Plasma-assisted absorption of CO_2 in AMP solution and chemical regeneration of AMP using calcium hydroxide

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Abstract: High energy consumption for thermal regeneration of amine remains a big challenge for large-scale application of amine-based CO_2 capture. In this work, aqueous solution of 2-amino-2-methyl-1-propanol (AMP) was used as CO_2 absorbent and mist and dielectric barrier discharge were introduced to enhance the CO_2 capture efficiency. Besides, chemical regeneration of AMP with calcium hydroxide was attempted, during which CO_2 was sequestrated in the form of $CaCO_3$ and AMP was regenerated via a pH swing.

Keywords: CO_2 capture, Amine, Chemical regeneration, $CaCO_3$, Dielectric barrier discharge.

1. Introduction

Amine-based chemical absorption of CO_2 has been widely studied and commercially used for post-combustion CO_2 capture [1-3]. CO_2 is generally absorbed by amine solutions at 25~45 °C and desorbed at 90~130 °C to regenerate the amine [3].

Amines used for CO_2 absorption can be divided into carbamate-formation and bicarbonate-formation amines according to the main absorption products [4]. Carbamate-formation amines include primary (e.g., monoethanolamine, MEA) and secondary (e.g., diethanolamine, DEA) amines, while bicarbonate-formation amines include tertiary (e.g., N-methyldiethanolamine, MDEA) and sterically hindered (e.g., 2-amino-2-methyl-1-propanol, AMP) amines [4]. The overall absorption reaction for these two groups of amines can be represented as follows [3, 4].

Formation of carbamate:

$$2\mathrm{RNH}_x + \mathrm{CO}_2 \rightleftharpoons \mathrm{RNH}_{x+1}^+ + \mathrm{RNH}_{x-1}\mathrm{COO}^- \ (x = 1,\ 2) \quad (1)$$

Formation of bicarbonate:

$$\mathrm{RNH}_x + \mathrm{H_2O} + \mathrm{CO}_2 \rightleftharpoons \mathrm{RNH}_{x+1}^+ + \mathrm{HCO}_3^- \ (x = 0 \sim 2) \quad (2)$$

Despite commercial applications, the amine-based technology still suffers from a significant energy penalty due to thermal regeneration of amine, which consumes 70~80% of the total energy used for CO_2 capture [3]. High temperature also aggravates the volatilization and degradation of amines during thermal regeneration [3, 5].

As an alternative strategy, chemical regeneration of amines using calcium oxide (CaO) or hydroxide ($Ca(OH)_2$) has gained increasing attention, during which CO_2 is sequestrated in the form of $CaCO_3$ and amine is regenerated through a pH swing [4, 6-8]. Mineralization of CO_2 into $CaCO_3$ occurs efficiently at a moderate temperature (e.g., 40~50 °C), thus reducing the energy requirement significantly while providing a value-added material ($CaCO_3$) [4, 6-8].

Considering that formation of bicarbonate facilitates subsequent mineralization process, a typical bicarbonate-formation amine, AMP was selected as the CO_2 absorbent in this study. Compared with the widely used MEA absorbent, AMP has higher absorption capacity (theoretically 1 mol CO_2/mol AMP) but lower absorption rate due to the sterically hindering effects [3, 4]. Aiming at accelerating the absorption of CO_2 by AMP, mist and dielectric barrier discharge (DBD) were introduced into the absorber in this work. Besides, chemical regeneration of AMP using $Ca(OH)_2$ was attempted for cyclic operation of the absorption-mineralization process.

2. Experimental

CO_2 absorption experiments were conducted at room temperature and atmospheric pressure using a tank reactor. A mixture of CO_2 and N_2 with 10 vol.% of CO_2 (relative to N_2) was prepared to simulate combustion flue gas of CH_4 (dry basis) and 1.1 L/min of the mixed gas was introduced into the tank reactor which contained 1.6 L of an aqueous solution of AMP (AMP content 5.1 wt.%). A mist generator was immersed in the solution and turned on when necessary to generate fine mist in the tank. A wire-cylinder DBD device was mounted at the outlet end of the tank reactor. DBD was generated by applying AC high voltage between the discharge (tungsten wire) and ground (stainless-steel mesh) electrodes.

Outlet gas from the DBD unit passed through a cold trap (−40 °C) first to separate water and then a quadrupole mass spectrometer (QMS, PrismaPlus, Pfeiffer Vacuum GmbH) to monitor the volumetric concentration of CO_2. Removal efficiency of CO_2 (%) and CO_2 loading in the liquid phase (mol CO_2/mol AMP) were calculated by Eqs. (3) and (4), respectively.

$$\text{Removal efficiency of } \mathrm{CO_2} = \frac{C_{\mathrm{CO_2,\,in}} - C_{\mathrm{CO_2,\,out}}}{C_{\mathrm{CO_2,\,in}}} \times 100 \quad (3)$$

$$\mathrm{CO_2} \text{ loading in the liquid phase} = \frac{n_{\mathrm{CO_2,\,absorbed}}}{n_{\mathrm{AMP,\,input}}} \quad (4)$$

where $C_{\mathrm{CO_2,\,in}}$ and $C_{\mathrm{CO_2,\,out}}$ denote the volumetric concentration of CO_2 (relative to N_2) before and after absorption, respectively; $n_{\mathrm{CO_2,\,absorbed}}$ and $n_{\mathrm{AMP,\,input}}$ denote the molar amount of CO_2 absorbed and that of AMP dosed into the absorption liquid, respectively.

For chemical regeneration of AMP, $Ca(OH)_2$ was added to the CO_2-rich solution at a dosage of 1 mol $Ca(OH)_2$/mol

CO_2 absorbed. After reaction at 40 °C for a given time, the slurry was filtered using a vacuum filter. The filtrate was then reused for CO_2 absorption. Regeneration efficiency of AMP was defined as the ratio of CO_2 absorption capacity of regenerated and fresh AMP solutions. To reflect changes in acidity-basicity of the absorption liquid, pH values of fresh, CO_2-rich and CO_2-lean (regenerated) AMP solutions were measured.

3. Results and Discussion

Fig. 1 shows the temporal variation of CO_2 removal efficiency and CO_2 loading in the liquid phase during CO_2 absorption in the AMP solution. It can be seen that the removal efficiency of CO_2 decreased with absorption time due to gradual consumption of AMP. The presence of mist in the tank greatly enhanced the absorption of CO_2, especially at the initial stage of the absorption process. CO_2 removal efficiency increased from 47.4% at the 20 min without mist to 61.4% at the 32 min with mist. Obviously, large surface area of the mist promoted the absorption of CO_2. Even with weak DBD in the cylinder, mist in the effluent gas could be effectively captured. Application of DBD is important for recovering mist particles and enhancing CO_2 absorption.

As also shown in Fig. 1, CO_2 loading in the liquid phase increased with absorption time, reaching 0.85 mol CO_2/mol AMP at the end (720 min) of the absorption experiment. The final CO_2 loading was less than the theoretical value of 1 mol CO_2/mol AMP, partially because the AMP solution was not fully saturated (5.9% of CO_2 was still absorbed) at the end of the experiment.

Chemical regeneration of AMP was attempted by adding $Ca(OH)_2$ powder into the CO_2-rich AMP solution at a dosage of 1 mol $Ca(OH)_2$/mol CO_2 absorbed. The slurry was stirred and kept at 40 °C for 2 h before being filtered. Test results show that pH values of fresh, CO_2-rich and regenerated AMP solutions were 14, 9 and 12, respectively. CO_2 absorption capacity of the regenerated AMP solution reached 0.62 mol CO_2/mol AMP, indicating a regeneration efficiency of 73% for AMP by adding $Ca(OH)_2$, which is comparable to that obtained with CaO under similar regeneration conditions [4].

4. Concluding Remarks

Combining amine-based CO_2 absorption with chemical regeneration of amine using CaO or $Ca(OH)_2$ appears to be a promising method for capturing and sequestering CO_2 at low energy consumption. By dosing CaO or $Ca(OH)_2$ into the CO_2-rich amine solution, Ca^{2+} and OH^- produced lead to mineralization of CO_2 into $CaCO_3$ and regeneration of amine at the same time.

In order to facilitate the mineralization process, a typical bicarbonate-formation amine, AMP was used as the CO_2 absorbent in this study. Mist and DBD were introduced into the absorber to enhance the absorption of CO_2. For fresh solution with an AMP content of 5.1 wt.%, CO_2 removal efficiency reached 61.4%, corresponding to an absorption rate of 2.8 mmol CO_2/(mol AMP·min). During an attempt of chemical regeneration using $Ca(OH)_2$, 73% of the AMP in CO_2-rich solution was regenerated.

For practical applications of this absorption-mineralization process, further optimization of the absorption and regeneration conditions is required to increase CO_2 absorption and AMP regeneration efficiency. Multicycle experiments are also necessary to investigate stability of the cyclic process. Besides, characterization of the fresh, CO_2-rich and regenerated AMP solutions, as well as the solid products (carbonates) is essential for clarifying the absorption and mineralization mechanisms of CO_2.

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6. References

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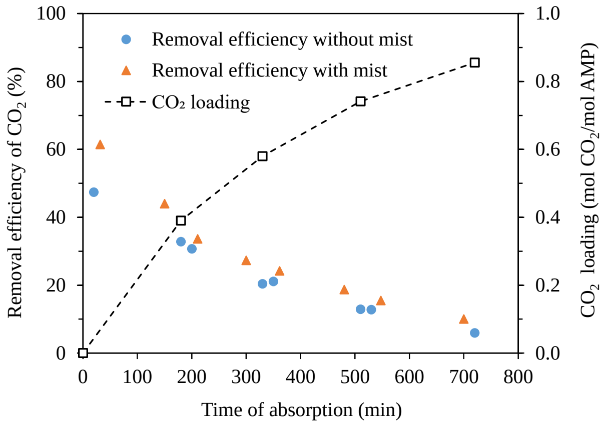

Fig. 1. Temporal variation of removal efficiency of CO_2 and CO_2 loading in the liquid phase during CO_2 absorption in the AMP solution.