Experimental study on CO₂ absorption into aqueous ammonia-based blended absorbents

Mengxiang Fang,* Qunyang Xiang, Xuping Zhou, Qinhui Ma, Zhongyang Luo

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou, 310027, P. R. China

Abstract
A crucial problem for the promising absorbent aqueous ammonia (NH₃) is the low CO₂ absorption rate and high ammonia volatile loss rate. This work investigated the effect of potential promoters for CO₂ absorption into aqueous ammonia solutions on a wetted wall column. Monoethanolamine, sarcosinate, taurinate, glycinate, piperazine and 1-methyl piperazine were introduced to NH₃ solutions as promoters. We found sarcosinate, piperazine and 1-methyl piperazine could increase the mass transfer coefficient of CO₂ into the ammonia-based solutions significantly. We further undertook a detailed mass transfer study of CO₂ into ammonia based blended solutions to investigate the effects of temperature and additive concentration. Besides, a novel ammonia separation method from low concentration ammonia solution by membrane vacuum regeneration was developed which could recover more than 80% of ammonia gas from low concentration ammonia.

Keywords: Aqueous ammonia; Carbon dioxide; Blended absorbent; Absorption mechanism, Membrane vacuum regeneration

1. Introduction
Carbon dioxide (CO₂) is believed to be a major contributor to global warming, with most emissions resulting from burning fossil fuel in power plants and other industrial processes.[1] Hence, it becomes a crucial issue to remove CO₂, especially in the fossil fuel power plants. Post combustion capture (PCC) technology using chemical absorbents is thought to be the most promising way to limit CO₂ emission for the existing coal fired power plants.[2] Development of absorbents for CO₂ capture is currently one of the most important tasks in PCC technologies.

Traditional amine-based absorbents, such as monoethanolamine (MEA), suffer from high energy consumption and thermal and oxidative degradation issues.[3,4] In contrast, aqueous ammonia solution has good thermal and oxidative stabilities, a large CO₂ cyclic capacity and a lower regeneration energy.[5-7] In spite of its advantages, aqueous ammonia-based PCC faces two major challenges: low CO₂ absorption rate and high volatility.[8,9] To make the ammonia-based process economically feasible, its CO₂ absorption rate must be significantly increased and its ammonia loss issue should be solved. Adding promoters or homogeneous catalysts to the aqueous ammonia solution is reported as an effective way to increase CO₂ absorption rate while limited studies have been published in the area of reducing ammonia volatile loss.[10]

In this work, we investigated the effect of potential promoters for CO₂ absorption into aqueous ammonia solutions. Six promoters were tested: monoethanolamine (MEA), sarcosinate (SAR), taurinate (Tau), glycinate (Gly), piperazine (PZ) and 1-methyl piperazine (1-MPZ). Besides, a novel ammonia...
separation method from low concentration ammonia solution by membrane vacuum regeneration was developed which could recover ammonia gas from low concentration ammonia solution (coming from washing water) and thus the washing water could be reused.

2. Experimental section

The CO₂ absorption experiments were performed on a wetted-wall column apparatus shown in Figure 1 (left). The apparatus allowed gas stream to be contacted with a falling thin liquid film on a known surface area. The solvent stored in a reservoir was pumped up the inside of the column and flowed out the top and down along the outside surface. The gas stream was introduced at the bottom of the column, passing the gap between the column surface and the glass tube before being exhausted from the top. Two flanges were used to fix the glass tube to ensure no gas leakage even at high pressure. A water bath was used to control the temperature during the experiments. The ammonia membrane vacuum regeneration experiments were performed on a membrane contactor shown as Figure 1(right). Ammonia solution was prepared and added into the tank and then heated to desired temperature before the inlet of membrane module. After pre-heating, ammonia solution was continuously pumped into the tube side of the membrane contactor by the peristaltic pump. The shell side of membrane contactor was kept at reduced pressure. Hence, ammonia would be regenerated from the rich solution due to the positive effects of reduced pressure and permeated the gas-filled membrane pores to the shell side. Finally, the regenerated ammonia gas could be collected from the vacuum pump.

3. Results and discussion

3.1 Promoted CO₂ absorption in aqueous ammonia solutions

Figure 2 shows the CO₂ mass transfer coefficients in blended solutions of ammonia with promoters at three CO₂ loadings. Only 0.3 M promoters especially sarcosinate, PZ and 1-MPZ can improve the CO₂ mass transfer coefficients in 3 M ammonia solutions significantly. The promotion effects of additives are still distinct at high CO₂ loading. In contrast, the mass transfer coefficients for CO₂ absorption in 5 M MEA decreases much faster than ammonia-based solutions.

Among the six promoters, sarcosinate, PZ and 1-MPZ shows the most significant effect on increasing CO₂ absorption rate in aqueous ammonia solutions. Sarcosinate is reported to have good oxidative and thermal stability and environmentally friendly characteristics which is thought to be a clean solvent. Figure 3(left) shows the overall mass transfer coefficients (K_G) as a function of temperature of three different solutions. The effect of temperature on the overall mass transfer coefficients is relatively small for all the three ammonia-based solutions. When the temperature increases from 279 to 298 K, the corresponding overall mass transfer coefficients are increased by only 5–12%. Figure 3(right) presents the effect of SAR⁻ concentration on the overall mass transfer coefficients for CO₂ absorption in 3 M NH₃+SAR⁻ solutions at 288 K. The effect of SAR⁻ additive concentration is pronounced when its concentration is low. However, when the SAR⁻ concentration reaches a relatively high value, K_G does not
increase with the increase of SAR\(^-\) concentration. The highest \(K_G\) of CO\(_2\) in 3 M NH\(_3\) + SAR\(^-\) solutions at 288 K is approximately 2.2 mmol/(s m\(^2\) kPa) which is quite close to the CO\(_2\) absorption performance into 5 M MEA at 313 K.

### 3.2 Ammonia membrane vacuum regeneration

Figure 4 (left) shows the effect of solvent flow rate on the ammonia vacuum regeneration efficiency. The ammonia concentration before regeneration is 0.3 M, the absolute pressure in the gas side is 40 kPa and the temperature is 333 K. The solvent flow rate is significant to the ammonia removal efficiency. The ammonia removal efficiency could reach a high value only at a very low solvent flow rate, for instance, the ammonia removal efficiency at a solvent flow rate of 5 ml/min is only 49%. Hence, we cycle the ammonia after regeneration back to the solvent tank as a continuous regeneration process. Figure 4 (right) shows the NH\(_3\) concentration and the NH\(_3\) removal efficiency as a function of time in a continuous membrane vacuum regeneration process. The experimental conditions are same to that in Figure 4 (left). The total volume of the solvent is 600 ml and the solvent flow rate is 50 ml/min which gives the time of one cycle as 12 minutes. In the continuous process, the ammonia removal efficiency could reach 80% in about 7 cycles (approximately 80 minutes). Taking the solvent handling capacity into consideration, the continuous process is much better than the one cycle process. The study for the ammonia membrane vacuum regeneration is primary and more detailed work is required for obtaining suitable operation conditions and better understanding of the process.

![Figure 2](image2.png)

**Figure 2.** Mass transfer coefficients for CO\(_2\) absorption in various ammonia-based blended solvents at three CO\(_2\) loadings. For 5 M MEA, temperature=313 K; for other solvents, temperature =288 K.

![Figure 3](image3.png)

**Figure 3 (left).** Overall mass transfer coefficients as a function of temperature of three different solutions. (right) Overall mass transfer coefficients as a function of SAR\(^-\) concentration for CO\(_2\) absorption in 3 M NH\(_3\)+SAR\(^-\) solutions at 288 K.
Conclusion

Sarcosinate, piperazine and 1-methyl piperazine promoters were found to increase the mass transfer coefficient of CO₂ into aqueous ammonia solution significantly. Novel ammonia separation technology from low concentration ammonia solution using membrane vacuum regeneration was developed. The primary tests showed that 80% of ammonia gas could be separated from low concentration ammonia solution at a suitable condition. More detailed work is required to obtain suitable operation conditions and have a better understanding of the ammonia membrane vacuum regeneration process.

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References

Biography
Prof. Mengxiang Fang got his Ph D degree on Engineering Thermophysics on July, 1991. He worked at Institute for Thermal Power Engineering of Zhejiang University and his interest is coal and biomass combustion and gasification, CO2 emission control. He got 10 patents and presented more than 100 papers in Journal and conference.