Study on the absorption-mineralisation for low-energy CO₂ capture in BDA activated DEEA aqueous solution using calcium chloride

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Abstract. The large amount of energy in the thermal regeneration process of the absorbent is a challenge for the CO₂ capture technology. The CO₂ absorption-mineralization was investigated, which is different from the traditional thermal method. 1,4-Diaminobutane (BDA) promoted 2-diethylaminoethanol (DEEA) aqueous solutions were used to capture CO₂. In the desorption process, adding anhydrous calcium chloride (CaCl₂) in CO₂ loaded amine solutions can rapidly removal CO₂ from the rich amine solutions. In addition, we also analyzed the mineralized products by X-ray diffractometer, and discussed the stability of cyclic absorption-mineralization technology.

1. Introduction
The post-combustion capture of carbon dioxide (CO₂) technology continues to receive increasing attention due to excessive emissions of CO₂ from coal-fired power plants, which has led to an increase in the global greenhouse effect[1]. The use amine solvents for chemical absorption of CO₂ has attracted widespread attention due to its maturity, cost-effectiveness and ability to handle large volumes of flue gas streams[2]. However, the problems cannot be ignored that alcohol amine degradation, corrosion equipment, amine volatilization, and high energy consumption for regeneration[3, 4]. Among them, the high energy consumption for the regeneration of alcohol amine solvents is the biggest obstacle to the development of CO₂ capture by amine solutions. For example, the solvent regeneration load accounts for about 70-80% of the total operating cost of a CO₂ capture plant[5]. Nowadays, the methods to reduce the energy consumption of solvent regeneration mainly include the development of energy efficient solvents, design of higher performance devices for mass and heat transfers, and improvement of absorption-desorption processes[6]. Although the various attempts mentioned have shown a certain reduction in the energy required for amine regeneration, the reduced thermal load in these CO₂ desorption processes is still based on thermal regeneration, which still requires a lot of energy.

Therefore, the mineral carbonation reaction is receiving more and more attention due to its favorable thermodynamic process and permanent isolation of CO₂[7]. The CO₂ mineralization forms a stable carbonate rock mineral, which can conduct at normal temperature without heating the regeneration
temperature to 100-140°C[8]. Murnandari et al.[9] studied the mineralization and fixation of CO$_2$ by using Ca$^{2+}$-rich aqueous solution. They used saturated 2-amino-2-methyl-1-propanol (AMP) solution as the carbonate source, and calcium chloride (CaCl$_2$) precipitates calcium carbonate as a source of calcium ions to, regenerates AMP. The experimental results show that during the mineralization reaction, the CO$_2$ in the absorbed AMP solution was instantly converted into a white calcium carbonate precipitate, with a conversion rate of 97.4%. However, the mineralization in the 1,4-Diaminobutane (BDA) promoted 2-diethylaminoethanol (DEEA) CO$_2$ loaded aqueous solution has not been rigorously studied.

In this work, all reactions related to CO$_2$ mineralization were carried out in a semi-batch reactor under different reaction conditions. When the CO$_2$ absorption reaches the maximum amine load level, a calcium source is injected into the system and the product is harvested at the end of the reaction. Qualitative analysis of mineralized products by XDR confirmed the shape and crystal structure of carbonized products of different amine mixed solvents. In order to the industrial application of mineralization technology, the stability of the mineralization process was verified through cyclic absorption-desorption experiments.

2. Another section of your paper

2.1. Materials

DEEA (≥99%) and BDA (≥98%) were all purchased from Aladdin Reagent (Shanghai) Co., Ltd, and anhydrous granular calcium chloride (analytically pure) was obtained from Xianshuigu Industrial Park, Nan District, Tianjin. All chemicals were without any additional purification. CO$_2$ with a purity of 99.9% (in mole fraction) were purchased from Baoding Hanjiangxue Trading Co., Ltd.

2.2. Apparatus and procedures

Before performing the regeneration experiment, all the aqueous amine solutions (DEEA solution and DEEA-BDA blends amine solution) were subjected to CO$_2$ absorption as shown in Figure 1. The absorption temperature was 313.2k.

![Figure 1. Schematic diagram for CO$_2$ absorption](image)

The completely absorbed three-necked flask was still placed in a thermostatic stirrer. The desorption temperature was 313.2k, and the rotation speed was set. Anhydrous calcium chloride powder is added to the fully absorbed rich liquid for desorption. When the MFM display is less than or equal to 0, the desorption experiment is completed. After reaching equilibrium, the precipitated calcium carbonate was removed from the solution by vacuum filtration, and the separation solution was recovered. The obtained calcium carbonate powder was dried in an oven at 80°C for 24 hours. The X-ray diffraction was used to detect the powdery calcium carbonate produced during the mineralization process.

In order to evaluate the stability of chemical regeneration, anhydrous calcium chloride was added to the amine-rich solution so that the molar concentration of CO$_2$ absorbed by the alcohol amine was the same. Repeat three times to remove calcium carbonate and add anhydrous calcium chloride. The calcium carbonate obtained by vacuum filtration was dried in an oven at 80°C for 24 hours. After measuring the weight of the calcium carbonate produced, the mass balance of carbon dioxide and calcium was calculated.
2.3. Calculation methods for different parameters
The CO$_2$ loading is defined as the number of moles of CO$_2$ captured per mole of amine. The CO$_2$ loading can be expressed as:

$$\alpha = \frac{m}{44} \left( \frac{m_1}{M_1} + \frac{m_2}{M_2} \right)$$  \hspace{1cm} (1)

Where $m$ is the mass of CO$_2$ absorbed; $m_1$ is the mass of DEEA in a compound solution without CO$_2$ absorption; $m_2$ is the mass of BDA in a compound solution without CO$_2$ absorption; $M_1$ is the molar mass of DEEA; $M_2$ is the molar mass of BDA.

In this work, the rich amine loading ($\alpha_{\text{rich}}$) is the largest CO$_2$ concentration in the amine solution after absorption. The lean amine loading ($\alpha_{\text{lean}}$) is the smallest CO$_2$ concentration in the amine after desorption. The CO$_2$ desorption efficiency ($\eta$) can be expressed by the following equation:

$$\eta = \frac{\alpha_{\text{rich}} - \alpha_{\text{lean}}}{\alpha_{\text{rich}}}$$  \hspace{1cm} (2)

3. Results and discussion
The values of the three cycles of absorption-mineralization process of $\alpha_{\text{rich}}$ and $\alpha_{\text{lean}}$ are shown in Table 1.

| $w_{\text{DEEA}}$ | $w_{\text{BDA}}$ | $\alpha_{\text{rich}}$/(molCO$_2$/mol amine) | $\alpha_{\text{lean}}$/(molCO$_2$/mol amine) |
|------------------|------------------|---------------------------------------------|---------------------------------------------|
|                  |                  | I | II | III | I | II | III |
| 0.30             | 0                | 0.91 | 0.131 | 0.102 | 0.061 | 0.046 | 0.090 |
|                  | 0.050            | 0.812 | 0.129 | 0.095 | 0.063 | 0.036 | 0.026 |
|                  | 0.100            | 0.752 | 0.120 | 0.116 | 0.047 | 0.044 | 0.037 |
|                  | 0.150            | 0.764 | 0.104 | 0.088 | 0.043 | 0.026 | 0.022 |

3.1. Effectiveness of Mineralization in the regeneration of DEEA and DEEA-BDA aqueous solutions
In this work, the effectiveness of mineralization in the regeneration of the DEEA and DEEA-BDA aqueous solution were tested. 2-(Diethylamino)ethanol (DEEA) is a common tertiary amine, which is generally used as the main absorber. 1,4-Diaminobutane (BDA) is a primary amine, which can greatly accelerate the absorption rate with a small amount. and is generally used as an accelerator. Therefore, DEEA and DEEA-BDA blend solutions were used to study the mineralization capacity of anhydrous calcium chloride (CaCl$_2$). When the alcohol amine solution is completely absorbed, the same molar ratio of anhydrous calcium chloride (CaCl$_2$) was added to the aqueous solution. Most of the absorbed CO$_2$ immediately reacted with calcium ions to produce white calcium carbonate CaCO$_3$ precipitation. The performance of regenerating alcohol amines using anhydrous calcium chloride CaCl$_2$ can be evaluated by CO$_2$ desorption efficiency. Fig. 2 shows the changes in the CO$_2$ loading of the alcohol amine solution before and after the addition of anhydrous calcium chloride (CaCl$_2$) powder. It seems that the mineralization efficiency of CO$_2$ is greater than 93% and the desorption efficiency of CO$_2$ is increased after the promoter BDA is added. It is worth noting that in 30wt% DEEA-5wt% BDA solution, the residual concentration of CO$_2$ is only 0.016 mol, and the efficiency of CO$_2$ conversion to mineral carbonate is 98.06%. These results indicate that mineralization may be an effective regeneration method to desorb CO$_2$ from DEEA solution and DEEA-BDA mixed solution.
3.2. **DEEA and DEEA-BDA Effects on Calcium Carbonate Crystal Production.**

The effect of DEEA and DEEA-BDA aqueous solution on the calcium carbonate crystals was studied. Fig. 3 shows the X-ray diffraction of the precipitates obtained by mineralization desorption of CO₂ with DEEA monoethanolamine and DEEA-BDA compound alanolamine system as absorbers, respectively. In this work, the X-ray diffraction analysis results showed that the calcium carbonate crystal product of a single process absorption is calcite for 30wt% DEEA aqueous solution. However, the formation of calcite and vaterite in the DEEA-BDA blends amine solution. The formation of calcite and vaterite in the DEEA-BDA compound system indicates that the system has higher saturation. Carbamate hydrolysis and the presence of bicarbonate in the system can cause mineralization and produce highly saturated conditions. This is consistent with the results of Murmandari et al.[10]. They showed that the composition of the mineralized desorption products of the MEA, DEA, MDEA and AMP systems was tested, and only calcite and vaterite were found in the AMP system.

The XRD peak was analyzed according to the Debye-Scherrer method. It was found that the largest crystal size was generated by 30wt% DEEA. The crystal sizes calculated according to XRD results are 30wt% DEEA (39nm), 30wt% DEEA-5wt% BDA (33nm), 30wt% DEEA-10wt% BDA (31nm), and 30wt% DEEA-15wt% BDA (30nm). It seems that DEEA system has higher carbonate content and
stronger alkalinity than DEEA-BDA system. It can be seen that in higher pH system, precipitation helps
more agglomeration. Therefore, the high pH rich solution can be obtained by increasing the solubility
of absorbent, and the mineralization efficiency can be improved.

3.3. Multicycle absorption-mineralisation performance of DEEA and DEEA-BDA
In order to realize the industrialized application of CO$_2$ demineralization technology, the stability of
the adsorption-mineralization process is very important. The absorption and mineralization cycle
experiments were carried out three times with DEEA solution and DEEA-BDA blends solution, and the
technical performance of the absorption and regeneration process was investigated. Fig. 4 shows the
CO$_2$ loading of 30wt% DEEA solution and 30wt% DEEA-15wt% BDA blends solution in three
absorption-mineralization cycles. The results indicate that the effect of the first absorption-
mineralization process of 30wt% DEEA and 30wt% DEEA-15wt% BDA solution to capture CO$_2$ is very
ideal. However, amine absorbents cannot be regenerated in the presence of CaCl$_2$. The reason is that
after removing calcium carbonate from the solution, the CO$_2$ load is only stabilized at 0.131 molCO$_2$/mol
amine after re-injecting CaCl$_2$ into a 30wt%DEEA solution. Similarly, the load of 30wt%DEEA-
15wt%BDA solution is stable at 0.104molCO$_2$/mol amine. Therefore, after the chemical regeneration
attempt, compared with the original absorbent, the amount of CO$_2$ loaded is greatly reduced, and it is no
longer suitable for industrialization. This is consistent with the experimental results of Ji et al.[11]. They
found that the use of CaCl$_2$ is not suitable for continuous CO$_2$ capture. Because the chloride prevented
the ammonium cations from being converted into free amines.

4. Conclusion
In this work, the mineralization method for the regeneration of amine-based absorbents was discussed.
Our results showed that:
(1) After the carbonation reaction with CaCl$_2$ at 40°C, the four groups of different ratios of amine
solutions all achieved good regeneration effects. Moreover, the absorbed CO$_2$ was effectively
precipitated. The 30wt%DEEA-5wt%BDA has the highest desorption efficiency (98.06%) in four
groups of different ratio amine solutions.
(2) The effects of different ratios of alcohol amine solutions on mineralized crystalline products were
studied. The DEEA alcohol amine system promoted the formation of mineralized products with larger
crystal radius due to higher carbonate solubility. However, the presence of carbamates for DEEA-BDA
blend solutions may lead to the formation of polymorphic mineralized products.

![Figure 4. CO$_2$ loading of 30wt% DEEA and 30wt%DEEA-15wt% BDA solution in three cycles of
CO$_2$ absorption-mineralisation using calcium chloride (R-i: rich solution of cycle i; L-i: lean solution
of cycle i).](image)
(3) The cyclic absorption-mineralization process of CaCl2 was studied, and experiments showed that the alcohol amine absorbent could not be recycled in the presence of Cl-

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