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Semi-batch experimental study on CO₂ absorption characteristic of aqueous ammonia

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Abstract

Absorption characteristics of CO₂ into aqueous ammonia are the key factors to achieve simultaneous removal of pollutants from coal-fired flue gas by ammonia scrubbing. An experimental study with a semi-continuous flow reactor was conducted to investigate the CO₂ absorption characteristic of aqueous ammonia solutions. Pure CO₂ was chosen in order to avoid the effect by the other gas components in this paper. The effect on solution CO₂ loading and CO₂ absorption capacity, which is caused by ammonia concentration, CO₂ inlet velocity and temperature, has been given. Furthermore, the effect on absorption characteristic and slippery characteristics of ammonia caused by additives is also covered. The experiment results show that, with increase of ammonia concentration, the solution CO₂ loading increases while the CO₂ absorption capacity decreases. Both the above two parameters decrease with the increase of CO₂ inlet velocity, but the total reaction rate acts reversely. When the temperature reaches 15°C or 35°C, the absorption characteristic can reach the extreme points. Adding AMP into ammonia can enhance the absorption of CO₂, and control the slippery of ammonia in the absorption process. What’s more, 3% is a better choice for addition concentration.

Keywords: Ammonia scrubbing; CO₂; AMP; Absorption characteristic; Ammonia slippery

1. Introduction

Although the amine-based chemical absorption process is currently the most effective means of CO₂ capture and storage, an amine-based absorption option such as ethanolamine (MEA) absorption process is still relatively too expensive to afford for large-scale power plants and other large-scale CO₂ emissions sources. In addition, there are still many inherent problems for amine-based decarbonisation methods, such as the relatively low CO₂ absorption efficiency, the weakness of absorption capacity due to oxidation, thermal degradation, irreversible reaction, evaporation and other reasons, system corrosion caused by degradation product in the rich-MEA solution, large regeneration energy consumption and relatively high initial capital and operating costs[1,2,3]. In 1997, Bai and Yeh apply ammonia as an alternative absorbent for removal of CO₂. Studies have shown that ammonia solution has a quicker reaction rate with CO₂ and low CO₂ regeneration energy consumption. The CO₂ absorption capacity of ammonia is triple of the CO₂ absorption capacity of MEA. There are less system erosion and oxidization

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degradation problems for ammonia [4]. It is more attractive that ammonia can be also applied to simultaneous removal of SOx, NOx, Hg and the other matters, which is demonstrated by the former studies [5,6,7].

Many research organizations worldwide has already undertaken the studies of decarbonisation by the ammonia scrubbing method. Powerspan, NETL and NRG cooperated to develop an aqueous ammonia decarbonisation method called ECO-ECO₂. Alstom and EPRI jointly developed chilled ammonia process named CAP. However, the current study result on the ammonia decarbonisation method is still relatively hard to find due to the commercial interest factors. In the aspect of mechanism studies by semi-continuous experiments, J.T.Yeh and K.P.Resnik applied a 3L glass container for continuous bubbling experiments with ammonia concentration (7% ~ 21%) and reaction temperature (15 ~ 38 °C) factors to investigate the CO₂ absorption rate and absorptive capacity [3]; Kim and You carried semi-batch studies under the condition that the ammonia concentration varies in the range of (7% ~ 17%) and reaction temperature keeps to be (10 ~ 80 °C). The effect caused by liquid PH value was also concerned [8]; Han-Ping Chen used semi-continuous bubbling absorbing device tested the CO₂ removal efficiency change and absorption ratio change under the concentration of ammonia (20 ~ 30%), reaction temperature (25 ~ 50 °C), flue gas flow rate (0.5 ~ 4L/min) and CO₂ concentration (10 ~ 18%) [9]. In the aspect of continuous absorption experiments, Diao applied sieved-plate tower to study the CO₂ removal efficiency and the process products under the condition that, the reaction temperature is from room temperature to 49 °C, the ammonia concentration is 0.066~0.140mol/L and CO₂ concentration is 8%~16%[10,11,12]. Li applied packed towers to study the effect on CO₂ removal efficiency caused by remaining time, ammonia concentration, inlet NH₃/CO₂ mole ratio, flue gas temperature and the other compositions in the flue gas.

Previous research has shown that almost all the studies focus on the simulated gas. There is a lack of investigation into pure CO₂ and real flue gas. Scientists have been unable to state the effect caused by the gas composition. Different with the former studies, pure CO₂ is injected into the ammonia solution which has been set in the semi-absorption devices to remove the effects caused by the other factors such as accompany gas and the flow parameters. In order to develop a wider experimental scale, ammonia concentration is set to be 0.2%~15%, inlet CO₂ velocity is around 0.06~0.20 m³/h, the absorption temperature is 5~40°C.The experiments obtain the effect on solution CO₂ loading, absorption capacity and absorption rate caused by the above operating factors. This paper also shows the effect on ammonia absorption characteristics and slippery characteristics caused by the AMP addition concentration.

2. Experimental Section

2.1. Experimental apparatus

The schematic diagram of the experimental system for studying the reaction between CO₂ and an ammonia solution is shown in Figure 1. The experimental system mainly includes the reactor, low-temperature oil bath system, CO₂ cylinder, gas buffer tank, rotor flow meter, processing system of the exhaust gas and CO₂ gas analyzer. The experimental CO₂ gas is supplied by a high-pressure CO₂ cylinder with purity 99.9%, while the ammonia solution is obtained by mixing of standard ammonia with mass concentration 25%~28% and deionised water. The CO₂ scrubber is a 50mm i.d. glass bottle containing 200 ml ammonia solution. The low-temperature oil bath system produced by Yu Hua Scientific Groups is used to control the ambient temperature of the reactor. The temperature range is between -10°C and 400°C with the increment 0.1°C. The CO₂ volume flow rate is measured by rotor flow meter, while U type manometer is applied to measure the pressure data. The experimental gas analyzer is Gasmet FT-IR Dx4000 infrared gas analyzer produced by Finland. In order to reduce the error caused by NH₃ slippery, acid wash is employed to control the ammonia slippery and chromo-tropic silica gel desiccators are used for removal of water.

2.2. Experimental method

All the experiments in this article were carried out at atmospheric pressure. CO₂ gas from the compressed gas cylinder firstly flows through the buffer tank and then enters the reactor system for chemical reactions. The gas is then sent to the gas analyzer and eventually vented to the air. During the whole absorption process, the flow volume
was controlled by rotor flow meter. The function of buffer tank is to balance the static pressure and dynamic pressure of the whole system and guarantee the stability of the output flow.

Both liquid-phase change and gas-phase change of the experimental system are supervised and analyzed during these studies. The liquid sampling time was adjusted according to the anticipated time of different reaction phases derived from the previous studies. Each sample does not exceed 1% of the total liquid volume and timely complement of fresh ammonia is guaranteed. The sample was analyzed by excess strong acid solution during these experiments. According to the height difference between the fixed liquid level and measured level, the volume of CO₂ loaded in the sample can be tested. The CO₂ loading of the sample is easily obtained by calculation.

This paper mainly studies the change of CO₂ absorption characteristic in aqueous ammonia solution at different experimental conditions, such as different ammonia concentrations, different CO₂ inlet velocities and different temperatures. The effect on slippery characteristic of ammonia caused by different concentrations of AMP additives is also studied. During these experiments in this paper, the concentration of ammonia was chosen as 0.2%, 0.4%, 0.6%, 0.8%, 2.5%, 5%, 10%, 12%, 15%. The reaction temperature of the absorber was set to be 5 ℃, 10 ℃, 15 ℃, 23 ℃, 30 ℃, 35 ℃, 40 ℃. The experimental CO₂ inlet velocities were 0.06m³/h, 0.1m³/h, 0.15m³/h, 0.2m³/h. The concentrations of AMP were respectively set as 1%, 3%, 5%. All these experiments were carried out when the ambient temperature was controlled to be 23 ± 1 ℃.

3. Results and discussion

3.1. Data analysis

In these experiments, the solution CO₂ loading data analysis obtained by the liquid sample, its specific method is shown in equation (1).

\[
A = \frac{\alpha (V_2 - V_1)}{22.4 V_0 M_{NH_3}}
\]  

\(A\) ——— CO₂ loading of the solution;
\(V_0\) ——— The volume of tested sample, L;
\(V_1\) ——— The initial volume of the gauges tube before titration, L;
\(V_2\) ——— The ending volume of the gauges tube after titration, L;
\(M_{NH_3}\) ——— The mole concentration of ammonia, mol/L;
\(\alpha\) ——— The gas volume correction factor when the experimental operating conditions are converted into standard operating conditions. It is a dimensionless coefficient and its calculation formula is as follows:
\[ \alpha = \frac{273}{(273+t)} \frac{P_0}{P} \]  

\( P_0 \) —— The standard pressure, 101.325KPa;  
\( P \) —— The real pressure for the experiment, KPa;  
\( t \) —— The real temperature for the experiment, °C.

AMP additives was hoped to control slippery of the ammonia. Experiments in this paper were undertaken at constant ambient pressure, 296K with 60% of the relative humidity. Under controlled conditions during these experiments, the saturation vapor pressure of water is far less than the vapor pressure of ammonia. Hence, the loss of absorbent can be viewed as the loss of ammonia. However, the production formed due to the reaction between ammonia and CO\(_2\) can affect the weight of solution. In order to avoid the affection by inlet CO\(_2\) velocity and contact mode, the weight loss of ammonia is tested by using still sample solution. The weight loss rate of absorbent by vaporization is the function of measured time. It can be written in this form:

\[ W_{\text{loss}} = \frac{(W_2 - W_1) - W}{W_0} \times 100\% \]  

Where,

\( W_{\text{loss}} \) —— Weight loss rate of absorbent by vaporization, dimensionless coefficient  
\( W_0 \) —— Initial weight of absorbent before the reaction, g;  
\( W_1 \) —— The weight of solution after sampling and replacing with fresh absorbent solution in same volume at certain time, g;  
\( W_2 \) —— The weight of solution before sampling and replacing with fresh absorbent solution in same volume at certain time, g;  
\( W \) —— The weight of CO\(_2\) loading in the sampling at that time, g

### 3.2. Effect of solvent concentration

Fig.3 Ammonia concentration effect on solution CO\(_2\) loading and absorption capacity 2.5%~15%  
Fig.4 Ammonia concentration effect on solution CO\(_2\) loading and absorption capacity 0.2%~0.8%

Fig.3 and Fig.4 are typical plots of solution CO\(_2\) loading and absorption capacity as the function of operation time under the condition that the operation pressure is atmospheric pressure, the atmospheric temperature is around 23 ± 1°C, the inlet CO\(_2\) velocity is 0.1 m\(^3\)/h and the controlled ammonia solution concentration is respectively during 2.5%~15% and 0.2%~0.8% without any additive. As seen from Fig.3, when the ammonia solution concentration is controlled to be 2.5%~15%, the solution CO\(_2\) loading and total reaction time increase while the absorption capacity decreases with the increase of ammonia solution concentration. However, the CO\(_2\) absorption capacity gradually decreases. The maximum CO\(_2\) loading reaches 4.29 mol/L and the minimum solution absorption capacity reaches 1.34 kg CO\(_2\)/kg NH\(_3\) for the ammonia solution with the weight concentration 15%. The maximum CO\(_2\) loading reaches 1.25 mol/L and the minimum solution absorption capacity reaches 2.22 kg CO\(_2\)/kg NH\(_3\) for the ammonia
solution with the weight concentration 2.5%. With the increase of ammonia solution concentration, the solution density has a much faster increase than the change of CO₂ mass. As seen from Fig.4, when the ammonia solution concentration is controlled to be 0.2%~0.8%, the trend curves of solution CO₂ loading, reaction time and CO₂ absorption capacity obtained are similar to those obtained from the relatively high concentration ammonia solution. It should be noticed that the CO₂ loading of ammonia solution with the concentration 0.8% is less than that of ammonia solution with the concentration 0.6%. The maximum CO₂ loading reaches 2.71mol/L for the ammonia solution with the weight concentration 0.6%, while the maximum CO₂ loading reaches 1.78mol/L for the ammonia solution with the weight concentration 0.2%. The CO₂ loading has the same tendency with the absorption capacity. The reason is that the density of ammonia solution does not change too much under the controlled ammonia solution concentration scale. The weight change due to the change of density can be compensated by the CO₂ weight absorbed into the solution. As can be easily deserved by the comparison of two figures, the CO₂ loading and absorption capacity of ammonia solution with high concentration is respectively higher than that of ammonia solution with low concentration. However, the former ammonia solution needs a relatively long reaction time. The total reaction time is less than 50 minutes for the ammonia solution with concentration lower than 1%. It is even less than 10 minutes. However, once the concentration of ammonia solution exceeds 5%, the reaction time is usually stable around 110 minutes. In general, the ammonia solution with weight concentration 12% has the optimal absorption characteristics such as high CO₂ loading, high absorption capacity and long reaction time. It is considered to be the best concentration under the controlled conditions.

3.3. Effect of inlet CO₂ velocity

![Fig.5 Inlet velocity effect on solution CO₂ loading](image1)

The inlet CO₂ velocity effect on solution CO₂ loading and absorption capacity is respectively shown in Fig.5 and Fig.6. These experimental conditions were controlled at the same experimental conditions discussed above. The ammonia solution of 12wt% without any additives is chosen as the experimental absorbent and the tested inlet CO₂ velocity is respectively 0.06m³/h, 0.1m³/h, 0.15m³/h and 0.2m³/h. Seen from the figures, with the increase of inlet CO₂ velocity, both solutions CO₂ loading and absorption capacity increase rapidly, that is to say, the reaction rate was enhanced. However, it does not guarantee the increase of final solution CO₂ loading and final absorption capacity. The reason is that the increase of inlet CO₂ velocity can decrease the contact time between CO₂ and ammonia although it can speed up the reaction and shorten the time of fast reaction. What’s more, the increase of inlet velocity can affect the reaction temperature and the pressure at the top of the absorber. As can be seen from the plot, the total reaction time is around 90 minutes when the inlet CO₂ velocity is respectively 0.15m³/h and 0.2m³/h, the total reaction time is around 110 minutes when the inlet CO₂ velocity is respectively 0.06m³/h and 0.2m³/h. The solution CO₂ loading and absorption capacity reach the maximum value, respectively 4.23mol/L and 1.63kgCO₂/kgNH₃, when the inlet CO₂ velocity is 0.06. The solution CO₂ loading and absorption capacity reach the minimum value, respectively 4.00mol/L and 1.54kgCO₂/kgNH₃, when the inlet CO₂ velocity is 0.2m³/h. The CO₂ absorption characteristic of ammonia solution is almost same when the inlet CO₂ velocity is respectively 0.15m³/h and 0.1m³/h. Hence, the best inlet CO₂ velocity should be 0.15m³/h under the tested conditions.
3.4. Effect of reaction temperature

Fig. 7 Relationship between CO₂ loading and reaction time at different operating temperatures

Fig. 8 Relationship between absorption capacity and reaction time at different temperatures

Fig. 9 Temperature effect on CO₂ absorption characteristics

Fig. 10 Addition concentration effect on ammonia slippery

3.5. Effect of AMP additives and the slippery of ammonia

Fig.11 and Fig.12 respectively shows the additive concentration effect on CO₂ loading and absorption capacity. A typical plot of CO₂ loading and absorption capacity as the functions of operation time is given. The ammonia solution concentration is 12% without AMP additive, the concentration of AMP additive solution is respectively 1%, 3%, 5%. As seen from the plots, AMP additives with any concentration can enhance the absorption characteristic of ammonia solution. Although AMP additives can increase the initial reaction rate obviously, the total reaction time of absorption process does not have a big cut. With the increase of AMP additive concentration, both maximum CO₂ loading and absorption capacity of ammonia solution are enhanced. The concentration 5% is the best choice in the tested concentrations. The two basic indicators of absorption properties are significantly increased about 4%. In addition, the two sets of experimental results of 3% AMP additive concentration and 5% additive concentration are quite close, which indicates that when the additive concentration reaches a certain value, continue to add AMP has little effect on the absorption properties. 3% is a better additive concentration.

Fig.10 is a typical plot of ammonia loss rate as a function of reaction time. At the beginning of the reaction, the ammonia loss is on the rise with the increase of reaction time. However, as the CO₂ loading increase, the ammonia loss rate has a slowly cut down. Seen from the Fig.10, during all the tested AMP concentration, 3% is the best concentration to control the slippery of ammonia. The ammonia loss can decrease 12%~30% relatively to ammonia solution without any additive, while AMP additive with concentration 1% and 5% has little effect on the slippery of ammonia. The reason is that AMP additives with low concentration has too little additive, which means that AMP additive has little impact on ammonia structure, that is to say, sterically -hindered effect is not obvious. When the concentration of AMP additive is too high, the original ammonia solution is equivalent to be diluted. The effect of molecular distance increase is greater than steric effect. Hence, the AMP additive of high concentration is not conducive to control of ammonia slippery.

4. Conclusions

(1) With the increase in ammonia concentration of the solution, the CO₂ loading increases and a corresponding increase in reaction time occurs, but the solution absorption capacity has been constantly reduced. The CO₂ loading of 12% NH₃ solution has a little difference with that value of 15% NH₃ solution, while the absorption capacity of 12% NH₃ solution is larger than that value of 10% NH₃ solution. For all the experimental ammonia concentrations, 12% is the best choice.

(2) With the increase in CO₂ inlet velocity, both the solution CO₂ loading and absorption capacity have rapid growth in the initial stage of the reaction, which means the increase of reaction rate. However, it does not necessarily lead to the increase of the final solution CO₂ loading and CO₂ absorption capacity.

(3) The overall impact on CO₂ absorption characteristics caused by temperature is not high. The maximum fluctuations of CO₂ loading is around 4% while the maximum fluctuations of CO₂ capacity is less than 5%.15℃ and 35℃ is two extreme points to reach the better CO₂ absorption characteristics.

(4) Adding any concentrations of AMP solution will be to some extent to promote absorption of ammonia solution. Although the initial reaction rate is significantly increased by adding AMP solution, little improvement can be achieved in the overall reaction time. When the additive concentration reaches a certain value, it has little effect on the absorption properties to continue to add AMP solution.
The ammonia loss rate grew with the increase of reaction time firstly and then stabilized. During the scope of the study, 3% is the best AMP concentration on the slippery control of ammonia. Relative to the ammonia solution without additives, the ammonia solutions with 3% AMP additives can reduce 12% ~ 30% of ammonia loss. In order to find the reasonable additives and their concentrations to control the slippery of ammonia, further discussions on other hinder amines and their concentrations should be carried out.

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Reference

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