Experimental Studies on the Influence of HCO$_3^-$ on Absorption and Desorption of CO$_2$ from Ammonia Solution

Shaojian Jiang, Wei Zhong, Rui Peng, Yong Jiang, Jun Zhang
School of Energy Science and Engineering, Central South University, Changsha, China

Received 2012

ABSTRACT

With aqueous ammonia in the process of CO$_2$ absorption and desorption to join sodium bicarbonate, the influence of HCO$_3^-$ on CO$_2$ absorption and desorption from ammonia solution was investigated through the experimental analysis of the desorption quantity of CO$_2$, desorption rate, CO$_2$ loading and the absorption rate. The experimental results showed that, in experimental conditions, the desorption rate decreased gradually with increasing ammonia concentrations. The desorption rate increased 12%, 17%, 19% and 28.8% when 1 mol/L of ammonia solution is added in 0.1 mol/L, 0.3 mol/L, 0.5 mol/L and 1 mol/L of sodium bicarbonate. The higher concentration of ammonium bicarbonate solution which was added sodium bicarbonate, the more observably the effect of CO$_2$ desorption was promoted. The absorption rate had dropped when absorption process added 0.3 mol/L sodium bicarbonate, the CO$_2$ loading was a little change.

Keywords: Ammonia Desorption; the Desorption Rate; CO$_2$ Absorption; CO$_2$ Loading

1. Introduction

As the rapid development of modern industry, a large number of the use of fossil fuels leads to increased CO$_2$ emissions, and CO$_2$ is climate change and the main cause of global warming. Therefore, carbon capture and storage (CCS) projects have been reported[1]. The chemical absorption capture of CO$_2$ has been studied and widely used as a reliable and cost-efficient method for CO$_2$ because of its characteristics such as higher absorption rate, higher CO$_2$ recovery rate, no absorbent degradation and lower desorption energy requirement, etc[2]. The traditional chemical absorption methods include alcohol amine solution, alkali solution, aqueous alkanolamine solution, etc. Among them, MEA, as a representative of the alcohol amine is the most traditional absorbent[3], it is used in industry early in the 19th century. However, because its higher desorption energy, amine degradation by O$_2$, SO$_2$ in flue gas which induces a high absorbent makeup rate and high equipment corrosion rate[4], on the actual plant there is still a limit used in decarbonization. Compared with MEA, aqueous ammonia which has higher CO$_2$ loading capacity (g CO$_2$ absorbed per g absorbent), no corrosion problem, no absorbent degradation problem, lower desorption energy[5,6], and the ability to capture all three major acid gases(SO$_2$, NO$_x$, CO$_2$), is becoming a hot research[7].

It has been concluded that the maximum CO$_2$ removal efficiency by NH$_3$ absorbent can achieve 95% and the major produced from the Aqua Ammonia Process including ammonium bicarbonate and ammonium carbonate etc[8]. Due to the process is reversible, therefore, a way to heat its bicarbonate salts to desorb the solution is used to make sorbent recycling. The process to CO$_2$ desorption which is not desorbed completely has resulted in absorption capacity is reduced. Liu Fang[9] researched the process of CO$_2$ desorption from ammonium bicarbonate, Zeng Qing[10] studied the characteristics of CO$_2$ desorption from Carbonated ammonia solution, which showed that desorption rate was influenced by temperature, CO$_2$ loading. Houping Huang[11] investigated a method to regenerate ammonia so as to allow for the ammonia scrubbing technique to be practical in the capture of CO$_2$ that a weakly basic ion-exchange resin containing amine functional groups is used. How to improve the desorption rate, and in the process of absorption recycling, keep the CO$_2$ loading capacity the same are a key research direction.

Research has shown that[12], with the increasing of the concentration of bicarbonate ions, CO$_2$ is easier to release from the solution. This paper studied the influence of HCO$_3^-$ (put NaHCO$_3$ into solution as a additives) on CO$_2$ absorption and desorption from ammonia solution which keep the concentration of NH$_4^+$ the same and change the solution of HCO$_3^-$ concentration.

2. Experiment

2.1. Theory

The desorption reaction of CO$_2$ into ammonia solution can be described as the following equations (1), (2), (3), it is shown the lowest enthalpy of dissociation for CO$_2$ release from (1).

2NH$_4$HCO$_3$(aq) ⇔ (NH$_4$)$_2$CO$_3$(aq)+CO$_2$(g)+H$_2$O(l) (1)

NH$_4$HCO$_3$(aq) ⇔ NH$_4$(aq)+CO$_2$(g)+H$_2$O(l) (2)

(NH$_4$)$_2$CO$_3$(aq) ⇔ 2NH$_4$(aq)+CO$_2$(g)+H$_2$O(l) (3)

For absorption reaction, it is typical chemical reaction process as following equations (4), (5), (6), (7).
\[
\begin{align*}
\text{CO}_2 + 2\text{NH}_3 & \rightarrow \text{NH}_2\text{COONH}_4 & (4) \\
\text{NH}_2\text{COONH}_4 + \text{H}_2\text{O} & \Leftrightarrow \text{NH}_4\text{HCO}_3 & (5) \\
\text{NH}_4\text{HCO}_3 & \Leftrightarrow (\text{NH}_4)_2\text{CO}_3 & (6) \\
(\text{NH}_4)_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} & \Leftrightarrow 2\text{NH}_4\text{HCO}_3 & (7)
\end{align*}
\]

2.2. The Experiment System

The experiments were divided into desorption and absorption process. The schematic diagrams for desorption process were represented in Figure 1. It was experimented with ammonium bicarbonate solution preparation simulation of the practical absorbent, through the adjustment of ammonium bicarbonate solution concentration and adding additives way to control simulation absorbent. The desorption solution was controlled the temperature by water-bath pot. CO\textsubscript{2} gas was purged the entire system before the start of the experiment. Then the solution was stirred by the magnetic stirrer. The gas was analysed by CO\textsubscript{2} Analyzer through a mixture of gases from desorption after pickling bottle and desiccating agent. In the process of desorption, the temperature controlled in 60°C ~ 99°C. The desorption rate is tested at 99°C.

The experimental system for studying CO\textsubscript{2} absorption is showed in the schematic diagram of Figure 2. The simulated flue gas consisted of 14 vol.% CO\textsubscript{2} and 86 vol.% Air. The temperature of the gases was 20°C, and the flow controlled by mass flow controlled which was 80 m\textsuperscript{3}/h. The temperature of the absorber was controlled in 40 ~ 50°C, and the flow was 1450 L/h (liquid/gas is about 18 L/m\textsuperscript{3}). The pressure of the whole experiment process was close to 1 atmosphere. In the experimental process, flue gas was flowing through absorption tower continuously and absorber was recycling. After the absorption the gas was analysed by CO\textsubscript{2} analyzer.

3. Result and Discussion

3.1. CO\textsubscript{2} Desorption Characteristics in Ammonium Bicarbonate Solution

Experiments of 100 mL ammonium bicarbonate solution was heated which the concentrations were 1 mol/L, 1.5 mol/L and 2 mol/L. From 55°C solution had been heated to a constant temperature when water-bath water was boiling. The desorption process was end when CO\textsubscript{2} analyzer show flow velocity was zero. Desorption started quickly when the solution was decomposed and a large number of small bubbles were emerged. With the rise of temperature, the bubbles on the surface of liquid level were becoming bigger, and bubbles was rising quickly as well as they burst. Finally, the bubbles become less and less. It was shown that CO\textsubscript{2} desorption from the method of ammonia absorber was obvious effective and with good reproducibility.

Typical CO\textsubscript{2} desorption curve of Ammonium bicarbonate solution changing with temperature rules was shown in Figure 3. With the rise of temperature, CO\textsubscript{2} desorption speeded rapidly, when the temperature reached 85°C, CO\textsubscript{2} desorption speed was about to the biggest, and the amount of CO\textsubscript{2} desorption increased quickly. It was closed to the best desorption temperature of 87.5°C which Liu Fang [13] confirmed in the desorption of the ammonia method of absorbent. With the temperature rise further, the concentration of HCO\textsubscript{3} was reduced gradually so that little CO\textsubscript{2} desorbed out, desorption speed was reduced. As the increasing concentration of HCO\textsubscript{3}, the higher concentration of desorption solution could desorb more over CO\textsubscript{2}. The final desorption rates of 1 mol/L, 1.5 mol/L, 2 mol/L of ammonium bicarbonate solution were 57%, 54% and 48%, it was shown that the higher the concentration of solution was, CO\textsubscript{2} desorption rate gradually reduced. Because the concentration of HCO\textsubscript{3} reduced and CO\textsubscript{3}\textsuperscript{2-} increased, leading to inhibit the reaction (1).
3.2. The Influence on the Desorption of Ammonium Bicarbonate Solution within Sodium Bicarbonate

The Figure 3 showed the higher the concentration of ammonium bicarbonate solution was, CO₂ desorption rate gradually reduced. The following experiments were conducted. Sodium bicarbonate was added into the ammonium bicarbonate solution to change the concentration of HCO₃⁻ and ensure NH₄⁺ concentration under the condition of invariable, to investigate HCO₃⁻ to the effect of CO₂ desorption. 100 mL, 1 mol/L of ammonium bicarbonate was added 0.1 mol/L, 0.3 mol/L, 0.5 mol/L and 1 mol/L of sodium bicarbonate to study its CO₂ desorption characteristics. The desorption of 1 mol/L ammonium bicarbonate solution as a function of sodium bicarbonate concentration was shown in Figure 4.

The CO₂ desorption quantity and rate were increased by adding sodium bicarbonate and intensified with higher concentration of sodium bicarbonate. The desorption rate was 58% for the solution of 1 mol/L ammonium bicarbonate solution. The CO₂ desorption rate with ammonium bicarbonate solution adding 0, 0.1 mol/L, 0.3 mol/L, 0.5 mol/L and 1 mol/L of sodium bicarbonate solutions were 58%, 65%, 68%, 69%, 74%, respectively, the efficiencies were increased 12%, 17%, 19% and 28.8%. The sodium bicarbonate solutions of 0.1~0.3 mol/L into 1 mol/L ammonium bicarbonate solution afforded the greatest rate of increased desorption. Over 0.3 mol/L the rate was slow. According to the chemical reaction kinetics, it was supposed to make positive reaction for desorption to make the amount of CO₂ desorption increased when the concentration of HCO₃⁻ continued to increase. The higher concentration of sodium bicarbonate which was weakly alkaline salt was, the degree of hydrolysis was more and more small. Meanwhile, it's inhibit effect to the NH₄HCO₃ ionization and makes the growth of desorption amount.

3.3. The Influence of the Desorption of Different Concentration of Ammonium Bicarbonate Solution within Sodium Bicarbonate

CO₂ desorption characteristics for 1 mol/L, 1.5 mol/L, 2 mol/L, 2.5 mol/L of ammonium bicarbonate solution were investigated which was joined 0.3 mol/L of sodium bicarbonate. The desorption of different concentration of ammonium bicarbonate solution as a function of sodium bicarbonate concentration was shown in Figure 5. The increasing desorption amount with increasing concentration expressed on approximate linear relationship. Nevertheless, the result that the higher the concentration of solution was, CO₂ desorption rate gradually reduced had been confirmed in Figure 3. The quantity of CO₂ desorption and the concentration had an inverse proportion relation. When adding sodium bicarbonate, CO₂ desorption rate increased and the higher concentration of ammonium bicarbonate solution the better effect of the CO₂ desorption rate bringing about by introducing HCO₃⁻, and the speed reduction of desorption rate slowed down. Compared with 1.5 mol/L plus 0.3 mol/L sodium bicarbonate into 2 mol/L of ammonium bicarbonate solution had only declined 3.2%. Add 2 mol/L of sodium bicarbonate ammonium bicarbonate solution of the CO₂ desorption rate than only 1.5 mol/L declined 3.2%. This shown that the higher concentration of absorbent plus sodium bicarbonate, the more observably the effect of CO₂ desorption was promoted.

3.4. Sodium Bicarbonate of CO₂ Absorption Effect

Using ammonia method to absorb CO₂, the absorbent circulated after desorption. When plus sodium bicarbonate, it had an influence on the absorption process. Carbon dioxide absorption rates for 5% ammonia solution and plus 0.3 mol/L sodium bicarbonate were measured in the experiment equipment (Figure 2). For each amine concentration about CO₂ loadings were tested. The experimental results were represented in Figure 6. Ammonia solution had an great effect on absorbing CO₂, the CO₂ absorption capacity reduced with increasing CO₂ loading. When added sodium bicarbonate, the absorption rate decreased.
There was so much free ammonia in low CO₂ loading in the early stage that carbamate(NH₂COO⁻) was the main species[14]. Meanwhile, the concentration of carbamate increased with increasing CO₂ loading. Moreover, Carbamate and carbonate ions would be gradually converted to bicarbonate ions as increasing absorbed amount of CO₂ in ammonia solution(Eq. 5) after a certain time. The process was inhibited by adding sodium bicarbonate and leading to the drop of the CO₂ absorption rate. While by changing the operation conditions, as well as the absorption tower structure could be improved the absorption rate. Along with the absorption process, the absorption rate reduced gradually with increasing CO₂ loading, and the CO₂ loading capacity reduced when added sodium bicarbonate, but the speed reduction of CO₂ loading slowed down. Respectively, the concentration of free ammonia decreased rapidly, while the speed reduction of that slowed down. The concentration of NH₄⁺ remained the same in whole solution, for the same absorption effect, CO₂ loading changed a little.

**4. Conclusion**

1) Using ammonia method had an good effect on CO₂ absorption and desorption. High concentration of absorbent could also have lower rates of desorption.

2) Sodium bicarbonate as additives, could greatly improve the CO₂ desorption rate, with the increasing of the concentration of HCO₃⁻, the speed reduction of CO₂ desorption rate slowed down.

3) For different concentration of absorbent, the higher concentration of absorbent plus sodium bicarbonate, the more observably the effect of CO₂ desorption was promoted.

The absorption process joined sodium bicarbonate, the absorption rate had reduced, CO₂ loading changed a little.

---

**REFERENCES**


