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Abstract. The large amount of energy in the thermal regeneration process of the absorbent is a challenge for the CO_2 capture technology. The CO_2 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 CO_2. In the desorption process, adding anhydrous calcium chloride ($CaCl_2$) in CO_2 loaded amine solutions can rapidly removal CO_2 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 (CO_2) technology continues to receive increasing attention due to excessive emissions of CO_2 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 CO_2 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 CO_2 capture by amine solutions. For example, the solvent regeneration load accounts for about 70-80% of the total operating cost of a CO_2 capture plant[5]. Nowdays, 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 CO_2 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 CO_2[7]. The CO_2 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.

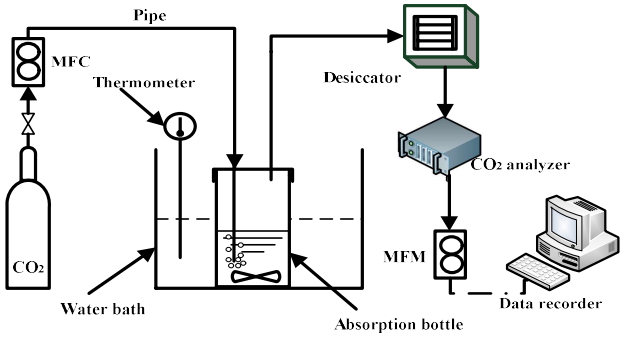

Figure 1. Schematic diagram for CO_2 absorption

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:

$$\alpha = \frac{m / 44}{m_1 / M_1 + m_2 / M_2} \tag{1}$$

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 (α_{rich}) is the largest CO_2 concentration in the amine solution after absorption. The lean amine loading (α_{lean}) is the smallest CO_2 concentration in the amine after desorption. The CO_2 desorption efficiency (η) can be expressed by the following equation:

$$\eta = (\alpha_{rich} - \alpha_{lean}) / \alpha_{rich} \tag{2}$$

3. Results and dicussion

The values of the three cycles of absorption-mineralization process of α_{rich} and α_{lean} are shown in Table 1.

Table 1. The values of α_{rich} and α_{lean} of the three cycles of absorption-mineralization process.

w_{DEEA}	w_{BDA}	α_{rich}/(molCO_2/mol amine)			α_{lean}/(molCO_2/mol amine)		
		I	II	III	I	II	III
0.30	0	0.891	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.

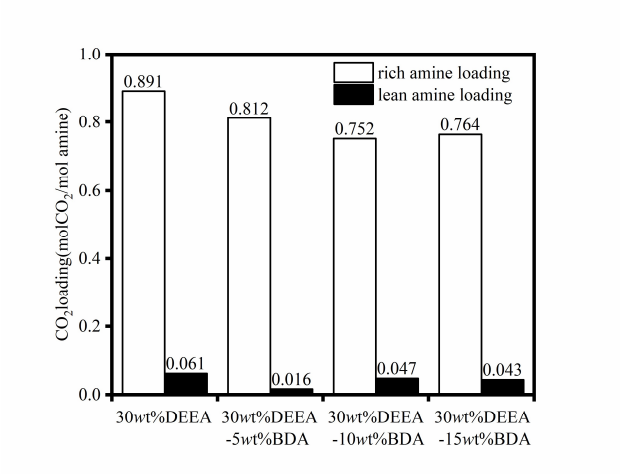

Figure 2. α_{rich} and α_{lean} of DEEA and DEEA–BDA blends solution at atmospheric pressure, 313 K (absorption temperature) and 313 K (desorption temperature)

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 CO_2 with DEEA monoethanolamine and DEEA-BDA compound alcoholamine 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 Murnandari 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 vateriter were found in the AMP system.

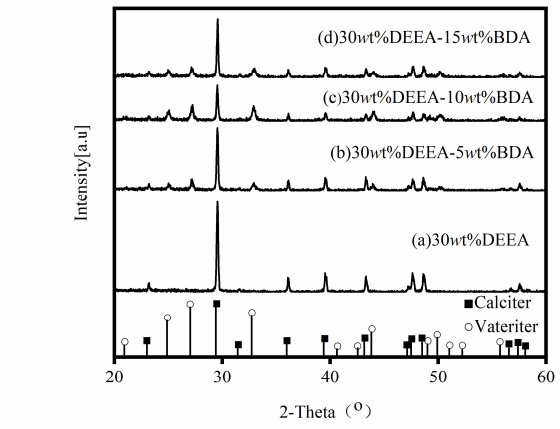

Figure 3. X-ray diffractogram of produced in different types of amine systems (a) 30wt%DEEA, (b) 30wt%DEEA-5wt%BDA, (c) 30wt%DEEA-10wt%BDA, and (d) 30wt%DEEA-15wt%BDA.

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 30*wt*% DEEA solution and 30*wt*% DEEA-15*wt*% 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 30*wt*%DEEA solution. Similarly, the load of 30*wt*%DEEA-15*wt*%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.

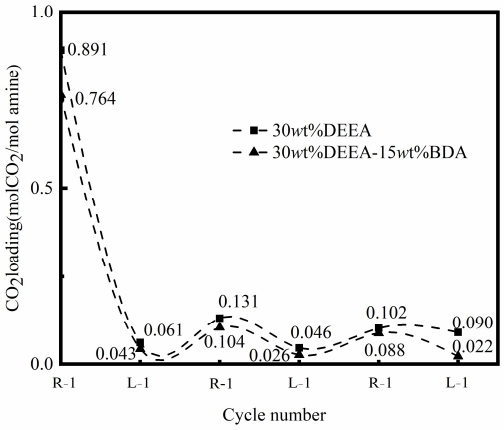

Figure 4. CO_2 loading of 30wt% DEEA and 30wt%DEEA-15wt%BDA solution in three cycles of CO_2 absorption-mineralisation using calcium chloride (R-i: rich solution of cycle i; L-i: lean solution of cycle i).

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 30*wt*%DEEA-5*wt*%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.

(3) The cyclic absorption-mineralization process of $CaCl_2$ was studied, and experiments showed that the alcohol amine absorbent could not be recycled in the presence of Cl^-.

References

[1] S.K. Wai, C. Nwaoha, C. Saiwan, R. Idem, and T. Supap, Absorption heat, solubility, absorption and desorption rates, cyclic capacity, heat duty, and absorption kinetic modeling of AMP-DETA blend for post-combustion CO_2 capture, Separation and Purification Technology. 194 (2018) 89-95.

[2] C. Nwaoha, C. Saiwan, T. Supap, R. Idem, P. Tontiwachwuthikul, W. Rongwong, M.J. Al-Marri, and A. Benamor, Carbon dioxide (CO_2) capture performance of aqueous tri-solvent blends containing 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) promoted by diethylenetriamine (DETA), International Journal of Greenhouse Gas Control. 53 (2016) 292-304.

[3] X. Zhao, Q. Cui, B. Wang, X. Yan, S. Singh, F. Zhang, X. Gao, and Y. Li, Recent progress of amine modified sorbents for capturing CO_2 from flue gas, Chinese Journal of Chemical Engineering. 26 (2018) 2292-2302.

[4] S. Delgado, B. Valentin, D. Bontemps, and O. Authier, Degradation of Amine Solvents in a CO_2 Capture Plant at Lab-Scale: Experiments and Modeling, Industrial & Engineering Chemistry Research. 57 (2018).

[5] F. Bougie and M.C. Iliuta, Analysis of regeneration of sterically hindered alkanolamines aqueous solutions with and without activator, Chemical Engineering Science. 65, 4746-4750.

[6] X. Zhang, K. Fu, Z. Liang, W. Rongwong, Z. Yang, R. Idem, and P. Tontiwachwuthikul, Experimental studies of regeneration heat duty for CO_2 desorption from diethylenetriamine (DETA) solution in a stripper column packed with Dixon ring random packing, Fuel. 136 (2014) 261-267.

[7] B. Yu, K. Li, L. Ji, Q. Yang, K. Jiang, M. Megharaj, H. Yu, and Z. Chen, Coupling a sterically hindered amine-based absorption and coal fly ash triggered amine regeneration: A high energy-saving process for CO_2 absorption and sequestration, International Journal of Greenhouse Gas Control. 87 (2019) 58-65.

[8] L. Ji, H. Yu, K. Li, B. Yu, M. Grigore, Q. Yang, X. Wang, Z. Chen, M. Zeng, and S. Zhao, Integrated absorption-mineralisation for low-energy CO_2 capture and sequestration, Applied Energy. 225 (2018) 356-366.

[9] A. Murnandari, J. Kang, M.H. Youn, K.T. Park, H.J. Kim, S.-P. Kang, and S.K. Jeong, Effect of process parameters on the $CaCO_3$ production in the single process for carbon capture and mineralization, Korean Journal of Chemical Engineering. 34 (2017) 935-941.

[10] M. Arti, M.H. Youn, K.T. Park, H.J. Kim, Y.E. Kim, and S.K. Jeong, Single Process for CO_2 Capture and Mineralization in Various Alkanolamines Using Calcium Chloride, Energy & Fuels. 31 (2017) 763-769

[11] J.M. Kang, A. Murnandari, M.H. Youn, W. Lee, K.T. Park, Y.E. Kim, H.J. Kim, S.-P. Kang, J.-H. Lee, and S.K. Jeong, Energy-efficient chemical regeneration of AMP using calcium hydroxide for operating carbon dioxide capture process, Chemical Engineering Journal. 335 (2018) 338-344.