

# Metal Oxides Enhance the Absorption Performance of N-Methyldiethanolamine Solution during the Carbon Dioxide Capture Process

Yuming Nie, Ye Li, Huanjun Wang, Dongfang Guo, Lianbo Liu, and Yonghong Fu\*



Cite This: ACS Omega 2023, 8, 11813–11823

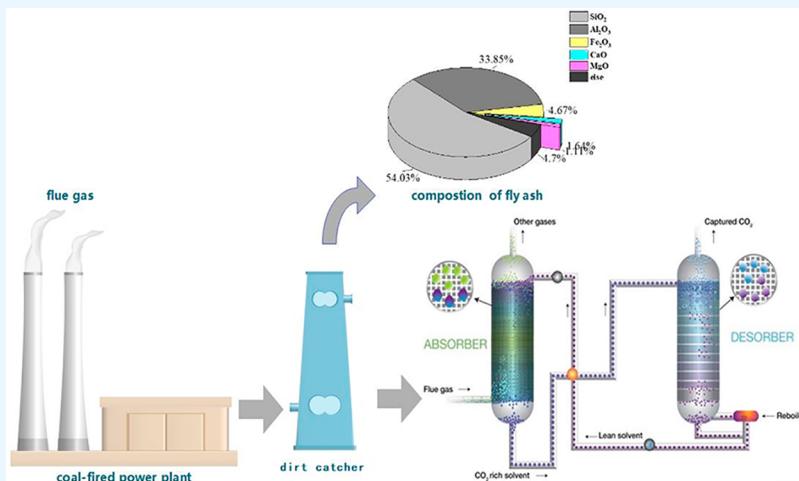


Read Online

ACCESS |

Metrics &amp; More

Article Recommendations



**ABSTRACT:** Fly ash from coal-fired power plants can enter chemical absorbents along with flue gas. Silica and metal oxides are the main components of fly ash. To explore the effect of the metal oxides on absorbents, we analyzed the integrated  $\text{CO}_2$  absorption–desorption process using *N*-methyldiethanolamine (MDEA) as the standard and an amine absorbent after adding different metal oxides. The effects of each metal oxide on  $\text{CO}_2$  capture by the MDEA solution, including  $\text{CO}_2$  reaction heat, absorption rate, cyclic loading, and carbonation rate, were assessed. It was found that supplementation with appropriate calcium oxide and magnesium oxide proportions accelerates the  $\text{CO}_2$  absorption rate and shortens the saturation time of the MDEA solution by 9%–17%. Magnesium oxide and calcium oxide were precipitated as carbonates during absorption. The  $\text{CO}_2$  reaction heat of the MDEA solution increased by 95% after adding magnesium oxide, thereby significantly increasing the energy consumption of the desorption process. On the basis of the experimental studies, the increase in  $\text{CO}_2$  absorption rate by MDEA after adding MgO and CaO may be mediated through two different mechanisms.

## 1. INTRODUCTION

Global warming, attributed to excessive carbon dioxide emissions, greatly impacts human health.<sup>1,2</sup> In 2019, China's carbon dioxide emission from coal combustion was 738 million tons,<sup>3</sup> with coal-fired power plants being the largest contributor. Carbon capture, utilization, and storage (CCUS) technology can effectively reduce these anthropogenic  $\text{CO}_2$  emissions.<sup>4</sup>

Currently, oxygen-rich combustion technology and carbon capture before and after combustion technologies are the three major types of  $\text{CO}_2$  capture methods used in coal-fired power plants.<sup>5</sup> Postcombustion carbon capture based on alcohol amine solutions is the most commonly applied in coal-fired power plants.<sup>6–8</sup> *N*-Methyldiethanolamine solution is also

widely used. Herein, the flue gas is pretreated to remove dust and sulfur before carbon capture through amine liquefaction. However, some impurities still remain in the absorbent.

Various studies have been conducted to test the effects of these impurities on the absorbent properties of amine solutions. For instance, Ling et al.<sup>9</sup> investigated the efficiency of  $\text{CO}_2$  absorption by amine solutions supplemented with

Received: October 11, 2022

Accepted: February 9, 2023

Published: March 21, 2023



ACS Publications

heat-stabilized salts (HSSs). The results showed that carboxylic acids reduced the initial pH, equilibrium solubility of CO<sub>2</sub>, adsorption rate, and circulating CO<sub>2</sub> solubility of MDEA (*N*-methyldiethanolamine) solution but enhanced the rate of CO<sub>2</sub> desorption of the solution. Metal ions enhanced the oxidative degradation of MDEA but they had no effect on its thermal degradation.<sup>10</sup> Metal ions, including Fe<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, and Mn<sup>2+</sup>, may be derived from solvent impurities and wall leaching. Liu et al.<sup>11</sup> investigated the effect of salt impurities on foaming in *N*-methyldiethanolamine (MDEA) solutions and found that Fe<sup>2+</sup>, Mg<sup>2+</sup>, and Sr<sup>2+</sup> induced foaming and stabilized the foam. Ca<sup>2+</sup> induced foaming but had no effect on foam stability. Bhatti et al.<sup>12</sup> further found that adding metal oxide catalysts such as Ag<sub>2</sub>O, NiO, and CuO to the CO<sub>2</sub> desorption column facilitated monoethanolamine (MEA) desorption at below 80 °C. However, the addition of other organic amines,<sup>15–17</sup> solvents, and ionic liquids<sup>18–20</sup> is required to improve the slow MDEA solution absorption rate.<sup>13,14</sup> Wang et al.<sup>21</sup> found through experiments with three different nanoparticles—SiO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>—employed to enhance CO<sub>2</sub> gas absorption by MEA solvent, that the nanoparticles present more obvious enhancement effect on mass transfer. In addition, the presence of nanoparticles also increases the desorption efficiency of the MEA solution. The main objectives of the previous study is to have a high-stability and low-cost organic amine solvent, and the adsorption load, desorption capacity, and low regeneration energy consumption of the solvent are the main indicators for evaluating the performance.<sup>22</sup>

Although the CO<sub>2</sub> capture process in coal-fired power plants requires dust removal, it is not possible to remove all the fly ash. Our analysis found that the fly ash at Shanghai Shidongkou Power Plant is mainly composed of four metal oxides (CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>) and silica. The main components of fly ash samples also vary between power plants.<sup>23</sup> To evaluate the absorbent performance of fly ash in coal-fired power plants, the influence of metal oxides on the absorbent is not negligible.

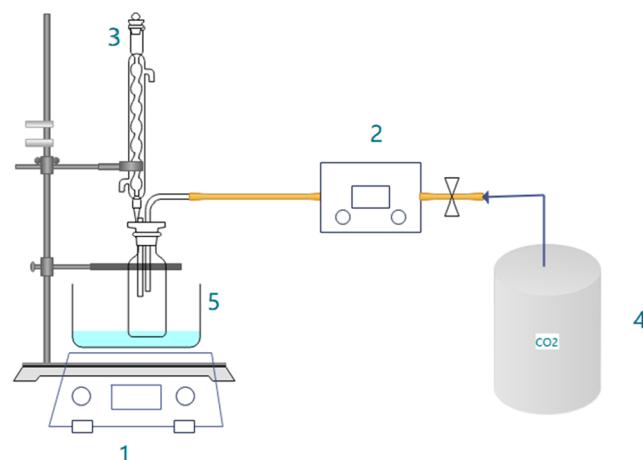
In this paper, we assessed the effects of the four metal oxides in fly ash on MDEA absorbent properties. The effects of each metal oxide on the CO<sub>2</sub> load, absorption rate, and absorption enthalpy of MDEA were analyzed. During the absorption process, temperature, gas flow rate, and solid–liquid ratio affect the mineralization efficiency of magnesium oxide and calcium oxide. However, we found that calcium and magnesium oxide enhanced the CO<sub>2</sub> absorption of MDEA, thereby shortening the saturation time for the complete conversion of carbonates during the absorption process. Accordingly, we propose the supplementation of MDEA with oxides of calcium and magnesium to enhance its CO<sub>2</sub> absorption.

## 2. MATERIALS AND METHODS

**2.1. Materials.** *N*-Methyldiethanolamine (MDEA) of 99% purity was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Calcium oxide (CaO) of 98% purity was purchased from Shanghai Xianding Biotechnology Co., Ltd. Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) was purchased from Shanghai Maclean Biochemical Technology Co. Magnesium oxide (MgO) was purchased from Shanghai Maclean Biochemical Technology Co., Ltd. Iron oxide (Fe<sub>2</sub>O<sub>3</sub>) was purchased from Shanghai Maclean Biochemical Technology Co. Magnesium chloride (MgCl<sub>2</sub>) was purchased from Shanghai Maclean

Biochemical Technology Co. Calcium chloride (CaCl<sub>2</sub>) of 96% purity was purchased from Shanghai Maclean Biochemical Technology Co., Ltd. Calcium carbonate (CaCO<sub>3</sub>) of 99.00% purity was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Magnesium carbonate (MgCO<sub>3</sub>) of 98% purity was obtained from Shanghai Bide Pharmaceutical Technology Co., Ltd. Highly pure CO<sub>2</sub> gas (≥99.99%) was purchased from Henan Heart to Heart Deep Cooling Energy Co., Ltd. Hydrochloric acid (HCl) (36%–38%) was purchased from Beijing Chemical Reagent Research Institute Co., Ltd. Deionized water was used where necessary.

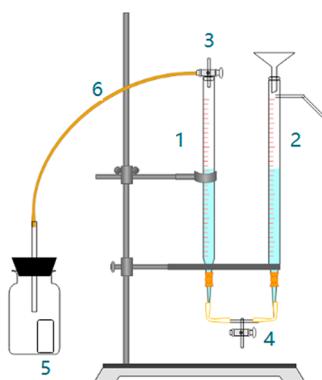
**2.2. Absorption/Desorption Experiment.** The apparatus and setup of the absorption–desorption experiment are shown in Figure 1. Carbon dioxide with a partial pressure of



**Figure 1.** Sketch of the absorption–desorption unit (1) magnetic stirrer, (2) digital readout and control unit, (3) condenser, (4) CO<sub>2</sub> cylinder, and (5) water bath

0.4 MPa in the cylinder was injected into the reactor at a speed of 100 mL/min through a gas distributor. Before the experiment, 2.7 mol L<sup>-1</sup> MDEA solutions were prepared. The reactor was a 25 mL bottle containing 20 g of amine solution. The system was heated using a water bath with a built-in magnetic stirrer (WIGGENS WH240-HT, China). The stirring was maintained at a constant rate (200 rpm), whereas the water bath was maintained at 40 °C during CO<sub>2</sub> absorption and at 90 °C during desorption. The absorption–desorption process was stopped when the weight of the reactor remained constant.

**2.3. Determination of Metal Oxide Carbonation.** Metal oxides that underwent carbonation were filtered from the organic amine solution and dried in a vacuum dryer oven. The degree of carbonate conversion was measured using a simple instrument on the basis of the principle of a linker, as shown in Figure 2. The gas volume tube was connected to the nearby side tube to form a simple communicator. First, 0.1 g of the substance to be measured was placed into the reaction flask, and the flat-bottomed finger-shaped tube containing hydrochloric acid solution was placed into the reaction flask. Then, the tee plug at the upper end of the gas volume tube was opened to make it connected, and the funnel from the upper end of the side tube was filled with water until the water level rose to the 0 scales. Then, the tee piston was turned to make only the upper part of the gas volume tube connected with the air guide tube, the reaction bottle was slowly tilted to make the hydrochloric acid in the finger-shaped tube mix with the



**Figure 2.** Device for carbonate conversion rate. Unit (1) gas volume tube, (2) side tube, (3) tee plug, (4) two-way piston, (5) flat-bottomed finger-shaped tube, and (6) air guide tube.

sample, and the reaction bottle was fully shaken. When the liquid level in the gas volume tube began to change, the piston underneath was opened to slowly drain it. When the water surface of the side tube dropped to the same level as the water surface of the gas volume tube, the draining was stopped, and the display was immediately read. The hydrochloric acid solutions were prepared at the ratio of 1:3 with water.

The degree of carbonate conversion was calculated as shown in eq 1.

$$\frac{m_1^* v_2}{m_2^* v_1} = (\text{carbonation efficiency})\% \quad (1)$$

where  $m_1$  is the standard carbonate mass (g),  $v_2$  is the amount of the gas to be measured (mL),  $m_2$  is the mass of the substance to be measured (g), and  $v_1$  is the amount of carbonate gas reading (mL).

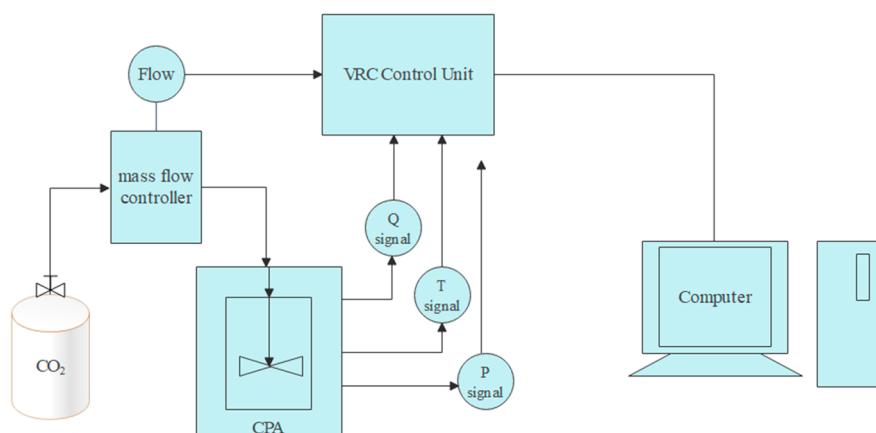
**2.4. Determination of the Reaction Heat.** The heat of carbon dioxide absorption by a mixture of N-methyldiethanolamine (MDEA) and metal oxides was determined using a reaction calorimeter (CPA-201 Sweden). A schematic representation of the process is shown in Figure 3. A 30 wt % MDEA preparation was used. Water was used as the solvent. Each metal oxide (2 g) was added separately to 150 mL of the MDEA solution.

### 3. RESULTS AND DISCUSSION

**3.1. CO<sub>2</sub> Absorption of Mixed Metal Oxides.** **3.1.1. CO<sub>2</sub> Absorption Rate and Absorption Amount of the MDEA–Metal Oxide Mixture.** The effect of the metal oxides on the CO<sub>2</sub> absorption by MDEA solution was assessed by adding 0.01 g of metal oxides to the amine. The amine concentration was maintained at 2.7 mol L<sup>-1</sup> in the MDEA–H<sub>2</sub>O system prior to CO<sub>2</sub> absorption. The CO<sub>2</sub> absorption rates and capacities of the MDEA–metal oxide solutions are shown in Figure 4. The rate of CO<sub>2</sub> absorption initially dropped rapidly, then increased gradually before decreasing again. The rate of CO<sub>2</sub> absorption by a mixture of MDEA and Al<sub>2</sub>O<sub>3</sub> solution remained relatively constant in the first 20 min. Notably, CaO and MgO significantly accelerated the CO<sub>2</sub> absorption rate of MDEA and shortened the saturation time. The MDEA–MgO solution reduced the CO<sub>2</sub> absorption saturation time by 16.4%. The MDEA–metal oxide mixtures also showed different CO<sub>2</sub> absorption capacities; the addition of CaO and MgO slightly enhanced the CO<sub>2</sub> uptake. However, the addition of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> reduced the CO<sub>2</sub> loading capacity of the MDEA solution.

The effect of the amount of the metal oxide on the absorption capacity of MDEA was analyzed by increasing the amount of MgO and CaO in the MDEA solution to 0.05 g (Figure 5). The CO<sub>2</sub> absorption capacity was higher at 0.05 g of MgO than at 0.01 g, with an increase from 1.9945 mol L<sup>-1</sup> at 0.01 g to 2.11 mol L<sup>-1</sup> at 0.05 g. The results indicate that only a given MgO concentration enhances the CO<sub>2</sub> absorption capacity of MDEA. From the perspective of chemical reaction equilibrium, the equilibrium of the MDEA reaction shifts in the direction of the CO<sub>2</sub> absorption reaction after the addition of magnesium oxide, which increases the capacity of MDEA to absorb CO<sub>2</sub>. Meanwhile, an increase of the CaO content increased the absorption rate but had no significant effect on the absorption capacity of MDEA. The increase in CO<sub>2</sub> absorption was higher for CaO than MgO. Particularly, the MDEA solution with 0.05 g of CaO reduced the CO<sub>2</sub> absorption saturation time by 17%.

**3.1.2. Cyclic CO<sub>2</sub> Capacity.** Considering that the solvent used for CO<sub>2</sub> capture in practical industrial applications needs to be reused, in addition to considering the influence of metal oxides on the maximum load of solvent CO<sub>2</sub>, it is also necessary to consider the performance of the solution in cyclic absorption.



**Figure 3.** Schematic diagram of the heat of reaction measurement process.

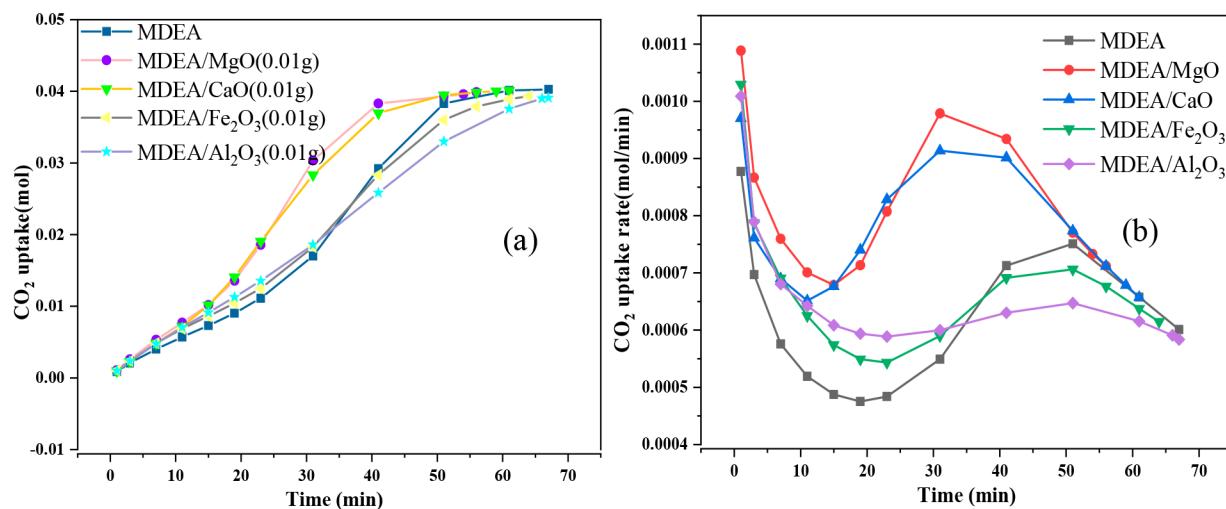


Figure 4. CO<sub>2</sub> uptakes in MDEA/0.01 g metal oxides solutions: (a) CO<sub>2</sub> absorption capacity and (b) CO<sub>2</sub> absorption rate.

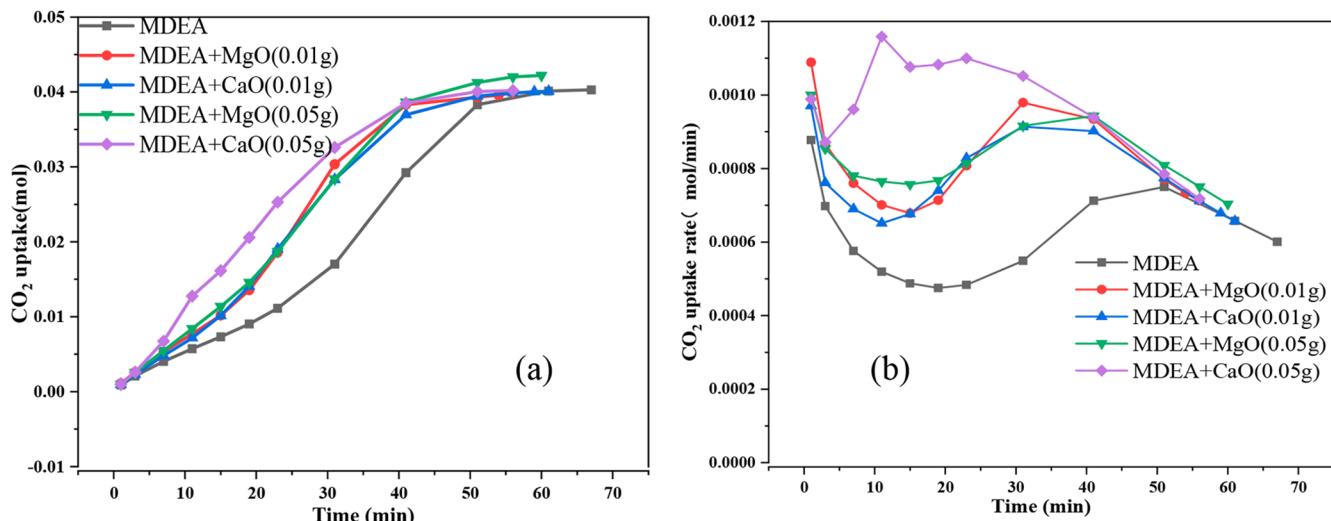


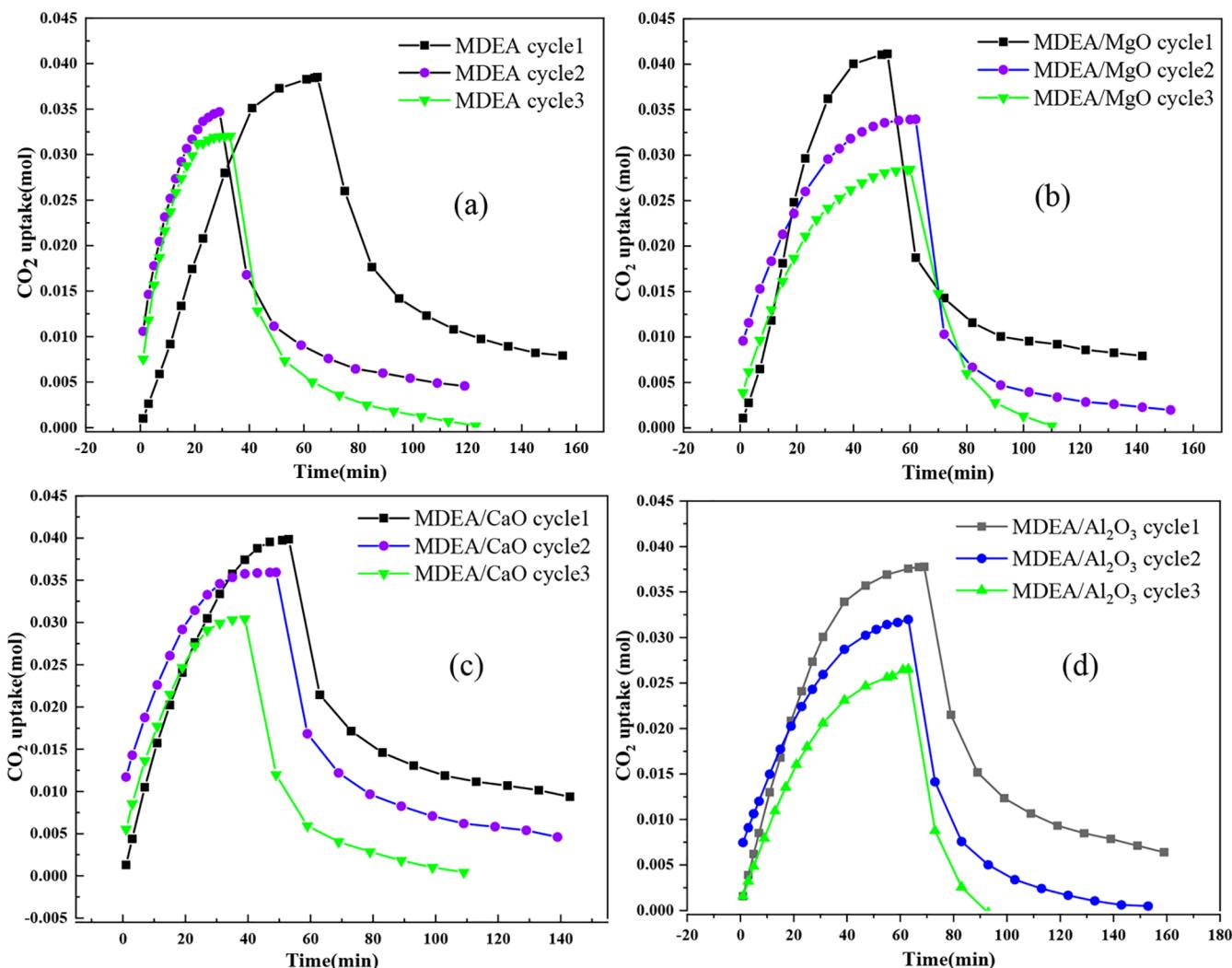
Figure 5. CO<sub>2</sub> uptakes of MDEA solution containing 0.05 g of magnesium oxide and 0.05 g of calcium oxide: (a) CO<sub>2</sub> absorption capacity and (b) CO<sub>2</sub> absorption rate.

Continuous CO<sub>2</sub> absorption is dependent on the recycling capacity of the amine solution, which is directly related to the absorption rate and regenerative energy consumption in the absorption–desorption process.<sup>24,25</sup> When metal oxides were added to MDEA solution, it affected the CO<sub>2</sub> cycle loading. In the present study, the cycle of the circulating CO<sub>2</sub> capacity was calculated on the basis of the difference between the CO<sub>2</sub> load at saturation and the CO<sub>2</sub> load after desorption. A 90 min regeneration cycle was performed using 2.7 mol/L MDEA solution containing three different metal oxides (MgO, Al<sub>2</sub>O<sub>3</sub>, and CaO). The results showed that the addition of the metal oxides reduced the cyclic CO<sub>2</sub> capacity of the MDEA solution in the following order: 2.7 mol/L MDEA/0.05 mol of MgO solution > 2.7 mol/L MDEA/0.05 mol of Al<sub>2</sub>O<sub>3</sub> > 2.7 mol/L MDEA/0.05 mol of CaO solution. The cyclic loading of 2.7 mol/L MDEA/0.05 mol of CaO was close to that of the MDEA solution in the first two absorption cycles (Figure 6). The difference in CO<sub>2</sub> capture efficiency may be attributed to variation in the suspension of fine solid particles in MDEA solution. Particles in three-phase systems affect the hydrodynamics of the system. The gas–liquid interface can

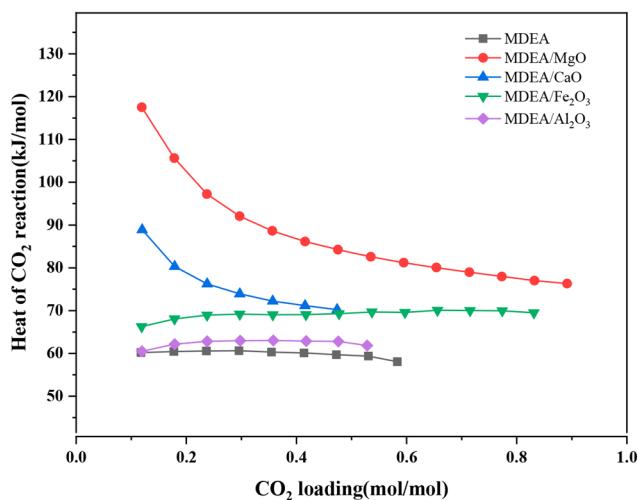
experience collisions and turbulence at the particle level, which results in a smaller diffusion layer at the interface.<sup>26</sup> From the experimental results, it can be seen that the metal oxide will weaken the MDEA capture efficiency during cyclic loading.

**3.2. Measurement of Absorption Heat.** Reduction of the regeneration energy consumption of the amine solution can make the carbon capture process more economical. The regeneration energy consumption of the absorbent is mainly composed of three heat parts: the sensible heat required to heat the absorbent to the desorption temperature, the reaction heat required to release CO<sub>2</sub> from the absorbent, and the evaporation heat of water from the absorbent during the desorption process.<sup>27,28</sup> The reaction heat of the desorption process is equal to the heat of the reaction of the absorption process and is the major part of the energy consumption for regeneration.

The reliability of the experimental equipment was verified using 150 g of MDEA solution without metal oxides. We found that the reaction heat of 30 wt % MDEA with CO<sub>2</sub> at 40 °C under an empty CO<sub>2</sub> load is 60.2 kJ/mol (Figure 7). This



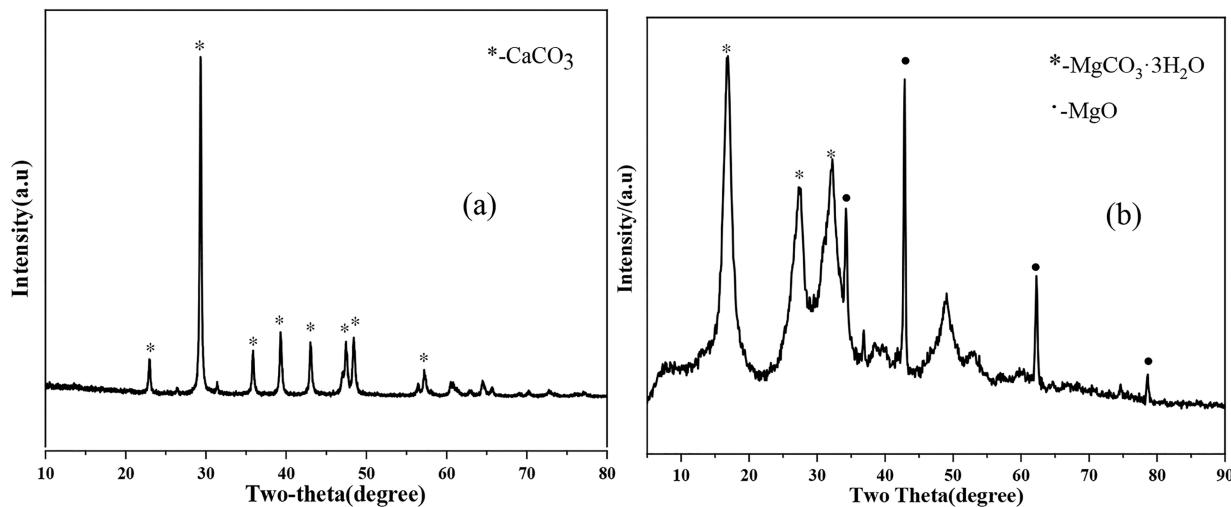
**Figure 6.** MDEA/metal oxides cyclic absorption and desorption capacities: (a) MDEA, (b) MDEA/MgO, (c) MDEA/CaO, and (d) MDEA/ $\text{Al}_2\text{O}_3$ .



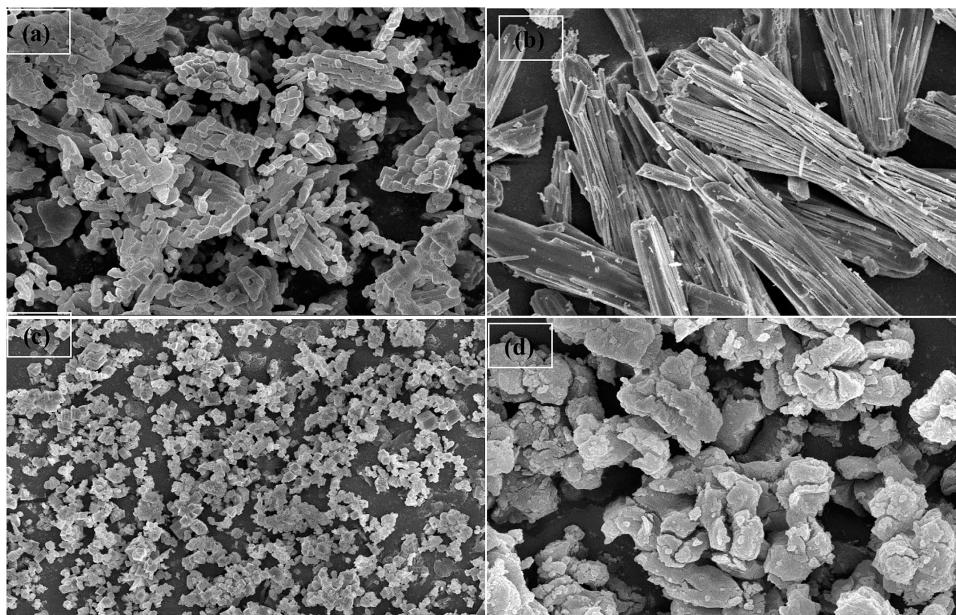
**Figure 7.** Reaction heat change in 30 wt % MDEA with  $\text{CO}_2$  after the addition of different metal oxides at 40 °C.

result was similar to that measured in the literature<sup>29</sup> for the same parameters. At 313 K, the differential enthalpy of absorption is close to constant, but when a metal oxide is

added to the solution, there is a significant increase in the reaction heat, and it is highest in the MgO solution. The maximum increase in reaction heat was 95%. As  $\text{CO}_2$  loading increased, the heat of absorption decreased substantially. The MDEA solutions containing CaO and MgO showed higher reaction heat at low  $\text{CO}_2$  loading. However, the absorption heat remained relatively stable with increasing  $\text{CO}_2$  loading after adding  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . The increase in the absorption heat was as follows: MgO > CaO >  $\text{Fe}_2\text{O}_3$  >  $\text{Al}_2\text{O}_3$  (the amount of metal oxide added was 2 g). On the one hand, magnesium oxide and calcium oxide undergo an exothermic reaction during the dissolution of an aqueous solution; in addition, the dissolved magnesium ions and calcium ions involved in the reaction affect the reaction process because calcium ions and magnesium ions react with carbonate in the solution to release a part of the heat. On the other hand, since  $\text{Al}_2\text{O}_3$  is insoluble in water, it had no effect on the absorption heat beyond a certain level. Because of the strong coloring power of iron oxide,<sup>30</sup> the absorption efficiency of MDEA solution was affected. Low absorption heat plays a vital role in improving the absorption performance of the absorbent and reducing energy consumption for desorption. Therefore, these four metal oxides increase the desorption of energy consumption.



**Figure 8.** XRD pattern of (a) CaO ( $\text{CO}_2$  absorption product) and (b) MgO ( $\text{CO}_2$  absorption product).



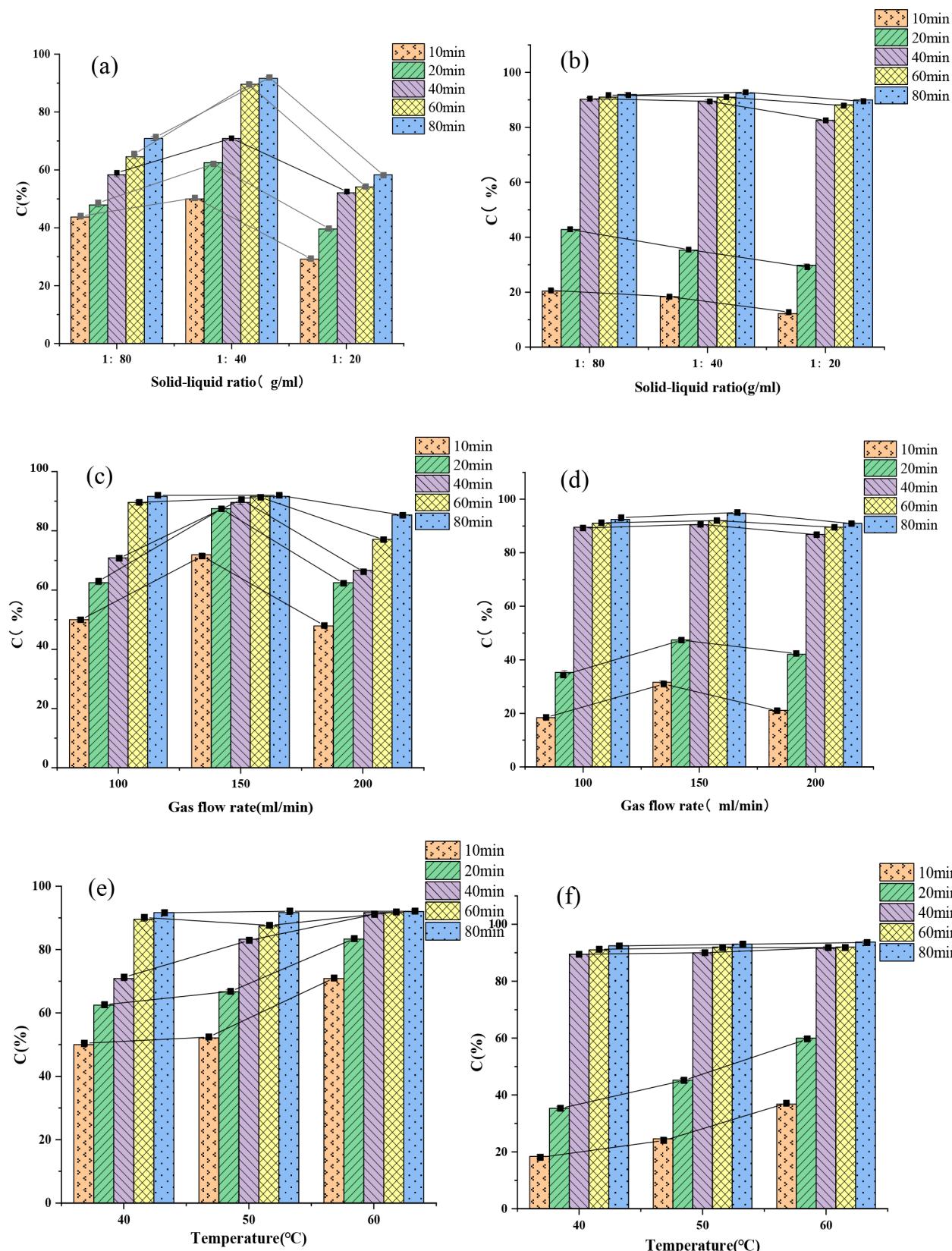
**Figure 9.** Comparison of the morphological changes in (a) unreacted magnesium oxide, (b) MgO reacted with MDEA ( $\text{CO}_2$  absorption product), (c) unreacted calcium oxide, and (d) CaO reacted with MDEA( $\text{CO}_2$  absorption product).

**3.3. Metal Oxide Carbonation.** X-ray diffraction (XRD) analysis was performed to identify the constituents in the solid phase after absorption (Figure 8). Comparison of the XRD patterns of pure  $\text{MgCO}_3$  and  $\text{CaCO}_3$  revealed that calcium oxide and magnesium oxide are mainly in the form of hydrochloride after absorption. The morphologies of MgO and CaO were determined before and after reaction with  $\text{CO}_2$  using scanning electron microscopy. As shown in Figure 9, most of the MgO and CaO dissolved and renucleated; MgO is present as needle-like magnesium carbonate after reaction with  $\text{CO}_2$ . The change of morphological characteristics found by scanning electron microscopy indicates that at a certain ratio of magnesium oxide and calcium oxide, the solidification of carbon dioxide can be achieved.

Because the addition of calcium oxide and magnesium oxide increased the absorption rate of MDEA for  $\text{CO}_2$ , we assessed the effects of temperature, solid-to-liquid ratio, and gas flow rate on the carbonation efficiency of CaO and MgO. For the

carbonation experiment, a 100 mL absorption glass flask reactor containing 80 mL of 30 wt % MDEA solution was used. The effects of the three factors on carbonation efficiency were evaluated using the controlled variable method.

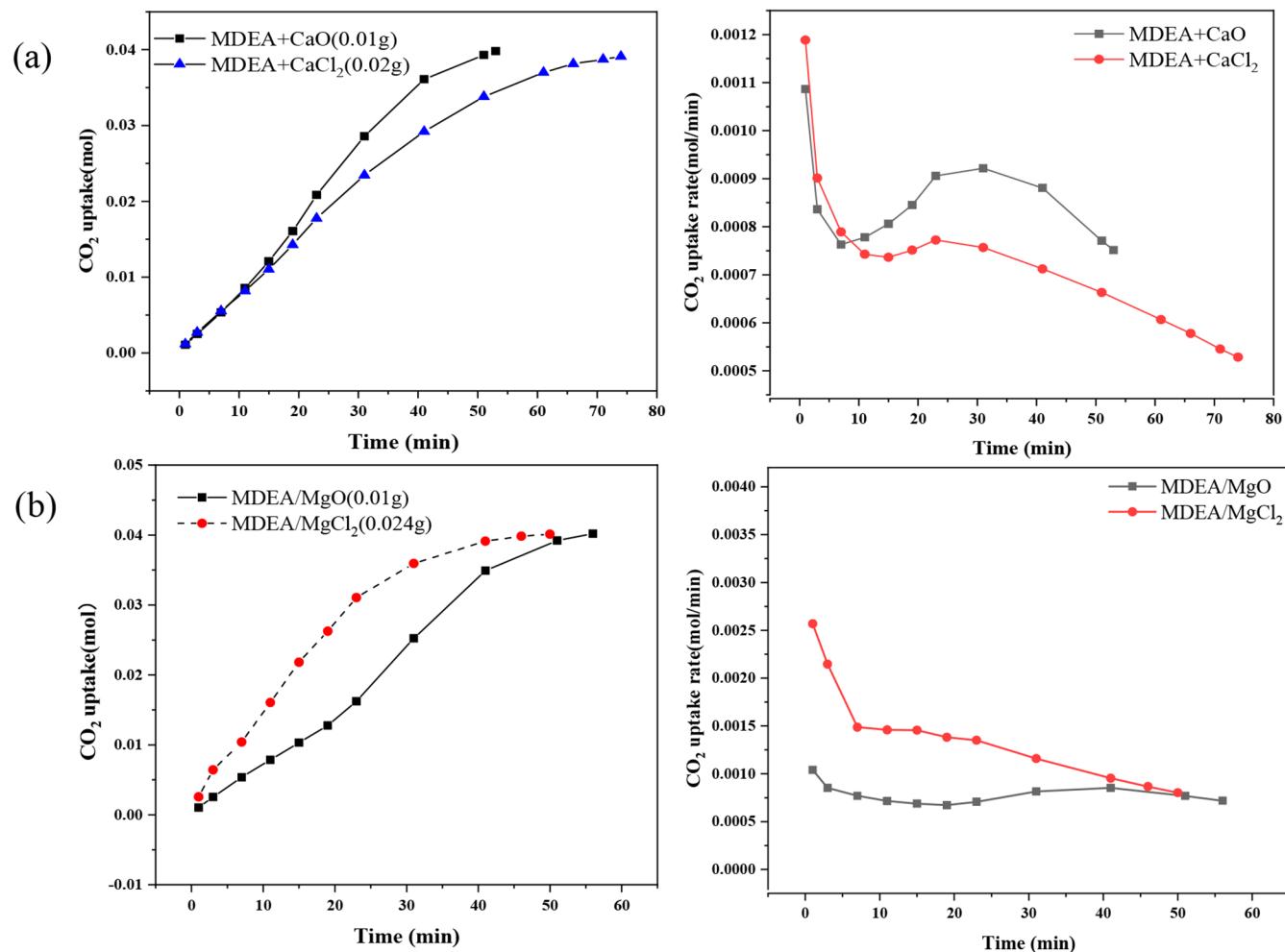
The carbonation experiment was conducted using different solid–liquid ratios (1 g/80 mL, 1 g/40 mL, and 1 g/20 mL) at 40 °C for 80 min. We found that the solid–liquid ratio affects the carbonation efficiency (Figure 10). The carbonation efficiency of MgO increased rapidly in the first 40 min before stabilizing. Meanwhile, the solubility of magnesium oxide gradually increased with the carbon dioxide content. A similar trend was observed for all the mixtures. However, the calcium oxide carbonation efficiency remained constant with a decreasing solid–liquid ratio. The carbonation efficiency at 1 g/40 mL was higher than at 1 g/80 mL, probably because of a higher density of the reactants, which provides a larger reaction area of exposure. The solubility of calcium and magnesium ions in a certain solution is limited. The experimental results



**Figure 10.** Effects of MDEA/metal oxide ratio, temperature, and gas flow rate on carbonation efficiency: (a,c,e) carbonation efficiency of calcium oxide, and (b,d,f) carbonation efficiency of magnesium oxide.

show that the optimal solid–liquid ratio provides maximum carbonation.

The effect of CO<sub>2</sub> gas flow rate on carbonation at a solid–liquid ratio of 1 g/40 mL at 40 °C was also assessed. The



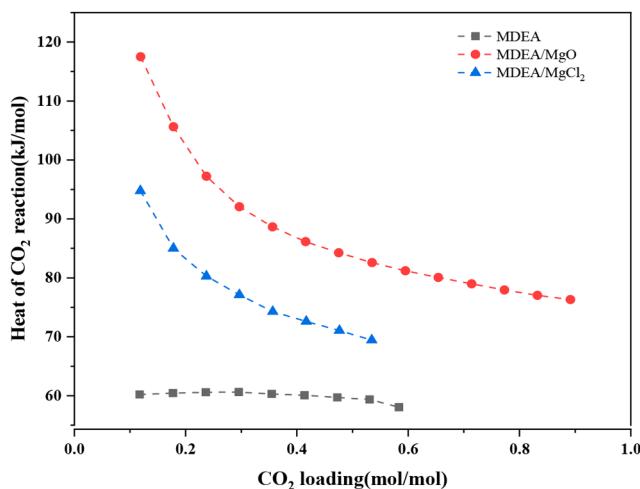
**Figure 11.** Effect of (a) calcium chloride, and (b) magnesium chloride on CO<sub>2</sub> absorption by MDEA.

average carbonation efficiency within 80 min of CaO at different gas flow rates decreased in the following order: 150 mL/min > 100 mL/min > 200 mL/min. At any given time, a higher gas flow rate increased CO<sub>2</sub> absorption by the MDEA solution. The carbonation rate decreased to lower than 100 mL/min when the gas flow rate increased to 200 mL/min. This might be because the gas flow rate exceeded the reaction equilibrium between calcium oxide and MDEA. The gas flow rate affects the mass transfer of the gas in the liquid, which in turn affects the kinetics of carbonation.<sup>31</sup> The carbonation efficiency of MgO remained constant regardless of gas flow. Magnesium oxide had poor solubility, but CO<sub>2</sub> enhanced the MgO dissolution. An increase in temperature enhanced the thermal movement of the molecules, which accelerated dissolution and the reaction rate (Figure 10). However, a very high temperature decreased CO<sub>2</sub> absorption by MDEA. Since the carbon dioxide solubility in solution increased with a decrease in temperature, the mineral carbonation conversion decreased with an increase in temperature. Beyond a certain temperature, the carbonation efficiency increased rapidly. However, very high temperatures did not significantly improve carbonation efficiency. Overall, the reaction temperature should be as low as possible to minimize energy consumption.

**3.4. Absorption Rate Analysis.** In order to understand the mechanism of increasing the CO<sub>2</sub> absorption rate in

MDEA solution by magnesium oxide and calcium oxide, we added CaCl<sub>2</sub> and MgCl<sub>2</sub> to the MDEA solution to exclude the effect of calcium and magnesium ions in the control experiment. Because calcium chloride and magnesium chloride were soluble in water, the solubility of the two substances in water were 74.5:100 and 54.2:100 g, respectively. This is shown in Figure 11. It was found that calcium ions had no effect on the uptake of MDEA, but Mg<sup>2+</sup> accelerated the uptake rate of MDEA; the Mg<sup>2+</sup>/MDEA solution exhibited a lower heat of reaction, as shown in Figure 12. This was due to the reduction of the heat released by the metal oxide dissolution process.

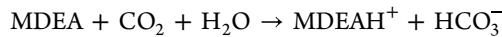
Therefore, we believe that MgO accelerates the absorption rate of CO<sub>2</sub> in MDEA solution because of the dissolution of magnesium ions. Since magnesium oxide is insoluble in pure water and organic solvents, its solubility in water increases because of the presence of carbon dioxide. In terms of the absorption rate of CO<sub>2</sub>, MgCl<sub>2</sub> was soluble in water, so Mg<sup>2+</sup> was easily provided by the dissociation of magnesium chloride in MDEA solution, thus reaching the reaction equilibrium faster than MgO. The continuous consumption of magnesium ions and CO<sub>3</sub><sup>2-</sup> promoted the positive reaction 2. With the decrease of magnesium ion, the adsorption rate became stable. Reaction eqs 2–4 are a schematic representation of the proposed mechanism. The precipitation of CaCO<sub>3</sub> and



**Figure 12.** Comparison of heat absorption of MDEA after addition of magnesium chloride and magnesium oxide.

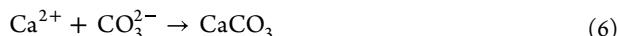
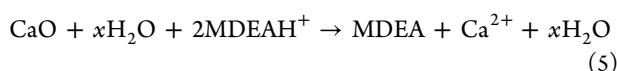
MgCO<sub>3</sub> products are related to the solubility product constant  $K_{sp}$  of Ca<sup>2+</sup>/Mg<sup>2+</sup> carbonate: since the solubility of Mg<sup>2+</sup> increased with the CO<sub>2</sub> content, the CO<sub>2</sub> uptake rate under

the MDEA/Mg<sup>2+</sup> system was greater than that of MDEA/MgO.

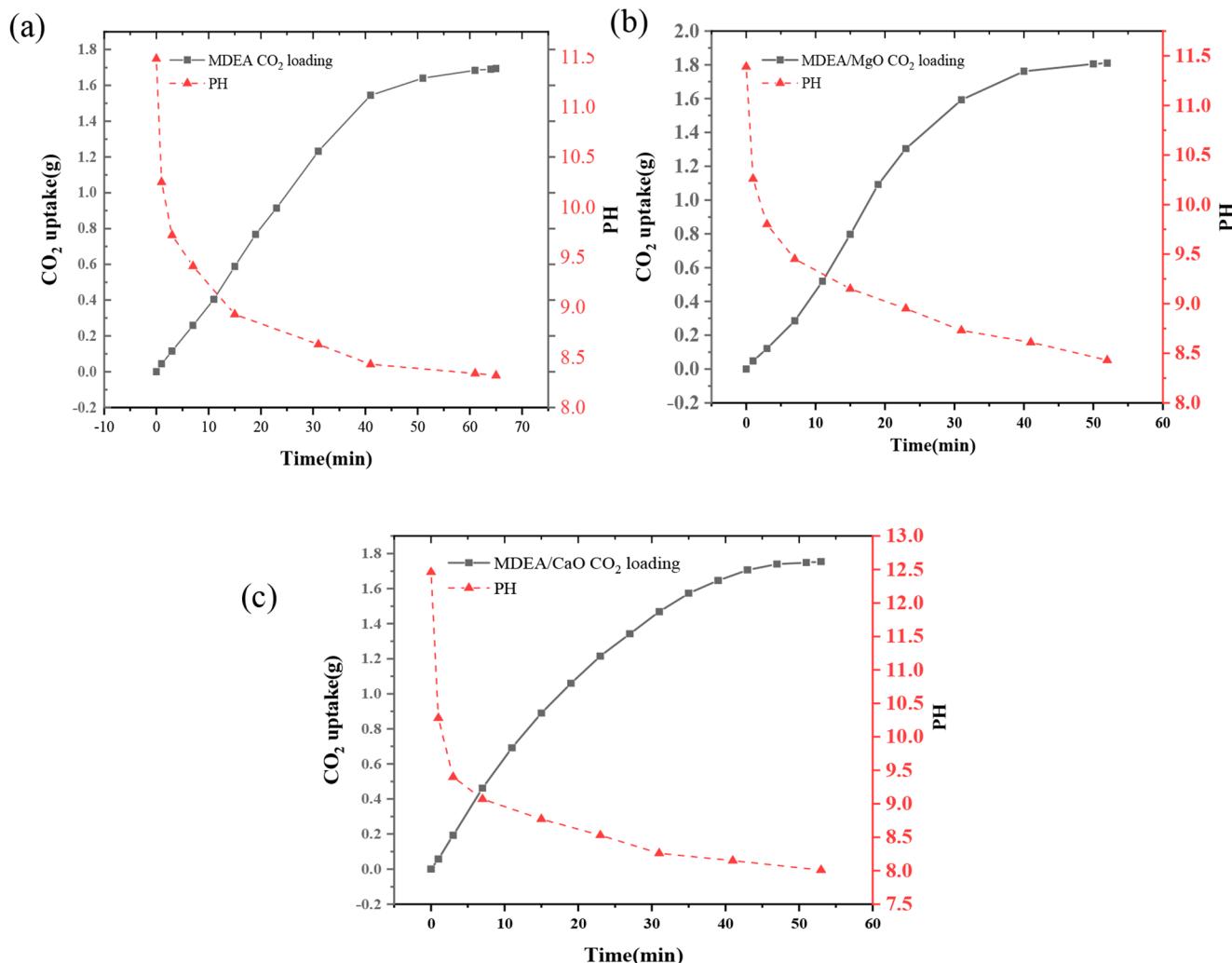


$$\Delta H_{abs} = 51 \text{ kJ/mol} \quad (2)$$

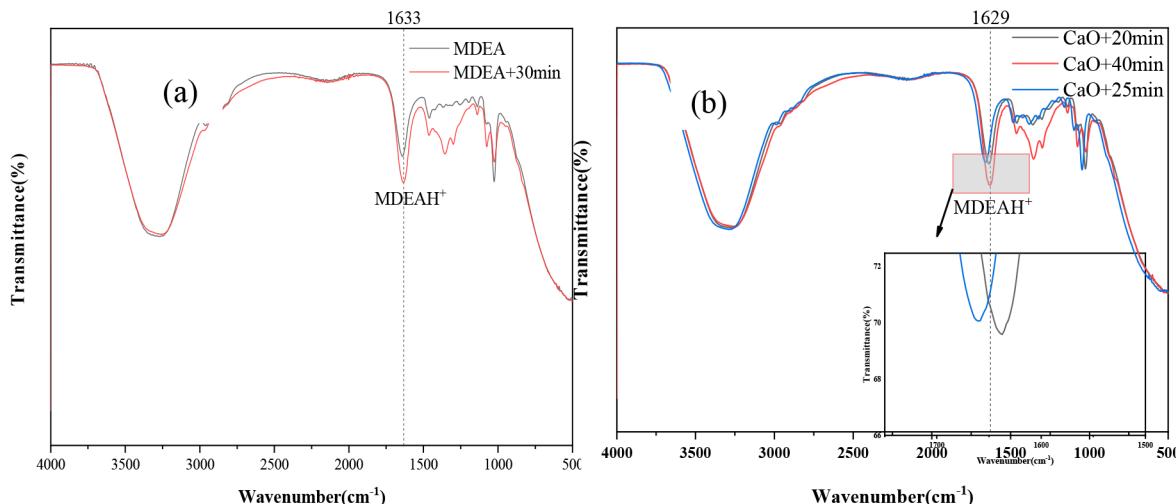
32



How calcium oxide accelerates CO<sub>2</sub> absorption was investigated further. Figure 13 shows the relationship between pH and CO<sub>2</sub> loading with reaction time. Under the same CO<sub>2</sub> loading, we found that calcium oxide increased the pH of the MDEA solution, but magnesium oxide had no effect on the pH of the solution. Tertiary amine (MDEA) did not form urethane during absorption. They acted as bases to receive protons from the slow reaction of CO<sub>2</sub> with H<sub>2</sub>O.<sup>33</sup> The regeneration



**Figure 13.** Effect of pH on the CO<sub>2</sub> loading of (a) MDEA solution, (b) MDEA–MgO solution, and (c) MDEA–CaO.



**Figure 14.** FTIR spectra of (a) MDEA absorption process and (b) MDEA/CaO absorption process at different times.

process of amine was the reverse process of the amine absorption process. The regeneration process of MDEA solution included deprotonation of  $\text{MDEAH}^+$  and decomposition of  $\text{HCO}_3^{2-}$ . Calcium oxide as an alkaline compound easily reacted with water and, because of hydration, a large amount of  $\text{OH}^-$ <sup>34</sup> reacted with the protonated amine  $\text{MDEAH}^+$  to convert it to neoamines. Given that the pH value was mainly related to MDEA content, we speculated that CaO achieved the regeneration of MDEA during the  $\text{CO}_2$  absorption process. As reaction eq 2 progresses, more protonated amines  $\text{MDEAH}^+$  are produced in the solution, and the characteristic peak of protonated amines in the wavenumber range of 1625–1645  $\text{cm}^{-1}$  gradually increases.<sup>35</sup> The FT-IR results (Figure 14) indicated that calcium oxide reduced the  $\text{MDEAH}^+$  content to achieve MDEA regeneration. The abundance of the characteristic peak of  $\text{MDEAH}^+$  was observed to be lower at 25 min of absorption than at 20 min. Reaction eqs 5 and 6 are a schematic representation of the proposed mechanism of action of calcium oxide.

#### 4. CONCLUSION

In this study, we elucidated the effect of metal oxides (calcium oxide, magnesium oxide, iron oxide, and aluminum oxide) on the  $\text{CO}_2$  absorption performance of MDEA. It was found that adding magnesium oxide and calcium oxide to the MDEA solution significantly accelerates the absorption of  $\text{CO}_2$ . However, accelerated  $\text{CO}_2$  uptake only occurred in the first cycle. Metal oxides limited the circulation of  $\text{CO}_2$  in the MDEA solutions. This was because calcium oxide and magnesium oxide form carbonates during the absorption of MDEA carbon dioxide and lose their effect. During the absorption process, temperature, gas flow rate, and solid–liquid ratio affect the mineralization efficiency of magnesium oxide and calcium oxide. The absorption heat of MDEA–metal oxide solutions is significantly higher. The 30 wt % MDEA–magnesium oxide solution required the highest absorption heat. Metal oxides would increase the energy consumption for the regeneration of MDEA solutions.

The composition of fly ash in coal-fired power plants is complex and uncontrollable. If fly ash enters the  $\text{CO}_2$  capture system, it will have a negative impact on the absorbent performance and may also increase the degradation of the absorbent, thereby resulting in increased operating costs.

However, if magnesium oxide or calcium oxide is used as a separate additive, and the process is matched to the relevant process, the capture performance can be well improved.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

**Yonghong Fu** — Xi'an University of Architecture and Technology, Xi'an 710055, China; Shaanxi Key Laboratory of Nanomaterials and Nanotechnology, Xi'an 710055, China; Xi'an Clean Energy Key Laboratory, Xi'an 710055, China; Email: 17771858340@163.com

##### Authors

**Yuming Nie** — Xi'an University of Architecture and Technology, Xi'an 710055, China; Shaanxi Key Laboratory of Nanomaterials and Nanotechnology, Xi'an 710055, China; Xi'an Clean Energy Key Laboratory, Xi'an 710055, China; [orcid.org/0000-0003-2175-2167](https://orcid.org/0000-0003-2175-2167)

**Ye Li** — Huaneng Clean Energy Research Institute, Beijing 100000, China

**Huanjun Wang** — Huaneng Clean Energy Research Institute, Beijing 100000, China

**Dongfang Guo** — Huaneng Clean Energy Research Institute, Beijing 100000, China

**Lianbo Liu** — Huaneng Clean Energy Research Institute, Beijing 100000, China

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.2c06482>

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

Throughout the writing of this dissertation, the authors have received a great deal of support and assistance from mentors and wonderful cooperation and patient support from teammates, groupmates, and team members. The Home for Researchers ([www.home-for-researchers.com](http://www.home-for-researchers.com)) is thanked for their guidance on grammar during the dissertation process. Finally, thanks are given to the China Huaneng Group Clean Energy Technology Research Institute for providing equipment and financial support.

## ■ REFERENCES

- (1) Iyer, G.; Clarke, L.; Edmonds, J.; Fawcett, A.; Fuhrman, J.; McJeon, H.; Waldhoff, S. The role of carbon dioxide removal in net-zero emissions pledges. *Energy and Climate Change* **2021**, *2*, 100043.
- (2) Beyeler, N.; Salas, R. N. An unequivocal call to climate action for the health sector. *bmj* **2022**, *376*, o680.
- (3) Ritchie, H.; Roser, M.; Rosado, P. CO<sub>2</sub> and Greenhouse Gas Emissions, *Our World in Data*, 2020. <https://ourworldindata.org/co2-and-greenhouse-gas-emissions>.
- (4) Supekar, S. D.; Skerlos, S. J. Reassessing the efficiency penalty from carbon capture in coal-fired power plants. *Environ. Sci. Technol.* **2015**, *49*, 12576–12584.
- (5) Rubin, E. S.; Mantripragada, H.; Marks, A.; Versteeg, P.; Kitchin, J. The outlook for improved carbon capture technology. *Progress in energy and combustion science* **2012**, *38* (5), 630–671.
- (6) Leung, D Y C.; Caramanna, G.; Maroto-Valer, M. M. An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews* **2014**, *39*, 426–443.
- (7) Shakerian, F.; Kim, K. H.; Szulejko, J. E.; Park, J. W. A comparative review between amines and ammonia as sorptive media for post-combustion CO<sub>2</sub> capture. *Applied Energy* **2015**, *148*, 10–22.
- (8) Vaidya, P. D.; Kenig, E. Y. CO<sub>2</sub>-alkanolamine reaction kinetics: a review of recent studies. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology* **2007**, *30* (11), 1467–1474.
- (9) Ling, H.; Liu, S.; Gao, H.; Liang, Z. Effect of heat-stable salts on absorption/desorption performance of aqueous monoethanolamine (MEA) solution during carbon dioxide capture process. *Sep. Purif. Technol.* **2019**, *212*, 822–833.
- (10) Léonard, G.; Voice, A.; Toye, D.; Heyen, G. Influence of dissolved metals and oxidative degradation inhibitors on the oxidative and thermal degradation of monoethanolamine in postcombustion CO<sub>2</sub> capture. *Ind. Eng. Chem. Res.* **2014**, *53* (47), 18121–18129.
- (11) Liu, Y.; Zhang, B.; Wu, D.; Zhou, Z. Influence of salt impurities on foaming properties of MDEA desulfurization solution. *Chemistry and Technology of Fuels and Oils* **2015**, *51* (4), 353–360.
- (12) Bhatti, U. H.; Sivanesan, D.; Lim, D. H.; Nam, S. C.; Park, S.; Baek, I. H. Metal oxide catalyst-aided solvent regeneration: A promising method to economize post-combustion CO<sub>2</sub> capture process. *Journal of the Taiwan Institute of Chemical Engineers* **2018**, *93*, 150–157.
- (13) Rinker, E. D.; Ashour, S. S.; Sandall, O. C. Absorption of Carbon Dioxide into Aqueous Blendeds of Diethanolamine and Methyldiethanolamine. *Industrial and Engineering Chemical Research* **2000**, *39*, 4346–4356.
- (14) Linek, V.; Sinkule, J.; Havelka, P. Empirical Design Method of Industrial Carbon Dioxide Mixed Solvent Absorbers with Axial Dispersion in Gas. *Industrial and Engineering Chemical Research* **1994**, *33*, 2731–2737.
- (15) Cheng, H. H.; Tan, C. S. Removal of CO<sub>2</sub> from indoor air by alkanolamine in a rotating packed bed. *Sep. Purif. Technol.* **2011**, *82*, 156–166.
- (16) Lu, J. G.; Zheng, Y. F.; He, D. L. Selective absorption of H<sub>2</sub>S from gas mixtures into aqueous solutions of blended amines of methyldiethanolamine and 2-tertiarybutylamino-2-ethoxyethanol in a packed column. *Sep. Purif. Technol.* **2006**, *52* (2), 209–217.
- (17) Xu, G. W.; Zhang, C. F.; Qin, S. J.; Gao, W. H.; Liu, H. B. Gas—Liquid Equilibrium in a CO<sub>2</sub>-MDEA-H<sub>2</sub>O System and the Effect of Piperazine. *Ind. Eng. Chem. Res.* **1998**, *37*, 1473–1477.
- (18) Feng, Z.; Cheng-Gang, F.; You-Ting, W.; Yuan-Tao, W.; Ai-Min, L.; Zhi-Bing, Z. Absorption of CO<sub>2</sub> in the aqueous solutions of functionalized ionic liquids and MDEA. *Chemical Engineering Journal* **2010**, *160* (2), 691–697.
- (19) Ahmady, A.; Hashim, M. A.; Aroua, M. K. Absorption of carbon dioxide in the aqueous mixtures of methyldiethanolamine with three types of imidazolium-based ionic liquids. *Fluid Phase Equilib.* **2011**, *309* (1), 76–82.
- (20) Zhao, Z.; Dong, H.; Zhang, X. The research progress of CO<sub>2</sub> capture with ionic liquids. *Chinese Journal of Chemical Engineering* **2012**, *20* (1), 120–129.
- (21) Wang, T.; Yu, W.; Liu, F.; Fang, M.; Farooq, M.; Luo, Z. Enhanced CO<sub>2</sub> absorption and desorption by monoethanolamine (MEA)-based nanoparticle suspensions. *Ind. Eng. Chem. Res.* **2016**, *55* (28), 7830–7838.
- (22) Liu, F.; Fang, M.; Dong, W.; Wang, T.; Xia, Z.; Wang, Q.; Luo, Z. Carbon dioxide absorption in aqueous alkanolamine blends for biphasic solvents screening and evaluation. *Applied energy* **2019**, *233*, 468–477.
- (23) Chandan, P.; Richburg, L.; Bhatnagar, S.; Remias, J. E.; Liu, K. Impact of fly ash on monoethanolamine degradation during CO<sub>2</sub> capture. *International Journal of Greenhouse Gas Control* **2014**, *25*, 102–108.
- (24) Gao, H.; Xu, B.; Liu, H.; Liang, Z. Effect of Amine Activators on Aqueous N,N-Diethylethanolamine Solution for Postcombustion CO<sub>2</sub> Capture. *Energy Fuels* **2016**, *30*, 7481–7488.
- (25) Gao, H.; Wu, Z.; Liu, H.; Luo, X.; Liang, Z. Experimental Studies on the Effect of Tertiary Amine Promoters in Aqueous Monoethanolamine (MEA) Solutions on the Absorption/Stripping Performances in Post-combustion CO<sub>2</sub> Capture. *Energy Fuels* **2017**, *31*, 13883–13891.
- (26) Kluytmans, J. H. J.; Van Wachem, B. G. M.; Kuster, B. F. M.; Schouten, J. C. Mass transfer in sparged and stirred reactors: influence of carbon particles and electrolyte. *Chem. Eng. Sci.* **2003**, *58* (20), 4719–4728.
- (27) Ye, J. X.; Jiang, C. K.; Chen, H.; Shen, Y.; Zhang, S. H.; Wang, L. D.; Chen, J. M. Novel biphasic solvent with tunable phase separation for CO<sub>2</sub> capture: role of water content in mechanism, kinetics, and energy penalty. *Environ. Sci. Technol.* **2019**, *53*, 4470–4479.
- (28) Zhou, X. B.; Jing, G. H.; Lv, B. H.; Liu, F.; Zhou, Z. M. Low-viscosity and efficient regeneration of carbon dioxide capture using a biphasic solvent regulated by 2-amino-2-methyl-1-propanol. *Appl. Energy* **2019**, *235*, 379–390.
- (29) Kim, I.; Svendsen, H. F. Comparative study of the heats of absorption of post-combustion CO<sub>2</sub> absorbents. *International Journal of Greenhouse Gas Control* **2011**, *5* (3), 390–395.
- (30) Arimoto, R.; Balsam, W.; Schloesslin, C. Visible spectroscopy of aerosol particles collected on filters: iron-oxide minerals. *Atmos. Environ.* **2002**, *36* (1), 89–96.
- (31) Bauer, M.; Gassen, N.; Stanjek, H.; Peiffer, S. Carbonation of lignite fly ash at ambient T and P in a semi-dry reaction system for CO<sub>2</sub> sequestration. *Applied geochemistry* **2011**, *26* (8), 1502–1512.
- (32) Muchan, P.; Saiwan, C.; Narku-Tetteh, J.; Idem, R.; Supap, T.; Tontiwachwuthikul, P. Screening tests of aqueous alkanolamine solutions based on primary, secondary, and tertiary structure for blended aqueous amine solution selection in post combustion CO<sub>2</sub> capture. *Chem. Eng. Sci.* **2017**, *170*, 574–582.
- (33) Yang, Q.; Puxty, G.; James, S.; Bown, M.; Feron, P.; Conway, W. Toward intelligent CO<sub>2</sub> capture solvent design through experimental solvent development and amine synthesis. *Energy Fuels* **2016**, *30* (9), 7503–10.
- (34) Ramachandran, V. S.; Sereda, P. J.; Feldman, R. F. Mechanism of hydration of calcium oxide. *Nature* **1964**, *201* (4916), 288–289.
- (35) Han, S.; Meng, Y.; Aihemaiti, A.; Gao, Y.; Ju, T.; Xiang, H.; Jiang, J. Biogas upgrading with various single and blended amines solutions: Capacities and kinetics. *Energy* **2022**, *253*, 124195.