Effect of the presence of HCl on cyclic CO₂ capture of calcium-based sorbent in calcium looping process

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HIGHLIGHTS
- HCl improves CO₂ capture capacity of limestone in the previous a dozen cycles.
- HCl sharply decreases limestone reactivity after a dozen cycles.
- HCl intensifies effects of carbonation and calcination temperature on CO₂ capture.
- HCl enlarges effects of particle size on CO₂ capture.
- HCl severely aggravates the sintering of limestone after a dozen cycles.

ABSTRACT
The effect of the presence of HCl on cyclic CO₂ capture behavior of calcium-based sorbent in the calcium looping process was investigated. When HCl was present in the carbonation atmosphere, the effects of carbonation temperature, calcination temperature, HCl concentration and particle size on CO₂ capture of the limestone in the multiple calcination/carbonation cycles were studied in a dual fixed-bed reactor. The presence of HCl in the carbonation atmosphere improves CO₂ capture capacity of the limestone in the previous a dozen cycles, but sharply decreases its reactivity with further increasing the cycle number above a dozen. The presence of HCl intensifies the effects of carbonation temperature and calcination temperature on CO₂ capture capacity of the limestone. The optimum carbonation temperature and the feasible calcination temperature for cyclic CO₂ capture of the limestone in the presence of HCl should be 700 °C and below 900 °C, respectively. The cyclic CO₂ capture capacity of the limestone in the previous a dozen cycles achieves the maximum in the presence of 300 ppm HCl with increasing the HCl concentration from 100 to 1000 ppm. The higher CO₂ capture capacity of the limestone is achieved with smaller particle size in the presence of HCl. The presence of HCl may destroy the compact CaCO₃ product layer and it is beneficial to CO₂ diffusion through the layer in the initial cycles. The chlorination conversion and the molten CaCl₂–CaCO₃ product layer thickness of the limestone in the presence of HCl increase with the number of calcination/carbonation cycles. It severely aggravates the sintering of the limestone once the cycle number is above about a dozen, which can be proved by microstructure analysis of the limestone experienced the multiple cycles in the presence of HCl.
1. Introduction

Calcium looping technology, as one of the most promising CO₂ capture technology for large-scale industrial applications, has aroused widespread interests, because of the potentially renewable and low cost sorbents, relatively energy-efficiency, high CO₂ capture capacity, the opportunity for integration with cement plants [1–5]. This process is proposed on the basis of the reversible reaction between CaO and CO₂ [6], as shown in Fig. 1. In this process, CO₂ from the flue gas of an existing power plant is removed by CaO in a calcinator at 600–750 °C to produce CaCO₃ (as shown in Eq. (1)). The produced CaCO₃ is transported to a calciner, where fuel is burnt under O₂/CO₂ stream (as shown in Fig. 1). The flue gas released from the calciner is a highly concentrated CO₂ stream for storage and reclaim. The process has been refined and used in specific CO₂ capture techniques, such as integrated gasification combined cycle (IGCC) plant with CO₂ capture [7–9] and post-combustion capture for coal-fired power plants [6].

CaO(s) + CO₂(g) → CaCO₃(s)
(1)

CaCO₃(s) → CaO(s) + CO₂(g)
(2)

Numerous studies have demonstrated that limestone is just high-efficiency in the initial cycles and its CO₂ capture reactivity decays sharply with the number of calcination/carbonation cycles mainly because of the sintering [10–13]. Many investigators utilized different methods such as steam reactivation [14,15], thermal pretreatment [16,17], the addition of manganese salts [18] or attapulgite [19], making pellets with aluminate cement [20], using chitosan as biotemplate [21], application of a high-intensity acoustic field [22] and use of nanomaterials [23–26] to improve CO₂ capture capacity and raise durability of calcium-based sorbents in the long-term calcination/carbonation cycles. The CO₂ capture capacity of calcium-based sorbents is not only affected by sintering, but also by competitive reactions with acidic gases in the flue gas, such as SO₂ and H₂S [27,28]. Iyer et al. [29], Sun et al. [30] and Ridha et al. [31] discovered that the presence of SO₂ impeded CO₂ capture of CaO, because SO₂ reacted with CaO and formed thermally stable CaSO₄ which plugged up lots of pores. Chen et al. [32] found that CO₂ capture of a calcium-based sorbent modified with rice husk ash decreased in the presence of SO₂. Manovic and Anthony [33] thought that when the calcium-based sorbent was relatively high reactivity, the negative effect of SO₂ on CO₂ capture was more pronounced. Sun et al. [34] investigated cyclic H₂S/CO₂ co-capture of three calcium-based sorbents in a pressurized TGA and found that H₂S had weaker influence than SO₂ on preventing CO₂ capture.

Various types of fuels such as biomass and refuse derived fuel (RDF) contain much chlorine which principally converts to HCl in combustion or gasification. Porbatzki et al. [35] found that the concentration of HCl could reach 1000 ppm in straw gasification. RDF contains more chlorine than biomass, so it produces more HCl. Calcium-based sorbents are usually used to remove HCl in biomass or RDF combustion or gasification process, as shown in Eqs. (3) and (4).

CaO(s) + 2HCl(g) → CaCl₂(s,l) + H₂O(g)
(3)

CaCO₃(s) + 2HCl(g) → CaCl₂(s,l) + H₂O(g) + CO₂(g)
(4)

Bie et al. [36] discovered that the HCl capture capacity of CaO achieved a maximum at 500–600 °C. Chyang et al. [37] found that CaO achieved the highest HCl capture capacity at 650 °C in the chlorination temperature range of 600–800 °C. Sun et al. [38] reported that CaO reached the fastest HCl capture rate at 550 °C in the range of 550–650 °C. The feasible temperature for CO₂ capture of calcium-based sorbents was also investigated. Manovic and Anthony [39] discovered that the optimum temperature for CO₂ capture of CaO was 650 °C in the range of 650–850 °C. Grasa et al. [40] found that the CO₂ capture capacity of calcium-based sorbent was relatively high at carbonation temperatures of 650–720 °C. Therefore, HCl and CO₂ can simultaneously react with calcium-based sorbents in the calcium looping process, when HCl is present in the carbonation atmosphere. Competitive reactions of carbonation and chlorination of CaO occur.

Several investigators have studied the effect of CO₂ on HCl removal of CaO. Partanen et al. [41] discovered that the presence of CO₂ induced higher HCl capture capacity of calcined limestone than that without CO₂ at 650 °C. It revealed that the presence of CO₂ improved HCl removal of limestone. Duo et al. [42] observed that HCl removal reactivity of CaO and Ca(OH)₂ both decreased with increasing CO₂ from 2 vol.% to 10 vol.% at 400 °C. Chin et al. [43] found that CaO reacted with CO₂ and converted to CaCO₃ which increased the diffusion resistance, leading to a premature termination of HCl removal at 100–300 °C.

The above investigations just focus on the effect of CO₂ on HCl removal of CaO, and they do not involve the calcium looping process. Furthermore, the effect of HCl on cyclic CO₂ capture behavior

![Fig. 1. Calcium looping process principle diagram.](image-url)
of calcium-based sorbent in the multiple calcination/carbonation cycles has been seldom discussed. Therefore, it is necessary to find out the effect of the presence of HCl on cyclic CO₂ capture behavior of calcium-based sorbent in the calcium looping process for biomass-fired or RDF-fired power plants. In this work, the cyclic CO₂ capture behavior of the limestone in the presence of HCl at various operating conditions involving carbonation temperature, calcination temperature, HCl concentration and particle size in the calcination/carbonation cycles was examined. In addition, the effect of the presence of HCl on microstructure of the limestone in the cycles was discussed.

2. Experimental

2.1. Experimental details

The natural limestone from Shandong Province, China was chosen as the sample and its chemical components are exhibited in Table 1. The limestone was crushed and sieved to three particle size ranges: <0.125 mm, 0.125–0.28 mm, 0.28–0.45 mm. The limestone particles sized in the range of <0.125 mm were utilized in all tests except for investigating the effects of particle size.

The experiment about the effect of HCl on cyclic CO₂ capture of the limestone was carried out in a dual fixed-bed reactor, which mainly comprises the carbonator and the calciner, as shown in Fig. 2. The limestone was firstly calcined into CaO in the calciner operated in the range of 850–950 °C and then produced CaO was moved into the carbonator to absorb CO₂ or HCl/CO₂. Then the first calcination/carbonation cycle was finished. To accomplish multiple calcination/carbonation cycles, the boat containing sample was shifted between the carbonator and the calciner. The variation of sample mass in the calcination/carbonation cycles was measured by a delicate electronic balance. The reacting gas was controlled by mass flow meter and constantly fed to the dual fixed-bed reactor.

In order to obtain the effect of HCl in the carbonation atmosphere on the carbonation, the experiments on cyclic CO₂ capture of the limestone in the absence and the presence of HCl were performed in the dual fixed-bed reactor, respectively. The specific experiment conditions in the absence and the presence of HCl are presented in Table 2. According to preliminary tests, the carbonation time and the calcination time were set as 20 min and 10 min, respectively. All tests were operated under atmospheric pressure. Mass change of the limestone in the presence of HCl in the calcination/carbonation cycles is plotted in Fig. 3. The reaction products of CaO derived from the limestone in the carbonation and chlorination are CaCO₃ and CaCl₂ in the presence of HCl according to Eqs. (1), (3), and (4). CaCO₃ can completely decompose into CaO and CO₂ in the calcination. The melting point of CaCl₂ is about 772 °C. A subset of tests was carried out to examine the mass loss of chlorinated CaO derived from the limestone in the range of 850–950 °C. The result indicates the mass of CaCl₂ keeps almost stable in the calcination for 10 min at 850–950 °C. The carbonation conversion and chlorination conversion of sample in the calcination/carbonation cycles were calculated by Eqs. (5) and (6), respectively, as follows.

\[ X_{CO_2N} = \frac{m_N - m_{calcN}}{m_0 \cdot A} \cdot \frac{M_{CaO}}{M_{CO_2}} \]  

\[ X_{HClN} = \frac{m_{calcN} - m_0}{m_0 \cdot A} \cdot \frac{M_{CaO}}{M_{CaCl_2} - M_{CaO}} \]  

where \( X_{CO_2N} \) represents carbonation conversion after \( N \) calcination/carbonation cycles which indicates the fractional conversion of CaO to CaCO₃ in the \( N \)th cycle. \( X_{HClN} \) is cumulative chlorination conversion.

![Fig. 2. Schematic diagram of the dual fixed-bed reactor.](image-url)
conversion in \( N \) calculation/carbonation cycles which denotes the cumulative fractional conversion of CaO to CaCl\(_2\) from 1st cycle to \( N \)th cycle. \( A \) is the content of CaO in initial sample, \%, \( m_{calc} \) is the mass of sample after \( N \) calculations, mg. \( m_{calc,N} \) is the mass of sample after \( N \) carbonations, mg. \( M_{CaO}, M_{CO_2} \) and \( M_{CaCl_2} \) are the mole mass of CaO, CO\(_2\) and CaCl\(_2\), respectively, g mol\(^{-1}\).

2.2. Phase and microstructure analysis

X-ray diffraction (XRD) was utilized to determine phase compositions of the sample after 10 calcination/carbonation cycles in the presence of HCl. Scanning electron microscope (SEM, JEOL JSM-7600F) analysis and energy dispersive X-ray (EDX, Oxford INCA sight X) analysis were performed to detect apparent morphology and elements on the surface of the sample. The nitrogen adsorption analyzer (Micromeritics ASAP 2020) was used to measure pore structure parameters of the sample in the cycles, including surface area, pore volume and pore volume distribution. The surface area and pore volume were computed according to BET (Brunauer–Emmett–Teller) method and BJH (Barrett–Joyner–Halenda) model, respectively.

3. Results and discussion

3.1. Cyclic CO\(_2\) capture of limestone in the presence of HCl

It is necessary to determine the phase compositions of the limestone after a series of calcination/carbonation cycles in the presence of HCl. Fig. 4(a) and (b) exhibits XRD spectrums of the limestone after 10 cycles in the absence (run 2) and the presence of HCl (run 1), respectively. The XRD analysis shows that the limestone experienced 10 calcination/carbonation cycles in the absence of HCl becomes CaCO\(_3\) and CaO, while it turns into CaCO\(_3\), CaO and CaCl\(_2\)-2H\(_2\)O in the presence of HCl. There is no H\(_2\)O in the reaction gas and CaCl\(_2\)-2H\(_2\)O also does not exist at 700 °C, so the CaCl\(_2\) absorbs H\(_2\)O from the air at the normal temperature to become CaCl\(_2\)-2H\(_2\)O. Thus, the real products of carbonation and chlorination of the limestone are CaCO\(_3\) and CaCl\(_2\), respectively. It indicates that the presence of HCl in the carbonation atmosphere results in a conversion of a portion of CaO to CaCl\(_2\). The carbonation conversions of the limestone after the various cycles in the absence (run 2) and the presence of 1000 ppm HCl (run 1) are shown in Fig. 5. The cyclic CO\(_2\) capture behavior of the limestone in the presence of HCl is significantly different from that in the absence of HCl. \( X_{CO_2,N} \) of the limestone in the presence of HCl is higher than that in the absence of HCl in the previous 13 cycles. \( X_{CO_2,1} \) of the limestone in the presence of HCl is 0.94, which is 18% higher than that in the absence of HCl. Nevertheless, the situation is reverse after 13 cycles. \( X_{CO_2,13} \) of the limestone in the presence of HCl is lower than that in the absence of HCl after 13 cycles. \( X_{CO_2,13} \) of the limestone in the presence of HCl presents an almost linear decrease with increasing the cycle number, until it approaches 0. Whereas the reduction of \( X_{CO_2,N} \) in the absence of HCl gradually disappears with cyclic process proceeding, and finally retains about 0.19 after 24 cycles. As seen in Fig. 5, the trend of \( X_{CO_2,N} \) in the absence of HCl is consistent with the semi-empirical equation proposed by Grasa and Abanades [44], as shown in Eq. (7).

\[
X_{CO_2,N} = \frac{1}{1/(1-Xr) + kN} + Xr
\]  

where \( Xr = 0.075 \) and \( k = 0.52 \). This equation is applicable to a wide range of limestone and operating conditions. \( X_{HCI,N} \) of the limestone in the presence of HCl increases with the number of cycles, achieving 42% after 24 cycles. It indicates that the presence of HCl enhances carbonation conversions of the limestone in a dozen cycles, but decreases carbonation conversions of the limestone with further increasing the cycle number above a dozen.

The effect of the presence of HCl could be explained by differences in the reaction pattern of the limestone. The CO\(_2\) concentration is obviously higher than the HCl concentration in the carbonation atmosphere, so the surface of the sorbent may firstly form CaCO\(_3\) product layer. And then HCl reacts with CaCO\(_3\) producing vapor and CO\(_2\). Vapor and CO\(_2\) release from the product layer in the chlorination and some pores in the product layer are left. It is beneficial to CO\(_2\) diffusion through CaCO\(_3\) product layer and CO\(_2\).
Carbonation temperature affects the cyclic CO₂ capture of the limestone. For example, the optimum carbonation temperature is still 700 °C in the presence of HCl. The presence of HCl elevates the cyclic CO₂ capture of the limestone, which is beneficial for CO₂ capture. It will be discussed in Section 3.6.

3.3. Effects of calcination temperature on cyclic CO₂ capture of limestone in the presence of HCl

Grasa and Abanades [44] reported that the calcination temperature above 950 °C accelerated the degradation in CO₂ capture capacity of calcium-based sorbents in the calcination/carbonation cycles, so the calcination temperature should be below 950 °C. It is necessary to discuss the effects of calcination temperature on CO₂ capture of the sorbent in the presence of HCl. The effects of calcination temperature in the range of 850–950 °C on X_{CO2,N} and X_{HCl,CO2} of the limestone in 10 cycles in the presence of HCl are depicted in Fig. 7. X_{CO2,N} decreases in the presence of HCl with the calcination temperature increasing from 850 to 950 °C. The effect of calcination temperature from 850 to 950 °C on X_{HCl,CO2} of the limestone is little, as found in Fig. 7. It is worth noting that the presence of HCl may accelerate the degradation in CO₂ capture capacity of the calcium-based sorbent reported by Chyang et al. [37]. The limestone in the cycles at 650 °C achieves a higher X_{HCl,CO2} than at 700 °C, which results in sharper drop in X_{CO2,N} at 650 °C than at 700 °C. Therefore, the optimum calcination temperature should be 700 °C in the presence of HCl.
very low. $X_{\text{CO}_2,N}$ of the limestone shows a slow decrease with increasing HCl concentration from 300 ppm to 1000 ppm in 10 cycles. $X_{\text{CO}_2,10}$ of the limestone in the presence of 300 ppm HCl is 31% higher than that in the presence of 1000 ppm HCl. That is because $X_{\text{HCl},N}$ increases visibly with increasing HCl concentration, which leads to a drop in $X_{\text{CO}_2,N}$ of the limestone. It indicates that when the HCl concentration varies in the range of 100–1000 ppm, $X_{\text{CO}_2,N}$ achieves the maximum value in the presence of 300 ppm HCl in the previous a dozen cycles.

### 3.5. Effects of particle size on cyclic CO$_2$ capture of limestone in the presence of HCl

Fig. 9 exhibits $X_{\text{CO}_2,N}$ and $X_{\text{HCl},N}$ of the limestone with different particle size in the calcination/carbonation cycles. Higher $X_{\text{CO}_2,N}$ of the limestone is achieved with smaller particles in the presence of HCl, which coincides with the trend in the absence of HCl. It is worth noting that the presence of HCl exacerbates influence of the particle size on carbonation conversions of the limestone, compared with that in the absence of HCl. In the presence of HCl, $X_{\text{CO}_2,10}$ of the limestone with the particle size of <0.125 mm is 0.41 after 10 cycles, which is 65% higher than that with the particle size of 0.28–0.45 mm. The chlorination conversions of the limestone increase with increasing the particle size. Due to the higher CO$_2$ concentration in the reaction atmosphere, the sorbent reacts with CO$_2$ and forms CaCO$_3$ product layer at first. The sorbent with the smaller particle size achieves the higher carbonation conversions and forms the thicker CaCO$_3$ product layer, which inhibits diffusion of HCl and decreases the chlorination conversions.

### 3.6. Microstructure analysis

Fig. 10(a) and (b) presents SEM images of the calcined limestone after 20 cycles in the absence (run 2) and the presence of HCl (run 1), respectively. The elements of surface zones (I) and (II) of the calcined limestone in Fig. 10(b) were detected by EDX, as shown in Fig. 11(a) and (b), respectively. Although the calcined limestone in the absence of HCl reveals pronounced sintering after 20 cycles, it keeps lots of small pores which interconnect with each other, as presented in Fig. 10(a). When HCl is present, it is observed that there are lots of smooth, compact and nonporous zones in the surface of the calcined limestone after 20 cycles, as seen in Fig. 10(b). These zones such as zones (I) and (II) contain much chlorine according to EDX analysis, as presented in Fig. 11. It reveals that the presence of HCl further aggravates the sintering of the limestone after the multiple cycles. The pore structure of the calcined limestone in the presence of HCl after 20 cycles is unfavorable.
for CO₂ capture. Thus, the limestone after 20 cycles achieves lower carbonation conversion in the presence of HCl.

BET surface areas and BJH pore volumes of the calcined limestone in the absence and the presence of HCl after 20 cycles are shown in Table 3. The high chlorination conversion in the presence of HCl decreases both the surface area and pore volume of the calcined limestone after 20 cycles. It demonstrates that the presence of HCl decreases the sintering resistance ability of the limestone, as the cycle number exceeds a dozen.

Fig. 12 exhibits the pore volume distribution of the calcined limestone in the absence (run 2) and the presence of HCl (run 1) after 20 cycles. In the entire measured pore size range, the calcined limestone in the presence of HCl processes less pores than that in the absence of HCl after 20 cycles. Especially, the volume of pores distributed in 10–100 nm for calcined limestone in the presence of HCl after 20 cycles is obviously smaller than that in the absence of HCl after 20 cycles. In the entire measured pore size range, the calcined limestone in the absence (run 2) and the presence of HCl (run 1) after 20 cycles. The optimum carbonation temperature of the limestone in the presence of HCl is 700 °C. In the presence of HCl, the calcination temperature above 900 °C drastically decreases CO₂ capture capacity of the limestone in the cycles. The HCl concentration in the carbonation atmosphere shows an important effect on cyclic CO₂ capture of the limestone. When HCl concentration varies in the range of 100–1000 ppm, the limestone in the presence of 300 ppm HCl remains higher CO₂ capture capacity in the previous a dozen cycles. The presence of HCl enlarges the differences of cyclic CO₂ capture capacity of the limestone with the different particle size. In the initial cycles, the presence of HCl destroys the CaCO₃ product layer and forms a few pores due to the vapor and CO₂ release in the chlorination. It is beneficial to CO₂ diffusion through the product layer. However, the formation of more CaCl₂ aggravates the sintering of the limestone with increasing the number of calcination/carbonation cycles above a dozen.

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