needed to evaluate the experimental results. Usually, three types of S/N ratio analysis are applicable: (1) lower is better (LB), (2) nominal is best (NB), and (3) higher is better (HB) [11]. Because the target of this study is to maximize the CO₂ removal from flue gas, the S/N ratio with HB characteristics is required, which is given by

\[
S/N = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} \left( \frac{1}{Y_i^2} \right) \right)
\]  \( (1) \)

Where n is the number of repetitions under the same experimental conditions, and Y represents the result of measurement, i.e. Y is the efficiency of the CO₂ capture [10].

\[
Y_i = \frac{y_{CO2, in} - y_{CO2, out}}{y_{CO2, in}}
\]  \( (2) \)

Where \( y_{in} \) and \( y_{out} \) stand for the mole fraction of CO₂ of the gas phase entering and leaving the absorption column respectively. All the experiments were carried out at atmospheric pressure.

| Table 1. Controllable process variable and their levels. |
|--------------------------------------|------|------|------|
| Parameter | Description | Level 1 | Level 2 | Level 3 |
| A | Gas flow rate (m³/hr) | 3 | 5 | 8 |
| B | CO₂ mole fraction (v/v%) | 5 | 10 | 15 |
| C | Liquid flow rate (ml/min) | 200 | 300 | 400 |
| D | Absorber temperature (°C) | 50 | 60 | 70 |
Table 2. Experimental conditions.

<table>
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<tr>
<th>Run Number</th>
<th>Gas flow rate (m³/hr)</th>
<th>CO₂ inlet percent (v/v%)</th>
<th>Liquid flow rate (ml/min)</th>
<th>Absorber temperature (°C)</th>
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4.1.2. Absorbent concentration

The effect of absorbent concentration on CO₂ absorption efficiency is shown in figure 2. The flow rate of flue gas, flow rate of liquid solvent, input temperature of absorbents and CO₂ concentration of flue gas were 3m³/h, 300 ml/min, 60 °C and 10%, respectively. The ratio of liquid to gas (L/G) kept constant with the value of 6 L/m³.

We can see from figure that CO₂ absorption efficiency increases with the concentration of absorbent increasing, then keep stabilized. When the absorbent concentration is low, increasing absorbent concentration, CO₂ absorption efficiency growth is large. However, when the absorbent concentration is high, CO₂ absorption efficiency growth is not obvious. These phenomenon’s are determined by reversible equilibrium conditions and gas liquid two phase mass transfer conditions. In the view of chemical dynamics, increasing absorbent concentration is equivalent to increasing the reactant concentration, resulting in response moving to the positive direction, improving the reaction rate and CO₂ absorption efficiency. Thus, in different operating conditions, it is feasible to improve CO₂ absorption efficiency by increasing the absorption concentration.

![Figure 2. Absorbent concentration effect on absorption efficiency](image_url)

4.1.3. Absorbent flow rate
The effect of absorbent flow rate on CO₂ absorption efficiency is shown in Figure 3. The other operation conditions are the same as basic operation conditions except ratio of the flow rate of liquid. It can be seen from Figure, CO₂ absorption efficiency is also increased as the absorbent flow rate increased. Flow rate is equivalent to increasing gas liquid two phase area of unit volume, enhancing gas liquid mass transfer rate, improving the CO₂ absorption efficiency. But there is a problem that while increasing the absorbent flow rate makes the droplets residence time cut down, reducing the CO₂ absorption efficiency.

![Figure 3. Absorbent flow rate effect on absorption efficiency.](image)

Combining two aspects of effect, CO₂ increased when absorbent flow rate increased. Therefore, in certain experimental conditions, it is possible to improve CO₂ absorption efficiency by increasing the absorbent flow rate.

5. Conclusion

CO₂ capture from flue gas produced by fossil fuels combustion is corresponding to the most widely applicable option in terms of industrial sectors and is compatible to a retrofit strategy. The main challenge for CO₂ capture systems is the large amount of energy consumption which reduces net plant efficiency significantly. Therefore, many researchers have examined the possibilities of enhancing the efficiency of these processes to reduce the effect of their drawbacks.

The bulk removal of CO₂ from process gas streams and flue gases is, in industry, usually carried out via an absorber-desorber combination. One promising solvent used in this process step is the amine proprietary blend (AIT 600). From the result obtained in the present study, it can be concluded that AIT 600 solvent appears to be an excellent solution for capturing CO₂ from flue gas. Since it combines the benefits of both, solvent with high rate of reaction with CO₂ and a low heat of reaction with —COO. This solvent has been analyzed in a pilot plant.

6. References


