ABSTRACT: The Ca-based sorbent cyclic calcination/carbonation reaction (CCCR) is a high-efficiency technique for capturing CO$_2$ from combustion processes. The CO$_2$ capture ability of CaO modified with sodium humate (HA-Na) (HA-Na/CaO) in long-term calcination/carbonation cycles was investigated. The enhancement mechanism of HA-Na on CCCR was proposed and demonstrated. The effects of carbonation temperature, reaction duration, and the addition amount of HA-Na on the carbonation rate of the CaO adsorbent were also studied. HA-Na/CaO is allowed to react 20 min at the optimum conditions for calcination (920 °C, 100% N$_2$) and for carbonation (700 °C, 15% CO$_2$, 85% N$_2$), respectively. HA-Na plays a key role in the CCCR process, and the carbonation conversion rate is lifted obviously. The maximum conversion rate of HA-Na/CaO is 23% higher than that of CaO in the first cycle. After 20 cycles, the conversion rate of HA-Na/CaO is still 0.28, while that of CaO is only 0.15. The carbonation conversion rate for HA-Na/CaO is improved by 86% compared to CaO. In addition, the characteristics of calcined sorbents are analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) methods.

1. INTRODUCTION

Nowadays, humanity is continuously using most of the fossil energy to live because renewable energy technologies are immature. The increase of the global atmospheric CO$_2$ concentration results from over a century of combustion of fossil fuels. The major impact of the CO$_2$ increase reflects on the global climate, environment, and economy. Thus, the development of effective methods for CO$_2$ capture is urgent.

CO$_2$ capture and storage (CCS) have the potential to isolate CO$_2$ from flue gas. The effective technologies of CCS include absorption, adsorption, membrane separation, cryogenic separation, mineral carbonation, and calcium looping process (CaLP). Among them, CaLP is thought to be one of the most promising methods to capture CO$_2$. The calcination/carbonation reaction is reversible (CaO + CO$_2$ ↔ CaCO$_3$). Figure 1 shows the process of the cyclic calcination/carbonation reaction (CCCR), which has several advantages, including the abundance of raw materials, low material cost, high absorption capacity, and good applicability and flexibility.

In spite of its low cost, the adsorption capacity of limestone dropped dramatically with the increase of cycle number because of sintering at a high temperature and the wearing effect, which are general disadvantages of CaO-based sorbents. A mass of fresh sorbents should be added into a carbonator to maintain the adsorption stability due to the

Figure 1. CO$_2$ capture process of the Ca-based sorbent cyclic calcination/carbonation reaction.
Figure 2. Reaction mechanism of HA-Na and Ca-based sorbents.

poor cycling stability of CaO-based sorbents like limestone. Therefore, the more frequent regeneration resulted in high cost. Ordinarily, to improve the sintering resistance of Ca-based sorbents, there are three methods: solution modification, controlling the reaction conditions, and the use of additives to modify Ca-based sorbents.

Researchers have suggested that alkali metal ions can effectively enhance the cyclic CO2 capture capacity of the sorbents. Xu et al. found that KCl, NaCl, and K2CO3 may boost the carbonation property of CaO markedly, while KOH, NaOH, and Na2CO3 were detrimental to the sorbents. The multicyclic CO2 capture capacity of CaO/La2O3 sorbents and the effect of the La2O3 additive were investigated, and the results indicate that the additive of La2O3 plays a positive role in the carbonation/calcination reactions. The NaBr-modified CaO showed improved activity and durability for carbonation. After 100 cycles, “NaBr/CaO-10/100” maintained a capacity of 0.202 g CO2/g sorbent, which was about 185% higher than that of the unmodified CaCO3 precursor. Kim et al. prepared MgAl2O4-stabilized Ca-based sorbent for CO2 capture. Hu et al. compared different metal skeletons of Ca-based sorbents and provided the basis for high-temperature CO2 capture sorbents. Monica et al. prepared Al2O3–CaO composites and studied the ability to capture CO2 under different conditions. Liu et al. presented the effect of five different elements in CaO on improving the cyclic stability and found the relationship between the carbonation conversion rate and the critical time.

Organic acid and organic acid salt have been investigated previously by researchers to improve the specific surface area of Ca-based sorbents. Two types of anionic surfactants, Dispex, consisting of sodium (N40V) or ammonium (A40) salt of a polycarboxylic acid, and calcium lignosulfonate, have been used to improve the surface area of Ca(OH)2 and CaCO3. The surface area increases from 31 m2/g in the absence of a surfactant to between 45 and 60 m2/g with the addition of 2 wt % surfactant. Both Dispex N40V and Dispex A40 improve the surface area to about 60 m2/g, while lignosulfonate shows about 47 m2/g. In addition, the performance of Ca-based sorbents for CO2 capture can be promoted by formic acid, acetic acid, propionic acid, and citric acid.

Sodium humate (HA-Na), a sodium salt of humic acid (HA), is soluble in water. HA-Na has a weak alkaline effect and a strong chelate effect on Ca2+, Mg2+, Fe3+, and other metal ions. HA has a wide range of origins, lower price, and special physical and chemical characteristics, which make it have potential advantages to modify CaO for CO2 capture. (1) HA-Na prevents the CaCO3 layer from growing by chelating Ca2+ ions with active groups of HA-Na. (2) In terms of the microstructure after cycling, HA-Na maintains a higher surface area of CaO. (3) The addition of HA-Na greatly improves the anti-sintering of Ca-based sorbents.

However, research studies using HA-Na to improve the CO2 capture capacity of sorbents are scarce. Sun et al. found that an appropriate amount of HA-Na can promote the desulfurization efficiency of limestone. Zhao et al. used HA to modify Ca-based adsorbents for flue gas desulfurization (FGD). The experimental results showed that the specific surface area can run up from 28 to 50 m2/g and the pore size becomes larger, while the SO2 removal rate is promoted from 38.4% of normal CaCO3 to above 70% with an increased amount of HA additive. HA-Na has not only Na+ but also an organic acid radical. Thus, it is supposed that Ca-based sorbents modified with HA-Na for the CCCR are promising for CO2 capture.

In this paper, it is proposed that HA-Na is used to improve the CO2 capture capacity of CaO in long-term CCCR cycles. There are some influences of the amount of HA-Na, reaction duration, reaction temperature, and the number of cycles on CO2 absorption during the CCCR. We focus on discussing the role of HA-Na in the CCCR cycles.

2. ENHANCEMENT MECHANISM

HA-Na can promote CO2 capture during the CCCR cycles, and the proposed reaction mechanism between HA-Na and Ca-based sorbents is illustrated in Figure 2. Absorption, complexation, and ion exchange may occur between the carboxyl, hydroxyl, carbonyl, and amino groups of HA-Na and metal ions such as Ca2+, Mg2+, and Zn2+. Among all functional groups of HA-Na, the carboxyl and hydroxyl groups are active and typical, respectively. The reactions of HA-Na with Ca2+ are as follows:

Chelation:

\[
R\left(\text{COO}^-\right)_2 + \text{Ca}^{2+} \rightarrow \text{RCOOCaOOOC}
\]
Complexation:
\[ \text{RO}^- + \text{Ca}^{2+} \rightarrow [\text{ROCa}]^+ \]  \hspace{1cm} (2)

Ion exchange:
\[ 2\text{RCOO}^- + \text{Ca}^{2+} \rightarrow (\text{RCOO})_2\text{Ca} \downarrow \]  \hspace{1cm} (3)

\[ (\text{RO})_2\text{Ca} + 2\text{RCOO}^- \rightarrow (\text{RCOO})_2\text{Ca} \downarrow +2\text{RO}^- \]  \hspace{1cm} (4)

Lattice distortion:
\[ [\text{Ca} (\text{CaCO}_3)_n]^{2+} + 2\text{RCOO}^- \rightarrow (\text{RCOO})_2\text{Ca} (\text{CaCO}_3)_n \downarrow \]  \hspace{1cm} (5)

where R-COO\(^-\) represents the carboxyl group and RO\(^-\) represents the hydroxyl group.

1) With the increase of the carbonation reaction, the amount of CaCO\(_3\) crystallite is increased, and a compact layer of CaCO\(_3\) is formed on the CaO surface, which prevents the contact of CO\(_2\) and unreacted CaO, thus affecting the further carbonation reaction. HA-Na additives may prevent the growth of the CaCO\(_3\) layer. Ca\(^{2+}\) ions on the surface are easy to be chelated by the active groups of HA-Na. The lattice growth of the CaCO\(_3\) crystallite is interfered since the surface active sites of the CaCO\(_3\) crystallite is chelated. HA-Na is adsorbed on the tiny crystals and doped in the lattice of CaCO\(_3\), which prevents the formation of compact and hard structures. This causes crystal lattice distortion, stress increase, and the instability of the crystal structures. Thus, the lattice growth of CaCO\(_3\) is disturbed. Besides, the pore size and specific surface area are increased.

2) After many cycles, it is possible that the defect concentration of the CaCO\(_3\) layer increased as the cycle numbers increased. Hence the carbonation conversion rate is improved since both the diffusion rate of unreacted Ca\(^{2+}\) passing the product layer and contact chance of CO\(_2\) and unreacted Ca\(^{2+}\) are increased.

3) Owing to the chelation and complexation of the active groups of HA-Na and Ca\(^{2+}\), the crystal form of CaO is affected and exhibits amorphous characteristics. Hence, the CaO structure is changed, and a stable pore structure is formed, while the pore size distribution and the specific surface area are regulated. The carbonation conversion rate of Ca-based sorbents during the CCCR cycles is improved because of HA-Na additives.

3. RESULTS AND DISCUSSION

3.1. Effect of Calcination Temperature. The calcination temperature is important for CO\(_2\) absorption. The low temperature of the calcination reaction leads to incomplete decomposition of CaCO\(_3\). On the other hand, CaCO\(_3\) is likely to be sintered when the temperature is too high. Generally, the limit temperature of the high-temperature flue of the power plant is less than 1000 °C. This experiment compared the calcination effects at 800, 850, and 920 °C. It can be seen from Figure 3 that the carbonation conversion rates of HA-Na-0 and HA-Na-7 change upon increasing the temperature from 800 to 920 °C. It is indicated that CaCO\(_3\) from the Ca-based sorbent modified with HA-Na-7 and HA-Na-0 decomposes more thoroughly at 920 °C. The influence of temperature is gradually obvious with an increase of the cycle number. The \(X_b\) value for HA-Na-0 and HA-Na-7 is 0.40 and 0.54 at 920 °C, respectively. The \(X_b\) values for HA-Na-0 and HA-Na-7 are 0.30 and 0.35, respectively, at 800 °C. Therefore, the optimum calcination temperature is 920 °C.

3.2. Effect of Carbonation Temperature. Figures 4 and 5 illustrate the effect of carbonation temperature at 550–750 °C. A carbonation temperature below 550 °C or over 750 °C is not conducive to the chemical reaction, and even it is hard for that above 750 °C. Hence, carbonization takes place in the range of 550–700 °C rather than at other temperatures. As can be seen from Figure 6 that the CO\(_2\) capture capacity of HA-Na-7 is stronger than that of HA-Na-0 in the range of 550–
It is explained that HA-Na has a significant effect on improving the CO₂ capture capacity at different carbonation temperatures.

The absorption reaction of the Ca-based absorbent is an exothermic reaction, the excessive absorption temperature is not conducive to the capture of CO₂, and the absorption temperature is too low to provide the activation energy required for the chemical reaction.

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3.3. Effect of Carbonation Time. Figures 6 and 7 show the effect of carbonation time on CO₂ absorption during the first and fourth cycles. The length of carbonation time has an effect on the modified CaCO₃. In the first 10 min, CaO and CO₂ react with each other quickly, while the reaction rate decreases after 10 min. It can be seen that the carbonation conversion rate remains basically unchanged after 20 min. The optimum carbonation time is 20 min in this experiment.

The optimum experimental conditions based on the above experiments are as follows: the calcination temperature is 920 °C, and the carbonation temperature is 700 °C. The calcination/carbonation reaction duration was 20 min. The carbonation atmosphere simulates the exhaust gas emissions from coal-fired power plants, such as 15 vol% CO₂ and 85 vol% N₂, and the calcination atmosphere is 100 vol% N₂.

3.4. Effect of Cycle Number. As shown in Figure 8, the different proportions of HA-Na have different carbonation conversion rates in optimum conditions (calcination, 920 °C, 100% N₂, 20 min; carbonation, 700 °C, 15% CO₂, 85% N₂, 20 min). The X₁ values for HA-Na-0 and HA-Na-9 are 0.55 and 0.78. This illustrates that HA-Na may improve obviously the carbonation conversion of Ca-based sorbents. Similarly, the X₂ values for HA-Na-0 is 0.15, while the X₂ value for HA-Na-9 is 0.28. Therefore, HA-Na/CaO has a higher carbonation conversion rate than CaO. However, the X_N values for HA-Na-5, HA-Na-7, and HA-Na-9 are not different with the increase of cycle numbers, while the optimum addition amount of HA-Na is 5%. With the increase of cycle reaction durations,
the CO₂ conversion rate gradually decreases, especially in the first five cycles, the conversion rate decreases rapidly. The reduced adsorption capacity is due to CaO sintering. After the addition of HA-Na, the sintering of CaO is weakened and the single adsorption capacity is improved, and then the ability of CO₂ adsorption in multiple cycles is improved.

3.5. X-ray Diffraction (XRD) Analysis. Figure 9 shows the XRD patterns of a Ca-based absorbent with HA-Na. Figure 9b displays the XRD patterns of CaO without HA-Na, and it corresponded to the (001), (100), (011), (012), (110), and (111) planes of the Ca(OH)₂ phase. This illustrates that the CaO combine with water to form Ca(OH)₂. Figure 9a shows the XRD patterns of the HA-Na/CaO adsorbent, and it is similar to that of pure Ca(OH)₂. The different peak at 37.50° corresponds to the (200) plane. This peak is HA-Na but very weak. It can be seen there is no new substance formed in the HA-Na/CaO adsorbent, which suggests that HA-Na does not change the nature of the Ca-based sorbent. There are no characteristic peaks shown in Figure 10, indicating that CaCO₃ is sufficiently decomposed. This also shows that 920 °C is the optimum temperature for calcination.

3.6. Characteristics of the Sorbents after Various Cycles. The scanning electron microscopy (SEM) micrographs of calcined sorbents of HA-Na-0 and HA-Na-9 after various cycles as shown in Figure 11. Comparing the SEM photomicrographs of HA-Na-0 (Figure 11a,c) and HA-Na-9 (Figure 11b,d), it is obvious that the pores between the particles of Ca modified with 9 wt % of HA-Na are abundant, and the accumulation is relatively loose, while the specific surface area is relatively large. Obviously, the surface pore and the pore volume of CaO decrease dramatically with an increase in the cycle number due to CaCO₃ blocking of the pores. The change in the surface of HA-Na-9 is because the active group in HA-Na increases the internal pores by chelation of Ca²⁺ ions. From the above analysis, it is proved that HA-Na can increase the surface pores and the pore volume of CaO and improve the carbonation conversion rate.
The Brunauer–Emmett–Teller (BET) specific surface area and pore volume changes with the variation of cycle number are depicted in Figures 12 and 13 and Table 1. The BET specific surface area and pore volume HA-Na/CaO are higher obviously than those of each CaO cycle. The BET specific surface area of fresh CaO is lifted 7 times due to the 9 wt % of HA-Na additive. The BET specific surface area of fresh CaO decreases from 4.83 to 1.28 m²/g upon increasing the cycle number from 1 to 20, while the BET specific surface area of HA-Na/CaO 33.71 m²/g reduces from 33.71 to 13.93 m²/g. In addition, the pore volume of fresh CaO is promoted 12.5 times (from 0.006 to 0.075 cm³/g) because of the addition of 9 wt % of HA-Na. The pore volume of HA-Na/CaO is still 0.12 cm³/g, which is far more than 0.002 cm³/g of CaO after 20 cycles. Therefore, it is demonstrated that HA-Na may improve the BET specific surface area and pore volume of CaO, which results in that the contact area of CO₂ with CaO is boosted, and the carbonation conversion rate is lifted obviously. This is in agreement with the results of the above SEM analyses.

**4. CONCLUSIONS**

The cyclic calcination/carbonation reaction of HA-Na/CaO was preliminarily investigated. The effects of carbonation temperature, reaction duration, and HA-Na addition on the carbonation rate of CaO were studied. The internal micro-structure of SEM and XRD was used to observe the effect of HA-Na on the properties of calcium reagent. The carbonation temperature of HA-Na/CaO is 700 °C, and the optimal time is 20 min. CaO modified with 5% of HA-Na was the optimum proportion. In the first cycle, the maximum carbonation conversion rate of HA-Na/CaO reaches 78%, and the carbonization conversion rate still remains 20% after 20 cycles, which is higher than that of CaO. The experimental results showed that HA-Na improves the CO₂ capture capacity of CaO in long-term CCCR cycles.

**5. EXPERIMENTAL SECTION**

The cyclic characteristic simulation experiment is implemented in a porcelain boat reactor in a calcining/carbonizing room, as shown in Figure 14. The porcelain boat is placed in the calcining/carbonating room for the reaction to occur. The depth of the samples is 2 mm, and the weight of the samples is about 2 g. The thermal resistance controller adjusts the reaction temperature. The reaction gas is provided by N₂ and CO₂ cylinders and is controlled by a mass flow controller (MFC). In this work, the total volume flow of the gas remained at 100 mL/min.

Cyclic characteristic experiments have two parts: calcination reaction and carbonation reaction. First, the N₂ gas enters and constant temperature calcination occurs. Second, the temperature is reduced to the carbonation temperature, and the atmosphere was made up of CO₂ and N₂. The sample is cooled and weighed at the end of each process. The calcination reaction and the carbonation reaction are carried out in a 100 vol % N₂ atmosphere and a 15 vol % CO₂ atmosphere, respectively. The calcination temperature ranges from 800 to 920 °C, and the carbonation temperature varied from 550 to 750 °C. The carbonation reaction duration is 10–30 min, and the calcination reaction duration is 20 min.

CaO derived from limestone is modified with 1, 3, 5, 7, and 9 wt % of HA-Na and marked HA-Na-1, HA-Na-3, HA-Na-5, HA-Na-7, and HA-Na-9. CaO hydrated with distilled water is marked HA-Na-0. The carbonation conversion rate of the sample in CCCR cycles is determined by a calculation formula. The calculation formula for eq 1

\[
X_N = \frac{M_{\text{NCO}_2}}{M_{\text{CaO}}}
\]

where \( N, X_N, M_{\text{NCO}_2}, \) and \( M_{\text{CaO}} \) are, respectively, the number of CCCR cycles, the carbonation conversion rate, the amount of CO₂ substance absorbed in the \( N \)th cycle, and the amount of CaO mass in the absorbent added at the beginning of the experiment. The samples are analyzed by X-ray diffraction (XRD, D/max-2500, Rigaku, Japan), scanning electron microscopy (SEM, S-4800, Hitachi, Japan), and Brunauer–Emmett–Teller (BET, ASAP-2020M, Micromeritics) methods.

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