EFFECT OF HCL ADDITION ON CYCLIC CARBONATION PERFORMANCE OF CALCIUM-BASED SORBENT DURING CALCIUM LOOPING CYCLES

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Abstract –Calcium looping, that is, using calcium-based sorbents for repeated calcination/carbonation cycles involving the reversible reaction between CaO and CO2, is considered to be one of the most feasible techniques for CO2 capture from fossil fuel-fired power plants and the hydrogen production process. The effects of the discontinuous addition of HCl under the various conditions on CO_2 capture performance of the limestone at the calcium looping conditions were investigated in a dual fixed-bed reactor. The results show that HCl addition during the initial several cycles leads to the formation of CaClOH and the appropriate amount of CaClOH in the carbonation product is favorable to CO_2 capture by the limestone. HCl addition only in the initial 3 cycles changes the effect of carbonation temperature on CO_2 capture by the limestone. The optimum carbonation temperature in the range of 650-750 °C for the limestone with the addition of HCl is 700 °C. Higher CO_2 volume fraction in the carbonation leads to lower CO_2 capture capacity of the limestone with the addition of HCl only in the initial 3 cycles. The addition of HCl during the various cycles significantly improves the CO_2 capture capacity of the limestone.

INTRODUCTION

Carbon capture, utilization and storage (CCUS) has been considered as one of the effective solutions to regulation of anthropogenic CO_2 emissions. Calcium looping, that is, using calcium-based sorbents for repeated calcination/carbonation cycles involving the reversible reaction between CaO and CO_2, is considered to be one of the most feasible techniques for CO_2 capture from fossil fuel-fired power plants and the hydrogen production process (Anthony, 2011). This technology has some potential advantages, including relatively low efficiency penalty, high CO_2 capture capacity, opportunity for regeneration of sorbents, potential for implementing in cement manufacture (Dean et al., 2011). In the calcium looping technology, the flue gas from a fossil-fired power plant enters a carbonator where CO_2 in the flue gas is captured by CaO derived from the calcium-based sorbents such as limestone and dolomite and converts to $CaCO_3$ at the optimum temperature range of 600-700 °C. And then the produced $CaCO_3$ is transported to a calciner, where $CaCO_3$ is heated to 850-950 °C and decomposes into CaO and CO_2. CO_2 from the calciner can be concentrated for storage. The generated CaO is fed into the carbonator. And the calcination/carbonation looping of CaO is operated repeatedly.

Unfortunately, CaO derived from the natural limestones can not be completely converted into $CaCO_3$ (Rodriguez et al.,). As $CaCO_3$ has the larger molar volume than CaO, the formation of the thick $CaCO_3$ product layer contributes to pore block of the sorbent. The compact product layer increases CO_2 diffusion resistance, which limits the carbonation of the inner CaO. In addition, the CO_2 capture capacity of CaO exhibits a sharp decay with the number of the calcination/carbonation cycles due to the sintering of sorbent in the calcination step (Grasa and Abanades, 2006). The sintering leads to collapse and block of pores in the sorbent, which decreases its CO_2 capture capacity in the cycles (Valverde, 2013). Thus, the CO_2 capture capacity of the calcium-based sorbent such as limestone and dolomite is not high after the long-term calcination/carbonation cycles because of the two reasons mentioned above. In order to maintain the CO_2 capture efficiency of the fossil-fired power plant, more fresh sorbents are required, which leads to the high operating cost and energy consumption for CO_2 capture.

Lots of methods have been developed to enhance the molar conversion of CaO derived from the natural limestone to $CaCO_3$ and improve its CO_2 capture durability during the multiple cycles by increasing the active surface area and porosity of the sorbent and maintaining the stable pore structure (Valverde, 2013). The strategies have been focused on use of porous materials as mechanical supports of CaO (Sun et al., 2016), use of solid-phase additives (Reddy and Smirniotis, 2014), use of organic and mineral acids for modification of sorbent (Valverde, 2013), use of hydration treatment (Blamey et al., 2016), use of thermal pretreatment (Manovic et al., 2008), etc. It should be noted that the methods for improvement in CO_2 capture capacity of limestone maybe increase cost and the economics need to be considered. Erans et al. (2016) pointed out that a compromise must be made between improving the sorbent performance and increasing its

cost. This is often neglected when developing new materials focusing only on very high adsorption capacity. The easy, simple and Inexpensive methods to improve CO_2 capture performance of calcium-based sorbent are welcome.

Our previous work (Wang et al., 2014) showed that when hydrogen chloride (HCl) was present in the flue gas from combustion of biomass or refuse derived fuel (RDF), cyclic CO_2 capture performance of the limestone was severely impacted during the calcium looping cycles. HCl and CO_2 simultaneously reacted with CaO derived from limestone at the carbonation temperature of 650-700 °C. We found that HCl increased CO_2 capture capacity of the limestone in the previous several cycles; however, as the cycle number increased further, HCl seriously hinders CO_2 capture capacity of the limestone. That was because too much chlorination product accumulated in the cycled sorbent led to the severe sintering, which almost deprived CO_2 capture capacity of the sorbent (Wang et al., 2014). It indicates that HCl like a double-edged sword exhibits a duple influence on cyclic CO_2 capture by limestone. How to increase the positive effect of HCl on CO_2 capture by the limestone and to reduce the negative influence?

According to our previous work, a novel method is proposed to improve cyclic CO_2 capture capacity of the limestone by discontinuously adding HCl in the carbonation step. It should be noted that HCl as a gas-phase additive is discontinuously added in the carbonation step in some cycles rather than in the each cycle, with a view to utilize the positive effect of HCl and avoid the negative effect of HCl on CO_2 capture by the limestone at the calcium looping conditions. If the method is effective to improve CO_2 capture behavior of the limestone, it would be low cost and easy to implement. A few biomass or RDF can be discontinuously added in the carbonator, where a certain amount of HCl will be generated. In this work, to better utilize HCl to improve the CO_2 capture at the calcium looping conditions, the effects of the discontinuous addition of HCl under the various conditions on CO_2 capture performance of the limestone at the calcium looping conditions were investigated.

EXPERIMENTAL

The chemical components of the limestone sample were determined by a ZSX Primus II X-ray fluorescence (XRF), as exhibited in Table 1. The limestone was crushed and screened to a particle size below 0.125 mm.

Table.1: Chemical components of limestone (wt. %).

CaO	MgO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	Others	Loss on ignition
52.08	1.32	3.32	0.53	0.03	0.02	0.47	42.23

The cyclic CO_2 capture experiment of limestone by adding HCl discontinuously was performed in a dual fixed-bed reactor including a carbonator and a calciner operated at the atmospheric pressure, as exhibited in Fig. 1. The reacting gas was controlled by the mass flow meters and constantly introduced into the reactor. The limestone sample in a boat was completely calcined into CaO at 850 °C in pure N_2 (99.999%) for 10 min in the calciner. And then the calcined sample was transported to the carbonator at 650-750 °C under pure N_2. When the sample temperature was the same as the carbonator temperature, N_2 atmosphere was switched to carbonation atmosphere for 20 min. The sample boat was moved between the calciner and the carbonator to implement the multiple calcination/carbonation cycles. The samples after the calcination and carbonation reactions in the each cycle were cooled for 3 min in a dyer under pure N_2, respectively. And then the samples were weighted by an electronic balance (Mettler Toledo-XS105DU). The carbonation conversion was used to describe the molar conversion of CaO derived from the limestone to $CaCO_3$, as computed by Eq.(1). The XRD analysis shows that the addition of HCl leads to the conversion of a part of CaO to CaClOH, and CaClOH is stable, which will be discussed later in section 3.1. Thus, the cumulative chlorination conversion is used to depict the cumulative molar conversion of CaO to CaClOH due to the addition of HCl in the carbonation step, as defined by Eq. (2).

$$X_{car,N} = \frac{m_{car,N} - m_{cal,N}}{m_0 \cdot A} \cdot \frac{M_{CaO}}{M_{CO_2}} \tag{1}$$

$$X_{chl,N} = \frac{m_{cal,N+1} - m_{cal,1}}{m_0 \cdot A} \cdot \frac{M_{CaO}}{M_{CaClOH} - M_{CaO}} \tag{2}$$

where, $X_{car,N}$ denotes the carbonation conversion of the sample after N calcination/carbonation cycles, mol/mol. $X_{chl,N}$ indicates the cumulative chlorination conversion after N cycles, mol/mol. A is the mass content of CaO in the initial sample, wt.%. m_0 is the mass of the initial sample, g. $m_{car, N}$ is the mass of the carbonated sample after N cycles, g. $m_{cal, N}$ is the mass of calcined sample after N cycles, g. M_{CaO}, M_{CO2} and M_{CaClOH} are respectively the molar mass of CaO, CO_2 and CaClOH, g mol^{-1}.

The discontinuous HCl addition conditions (runs 1-13) in the carbonation step are shown in Table 2. The cyclic CO_2 capture behavior of the limestone without the addition of HCl was also examined (runs 14-18 in Table 2). The phase of the sample during the calcination/carbonation cycles under the various reaction conditions was examined by a D/Max-IIIA X-ray diffraction (XRD).
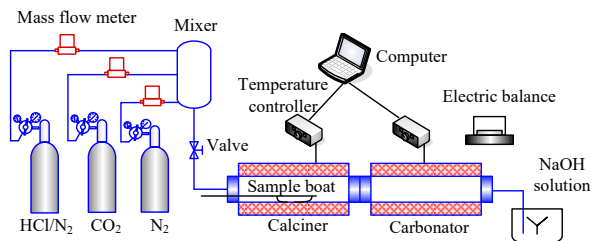

Fig. 1 Schematic of dual fixed-bed reactor.

Table. 2: Summary of run details (Calcination conditions: Pure N_2, 850 °C, 10 min) .

Run No.	Carbonation conditions
1	0.1%HCl/15%CO_2/N_2 only in 1 cycle, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
2	0.1%HCl/15%CO_2/N_2 only in previous 2 cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
3	0.1%HCl/15%CO_2/N_2 only in previous 3 cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
4	0.1%HCl/15%CO_2/N_2 only in previous 4 cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
5	0.1%HCl/15%CO_2/N_2 only in previous 5 cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
6	0.1%HCl/15%CO_2/N_2 only in previous 6 cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
7	0.1%HCl/15%CO_2/N_2 only in previous 3 cycles, 15% CO_2/85% N_2 in other cycles, 650 °C, 20 min
8	0.1%HCl/15%CO_2/N_2 only in previous 3 cycles, 15% CO_2/85% N_2 in other cycles, 750 °C, 20 min
9	0.1%HCl/30%CO_2/N_2 only in previous 3 cycles, 30% CO_2/70% N_2 in other cycles,700 °C, 20 min
10	0.1%HCl/60%CO_2/N_2 only in previous 3 cycles, 60% CO_2/40% N_2 in other cycles, 700 °C, 20 min
11	0.1%HCl/15%CO_2/N_2 only in the 1st, 2nd, 3rd, 21st, 22nd and 23rd cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
12	0.1%HCl/15%CO_2/N_2 only in the 1st, 2nd, 3rd, 27th, 28th and 29th cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
13	0.1%HCl/15%CO_2/N_2 only in the 11th, 12th and 13th cycles, 15% CO_2/85% N_2 in other cycles, 700 °C, 20 min
14	15%CO_2/85%N_2 in each cycle, 650 °C, 20 min
15	15%CO_2/85%N_2 in each cycle, 700 °C, 20 min
16	15% CO_2/85%N_2 in each cycle, 750 °C, 20 min
17	30% CO_2/70%N_2 in each cycle,700 °C, 20 min
18	60% CO_2/40%N_2 in each cycle, 700 °C, 20 min

RESULTS AND DISCUSSION

The XRD spectra of the limestone with the addition of HCl only in the first 3 carbonations during the calcination/carbonation cycles (run 3) are exhibited in Fig. 2. $CaCO_3$, CaO and CaClOH are found in the reaction product of the limestone after the 3rd carbonation with the addition of HCl (run 3), as presented in Fig.2(a). This indicates that the addition of HCl in the carbonation step leads to simultaneous carbonation

and chlorination of CaO and their corresponding products are $CaCO_3$ and CaClOH, respectively. The possible reactions in the carbonation of CaO derived from the limestone are presented in Eqs. (3) - (5). Most of CaClOH is maybe generated according to Eq.(4). That is because the volume fraction of CO_2 is 150 times as high as that of HCl, and $CaCO_3$ is more easily generated. After the 4th or the 7th calcinations, the carbonation product ($CaCO_3$) completely decomposes into CaO and CO_2, but the chlorination product (CaClOH) does not change. In addition, $m_{cal, 7}$ of the sorbent is the same to $m_{cal, 4}$. It indicates that CaClOH remains stable during the CO_2 capture cycles.

$$CaO + CO_2 \longrightarrow CaCO_3 \tag{3}$$

$$CaCO_3 + HCl \longrightarrow CaClOH + CO_2 \tag{4}$$
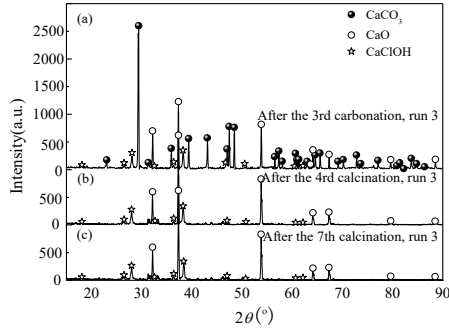
$$CaO + HCl \longrightarrow CaClOH \tag{5}$$

Fig. 2 XRD spectra of limestone with addition of HCl only in the previous 3 carbonations (run 3): (a) after the 3rd carbonation; (b) after the 4th calcination; (c) after the 7th calcinations.

The effect of 0.1% HCl addition in the carbonation step only during the initial N cycles ($N<7$) on carbonation conversions of the limestone in 10 cycles is depicted in Fig.3(a). It can be found that HCl addition during the initial N cycles ($N<7$) enhances the carbonation conversions of the limestone in 10 cycles. $X_{car, N}$ of the limestone without the addition of HCl (run 15) drops more sharply with the number of CO_2 capture cycles, compared to that with the addition of HCl. $X_{car, N}$ of the limestone with the addition of HCl only during the previous 3 cycles drops by 24% with increasing cycle number from 1 to 10, whereas that without the addition of HCl decreases by 63%. After the same cycles, $X_{car, N}$ of the limestone with the addition of HCl only during the previous 3 cycles (run 3) is higher than that with the addition of HCl during the previous N cycles ($N<7$, runs 1-6). Fig.3(b) shows the cumulative chlorination conversions of the limestone with the addition of HCl in the carbonation step during the initial cycles. It suggests that the formation of CaClOH in the reaction product is beneficial for CO_2 capture. However, it does not mean that more CaClOH leads to higher cyclic CO_2 capture capacity of the limestone. When HCl is added in the carbonation step during the initial 3 cycles, the limestone retains higher CO_2 capture capacity in 10 cycles and the corresponding $X_{chl, 3}$ is about 0.055. It reveals that the appropriate amount of CaClOH in the carbonation product is favorable to CO_2 capture by the limestone.
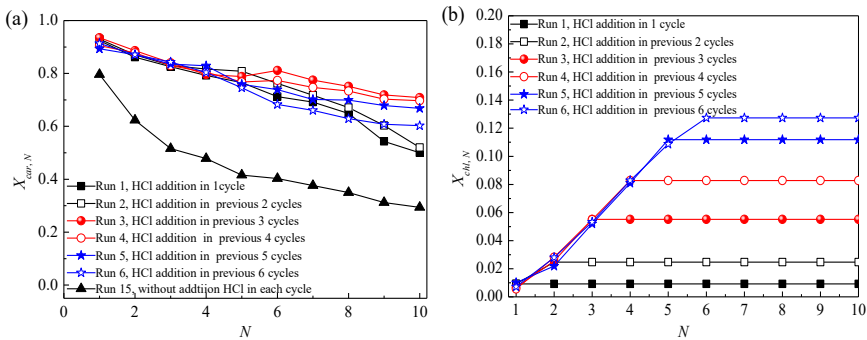

Fig.3. Effect of HCl addition in initial several cycles on $X_{car, N}$ and $X_{chl, N}$ of limestone during 10 cycles: (a) $X_{car, N}$, (b) $X_{chl, N}$

Fig. 4 exhibits the effect of the carbonation temperature on CO_2 capture by the limestone with the addition of HCl only during the initial 3 cycles. The carbonation temperature in the range of 650-750 °C shows a little effect on $X_{car, N}$ without the addition of HCl, but it exhibits a great effect on $X_{car, N}$ with the addition of HCl only during the initial 3 cycles. $X_{car, N}$ of the limestone at 700 °C (run 3) and 750 °C (run 8) with the addition of HCl are significantly higher than those at the corresponding temperatures without the addition of HCl, as shown in Fig.4(a). However, $X_{car, N}$ at 650 °C with the addition of HCl (run 7) is slightly higher than that without the addition of HCl (run 14) in the initial 5 cycles and their difference becomes little with the number of cycles. It indicates that HCl addition only in the initial 3 cycles changes the effect of carbonation temperature on CO_2 capture by the limestone. The optimum carbonation temperature for the limestone with the addition of HCl in the carbonation step only during the initial 3 cycles is 700 °C. The cumulative chlorination conversion of the limestone at 650 °C exhibits obviously higher value than that at 700 °C and 750 °C, as presented in Fig.4(b). $X_{chl,3}$ at 650 °C (run 7) is 0.11, which is 2 and 1.4 times as high as that at 700 °C (run 3) and 750 °C (run 8), respectively. The limestone absorbs more HCl at 650 °C. Partanen et al. (2005) also pointed out the limestone possessed highest HCl absorption capacity at about 650 °C. Too much CaClOH generated in the carbonation product not only decreases the conversion of CaO to $CaCO_3$, but also aggravates the sintering of the limestone during the CO_2 capture cycles. Therefore, the carbonation temperature of 700 °C with the addition of HCl in the carbonation step only during the initial 3 cycles is appropriate.
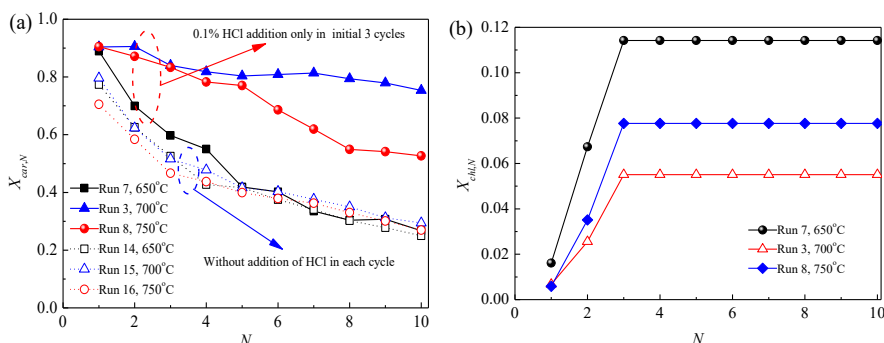

Fig.4. Effect of carbonation temperature on $X_{car, N}$ and $X_{chl, N}$ of limestone with addition of HCl only in previous 3 cycles during 10 cycles: (a) $X_{car, N}$, (b) $X_{chl, N}$

CO_2 capture capacities of the limestone with the discontinuous addition of 0.1% HCl in the various cycles are illustrated in Fig. 5. The discontinuous addition methods of HCl are performed in the following three ways: HCl addition only in the 1st, 2nd, 3rd, 21st, 22nd and 23rd cycles (run 11), HCl addition only in the 1st, 2nd, 3rd, 27th, 28th and 29th cycles (run 12) and HCl addition only in the 11th, 12th and 13th cycles (run 13). Compared to that without addition of HCl (run 15), $X_{car, N}$ of the limestone with the vinous addition methods of HCl (runs 11-13) is higher, as presented in Fig.5. $X_{car,20}$ of the limestone after run 11 is 1.8 time as high as that after run 15. Although $X_{car,N}$ of the limestone is improved with the addition of HCl only in the previous 3 cycles, it still drops with the number of CO_2 capture cycles, as shown in Fig.5. And then HCl is added again in the following cycles such as the 21st, 22nd and 23rd cycles (run 11) or the 27th, 28th and 29th cycles (run 12), $X_{car, N}$ of the limestone in the subsequent cycles after runs 11 or 12 is enhanced again. When HCl is only added in the 11th, 12th and 13th cycles (run 13), the reaction activity of the limestone are activated again, thus $X_{car, 11}$, $X_{car, 12}$ and $X_{car, 13}$ increase by 14%, 99% and 123%, respectively. And after stopping adding HCl, $X_{car,N}$ in the subsequent cycles is still improved. For example, $X_{car, 14}$ and $X_{car, 30}$ after run 13 are 134% and 86% higher than those after run 15, respectively. Therefore, the discontinuous addition of HCl during the various cycles improves the CO_2 capture capacity of the limestone.
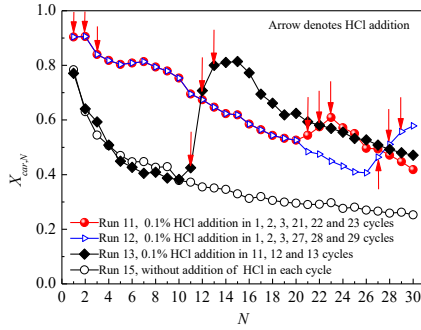
Fig.5. $X_{car,N}$ of limestone with discontinuous addition of 0.1% HCl in various cycles

The SEM images of the calcined limestone after 20 cycles without the addition of HCl (run 15) and with the addition of HCl (run 3) are presented in Fig.6(a) and (b), respectively. The few pores is observed in the surface of the calcined limestone experienced 20 cycles after run 15 and the obvious fusion phenomenon in the lots of the adjacent CaO grains is also observed, as illustrated in Fig.6(a). It indicates that the calcined limestone without the addition of HCl suffers the serious sintering after the 20 cycles. However, with the addition of HCl only in the previous 3 cycles (run 3), the surface of the calcined limestone which has experienced 20 cycles seems porous and loose, as shown in Fig.6(b). The obvious fusion phenomenon of CaO grains is not found in the surface of the calcined limestone after run 3. It proves that the addition of HCl in the carbonation stage during only the initial 3 cycles improves the pore structure of the calcined limestone and retards the fusion of CaO grains during the multiple CO_2 capture cycles. Al-Jeboori et al. (2013) also found the pore structure of the calcined limestone was improved significantly by doping Cl^- ion. The microstructure analysis shows that the addition of HCl in the carbonation step only in the initial 3 cycles improves the pore structure of the calcined limestone and enhances its sintering resistance during the multiple CO_2 capture cycles.
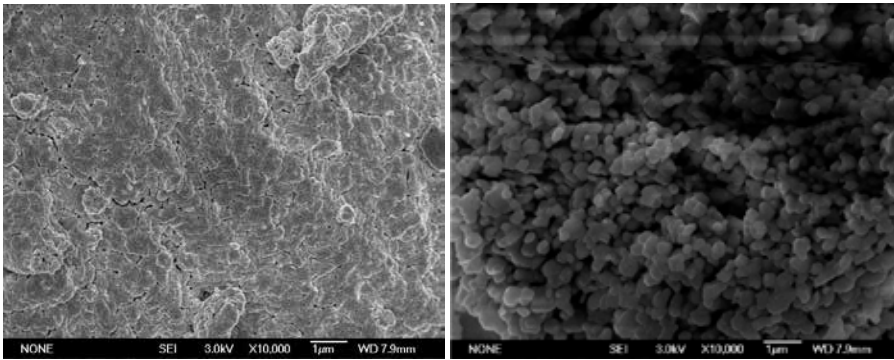

Fig. 6 SEM images of calcined limestone after 20 cycles under different reaction conditions: (a) without addition of HCl (run 15); (b) with addition of HCl only in initial 3 cycles (run 3).

ACKNOWLEDGEMENTS

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