

Effect of steam hydration on reactivity and strength of cement-supported calcium sorbents for CO₂ capture

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Highlights:

- Cracks did not emerge with steam-hydrated synthetic pellets, whereas they were common for hydrated limestone.
- The hydrated pellets showed better porosity and reactivity enhancement than hydrated limestone.
- The mechanical strength of hydrated pellets was worse than that of hydrated limestone based on tests with a vertical particle impact apparatus.
- Superheating treatment was found to be effective in improving the strength of hydrated synthetic pellets.

Abstract

Steam hydration was used to reactivate spent cement-supported CO₂ sorbent pellets for

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recycle and 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 the reactivated pellets as well as determine the effect of “superheating”. It was found that the reactivity of synthetic pellets was significantly elevated over that of raw limestone after steam hydration. The CaO conversion of spent pellets increased from 0.113 to 0.419 after hydration, whereas that of spent limestone ranged from 0.089 to 0.278. The CaO conversions of hydrated samples calcined under different conditions achieved the identical level, proportional to the degree of hydration. As expected, the mechanical strength of synthetic pellets declined severely after reactivation. Large cracks emerged on hydrated limestone as seen in scanning electron microscope images. By contrast, similar cracks were not observed for synthetic pellets after hydration, although hydration did produce higher porosity than seen with limestone and an increased surface area, which enhanced CO₂ capacity and was associated with an increase in strength loss. The breakage rate of superheated steam-activated limestone derived pellets was about half that of hydrated samples. This demonstrates that superheating treatment (which allows the annealing of stacking faults and mechanical strain produced by hydration) enhances the strength of hydrated pellets. This work demonstrated that combining steam hydration with superheating can both reactivate the spent synthetic pellets and reduce strength decay associated with the hydration process.

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

1. Introduction

The calcium looping (CaL) process is a promising technique for post-combustion CO₂ capture. Its advantages include greater operability for existing plants and lower cost than amine scrubbing¹. Such a process will be typically be carried out in a dual interconnected fluidised bed system, with one unit operating as a carbonator and the other as a calciner. Generally, the calciner is run as an oxy-fuel combustor at 900-950°C, which provides heat for calcination of CaCO₃; the CO₂ in flue gas is captured by the regenerated CaO in the carbonator, at a temperatures 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 their lifetime². Many methods have been proposed to improve sorbents such as chemical doping³⁻⁵, organic acid treatment⁶, synthesis techniques including the sol-gel method⁷⁻⁸, co-precipitation method⁹, and so on. Although many of the preparation methods produce particles with excellent reactivity, the resulting sorbents are often unsatisfactory for fluidised bed operation due to their low mechanical strength. Another drawback of sorbent modification methods is that they typically produce only small batches of material, and are potentially difficult to scale up to industrial levels required for commercial operation.

A mechanical granulator has been proposed recently for large-scale sorbent pelletisation, which allows the addition of various dopants (*i.e.*, biomass, metallic oxides, SiO₂, *etc.*) along with employing cement or kaolin as binders to support sorbents¹⁰⁻¹². The superior attrition

resistance and CO₂ capacity of synthetic pellets has also been demonstrated in other work¹³.

However, the decay in reactivity for such pellets is still inevitable during long-term cycling under harsh regeneration conditions, even where advanced techniques are used to produce a “superior” sorbent. In consequence, the deactivated sorbents must be purged and replaced by fresh sorbent to maintain overall efficiency. Telesca *et al.*¹⁴ reported that the spent limestone could serve as an excellent substitute for lime in the cement industry for producing Portland cement and calcium sulphoaluminate cement (4CaO₃·Al₂O₃·SO₃). Moreover, the use of such material was associated with considerable reduction of CO₂ emission and energy consumption compared with the calcination of limestone. Such spent sorbent can also be used for flue gas desulphurisation¹⁵, H₂S desorption and mercury removal¹⁶. In addition, the deactivated sorbents produced after grinding can be granulated again by mixing with binder¹⁷, although this may be uneconomical for synthetic sorbents due to their high cost of production. It has been widely reported that spent limestone can be reactivated by steam hydration¹⁸⁻²⁰, which may be a suitable way for reuse of spent synthetic pellets. However, studies on the characteristics of such reactivated synthetic sorbents are largely lacking.

Many workers²¹⁻²² have reported that large cracks emerged on the surface of limestone after hydration. In consequence, hydrated limestone shows poor strength and more serious elutriation in the fluidised reactor than the original material. Whether the pelletised sorbents are seriously affected after steam hydration is still an open question due to the lack of studies in this area. However, it can be concluded that the mechanical strength of pellets may decline to a greater or lesser degree after hydration. So, it is necessary to balance the needs for

reactivity recovery with any strength decay due to reactivation. Materic *et al.*²³ noted that the presence of 40-100% CO₂ during the dehydration step increased the initial decomposition temperature of Ca(OH)₂ from 445 to 618 °C. Under these conditions, the Ca(OH)₂ was presumed to be in the “superheated state”. Further research by Blamey *et al.*²⁴ and Materic *et al.*²⁵ 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 and then measure the elutriation and the particle size evolution of sorbents after a few reaction cycles²⁶. Another approach that can be employed is an air jet²⁷, as proposed by the American Society for Testing and Materials with the development of an Air Jet Index (AJI, a unitless index numerically equal to the percent attrition loss at 5 h). However, these methods mainly focus on the abrasion and exfoliation of particles. In actual dual fluidised beds, the sorbents frequently experience high-speed impact against rigid walls and other particles, especially in the cyclone and near the air distributor. Given that such abrasion results from the impact breakage on the surface. Scala *et al.*²⁸⁻²⁹ proposed an impact apparatus for single particle testing, in which the particle accelerated by the gas stream strikes a target and then the breakdown fragments are collected and measured. This setup focuses on attrition by impact damage which is frequently dominant in fluidised beds. Recently, Duan *et al.*³⁰ have employed this approach to evaluate the effect of biomass

addition on the mechanical strength for synthetic pellets and showed that it works well.

In this work, cement-supported Ca-sorbent was pelletised with a 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 pellets (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 a size range of 0-1 mm were prepared with a mechanical granulator (Xinyite G6 version, China). Prior to pelletisation, natural limestone was calcined at 850 °C in a muffle furnace for two hours. The general procedure of granulation was as follows: 90 wt. % calcined limestone powder (less than 50 µm) and 10 wt. % cement powder were added into the pelletiser vessel. Initially, the powder was mixed for 10 min, stirred by the agitator at a speed of 360 rpm. Then, a chopper on the side of the vessel and an agitator were started simultaneously at speeds of 2800 and 480 rpm, respectively. The blade speed was controlled by a PLC system on a digital panel. Deionised water *via* an atomising nozzle was sprayed progressively during the operation. The final size of particles was closely related to the water quantity and size of atomising droplets. Finally, the resulting

material was air dried for 12 h before being stored in a desiccator for fresh pellets. The compositions of sorbents measured by X-ray fluorescence (XRF) are shown in Table 1, indicating that the LC pellets contain a relatively high quantity of Al_2O_3 due to cement addition.

2.2. Fluidised bed experiments

The schematic of the bubbling fluidised reactor used for CaL cycles and hydration tests is shown in Fig.1. A 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 then supplied from the bottom of the reactor. A steam generation system consisting of a syringe pump, rotameter, temperature controller and steam generator, was connected to the inlet tube bypass. The inlet tube was heated externally by heating tapes in order to avoid steam condensation. The CO_2 concentration in the 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.

2.2.1 Calcination/carbonation cycles

About 30 g of pellets in the size range of 0.35-0.5 mm were employed for each FB test. Bed material was not used in the fluidised bed. The gas superficial velocity was 0.4 m/s, which was 3 times the minimum fluidisation velocity of sorbents at 650 °C as calculated by the well-known Wen & Yu equation³¹. Mild and severe calcining temperatures were employed and the detailed operating conditions are listed in Table 2. Here, 15 vol. % CO_2 was

introduced to the reactor when its temperature dropped to 650 °C under pure N₂.

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

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

where C_N is the carbonation conversion of samples after N cycles; t is carbonation time (min); Q is volume flow rate (L/min); $\varphi_{CO_2,0}(t)$ denotes CO₂ concentration at the outlet in the absence of sorbent at t min (vol. %); $\varphi_{CO_2}(N,t)$ represents CO₂ concentration in the presence of sorbent at t min (vol. %); m_{cal} is the mass of sorbent (g); A is the CaO content in the sample (%); and M_{CaO} is the molecular weight of CaO, (g/mol).

2.2.2 Hydration and superheating treatment

The sorbent retrieved from the bed after the eighth calcination was considered to be spent sorbent and steam hydration was performed *in situ* in the apparatus with a reaction temperature of 220 °C. This temperature was chosen based on the trade-off between hydrated reactivity and steam consumption¹⁸. The gas velocity was 0.35 m/s, with 50 vol. % steam (balance N₂). That corresponded to a mass flow rate of liquid water of 1.3 mL/min. The duration of steam hydration was 15 min, but tests with an extended 10 min steam treatment at 150 °C in N₂ atmosphere to remove the free water from the hydrated sorbent were also carried out. After this, the materials were removed from the reaction vessel and weighed to determine the hydration degree, C_{hy} , according to Eq. (2). Finally, an additional five CaL cycles was carried out under the same conditions given in Table 2.

$$C_{hy} = \frac{(m_{hy} - m_{cal} \cdot (1 - LOI)) \cdot M_{CaO}}{M_{H_2O} \cdot m_{cal} \cdot A} \quad (2)$$

where m_{hy} is the mass of hydrated sorbent after removal of the free water (g); LOI is mass loss on ignition; M_{H_2O} is the molecular weight of H_2O (g/mol).

A superheating process which kept the hydrated sorbent at 510 °C under 100% CO_2 for 25 min was also carried out in the fluidised bed to produce a “superheated” sorbent. In this situation, the dehydration of $Ca(OH)_2$ did not occur (as has been confirmed elsewhere²³), and the $Ca(OH)_2$ was considered in a “superheated state”.

2.2.3 Attrition in bed

The elutriated fines were captured by fiber filter located at reactor outlet. The elutriation (E) was calculated by Eq. (3) described as follow.

$$E = (m_t - m_0) / M \quad (3)$$

Where m_t was the mass of filter after cycles; m_0 was the mass of fresh filter; M was total mass of given sorbents.

2.3. Impact fragmentation tests

The impact testing of the pellets was performed in the impact apparatus shown in Fig.2. The apparatus consisted of a feeding device (1 mm i.d. at the bottom section), vertical eductor (10 mm i.d. and 1.1 m long) and dismountable collection chamber. The gas flowed into the tube from the side and velocity was controlled by a mass flow meter. The particles, accelerated by the gas flow and gravity, impacted a stainless steel target, which was inclined by 60° with respect to the vertical. The inclination was chosen by considering the effect of rebounding particles²⁸. The top section of the chamber was a sintered porous metal plate which filtered the entrained fine particles from the escaping gas.

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. According to the calculations, the particles approach terminal velocity after accelerating through the eductor (1.1 m length). If the mass of fragments collected after the impact test deviated by less than 1% from the initial mass, the test was deemed to be satisfactory. Debris was sieved to determine the size distribution after each impact test.

The definition of breakage probability (f) is given by Eq. (4). The Sauter mean diameter (d_{sv}) are calculated by Eq. (5).

$$f = \frac{m_{\text{Debris}}}{m} \quad (4)$$

$$d_{sv} = \frac{1}{\sum x_i / d_{pi}} \quad (5)$$

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 .

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

The SEM images of limestone and LC pellets that underwent eight cycles are shown in Fig. 3 (a), (b) and (e), (f). It can be seen that the sintering and merging of grains was significant for

both sorbents, but LC showed a surface feature that grains stacked together which resulted in a coarse surface. Fig. 3 (c), (g) and (d), (h) show the morphology of steam-hydrated spent limestone and LC pellets and their calcines, respectively. Numerous large-scale cracks emerged on the surface of hydrated limestone. These can be explained by the swelling of CaO grains during hydration as a result of the change of the molar volume from $16.9 \text{ cm}^3 \cdot \text{mol}^{-1}$ of CaO to $33.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ of $\text{Ca}(\text{OH})_2$. Blamey *et al.*³² concluded, based on theoretical calculations, that the tensile stress in the limestone hydroxide layer could reach 2 MPa. That is twice the Young's modulus of Portland cement and it is more likely to form cracks in particles with a lower porosity. Notably, even micro-sized cracks were not observed on hydrated LC sorbent, which may result from the fact that the LC pellet was physically supported by the cement, which provided a comparatively larger framework than the raw limestone. As a result, larger grain space and unconsolidated structure were formed in LC during granulation, which was beneficial for releasing swelling stress. The LC sorbent was more easily penetrated by steam to form non-compact surface, as can be inferred from the comparison between Fig. 3 (d) and (h).

The evolution of Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume of LC and limestone after the first calcination, the 9th calcination and hydration were explored by nitrogen physisorption and the results are listed in Table 3. The pore volume distributions are shown in Fig. 4. The BET surface area and BJH pore volume of LC after the 9th calcination declined to $2.69 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.0146 \text{ cm}^3 \cdot \text{g}^{-1}$, while those of limestone were $1.31 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.0113 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively. LC sorbents experienced less

porosity decay than limestone after multiple cycles, owing to the formation of mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$), that can be regarded as a material which prevents sintering as reported in numerous studies^{10, 11}. However, the surface area and pore volume of spent LC after hydration increased to $7.81 \text{ m}^2\cdot\text{g}^{-1}$ and $0.0345 \text{ cm}^3\cdot\text{g}^{-1}$, respectively. Hydrated limestone showed similar improvement in terms of these data. The pore volume in ranges of 3-180 nm diameter were effectively improved by hydration, as illustrated in Fig. 4. Especially notable, is that pore volumes in the range of 4-30 nm diameters were present at a higher level than those of the initial calcined sorbent. This indicates that the meso-porous fraction, which was most beneficial for reaction with CO_2 , could be significantly regenerated. Hydrated LC also showed better porosity enhancement than limestone, which was probably associated with improved penetration by steam due to better pore structure of LC before hydration and the absence of compression during granulation compared with natural limestone formation.

3.2. Effect of steam hydration on CO_2 capture capacity

The effect of steam hydration on cyclic reactivity of LC and limestone was further studied in a lab-scale fluidised reactor. Carbonation was performed immediately after hydration. Fig. 5 illustrates the CO_2 concentration curves for LC and limestone during the following cycles: 1st, 8th, 1st after hydration and 5th after hydration carbonation when calcined at 950°C . A fast initial reaction stage is clearly present for both reactivated sorbents during the first carbonation. However, the duration of this stage for LC was about 300s compared to 200s for limestone. Furthermore, hydrated LC showed different conversion profiles when compared with that of natural limestone. The carbonation of hydrated LC still demonstrated a noticeable

diffusion-controlled stage and the shift between the kinetically- and diffusion-controlled stages was not as sharp as in the case of hydrated limestone. It can be argued that the diffusion reaction is usually related to pore configuration. The different carbonation profiles suggest both a more active surface and porosity in LC than limestone after hydration treatment as demonstrated by the results shown in Table 3.

The cyclic conversions of CaO in LC pellets and limestone under three different calcination conditions are given in Fig. 6. The reactivity of both sorbents declined monotonically with repeated reaction cycles and decay was more significantly under calcination at 950°C. The CaO conversions of limestone at the 8th cycle were 21.9% and 8.9% for calcination at 850°C and 950°C respectively, lower than those of LC which were 27.1% and 11.3%. The literature is clear that only $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ formed at 800-1000°C can increase the resistance to sintering^{10, 33}, while $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ could react with CaO to form $\text{Ca}_3\text{Al}_2\text{O}_6$ in temperature above 1000°C which reduces the ability of the sorbent to resist sintering³². Fortunately, 1000°C is well beyond the calcination temperature. Also, it should be noted that the carbonation still continued noticeably when the pores on the surface were covered by CaCO_3 . As first proposed by Bhatia and Perlmutter³⁴, Sun *et al.*³⁵ experimentally verified that after the CaCO_3 layer is formed, the gaseous CO_2 reacts with the O^{2-} anions to form CO_3^{2-} anion groups. This permits the CO_3^{2-} to diffuse inward through the CaCO_3 layer to react with internal CaO. Meantime, the O^{2-} anions must diffuse outward from the internal CaO to the solid surface. The molar ratio of inward CO_3^{2-} to outward O^{2-} should be 1:1 in order to satisfy the charge balance. Fortunately, the $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ can serve as a carrier to provide O^{2-} anions. This means

that the O^{2-} on the surface may well react with CO_2 to form CO_3^{2-} directly. The outward O^{2-} concentration could be enhanced by the addition of Al_2O_3 , whose presence should allow more CO_3^{2-} to diffuse inward according to the charge balance. As a result, the carbonation can be expected to be accelerated.

The hydration degrees from CaO to $Ca(OH)_2$ and carbonation conversions are given in Table 4. It can be seen that the hydration degrees of spent LC at all calcination temperatures were higher than those of limestone. This is related to weaker sintering of spent LC reflected by better porosity than that of spent limestone. After hydration, The CaO conversion of LC calcined at $950^\circ C$ enhanced from 0.113 to 0.419, compared to that for limestone which was from 0.089 to 0.278. The reactivity recovery by steam hydration was more effective for spent LC than for limestone. Interestingly, the CaO conversions approached the same level for each type of sorbent after hydration, although they were calcined under different temperatures. This behaviour appears to be caused by the similar conversion from CaO to $Ca(OH)_2$ which reached the hydration limit in the presence of excess steam.

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 increased its activated surface. The possible reason for this is that the LC sorbent pelletised by powder without compression was more easily penetrated by steam. Accordingly, hydration produced larger porosity in LC. Beside porosity increase after hydration, the other reason for hydrated samples demonstrating an improved reactivity is an increasing anion diffusion in the $CaCO_3$ layer promoted by H_2O , as reported by Li *et al.*³⁶ based on the defect chemistry theory.

The 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 the CaCO_3 product layer to react with O^{2-} to form OH^- . Then, OH^- diffuses outward to the CaCO_3/gas interface. It has been shown that OH^- migrates faster than oxygen vacancy in the work of Li *et al.*³⁶. It should be noted that the existence of OH^- ions, which possess high migration speed in $\text{Ca}(\text{OH})_2$, must significantly enhance carbonation rate. Finally, the H^+ generated when OH^- reacts with CO_2 , diffuses through the 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-} ions diffuse inward to satisfy the charge balance, which indicates higher carbonation conversion.

3.3 Mechanical strength evaluation

3.3.1 Attrition in bubbling bed

Fig. 7 displays the particle size distributions of sorbents inside the bed after 13 cycles, and the corresponding elutriations are shown in Table 5. It is clear that the elutriations of LC at all calcination 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 fraction less than 0.2 mm was minimal, which indicated the superior total attrition resistance of LC. Calcium aluminate probably forms a stable cross-linked nano-sized framework and CaO grains were embedded in the framework. So, a more attrition-resistant structure of the LC pellet is produced. In addition, the higher sphericity also contributed to improved resistance.

3.3.2 Impact fragmentation

The spent sorbent, hydrated sorbent, calcined hydrated sorbent and calcined superheated

hydroxide were prepared in parallel fluidised experiments and the schematic is displayed in Fig. 8. The breakage probability and the Sauter mean diameter of LC and limestone in the size range of 0.35-0.5 mm following different pre-treatments are displayed in Fig. 9 and Fig. 10. The breakage probability and Sauter mean diameter of spent LC at impact velocity range of 5-34 m/s were 0.6-18.6% and 0.42-0.38 mm, and those of spent limestone were 2.6-17.2% and 0.42-0.37 mm, respectively. Interestingly, the spent LC and limestone retained similar breakage probability and mean size after impact. It seemed that cement-supported sorbent after calcination could reach the same resistance to impact fragmentation as the original limestone.

From the Fig. 9(a) and Fig. 10(a), it is evident that the breakage probability of both hydrated spent LC and limestone always had the highest values for all treated sorbents at all impact velocities. The breakage probability and Sauter mean diameter of hydrated spent LC were 13.8-83.7% and 0.36-0.15 mm, much higher than those of hydrated spent limestone which were 6.5-35.7% and 0.41-0.28 mm. This means that LC suffered higher strength decay after steam hydration compared to limestone. After calcination, the hydrated pellets showed slightly enhanced strength in view of their relatively lower breakage rate. One reason for this is that the strength of Ca(OH)_2 is weaker than CaO , which is reflected by the lower breakage probability curve of calcinate from hydrated sorbent. However, hydrated LC exhibited much more severe breakage. It appears that the LC pellet made from powder has larger grain space and unconsolidated structure after hydration, as shown in Fig. 3 (h), which promoted easier penetration by steam.

In order to improve the strength of steam-reactivated spent sorbents, additional superheating treatment under 510°C/100% CO₂ for 25 min was performed. From Fig. 9, it can be seen that the curves of calcined superheated LC were effectively located in the middle of those of calcined hydrated LC and spent LC. Typically, the breakage probability at impact velocities 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 those of the calcined hydrated LC. Here it is clear that the strength of superheated LC was significantly enhanced and reached an acceptable level to justify the treatment step. Notably, the impact breakage parameter curves of superheated limestone approached those curves of spent sorbents, which indicated the strength of limestone recovers effectively under superheated treatment.

Materic's experiment²³ noted that the decomposition temperature of Ca(OH)₂ in the presence of 40-100% CO₂ increases from 445 to 618°C. Hence, the Ca(OH)₂ can be considered to be in a superheated state under 100% CO₂/510°C since dehydration does not occur. Two possible explanations for this phenomenon were proposed in the literature. Blamey *et al.*²⁴ suggested that the formation of a protective carbonate layer prevented the mass transfer of H₂O from the centre of the particle to the surface, because of the larger molar volume of CaCO₃. By contrast, Materic *et al.*²³ claimed that the dehydrated H₂O chemisorbed on the surface can react with CO₂ to release H⁺ ions. H⁺ is injected into the lattice to combine with O²⁻ to form OH⁻. Hence, the dehydration is suppressed and higher temperature is necessary to break the equilibrium. The latter explanation appears to be more reasonable if we consider dehydration occurs through ionic diffusion.

The role of superheating treatment was similar to the annealing process of metal materials. The ions in the sorbent under the superheated state have enhanced motion activity, causing improved ionic migration. Here, the atoms tend to rearrange and distribute homogeneously. On the micro level, this allows the annealing of stacking faults inside the lattice and the reduction of mechanical strain. Employing transmission electron microscope (TEM) to detect the evolution of lattice defects inside sorbents during hydration will be explored in later work. 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 was pelletised with a mechanical granulator. Large cracks were observed on the surface of hydrated spent limestone, while even 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 clearer CO₂ capacity improvement after steam hydration. The pore volume in the size range of 4-30 nm was enhanced over that of the initial calcined sorbent, a result of steam reactivation. As expected, the impact breakage resistance of LC pellets declined significantly after hydration, similarly to limestone. Enlarged grain space in LC sorbents, as demonstrated in SEM images, appears to be responsible for this. However, superheating treatment under 510°C/100% CO₂ was employed for hydrated sorbents, and this clearly enhanced the strength of the sorbent particles. The impact

fragmentation extent of superheated reactivated LC was almost half that of hydrated LC. Furthermore, the strength of superheated reactivated limestone was almost comparable to that of the spent sorbent without reactivation. 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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Table 1. Composition of sorbents (wt. %) by XRF

Sample	CaO	Al ₂ O ₃	MgO	Fe ₂ O 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

LOI = Loss on ignition.

Table 2. Experimental conditions during the calcium looping tests

Temperature, °C	Calcination			Carbonation
	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
fluidising velocity, m·s ⁻¹		0.40		0.40

Table 3. BET surface area and BJH pore volume of LC and limestone (calcination at 950°C

pure CO₂)

Samples		S _{BET} , m ² ·g ⁻¹	V _{BJH} , cm ³ ·g ⁻¹
LC	1 st calcination	8.32	0.0404
	9 th calcination	2.69	0.0146
	hydration after 9 th	7.81	0.0345
limestone	1 st calcination	9.91	0.0662
	9 th calcination	1.31	0.0113
	hydration after 9 th	6.97	0.0308

Table 4. Hydration degree and cyclic conversion of CaO before and after hydration

Calcining temperature, °C	Limestone			LC		
	850	900	950	850	900	950
hydration degree	0.469	0.442	0.492	0.604	0.629	0.614
C_N before hydration	0.219	0.159	0.089	0.271	0.154	0.113
C_N 1 st after hydration	0.309	0.300	0.278	0.425	0.413	0.419
C_N 5 th after hydration	0.210	0.133	0.093	0.294	0.192	0.142

Table 5. Elutriations after 13 cycles for limestone and LC sorbent

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



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