EFFECT OF STEAM HYDRATION ON REACTIVITY AND STRENGTH OF CEMENT-SUPPORTED CALCIUM SORBENTS FOR CO₂ CAPTURE

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Abstract - Steam hydration was used to reactivate the spent cement-supported pellets for recycle. The effect of steam hydration on the reactivity of sorbents was investigated in a bubbling fluidised reactor. A specially designed impact apparatus was developed to evaluate the strength of reactivated pellets as well as determine the effect of "superheating". It was found that the reactivity of synthetic pellets was elevated significantly over that of raw limestone treated with steam hydration. The CaO conversion of spent pellets increased from 0.113 to 0.419 after hydration, whereas that of spent limestone was from 0.089 to 0.278. The conversions of hydrated samples calcined at different conditions achieved the identical level, and were proportional to hydration degrees. As expected, the mechanical strength of synthetic pellets declined severely after reactivation. Large cracks emerged on hydrated limestone as seen with Scanning Electron Microscope (SEM) images. By contrast, similar cracks were not observed for synthetic pellets after hydration, although hydration did produce higher porosity than seen limestone and an increased surface area, which enhanced CO₂ capacity and was associated with a small decrease in strength loss. It was proved that superheating treatment was able to enhance the strength of hydrated pellets.

Key words: Calcium sorbent; cement support; calcination/carbonation cycle; steam hydration; mechanic strength; superheating treatment

1. INTRODUCTION

The calcium looping process is a promising technique for post-combustion CO₂ capture. Its advantages include greater operability for existing plants and lower cost than amine scrubbing [1-2]. Such a process will be typically carried out using in dual interconnected fluidised bed with one unit operating as a carbonator and the other a calciner. Typically, the calciner is run as an oxy-fuel combustor at 900-950°C which provides heat for calcination of $CaCO_3$ and the CO₂ in flue gas is captured by the regenerated CaO in carbonator, at temperatures in the range of 650-700°C.

However, two major drawbacks emerge from this approach: (1) first there is a pronounced decay of sorbent reactivity due to thermal sintering and (2) sorbents experience attrition/fragmentation in actual fluidised-bed units, which decreases the lifetime of sorbents. A mechanical granulator has been proposed recently for large-scale sorbent pelletisation, which allows the addition of various dopants (i.e. biomass, metallic oxide, SiO_2, etc.) and employing cement or kaolin as binders to support sorbents [3-5]. The superior attrition resistance and CO₂ capacity of synthetic pellets had also been demonstrated in other work [6].

The decay of reactivity for such pellets is still inevitable during long-term cyclic reaction under harsh regeneration conditions. In consequence, the deactivated sorbents must be purged and replaced by fresh sorbent to maintain overall efficiency. It has been widely reported that spent limestone can be reactivated by steam hydration [7-9]. But studies on the characteristics of such reactivated synthetic sorbents are largely lacking. Materic et al. [10] noted that the presence of 40-100% CO_2 during the dehydration step increased the initial decomposition temperature of $Ca(OH)_2$ from 445 to 618 ℃ and indicated that the strength of hydrated limestone was enhanced after superheating. If the superheating treatment is also effective for hydrated synthetic pellets, then an approach combining steam hydration and superheating treatment seems potentially interesting for reactivating spent pellets.

There are several methods to evaluate the strength of sorbents. The most direct way is to perform attrition tests in a fluidised bed then measure the elutriation and the particle size evolution of sorbents after a few reaction cycles [11]. In actual dual fluidised beds, the sorbents experience frequently high-speed impact against rigid walls and other particles. Scala et al. [12-13] proposed an impact apparatus for single particle test, in which the particle accelerated by the gas stream strike a target. This setup focused on attrition by impact damage which is frequent dominant in fluidised beds. Recently, Duan et al. [14] have employed this approach to evaluate the effect of biomass addition on the mechanical strength for synthetic pellets showed that it works well.

In this work, cement-supported Ca-sorbent was pelletized by granulator and the reactivity of hydrated spent pellets was investigated in a bubbling fluidised reactor. In addition, a vertical impact apparatus was employed to evaluate the effect of steam hydration and superheating treatment on particle strength. Finally, the microstructure differences between hydrated LC and limestone were analysed.

2. EXPERIMENTAL

2.1. SORBENTS

Two sorbents were used in this work: natural limestone (L) and pellets (LC) prepared from calcined limestone powder supported by 10 wt. % calcium aluminate cement. The limestone and CA75 aluminate cement came from Nanjing and Zhengzhou Lvdu Refractory Material Co., Ltd., China, respectively. Pellets with size range of 0-1 mm were prepared by mechanical granulator (Xinyite G6 version, China). Prior to pelletisation, natural limestone was calcined at 850 °C in a muffle furnace for two hours. 90 wt. % calcined limestone powder (less than 50μm) and 10 wt. % cement powder were added into pelletiser vessel. Initially, the powder was mixed sufficiently for 10 min, stirred by the agitator at speed of 360 rpm. Then, a chopper on the side of the vessel and an agitator were started simultaneously. The deionized water via atomizing nozzle was sprayed progressively during the operation. The compositions of sorbents measured by X-ray fluorescence (XRF) are shown in Table.1.

Table.1. Composition of sorbents (wt. %) by XRF

Sample	CaO	Al_2O_3	MgO	Fe_2O_3	SiO_2	Others	LOI
Limestone	55.0	0.084	0.189	0.015	0.715	0.217	43.78
LC	57.9	5.585	0.206	0.033	1.190	0.266	34.82

2.2. FLUIDISED BED EXPERIMENTS

The schematic of bubbling fluidised bed reactor used for CaL cycles and hydration tests is shown in Fig.1. A long quartz tube was used as the reaction vessel with an inner diameter of 24 mm and length of 1100 mm. The gas distributor was a sintered plate. The height from the top of the reactor to the air distributor is 500 mm. Fluidisation gas, premixed using a mass flowmeter controller, was supplied from the bottom of the

reactor. Steam generation system consisting of syringe pump, rotameter, temperature controller and steam generator, was connected with inlet tube by pass. The CO_2 concentration in simulated flue gas after filtering during carbonation was analysed by a non-dispersive infrared analyser (Rosemount, NGA 2000) whose range and precision for CO_2 detection were 50% and 0.5%, respectively.
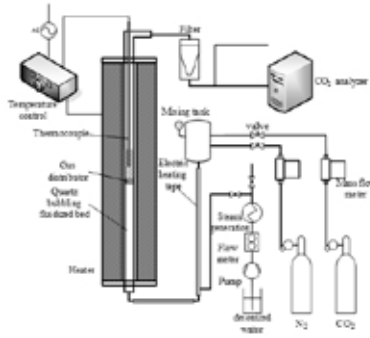

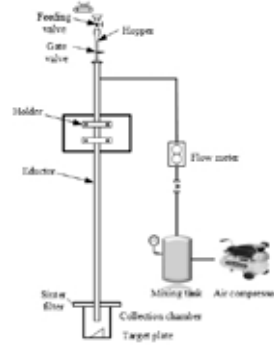Fig.1. Schematic of the bubbling fluidized bed.

Fig.2. Impact apparatus diagram.

2.2.1. CALCINATION/CARBONATION CYCLES

Table.2. Experimental conditions during the calcium looping tests

Temperature	Calcination			Carbonation
/°C	850	900	950	650
atmosphere	100% N_2	80% CO_2/20%N_2	100% CO_2	15% CO_2/85% N_2
time/min		10		20
fluidized velocity/m·s^{-1}		0.40		0.40

About 30g pellets in size range of 0.35-0.5 mm were employed for each FB test. Bed material was not used in the fluidized bed. The gas superficial velocity was 0.4m/s, which was 3.0 times the minimum fluidisation velocity of sorbents at 650 °C as calculated by Wen & Yu formula. Mild and severe calcined temperatures were employed and the detailed operating conditions are listed in Table.2. Here, 15 vol. % CO_2 was introduced to reactor when its temperature dropped to 650 °C under pure N_2.

Carbonation conversion was calculated by Eq. (1) as follow:

$$C_N = \frac{\int_0^t Q[\varphi_{CO_{2,0}}(t) - \varphi_{CO_2}(N,t)]dt}{22.4m_{cal}A/M_{CaO}} \tag{1}$$

Where C_N is the carbonation conversion of samples after N cycles; t is carbonation time [min]; Q is volume flow rates [L/min]; $\varphi_{CO_{2,0}}(t)$ denotes CO_2 concentration at the outlet in the absence of sorbent at t min, vol. %; $\varphi_{CO_2}(N,t)$ represents CO_2 concentration in the presence of sorbent at t min, vol. %; m_{cal} is the mass of sorbent (g); A is the CaO content in samples (%); M_{CaO} is the molecular weight of CaO, [g/mol].

2.2.2. HYDRATION AND SUPERHEATING TREATMENT

The sorbent retrieved from the bed after eighth calcination was considered to be a spent sorbent and steam hydration was performed *in situ* apparatus with a reaction temperature of 220 °C. The gas velocity was

0.35m/s, with 50 vol. % steam (balance N_2). That corresponded to a mass flow rate of liquid water of 1.3ml/min. The duration time for steam hydration was 15 min, but tests with an extended 10 min stream treatment to remove the free water from the hydrated sorbent at 150 °C in N_2 atmosphere were also carried out. After this, the materials were removed from the reaction vessel and weighed to determine the hydration degrees. Finally, an additional five CaL cycles were carried under the same conditions given in Table.2.

A superheating process which retained the hydrated sorbent at 510 °C under 100% CO_2 for 25min was also carried out in the fluidised bed to produce a "superheated" sorbent.

2.3. IMPACT FRAGMENTATION TESTS

The impact testing of the pellets was performed in the impact apparatus shown in Fig.2. The gas flowed into the tube from the side and velocity was controlled by a mass flow meter. The particles impacted a stainless target, which was inclined by 60° with respect to the vertical. About 2 g of pellets were used for each impact test at room temperature. The impact velocities were 5, 10, 18, 26, and 34 m/s, conforming to particle impact conditions near the gas distributor, in the bed and cyclone. If the mass of fragments collected after the impact test deviated by less than 1% from initial mass, the test was seen as satisfactory.

The definition of breakage probability, f, is given by Eq. (3). Using Eq. (4) to calculate the Sauter mean diameter (d_{sv}) and size reduction of d_{sv} are calculated.

$$f = \frac{m_{Debris}}{m} \tag{3}$$

$$d_{sv} = \frac{1}{\sum x_i / d_{pi}} \tag{4}$$

where m_{Debris} is the mass of debris whose size falls below the lower limit of the feed size interval; m is the total mass of particles; x_i is the mass fraction of particles in size interval of i; d_{pi} is the length of size interval of i; and d_0 is the initial mean size.

The morphology was observed by using a Hitachi S-4800 Scanning Electron Microscope (SEM). The pore microstructure was also measured by nitrogen adsorption/desorption on a Micromeritics ASAP 2020-M analyser.

3. RESULTS AND DISCUSSION

3.1. MICROSTRUCTURE OF STEAM-HYDRATED PELLETS

Fig.3 show the morphology of steam-hydrated spent limestone and LC pellets, respectively. Numerous large scale cracks emerged on the surface of hydrated limestone. These can be explained by the swelling of CaO grain during hydration as a result of the change of the molar volume from 16.9 cm³·mol⁻¹ of CaO to 33.7 cm³·mol⁻¹ of Ca(OH)₂. Notably, cracks even those with micro size were not observed on hydrated LC sorbent, which many result from the fact that LC pellet was physically supported by the cement, which provided a comparatively larger framework than the raw limestone. And it was beneficial for releasing swelling stress.
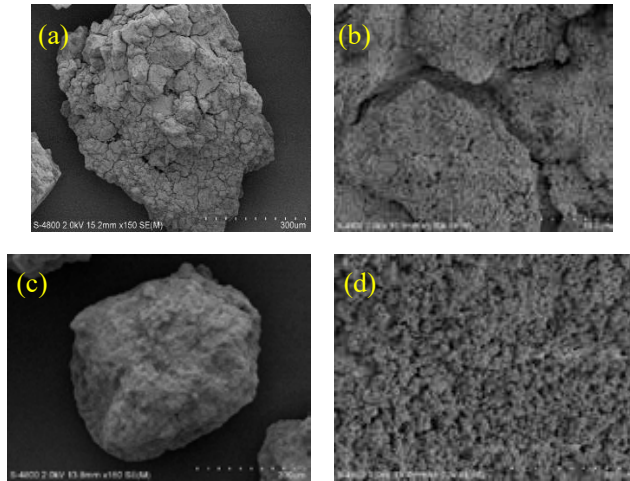
Fig.3. SEM images of limestone and LC sorbent at different stages: (a) (b)steam-hydrated spent limestone, (c) (d) steam-hydrated spent LC
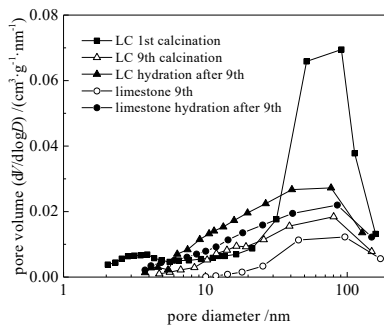

Fig.4. Pore volume distributions of LC and limestone during different stages.

The pore volume distributions of LC and limestone during different stages are shown in Fig.4. The BET surface area of LC after the 9th calcination declined to 2.69 $m^2 \cdot g^{-1}$, while that of limestone were 1.31 $m^2 \cdot g^{-1}$. LC sorbents experienced less porosity decay than limestone after multiple cycles, which owed to the formation of mayenite. For LC after hydration, the surface area increased to 7.81 $m^2 \cdot g^{-1}$. The pore volume in ranges of 3-180 nm diameter were effectively improved. Especially, pore volumes with 4-30 nm diameter were present at a higher level than that of initial calcined sorbent. This indicates that the meso-porous fraction, which was most beneficial for CO_2 reaction, could be significantly regenerated. Hydrated LC also showed better porosity enhancement than limestone, which was probably associated with by improved penetration by steam due to being absence of compression during granulation and better pore structure of LC before hydration.
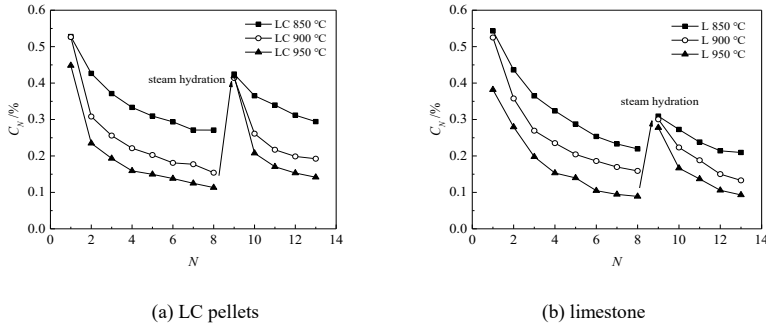
3.2. EFFECT OF STEAM HYDRATION ON CO₂ CAPTURE CAPACITY

(a) LC pellets   (b) limestone

Fig.5. Cyclic conversions of CaO in LC sorbent and limestone (carbonation at 650°C 15%CO_2/balance N_2, hydration at 220°C 50%steam/balance N_2).

Table.3. Hydration degree and cyclic conversion of CaO before and after hydration

Calcined	Limestone			LC		
temperature/°C	850	900	950	850	900	950
hydration degree	0.469	0.442	0.492	0.604	0.629	0.614
before hydration C_N	0.219	0.159	0.089	0.271	0.154	0.113
1st after hydration C_N	0.309	0.300	0.278	0.425	0.413	0.419

The cyclic conversions of CaO in LC pellet and limestone under three different calcined conditions are given in Fig.5. The reactivity of both sorbents declined monotonically with repeated reaction cycles. The CaO conversions of limestone at 8th cycle were 21.9% and 8.9% for calcination at 850°C and 950°C, higher than those of LC were 27.1% and 11.3%, respectively. The literature is clear that $Ca_{12}Al_{14}O_{33}$ formed during 800-1000°C can increase the resistance to sintering [12].

The hydration degrees from CaO to $Ca(OH)_2$ and carbonation conversions are given in Table.3. It can be seen that the hydration degrees of spent LC at all calcined temperatures were higher than those of limestone. After hydration, The CaO conversion of LC calcined at 950°C enhanced from 0.113 to 0.419, compared to that for limestone was from 0.089 to 0.278. The reactivity recovery by steam hydration was more effective for spent LC than that for limestone. Interestingly, the CaO conversions approached same level for each kind of sorbents after hydration, although they were calcined under different temperature.

The deactivated LC achieved higher reactivity enhancement after hydration than did limestone, but no similar cracks were seen as was the case for hydrated limestone which increase activated surface. There appears to be two reasons in this case. One is that the LC sorbent pelletized by powder without compression was more easily penetrated by steam. Accordingly, hydration produced larger porosity in LC. The other reason was increasing inion diffusion in $CaCO_3$ layer promoted by H_2O, as reported by Li et al. [15] based on the defect chemistry theory. H_2O molecule can dissociate into H^+ and OH^- at 650°C. OH^- reacts with CO_2 directly to form CO_3^{2-}, while H^+ which has a very small ionic radius can easily diffuse through $CaCO_3$ product layer to react with O^{2-} to form OH^-. Then, OH^- diffuses outward to $CaCO_3$/gas interface. It should be noted that the existence of OH^- ions which possessed high migration speed in $Ca(OH)_2$, must significantly enhance. Finally, the H^+ generated when OH^- react with CO_2, diffuses through product layer to react with O^{2-} in CaO to form fresh OH^-. In this way, more OH^- ions shift outward and more CO_3^{2-} diffuse inward to satisfy charge balance, which indicates higher carbonation conversion.

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3.3 MECHANICAL STRENGTH EVALUATION
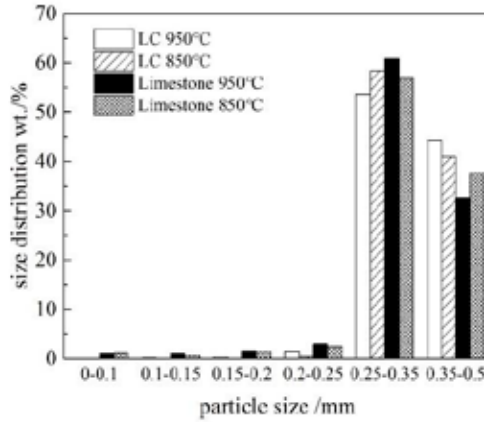
3.3.1 ATTRITION IN BUBBLING BED

Fig.6. Particle size distributions of sorbents after 13 cycles.

Table.4. Elutriations after 13 cycles for limestone and LC sorbent

Calcination temperature	Elutriation /%	
/°C	limestone	LC
850	0.89	0.18
900	1.66	0.73
950	2.29	1.35

Fig.6 displays the particle size distributions of sorbents inside bed after 13 cycles, and the corresponding elutriations is shown in Table.4. It is clear that the elutriations of LC at all calcined temperature were lower than those of limestone. The particle mass fraction of LC within the original size range was also high and the particle mass less than 0.2 mm was few, which indicated the better total attrition resistance of LC. Calcium aluminate formed a stable cross-linked nano-sized framework and CaO grains were embedded in the framework. So a tougher structure of LC pellet was acquired. In addition, the superior sphericity also contributed to resistance improvement.

3.3.2 IMPACT FRAGMENTATION

The breakage probability and the Sauter mean diameter of LC in size range of 0.35-0.5mm following different pre-treatments are displayed in Fig.7. The breakage probability and Sauter mean diameter of spent LC at impact velocity range of 5-34m/s were 0.6-18.6% and 0.42-0.38mm. It is evident that the breakage probability of hydrated spend LC was always the highest for all treated sorbents at all impact velocity.
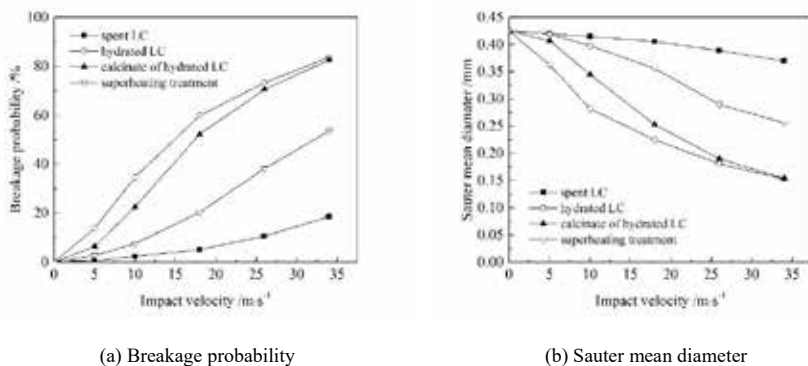
(a) Breakage probability (b) Sauter mean diameter

Fig.7. Breakage probability and Sauter mean diameter of LC sorbent experienced different treatments (calcination at 950°C pure CO_2; carbonation at 650°C 15%CO_2/balance N_2; hydration at 220°C 50%H_2O/balance N_2; superheating at 510°C pure CO_2).

In order to improve the strength of steam-reactivated spent sorbents, additional superheating treatment under 510°C/100%CO_2 for 25 min was performed. It can be seen that the curves of calcinate of superheated LC were almost located in the middle of those of calcined hydrated LC and spent LC. Typically, the breakage probability at impact velocity of 18 and 34 m/s was reduced by 32% and 33%, and the mean diameter of samples impacted at those velocities increased by 70% and 67%, as compared to that of the calcined hydrated LC. Here it is clear that the strength of superheated LC was significant enhancement and reached an acceptable level to justify the treatment step.

The role of superheating treatment was similar to the annealing process of metal materials. The ions in sorbent under superheated state had enhanced motion activity, caused improved ionic migration. Here, the atoms tended to rearrange and distribute homogeneously. On the micro level, this allows the annealing of stacking flaws inside lattice and the reduction of mechanical strain. On the macro level, this strengthens the pellets, allowing them to better resist impact force by eliminating residual stress, crack tendency and deformation.

4. CONCLUSION

Lime supported by 10 wt. % aluminate cement were pelletized with a mechanical granulator. Large cracks were observed on the surface of hydrated spent limestone, while micro-scale cracks were not found on hydrated LC. It is possible that the LC granulated in the absence of compression also reduces swelling stress. The superior cyclic reactivity of synthetic pellets over that of limestone was clearly observed during bubbling fluidised experiments. Compared to limestone, the LC showed clear CO_2 capacity improvement after steam hydration. The pore volume in size range of 4-30 nm was enhanced over that of the initial calcined sorbent, which contributed to steam-reactivation. As expected, the impact breakage resistance of LC pellets declined significantly after hydration. However, superheating treatment under 510°C/100% CO_2, was employed for hydrated sorbents, and this clearly enhanced the strength of sorbent particles. It is concluded that "superheating", (which appears to allow the annealing of stacking faults and mechanical strain formed by hydration) is clearly shown to be effective in terms of enhancing the strength of hydrated LC pellets.

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