INTRODUCTION

Large amount of industrial wastes are discharged from commercial production every year.\textsuperscript{1} Lime mud is a kind of industrial waste that produced during the causticization process in paper mill. China is one of the papermaking and paper consumption powerhouses. In China, about 50 million tons of paper was produced every year, which means dozens of million tons of lime mud were discharged to the environment. The discharge of such a large amount of lime mud leads to serious environmental aspects including water pollution and land occupation.\textsuperscript{2} Therefore, how to recycle the lime mud in environmentally friendly ways is an interesting topic and has drawn lots of researchers’ attentions.

Lime mud was firstly recovered as soil amendments and building materials.\textsuperscript{3} Qin et al\textsuperscript{4} have proved that recycling of lime mud as raw materials of anorthite ceramic was a feasible approach to solve the solid wastes. Madrid et al\textsuperscript{5} successfully reused lime mud to produce concrete masonry units that with better thermal properties. In recent years,
lime mud was widely investigated to remove pollutants in different phase and as catalysts in chemical industry. Li et al. used lime mud to prepare heterogeneous base transesterification catalyst by doping with potassium fluoride, and up to 99% oil conversion can be achieved under the optimum conditions. Lime mud was also investigated to absorb SO2 at fluidized bed conditions. The result shows that lime mud exhibits much better SO2 capture capacity compared with limestone due to the beneficial microstructure of the calcined lime mud for SO2 removal. CO2 emission from fossil fuel combustion has been identified as one of the major greenhouse gases and leads to global warming. Since fossil fuel fired power plants are the major sources of CO2 emission, how to capture the CO2 from flue gas in power plant has drawn public attentions. The reuse of the lime mud in environmentally friendly way and CO2 capture from flue gas can be simultaneously realized if lime mud can be used as CO2 sorbent in carbon capture system. Calcium looping process is widely considered as one of the most potential methods that can achieve deep CO2 emission reduction in view of its advantages including low-cost CO2 sorbent and proven CFB technology. The CO2 capture capacity of the calcium-based sorbent can be further enhanced by synthesizing inert supported sorbent and template-assisted synthesis approach. Therefore, the cost of this technology can be further reduced.

Our previous research has proposed lime mud as CO2 sorbent in calcium looping process. After prewash and prolonged carbonation treatment, the lime mud presented relatively higher CO2 capture capacity compared with limestone. Ma et al. used lime mud as CaO precursor to synthesize highly reactive calcium-based sorbent. The carbonation conversion of the obtained calcium-based sorbent can be higher than 38% after 50 cycles. The carbonation time, that is the time duration of the carbonation stage, was chosen in the range of 10-40 minutes when testing the CO2 capture capacity of the sorbents. However, the lasting time that the sorbent can stay in the carbonator was only 1-5 minutes in calcium looping process. Therefore, the carbonation conversion that the sorbent can obtain during the initial fast chemical reaction controlled stage, usually lasts for 1-3 minutes, is relatively significant to judge the CO2 capture capacity of the sorbents. A surface reaction-controlled kinetic model with a Boltzmann equation, developed by Lan and Wu, was proven to be more appropriate than the core shrinking model and the random core model to describe the carbonation reaction between CO2 and CaO during the chemical reaction controlled stage. In this manuscript, the carbonation kinetics of the lime mud in the chemical reaction controlled stage was analyzed by this surface reaction-controlled kinetic model. The effects of prewash and prolonged carbonation treatment on the carbonation kinetics of the lime mud were also discussed in detail.

**FIGURE 1** XRD spectrum of lime mud and calcined lime mud

## 2 | EXPERIMENTAL

### 2.1 | Samples

The lime mud (LM) in this research was sampled from a paper mill located in Shandong province, China. The components of the LM, detected by XRD analysis, were CaCO3 and a small amount of Ca(OH)2, as shown in Figure 1. All the CaCO3 and Ca(OH)2 in LM decomposed to CaO after calcination. A kind of limestone was employed as contrast sample. The X-ray fluorescence (XRF) results of the LM and limestone are shown in Table 1. CaCO3 was doped with CaCl2 by wet impregnation method to check the effect of Cl on carbonation performance of the LM, with the Cl/Ca molar ratio differed from 0.25:100 to 2:100. The detailed modification process was presented elsewhere. In order to mitigate the adverse effect of Cl on the CO2 capture capacity, the LM was prewashed to decrease the content of Cl. The prewash process was presented as follows: 100 g LM and 400 mL distilled water were firstly mixed in a beaker at ordinary temperature. After stirring for 2 hours, the mixture was filtered to remove the liquid. Then, the solid residue and 200 mL distilled water were mixed and stirred for 2 hours. After filtration, the mixture was dried in the oven at 120°C. Then, the solid residue obtained was called prewashed lime mud (PLM). The particle sizes of all the sorbents were below 0.125 mm.

A prolonged carbonation process was proposed to improve the microstructure and enhance the CO2 capture capacity of the calcined LM and PLM. The prolonged carbonation of the calcined sample was only performed in the 1st carbonation. Before used as CO2 sorbent, the calcined PLM was firstly carbonated in 100% CO2 for 3-12 hours at 700°C. Then, the PLM after prolonged carbonation treatment was sent for carbonation kinetics test in the dual-fixed bed reactor and the thermogravimetric analyzer.
2.2 | Carbonation kinetics performance of the sorbent

The cyclic calcination/carbonation tests of the LM, PLM, and limestone were accomplished in a dual-fixed bed reactor (DFR), as shown in Figure 2. The internal diameter of the DFR is 30 mm, and the constant temperature zone of the reactor is about 300 mm, which can make sure that the samples stay in the constant temperature zone at any operating mode. The N2 and CO2 feed were controlled by mass flow controllers and introduced into the reactor. The sample was firstly calcined for 10 minutes at 850°C in pure N2 and then was carbonated at 700°C for 20 minutes. The sample mass after calcination and carbonation was measured by a delicate electronic balance, and the carbonation conversions of the sorbents were calculated according the mass change during the carbonation and calcination stage, as shown in Equation (1).

\[
X_N = \frac{m_N - m_{cal}}{m_0 A} \cdot \frac{M_{CaO}}{M_{CO_2}}
\]  

(1)

where \(X_N\) is the carbonation conversion of the sample after \(N\) cycles. \(m_0\) is the initial mass of the sample. \(m_N\) is the mass of the carbonated sample after \(N\) cycles. \(m_{cal}\) is the mass of the completely calcined sample (the mass of the sample after each calcination is the same). \(M_{CaO}\) and \(M_{CO_2}\) are molar masses of the CaO and CO2, respectively. \(A\) is the content of CaO in the initial sample.

A thermogravimetric analyzer (TGA) was employed to investigate the carbonation kinetics of the sorbent during multiple cycles. After multiple calcination/carbonation cycles, the sorbents were sampled from the DFR and sent for TGA analysis. The crucible containing 10 ± 0.1 mg sample was firstly put into the furnace of the TGA. The reaction temperature was increased to 850°C at a heating rate of 30°C/min, and then, the temperature was constant for 10 min in pure N2. The sample was completely calcined in this period. Then, the temperature decreased to 700°C at 30°C/min in pure N2. The gas mixture was switched to the carbonation atmosphere (15% CO2 balanced with N2) at the moment when the temperature reached 700°C, and the temperature was constant at 700°C for 30 minutes for carbonation reaction. One data were collected per 3 second during the carbonation process. The gas flow was 120 mL/min. The carbonation rate of the sample was calculated according to Equation (2).

\[
r_N = \frac{dX_N}{dt}
\]  

(2)

where \(r_N\) is carbonation rate of the sample at \(t\) (carbonation time) in the \(N\)th carbonation, s\(^{-1}\). \(t\) denotes the reaction time, s.

2.3 | Kinetics analysis model

A surface reaction-controlled kinetic model with a Boltzmann equation was employed to describe the reaction of CO2 and CaO during the chemical reaction-controlled stage, the curve of which is an S-type. The fitting equation is shown in Equation (3):

\[
X_{N,t} = X_u - \frac{X_u}{1 + \exp \left[ \frac{(t-t_0)k}{X_u} \right]} \quad (0 \leq X_{N,t} \leq X_u)
\]  

(3)

### TABLE 1

| Sample   | CaO    | MgO    | SiO2   | Al2O3  | Fe2O3  | SO3    | TiO    | K2O    | Na2O   | Cl     | Others | LOI    |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| LM       | 52.39  | 0.7    | 2.52   | 1.49   | 0.29   | 0.31   | 0.056  | 0.013  | 0.14   | 0.88   | 0.049  | 41.16  |
| PLM      | 52.52  | 0.73   | 2.64   | 1.71   | 0.27   | 0.3    | 0.066  | 0.013  | 0.044  | 0.30   | 0.051  | 41.36  |
| Limestone| 52.08  | 1.32   | 3.32   | 0.53   | 0.03   | -      | -      | -      | 0.02   | -      | 0.47   | 42.23  |

**FIGURE 2** Schematic diagram of dual-fixed-bed reactor (DFR)
where $X_u$ is the ultimate carbonation conversion in the chemical reaction controlled stage, mol/mol; $k$ is the reaction rate constant in the chemical reaction controlled stage, s\(^{-1}\); $t_0$ is the time at which the carbonation achieves highest carbonation rate, s.

The carbonation rate $r_{N,t}$ is described in Equation (4)

$$r_{N,t} = \frac{dX_{N,t}}{dt} = k \times \frac{X_{N,t}}{X_u} \left(1 - \frac{X_{N,t}}{X_u}\right)$$  \hspace{1cm} (4)

perform the differential calculation according to Equation (4), and Equation (5) is obtained:

$$\frac{dr_{N,t}}{dt} = \frac{d^2X_{N,t}}{dt^2} = \frac{k}{X_u^2} \left(X_u - 2X_{N,t}\right) \frac{dX_{N,t}}{dt}$$  \hspace{1cm} (5)

when $\frac{dr_{N,t}}{dt} = 0$, it is related to the point of maximum carbonation rate. Here, $X_{N,t}$ is equal to half the value of $X_u$. According to this, the value of $X_u$ can be obtained by 2 times of the conversion at the point of maximum carbonation rate. Then, the carbonation process of the sorbent can be divided into chemical reaction controlled stage and diffusion controlled stage by the value of $X_u$. Here, this surface reaction-controlled kinetic model was employed to discuss the carbonation kinetics of the LM and PLM during the chemical reaction controlled stage.

2.4 | Microstructure analysis

The chemical components of the LM, PLM, and limestone were examined by X-ray fluorescence (XRF). The pore volume and pore area distributions of the calcined LM, PLM, and limestone after different cycles were examined by a nitrogen adsorption analyzer (Micromeritics, ASAP 2020-M). The pore volume and pore size distribution of the sample were computed by BJH (Barrett-Joyner-Halenda) model, the BET surface of the sample was calculated by BET model.

3 | RESULTS AND DISCUSSIONS

3.1 | Carbonation kinetics of LM in multiple cycles

Figure 3 shows the carbonation conversions of the LM and limestone in multiple calcination/carbonation cycles. The LM exhibits more stable CO\(_2\) capture capacity with cycle number, while it shows lower carbonation conversions in the initial cycles compared with the limestone. The carbonation conversions of the LM were higher than those of the limestone after 15 cycles. However, this result was obtained in a dual-fixed bed reactor with a relatively long carbonation time. Figure 4A,B present the carbonation conversions and carbonation rates of the LM and limestone with carbonation time during multiple cycles.
time in multiple cycles. It can be seen that the LM shows much slower carbonation rate during the initial fast reaction stage, while it presents higher carbonation rate during the following diffusion controlled stage compared with the limestone in the same cycle.

The point of maximum carbonation rate in each carbonation process can be obtained from Figure 4B, according to which the $X_u$ can be confirmed from Figure 4A. Then, the carbonation curves of the LM and limestone during the chemical reaction controlled stage were fitted by Equation (3), as shown in Figure 5. The correlation coefficients of all the curves are in the range of 0.980-0.998, which means it is feasible to use this surface reaction-controlled kinetic model to describe the carbonation of the LM and limestone during the chemical reaction controlled stage. The kinetic parameters obtained by this model are shown in Table 2. The parameter $t_{crcs}$ in Table 2 denotes the time duration of the chemical reaction controlled stage of the sorbents.

The values of $k$ and $t_{crcs}$ of the LM are much smaller compared with those of the limestone in the same cycle, as can be seen in Table 2. Taking the 1st cycle as an example, the values of $k$ and $t_{crcs}$ of the LM are only 62.6% and 31.3% those of the limestone, which means that the LM shows much slower carbonation rate and much shorter time duration in the chemical reaction controlled stage. Thus, the $X_u$ that can be achieved in this stage for the LM, which is mainly determined by $k$ and $t_{crcs}$, is much smaller than that for the limestone. We also can see from Table 2 that the values of $X_u$ of the LM in different cycles are very small, with a value that no more than 0.03 after 15 cycles. Such a low CO$_2$ capture capacity of the LM in the chemical reaction controlled stage makes it not suitable to be used as CO$_2$ sorbent in calcium looping process. The main components of the LM and limestone are all CaCO$_3$, and the corrected CaO contents that in the LM and limestone are almost the same, as shown in Table 1. Maybe, the complex impurities in the LM or the specific microstructure characteristics of the calcined LM were the reasons why the LM showed such low carbonation capacity during the chemical reaction controlled stage.

### 3.2 Effect of Cl on the carbonation kinetics of calcium-based sorbent

As shown in Table 1, the chemical components of the LM are much more complex compared with the limestone. Especially, the content of Cl in the LM is relatively high. The other impurities except Cl have been proved to be beneficial or not attributable to CO$_2$ capture capacity of the calcium-based sorbents.\(^{21,22}\) The effect of Cl on CO$_2$ capture capacity of the calcium-based sorbent was detected by doping CaCl$_2$ into CaCO$_3$ through wet impregnation method. The carbonation conversion and carbonation rate of Cl-doped CaCO$_3$ with carbonation time during the first cycle are shown in Figure 6, and the fitting results of the carbonation process of Cl-doped CaCO$_3$ with different Cl/Ca molar ratio during the chemical reaction controlled stage are shown in Figure 7. The obtained kinetic parameters were presented in Table 3.

We can see from Figures 6 and 7 and Table 3 that addition of Cl has adverse effect on the CO$_2$ capture performance of the calcium-based sorbent, especially the carbonation process during the chemical reaction controlled stage. The values of $k$ and $t_{crcs}$ of Cl-doped CaCO$_3$ decrease dramatically with increasing the Cl/Ca molar ratio. It indicates that the Cl-doped CaCO$_3$ shows much slower carbonation rate and shorter duration time during the chemical reaction controlled stage with increasing the additive amount of Cl in CaCO$_3$. Therefore, smaller carbonation conversion in chemical reaction controlled stage is achieved. When the Cl/Ca molar ratio is larger than 2:100, the $X_u$ that can be achieved is very low. It has been proven that doping the calcium-based sorbent with small amount of chloride can improve the long-term CO$_2$ capture capacity, while larger doping leads to decrease in pore volume and gives marked reduction in capacity.\(^{23,24}\) The similar result was obtained here. As is shown in Table 3, the pore volume and BET surface area decreased dramatically with the molar ratio of Cl/Ca when the value was higher than 0.25:100. The pore volume and surface area of the calcined sorbent decreased by 71.3% and 44.5% respectively when the molar ratio of Cl/Ca in the sorbent was increased from 0 to 2:100. After Cl doping, the CO$_2$ diffusion and carbonation reaction were limited during the carbonation process. The corresponding lower $X_u$, $k$, and $t_{crcs}$ were achieved for Cl doped sorbent. The Cl/Ca molar ratio in the LM which can be calculated according to the XRF results shown in Table 1 is 2.6:100. Therefore, the relatively high content of Cl in the LM can be judged as one of the major reasons that lead to

![FIGURE 5](image-url)  
**FIGURE 5** Fitting results of the carbonation conversions of LM and limestone during the chemical reaction controlled stage in multiple cycles
the poor CO₂ capture performance of the LM in chemical reaction controlled stage. Figure 8 shows the pore volume distribution of the calcined LM, CaCO₃, and Cl-doped CaCO₃ with a Cl/Ca molar ratio of 2:100 at the first cycle. The calcined LM and Cl-doped CaCO₃ with a Cl/Ca molar ratio of 2:100 show similar pore volume distribution characteristics, with less pores distributed in the range of 10-100 nm compared with calcined CaCO₃.

**TABLE 2** Carbonation kinetic parameters of the LM and limestone during the chemical reaction controlled stage

| Sample          | N  | k     | X₀  | t₀ (s) | tₓ (s) | tₓ (s) | R²  | Pore volume (cm³/g) | Surface area (m²/g) |
|-----------------|----|-------|-----|--------|--------|--------|-----|---------------------|---------------------|
| LM              | 1  | 0.0127| 0.090| 39     | 60     | .998   |     |                     |                     |
|                 | 5  | 0.0040| 0.032| 33     | 72     | .993   |     |                     |                     |
|                 | 10 | 0.0033| 0.031| 27     | 66     | .993   |     |                     |                     |
|                 | 15 | 0.0027| 0.026| 30     | 75     | .980   |     |                     |                     |
| PLM             | 1  | 0.0165| 0.238| 48     | 132    | .988   |     |                     |                     |
|                 | 5  | 0.0084| 0.100| 33     | 96     | .962   |     |                     |                     |
|                 | 10 | 0.0079| 0.097| 33     | 91     | .950   |     |                     |                     |
|                 | 15 | 0.0066| 0.095| 33     | 96     | .962   |     |                     |                     |
| PLM after 9 h carbonation | 1  | 0.0250| 0.361| 51     | 102    | .996   |     |                     |                     |
|                 | 15 | 0.0169| 0.140| 36     | 67     | .996   |     |                     |                     |
| Limestone       | 1  | 0.0203| 0.634| 102    | 192    | .996   |     |                     |                     |
|                 | 5  | 0.0146| 0.421| 90     | 177    | .996   |     |                     |                     |
|                 | 10 | 0.0080| 0.216| 78     | 153    | .995   |     |                     |                     |

a tₓ (s) denotes the time duration of the chemical reaction controlled stage.

**FIGURE 6** Effect of Cl content on CO₂ capture capacity of calcium-based sorbent in the 1st cycle

**FIGURE 7** Fitting results of the carbonation conversions of Cl-doped CaCO₃ with different Cl/Ca molar ratio during the chemical reaction controlled stage in the first cycle

**TABLE 3** Carbonation kinetic parameters of Cl-doped CaCO₃ during chemical reaction controlled stage during the 1st cycle

| Sample          | Cl/Ca molar ratio | k     | t₀ (s) | X₀  | tₓ (s) | Xₓ (s) | R²  | Pore volume (cm³/g) | Surface area (m²/g) |
|-----------------|-------------------|-------|--------|-----|--------|--------|-----|---------------------|---------------------|
| CaCO₃           | 0                 | 0.0234| 72     | 0.480| 141    | .993   | 0.08| 12.01               |                     |
| CaCO₃ + CaCl₂   | 0.25:100          | 0.0231| 57     | 0.448| 111    | .993   | 0.06| 12.2                |                     |
| CaCO₃ + CaCl₂   | 0.50:100          | 0.0229| 48     | 0.358| 90     | .993   | -   |                     |                     |
| CaCO₃ + CaCl₂   | 1:100             | 0.0220| 42     | 0.314| 84     | .992   | 0.042| 10.62               |                     |
| CaCO₃ + CaCl₂   | 2:100             | 0.0174| 24     | 0.110| 42     | .997   | 0.023| 6.67                |                     |
| CaCO₃ + CaCl₂   | 4:100             | 0.0174| 21     | 0.108| 39     | .998   | -   |                     |                     |

...
CaCO₃. It indicates that the Cl can aggravate the sintering of the LM during the calcination at high temperature, leading to reduction of pores distributed in 10-100 nm, which have been proved to be beneficial to diffusion of CO₂ in the sorbent to react with CaO. Therefore, it is predictable that reducing the Cl content in the LM can enhance its CO₂ capture capacity.

### 3.3 Effect of prewash treatment on the carbonation kinetics of LM

A prewash treatment process was proposed to decrease the Cl content in the LM. As shown in Table 1, the Cl content in the LM decreases dramatically after the prewash treatment process. The carbonation conversions and carbonation rates of the PLM with carbonation time during different cycles are shown in Figure 9. The fitting results of the carbonation process of the PLM during the chemical reaction controlled stage are shown in Figure 10, and the obtained kinetic parameters were presented in Table 2.

As can be seen in Table 2, the PLM shows much better carbonation performance compared with the LM. The values of $k$ and $t_{crcs}$ of the PLM are all higher than those of the LM during the same cycle. For example, the values of $k$ and $t_{crcs}$ during the 1st cycle are respectively increased by 29.9% and 120% after prewash treatment. The values of $k$ and $t_{crcs}$ of the PLM in the 15th cycle are 144% and 28.0% higher than those of the LM in the same cycle. In other words, the PLM shows faster carbonation rate and longer duration time in the chemical reaction controlled stage in the same cycle. Certainly, higher carbonation conversion can be achieved for the PLM during the chemical reaction controlled stage. The $X_u$ of the PLM in the 1st and 15th cycles is 2.64 and 3.65 times as those of the LM in the same cycle.

If the LM cannot be reused effectively, the major disposal for LM is landfill. Simultaneously, the Cl in the LM will penetrate into the underground water and lead to serious pollution. Therefore, the Cl in the LM was hard to handle and should be heavily focused on. In this manuscript, the LM was proposed to be CO₂ sorbent in calcium looping process. A prewash process was raised to decrease the Cl in the LM. Not only the CO₂ capture capacity of the LM was enhanced after prewash process, the Cl in the LM was also transferred into the discharged water, in which the Cl can be removed in more convenient ways. Dechloridation equipment can be employed to remove most of the Cl in the discharged water. After that, the spent water can be sent to the nearby sewage treatment plant for fine treatment before discharged to the environment. In this research, 400 g deionized water was used for 100 g LM during the prewash process. When applied to the practice, the deionized water can be replaced by the surface freshwater or the collected rainwater. Also, intense agitation can also be employed to enhance the dissolution of the Cl into the water and decrease the needed water.
3.4 Effect of prolonged carbonation treatment on the carbonation kinetics of the PLM

We can see from the above discussion that prewash treatment process dramatically enhances the CO₂ capture capacity of the LM during the chemical reaction controlled stage. However, the CO₂ capture capacity of the PLM is still lower than that of the limestone during the chemical reaction controlled stage. One of the major problems for the LM is that the pores of the calcined LM distributed in 10-100 nm were very less. Here, we proposed a prolonged carbonation process to improve the microstructure of the calcined PLM, in the hope of further enhancing the CO₂ capture capacity of the PLM. The CO₂ capture performance of the PLM after prolonged carbonation treatment is shown in Figure 11. As shown in Figure 11A, prolonged carbonation treatment successfully improves the carbonation conversion of the PLM in multiple cycles. The CO₂ capture capacity of the PLM increases with increasing the prolonged carbonation time when the prolonged carbonation time is shorter than 9 hours. Further extending the prolonged carbonation time has little effect on the CO₂ capture of the PLM when longer than 9 hours. It seems that 9 hours is the optimum prolonged carbonation time for the PLM. The fitting results of the carbonation process of the PLM after 9 hours prolonged carbonation in different cycles are shown in Figure 11B. The values of k and t_{crcs} of the PLM are increased by 51.5% and 6.3% after prolonged carbonation treatment in the 1st cycle, and the value of X_u is finally increased by 51.7%. The values of X_u of the PLM after prolonged carbonation treatment is still higher than that of the PLM in the 15th cycle. It means that prolonged carbonation treatment further enhances the carbonation performance of the PLM during the chemical reaction controlled stage. Though still lower compared with that of the limestone, the CO₂ capture capacity of the LM during the chemical reaction controlled stage is effectively enhanced by prewash treatment and subsequent prolonged carbonation treatment. The PLM after prolonged carbonation treatment shows higher carbonation rate but shorter duration time during the chemical reaction controlled stage compared with the limestone. The final values of X_u for the PLM after prolonged carbonation treatment are approximate to those of the limestone during multiple cycles, which means that the LM can be effectively utilized as an alternative of the limestone to capture CO₂ in calcium looping process after prewash and following prolonged carbonation treatment process.

Table 4 showed the pore distribution parameters of the limestone, LM, PLM before and after prolonged carbonation treatment in the 1st calcination. Figure 13A,B showed the pore volume distributions and cumulative pore volumes of the calcined limestone, LM, PLM before and after prolonged carbonation treatment in the 1st cycle. The BET surface area of the calcined LM is even larger than that of the calcined limestone, which means that the calcined LM can afford more places for the carbonation reaction. It seems that the LM should present higher carbonation conversion compared with limestone. However, the pore volume distributes in 1-100 nm (V_{1-100nm}) of the calcined LM is less than that of the calcined limestone, which means that the calcined LM can afford more places for the carbonation reaction. Though still lower compared with that of the limestone, the CO₂ capture capacity of the LM during the chemical reaction controlled stage is effectively enhanced by prewash and following prolonged carbonation treatment process.

![Figure 11](image-url) The CO₂ capture performance of the PLM after prolonged carbonation treatment during multiple cycles. A, X_N with cycle number and B, X_N and r_N with carbonation time
CO₂ capture of calcium-based sorbent,²⁶ is only 4.4% that of the calcined limestone. The diffusion resistance of CO₂ in the calcined LM is larger than that in the calcined limestone. Since most of the pores of the calcined LM distributes in 1-10 nm, it is easily to be blocked during carbonation process of the sorbent, because of which much of the surface is coated in the product layer and cannot be effectively utilized for carbonation reaction. Therefore, the LM shows much poorer carbonation performance compared with the limestone during the chemical reaction controlled stage. The prewash treatment obviously improves the microstructure of the LM. The surface area and \( V_{1-100 \text{ nm}} \) of the calcined PLM are increased by 74% and 56% compared with those of the calcined LM. Especially, the value of \( V_{10-100 \text{ nm}} \) of the calcined PLM is 4.5 times that of the calcined LM. The prolonged carbonation treatment further enhances the microstructure of the calcined PLM. Though the surface area is decreased, the value of \( V_{10-100 \text{ nm}} \) for the PLM is increased by 3.4 times through prolonged carbonation process. The microstructure of the PLM after prolonged carbonation process is much more beneficial to CO₂ capture compared with the LM, with

![Figure 12](image1.png)

**FIGURE 12** Fitting results of the carbonation conversions of the PLM after prolonged carbonation treatment during chemical reaction controlled stage

| Sample                 | Cycle | Surface area (m²/g) | \( V_{1-100 \text{ nm}} \)(cm³/g) | \( V_{1-10 \text{ nm}} \)(cm³/g) | \( V_{10-100 \text{ nm}} \)(cm³/g) |
|------------------------|-------|---------------------|---------------------------------|---------------------------------|---------------------------------|
| LM                     | 1     | 6.2                 | 0.016                           | 0.014                           | 0.002                           |
| P LM                   | 1     | 10.8                | 0.025                           | 0.016                           | 0.009                           |
| PLM after prolonged carbonation | 1     | 5.6                 | 0.051                           | 0.011                           | 0.040                           |
| Limestone              | 1     | 4.25                | 0.047                           | 0.002                           | 0.045                           |

**TABLE 4** Effect of prewash and prolonged carbonation treatment on pore distribution parameters of the calcined sorbents

![Figure 13](image2.png)

**FIGURE 13** Pore volume distributions of the calcined limestone, LM, PLM before and after prolonged carbonation treatment in the 1st cycle. A, Pore volume distribution and B, cumulative pore volume

As is shown in Table 4, the values of surface area for the calcined PLM after prolonged carbonation treatment is a
little larger compared with that for the calcined limestone, which means that the calcined PLM after prolonged carbonation treatment can afford much more surface for the carbonation reaction. Thus, the value of $k$ for PLM after prolonged carbonation treatment is larger than that of limestone. We can see from Figure 13A that the pores distributed in 10-30 nm for the calcined PLM after prolonged carbonation treatment are more than the calcined limestone, while the pores in 30-100 nm are fewer. Thus, the average pore diameter for the calcined PLM after prolonged carbonation treatment is smaller, which means that the pores of the calcined PLM after prolonged carbonation treatment are more easily to be blocked. Therefore, the $t_0$ for the calcined PLM after prolonged carbonation treatment is shorter than that for the limestone.

4 | CONCLUSIONS

Lime mud, a kind of industrial waste produced in paper mill, was proposed as CO$_2$ sorbent in calcium looping process in this research. The higher content of Cl in the LM leads to more serious sintering of the sorbent when calcined at high temperature. Therefore, the LM shows relatively lower CO$_2$ capture capacity compared with the limestone during the chemical reaction controlled stage. A prewash treatment process was proposed to decrease the Cl content in the LM and enhance the CO$_2$ capture capacity of the LM. The values of surface area and pore volume in 10-100 nm of the PLM are higher than those of the LM, which makes it easier for the diffusion of CO$_2$ in the sorbent to react with CaO. Therefore, the PLM shows faster carbonation rate and carbonation conversion in chemical reaction controlled stage compared with the LM. A prolonged carbonation treatment was proposed to further improve the microstructure of the PLM. Though the value of the surface area is decreased, the pore volume distributed in 10-100 nm for the PLM after prolonged carbonation treatment is increased, leading to less CO$_2$ diffusion resistance and more efficient utilization of the surface area in the sorbent. After prewash treatment and the following prolonged carbonation treatment, the LM shows similar carbonation performance compared with the limestone. It seems that the LM after prewash treatment and subsequent prolonged carbonation treatment can be effectively used as CO$_2$ sorbent in calcium looping process.

ACKNOWLEDGMENT

Financial supports from National Natural Science Foundation of China (51706094, 51661145011) are sincerely acknowledged.

ORCID

Rongyue Sun https://orcid.org/0000-0002-9984-5016

REFERENCES

1. Correa THA, Toledo R, Silva NS, Holanda JNF. Novel nano-sized biphasic calcium phosphate bioceramics (β-CPP/β-TCP) derived of lime mud waste. Mater Lett. 2019;243:17-20.
2. Said AEAA, Aly AAM, Ahmed HS. Development and utilization of lime-mud waste as filler for production of green paper. Environ Prog Sustain. 2019;38:e13022.
3. Zhang J, Zheng P, Wang Q. Lime mud from papermaking process as a potential ameliorant for pollutants at ambient conditions: a review. J Clean Prod. 2015;103:828-836.
4. Qin J, Cui C, Cui X, Hussain A, Yang C, Yang S. Recycling of lime mud and fly ash for fabrication of anorthite ceramic at low sintering temperature. Ceram Int. 2015;41:5648-5655.
5. Madrid M, Orbe A, Carré H, García Y. Thermal performance of sawdust and lime-mud concrete masonry units. Constr Build Mater. 2018;169:113-123.
6. Li H, Niu S, Lu C, Liu M, Huo M. Transesterification catalyzed by industrial waste-Lime mud doped with potassium fluoride and the kinetic calculation. Energy Convers Manage. 2014;86:1110-1117.
7. Chen Y, Huang B, Huang M, Lu Q, Huang B. Sticky rice lime mortars-inspired in situ sustainable design of novel calcium-rich activated carbon monoliths for efficient SO$_2$ capture. J Clean Prod. 2018;183:449-457.
8. Fashi F, Ghaemi A, Moradi P. Piperazine-modified activated alumina as a novel promising candidate for CO$_2$ capture: experimental and modeling. Greenhouse Gas Sci Technol. 2019;9:37-51.
9. Zhao N, Xu T, Wang K, Tian H, Wang F. Experimental study of physical-chemical properties modification of coal after CO$_2$ sequestration in deep unmineable coal seams. Greenhouse Gas Sci Technol. 2018;8:510-528.
10. Xu Y, Jin B, Zhao Y, Hu EJ, Chen X, Li X. Numerical simulation of aqueous ammonia-based CO$_2$ absorption in a sprayer tower: an integrated model combining gas-liquid hydrodynamics and chemistry. Appl Energ. 2018;211:318-333.
11. He D, Qin C, Manovic V, Ran J, Feng B. Study on the interaction between CaO-based sorbents and coal ash in calcium looping process. Fuel Process Technol. 2017;156:339-347.
12. Zhou L, Duan L, Anthony EJ. A calcium looping process for simultaneous CO$_2$ capture and peak shaving in a coal-fired power plant. Appl Energ. 2019;235:480-486.
13. Benitez-Guerrero M, Valverde JM, Perenon A, Sanchez-Jimenez PE, Perez-Maqueda LA. Calcium-Looping performance of mechanically modified Al$_2$O$_3$-CaO composites for energy storage and CO$_2$ capture. Chem Eng J. 2018;346:549-556.
14. Zhang Y, Gong X, Chen X, Yin L, Zhang J, Liu W. Performance of synthetic CaO-based sorbent pellets for CO$_2$ capture and kinetic analysis. Fuel. 2018;232:205-214.
15. Sun J, Liang C, Tong X, et al. Evaluation of high-temperature CO$_2$ capture performance of cellulose-templated CaO-based pellets. Fuel. 2019;239:1046-1054.
16. Chen J, Duan L, Sun Z. Accurate control of cage-like CaO hollow microspheres for enhanced CO$_2$ capture in calcium looping via a template-assisted synthesis approach. Environ Sci Technol. 2019;53:2249-2259.
17. Sun R, Li Y, Liu C, Xie X, Lu C. Utilization of lime mud from paper mill as CO$_2$ sorbent in calcium looping process. Chem Eng J. 2013;221:124-132.
18. Ma A, Jia Q, Su H, et al. Study of CO₂ cyclic absorption stability of CaO-based sorbents derived from lime mud purified by sucrose method. Environ Sci Pollut Res. 2016;23:2530-2536.
19. Duelli G, Bidwe AR, Papandreou I, Dieter H, Scheffknecht G. Characterization of the oxy-fired regenerator at a 10 kWth dual fluidized bed calcium looping facility. Appl Therm Eng. 2015;74:54-60.
20. Lan P, Wu S. Synthesis of a porous Nano-CaO/MgO-based CO₂ adsorbent. Chem Eng Technol. 2014;37:580-586.
21. Ma X, Li Y, Zhang W, Wang Z, Zhao J. DFT study of CO₂ adsorption across a CaO/CA₁₂Al₁₄O₃₃ sorbent in the presence of H₂O under calcium looping conditions. Chem Eng J. 2019;370:10-18.
22. Pi S, Zhang Z, He D, Qin C, Ran J. Investigation of Y₂O₃/MgO-modified extrusion- spheronized CaO-based pellets for high-temperature CO₂ capture. Asia-Pac J Chem Eng. 2019;14(6):e2366. https://doi.org/10.1002/apj.2366
23. Al-Jeboori MJ, Fennell PS, Nguyen M, Feng K. Effects of different dopants and doping procedures on the reactivity of CaO-based sorbents for CO₂ capture. Energ Fuel. 2012;26:6584-6594.
24. Xu Y, Ding H, Luo C, et al. Potential synergy of chlorine and potassium and sodium elements in carbonation enhancement of CaO-based sorbents. ACS Sustain Chem Eng. 2018;6:11677-11684.

How to cite this article: Sun R, Xiao R, Ye J. Kinetic analysis about the CO₂ capture capacity of lime mud from paper mill in calcium looping process. Energy Sci Eng. 2020;8:4014–4024. https://doi.org/10.1002/esee.3792