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Effect of steam addition during carbonation, calcination or hydration on re-activation of CaO sorbent for CO₂ capture

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ABSTRACT

Keywords:

Calcium looping
Cyclic carbonation/calcination
CO₂ capture
Steam
Morphology changes

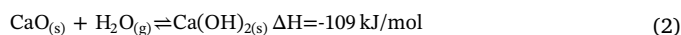
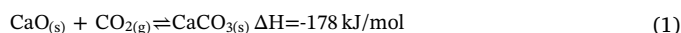
Calcium looping (CaL), based on cyclic carbonation/calcination using lime-based sorbents, is a promising technology for post-combustion CO₂ capture. An important obstacle of this technology is the decay of sorbent over multiple cycles. Steam re-activation is a potential approach to improve the sorbent reactivity, however, the effects of both *in-situ* high-temperature steam (in carbonator or/and calcinator) and *ex-situ* low-temperature steam (steam hydration in hydrator) are still a matter of debate. Here, a bubbling fluidised bed reactor was used to investigate three steam addition options: steam addition during carbonation stage, or during calcination stage, or intermediate steam hydration after each CaL cycle. A CaO sorbent was tested under varying steam concentrations up to 40 vol.% for 10 CaL cycles (carbonation: 650 °C, calcination: 900 °C). Compared to the dry condition, steam addition during carbonation and intermediate steam hydration were both found effective for CaO re-activation. For the former, the improved sorbent reactivity was mainly attributed to an increased pore volume enhancing the extent of carbonation in kinetic regime; while for the latter, the formation of cracks accelerated the rate of diffusion. Nevertheless, decreasing the hydration temperature was detrimental to sorbent reactivity due to enhanced sintering upon cooling. In case of steam addition during calcination, the sorbent was affected negatively or positively depending on the concentration of steam. At higher steam concentrations (20, 40 vol.%), the sorbent reactivity was significantly decreased due to sintering associated with larger pores and lower surface areas. Overall, steam addition during carbonation was recommended for sorbent re-activation.

1. Introduction

Recognizing the continuing global reliance on fossil fuels, CO₂ emission from fossil fuels combustion, such as coal-fired power plants, has become one major source of greenhouse gas emissions. The alarming impact of climate change becomes a powerful driving force for the developing guidelines, such as Kyoto Protocol and The Paris Agreement, to lessen the related environmental loads [1].

In the context of reducing CO₂ emission, a potential approach is to capture it from combustion systems followed by sequestration in underground geological formations or on the ocean floor, named, carbon capture and storage (CCS) [2,3]. Calcium Looping (CaL), based on reversible carbonation/calcination cycles of CaO-based sorbents, is one of the promising CCS technologies in post-combustion systems. The process involves the reaction of CaO with CO₂ from combustion flue gas or gasification syngas in a carbonator (see Eq. 1 forward), followed by regeneration of sorbent in a calcinator (see Eq. 1 backward). The CaO

sorbent is repeatedly cycled between the two reactors, which exhibits a number of advantages, such as: (1) high theoretical CO₂ capture capacity of 0.78 g(CO₂)/g(CaO) and fast reaction kinetics; (2) recycling of sorbent at lower energy penalty and operating cost; (3) relatively cheap and abundant CaO sorbent which could be derived from limestone [4,5].

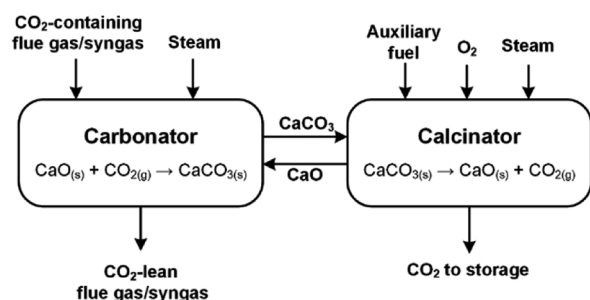


However, one drawback of the CaO sorbent is the decrease of CO₂ capture capacity upon iterated carbonation/calcination cycles. This has resulted in additional consumption of fresh sorbent to compensate for sorbent de-activation and accordingly, an increased overall cost of the CaL process [6,7]. Aspects which deserve consideration when designing CaL therefore, requires the improvement of sorbent reversibility for its extended use in industrial plants.

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(a) CaL process with presence of steam in carbonator or/and calcinator



(b) CaL process with steam hydration

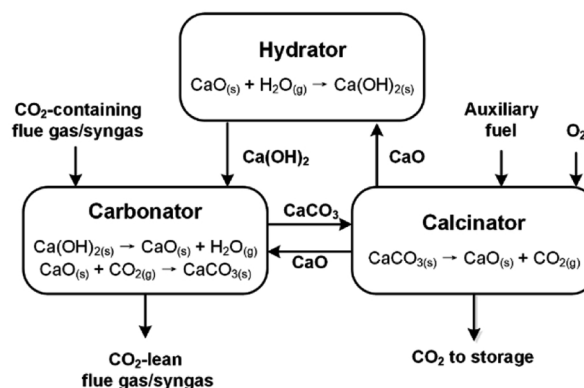


Fig. 1. Simplified schematic of CaL process with the addition of steam (a) in the carbonator or/and calcinator, and (b) in an external hydrator for steam hydration, as potential approach for sorbent re-activation.

The use of steam is a potential method to periodically re-activate the spent CaO sorbent. This can be achieved through two potential approaches: (i) by adjusting the concentration of steam in the carbonator or/and calcinator (see Fig. 1(a)); and (ii) by adding an external vessel between the carbonator and calcinator, within which steam hydration occurs (see Fig. 1(b)). The former approach considers that steam is usually present in the combustion flue gas (5–10 %) or gasification syngas (~20 %) to be treated in the carbonator [8], and also as a combustion product of the supplementary fuel in the calcinator [6]. This arises the possibility to utilise the high-temperature steam as an *in-situ* re-activation approach during the CaL process. While the temperature and pressure of the carbonator and calcinator are such that the formation of Ca(OH)_2 would not be thermodynamically favoured in these reactors, in the latter approach, a hydration reactor is installed for *ex-situ* re-activation of the spent sorbent retrieved from the calcinator (Eq. 2 forward). This is followed by Ca(OH)_2 de-hydration as the sorbent from the hydrator is reinjected into the carbonator (Eq. 2 backward), the recrystallisation of the sorbent has the potential to increase its reactivity [9].

Based on existing works there is a consensus that the presence of steam in the CaL process may significantly impact the sorbent performance; however, the effects and mechanisms of steam on the reactivity of CaO sorbent are still a matter of debate. Concerning the effect of steam addition during carbonation, most studies reported an improved sorbent performance, but there are studies to the contrary. For example, Manovic et al. [10] found that the addition of 15 % steam during carbonation has a beneficial effect on CO_2 capture of a CaO-based synthetic sorbent. However, Lu et al. [11] reported a deleterious effect of steam based on similar reaction conditions. In some studies, the enhancement of sorbent reactivity was attributed to the increase of carbonation rate in fast-kinetic stage [12–16]. This was explained by the steam catalysis effect between CaO and CO_2 [12–14], or the formation of transient Ca(OH)_2 which is more reactive than CaO [15,16]. The findings were contrary to another group of studies showing that steam just enhanced carbonation at the diffusion-controlled stage, whereas there was little influence on the kinetic stage [17–19]. The enhanced carbonation by steam addition could also probably be ascribed to OH^- formation from H_2O dissociation [20].

Regarding the effect of steam addition during calcination, several studies reported an improvement of the sorbent reactivity [8,21–23]. Donat et al. [8] showed that steam injection during calcination enhanced CO_2 capture at concentration up to 1% with no significant improvement thereafter. However Chou et al. [21] found that a higher steam concentration up to 80 % continued to enhance the sorbent reactivity. The increased capture capacity was due to a shift from smaller to large pores, possibly eliminating the trigger time retard in the fast-

kinetic stage and increasing carbonation rate in the diffusion regime. These findings contrast with a few works of a negative impact of steam which enhanced sorbent sintering during calcination, resulting in a decreased specific surface area for CO_2 capture [6,13,24]. Yancheshmeh et al. [13] in turn suggested that the positive effect of enhanced CO_2 diffusion through large pores and the negative effect of lower surface area can reach a trade-off. Only at a higher steam concentration (e.g. 9.5 %), the intensified sintering was sufficient to develop a stable sorbent structure for increased CO_2 capture.

Otherwise, steam hydration is also proven to be a feasible method of re-activating the CaO sorbent. The mechanism of enhancement has been under discussion: most studies suggested the development of particle pore structure [23,25,26], while Anthony et al. [27] mentioned that H_2O molecules penetrated the product layer more readily over that of CO_2 and resulted in a large increase of the reaction surface. Based on existing studies, the effect of steam hydration is dependent on several operating parameters, such as hydration temperature, duration and steam concentration. Blamey et al. [28] found that, at temperature ranges of 200 – 400 °C, decreasing hydration temperature favoured the increase of hydration extent, which subsequently led to a higher carbonation conversion. Instead, Rong et al. [24] reported that the sorbent hydrated at 300 °C was more reactive over that conducted at 200 °C, probably because the latter underwent a longer cooling residence time that led to more severe sintering. The authors also claimed that hydration temperature of 500 °C would worsen the sorbent reactivity than the case without hydration, due to thermodynamic constraint of Ca(OH)_2 formation at higher temperature. As can be summarised from the existing works [9,25,29,30], the optimal steam hydration temperature should consider a trade-off between kinetics constraints on one hand, which pushes towards a higher temperature; and on the other hand, the thermodynamic constraint calling for a lower temperature. Regarding the effect of hydration duration, Coppola et al. [25] reported that increasing the hydration duration was associated with larger degree of hydration and more extensive cold sintering of the sorbent. These two competitive effects led to non-monotonic trend of sorbent properties versus hydration duration: the sample hydrated for 30 min was the most micro- and mesoporous; while the sample hydrated for 60 min was more reactive towards CO_2 capture and was less prone to fracture. The hydration steam concentration also has a strong effect on re-activation performance. Often the largest improvement of sorbent reactivity came at the highest concentration of steam added [24,31]. However this has to be balanced with the cost of steam consumption based on economic grounds [31].

To facilitate industrial applicability of the CaL process, there is a need to recommend an optimal option for re-activating the spent sorbent. However such works have received only limited attentions.

Champagne et al. [32] studied the influence of steam injection during both calcination and carbonation and found that steam had a greater impact on sorbent reactivity for carbonation than for calcination. Li et al. [23] claimed that steam activation in calcination and carbonation processes and hydration treatment were all effective, and they suggested the use of these three ways in an improved CaL process. Overall current studies are not sufficient and more work is required to better address this aspect.

Accordingly, this study reports on re-activation of spent sorbent by steam addition. CaL experiments were carried out using a CaO sorbent in a lab-scale fluidised bed reactor. The influence of three steam addition options was examined, which in detail included: steam addition during carbonation stage, steam addition during calcination stage, and intermediate steam hydration after each iterated CaL cycle. The aim is to clarify the relationships among exposure to steam, sorbent microstructural properties, morphology changes and CO₂ capture. The results can help further develop CaL process and improve reactivity of calcium-based sorbents.

2. Experimental section

2.1. Experimental materials

Reagent-grade CaO, received at 99 % purity and with a calcination weight loss lower than 2%, was used. After being sieved, a fraction of 430–850 µm was selected. Since CaO is hygroscopic, it was dried at 105 °C for 12 h and stored in a sealed tank prior to experiments.

2.2. Apparatus and experimental procedures

A laboratory bench-scale bubbling fluidised bed (BFB) was used to simulate continuous operation of CO₂ capture process. This was achieved by periodically changing the reaction temperatures and inlet gases between the requirements for carbonation and calcination. A schematic of the system is depicted in Fig. 2. The furnace was electrically heated, with the main reaction chamber 600 mm in height and

60 mm in inner diameter. The temperature was measured by ten vertically positioned K-type thermocouples. The target temperature was controlled by a thermocouple placed close to the middle of the reactor. Two frits were equipped respectively on the bottom and top of the furnace. The bottom one was to hold the fed sample, and the top one was to prevent sample escaping from the reactor. The reactant gases, CO₂ and N₂, were fed from the bottom of the furnace by a mass flow controller. Steam was supplied by a steam generator at 150 °C and its flow was controlled at 0–1 NL/h. For all experiments, the total inlet gas flow was kept constant at 0.6 Nm³/h. The exit gas was dried by passing through a series of impingers immersed in an ice-water bath before evacuating to the atmosphere. Throughout the test, the CO₂ concentration in the exhaust gas was measured regularly to ensure the completion of carbonation and calcination reactions.

The aim of this study is to investigate the effects of steam addition during different stages of the CaL process. One sample (*Dry condition*) with no steam present was set as a base-case comparison for the other tests. The experimental conditions are detailed in Table 1. For each test, the cyclic CaL was repeated for 10 times. The carbonation was conducted at 650 °C for 30 min and the calcination was performed at 900 °C for 10 min. Three levels of steam (10, 20 and 40 vol.%) were chosen to be evaluated. Steam concentrations exceeding 40 vol.% were not considered because the reaction temperature cannot be kept stable under these conditions.

The experimental procedures are presented briefly as follows. The test was started by preloading with ~30 g of CaO. The furnace was heat up from ambient temperature to 650 °C at 20 °C/min under 100 vol.% N₂. Once the pre-set temperature reached, the gas stream was switched to carbonation (20 vol.% CO₂, 0/10/20/40 vol.% steam and N₂ balance) for 30 min. Thereafter the temperature was increased to 900 °C under 100 vol.% N₂, followed by calcination (0/10/20/40 vol.% steam and N₂ balance) for 10 min. So far these combined steps accounted for one CaL cycle. Then, a second cycle started: the furnace was cooled naturally in N₂ to 650 °C for carbonation, which was kept for 30 min before reheating to 900 °C for calcination.

A number of experiments considered an intermediate steam

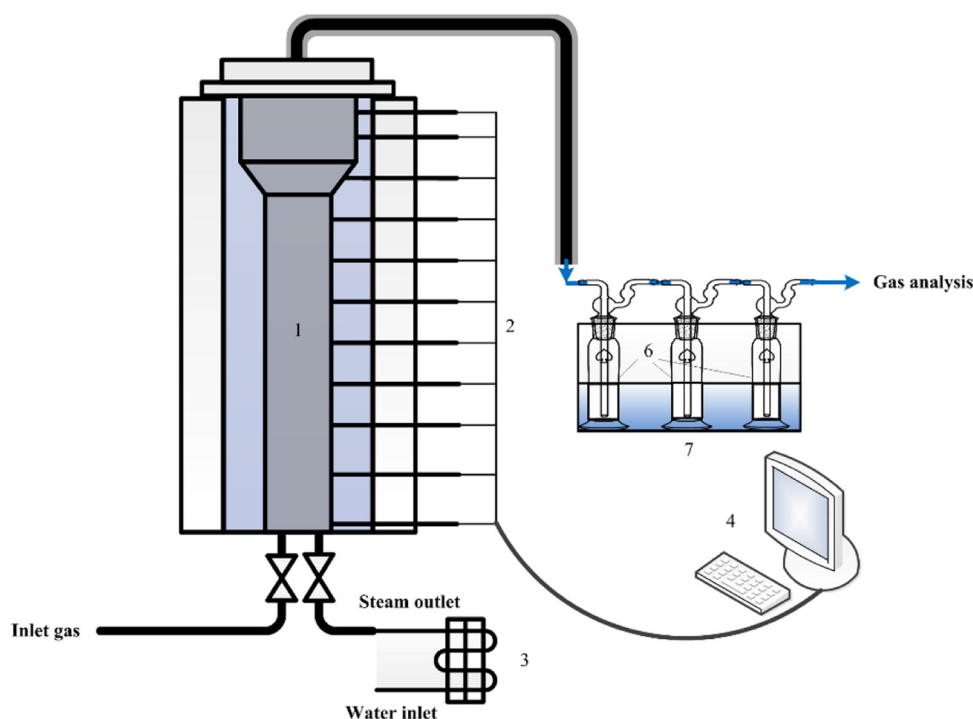


Fig. 2. Schematic diagram of the bubbling fluidised bed reactor: 1, reaction chamber; 2, thermocouples; 3, steam generator; 4, controller; 5, outlet pipe with heating tape; 6, empty impingers for steam condensation and removal; 7, ice-water bath.

Table 1

Definition and operating setup of samples used in different experimental runs.

Sample	Carbonation			Calcination		Intermediate steam hydration			
	CO ₂ (vol.%)	Steam (vol.%)	N ₂ (vol.%)	Steam (vol.%)	N ₂ (vol.%)	Steam (vol.%)	N ₂ (vol.%)	Temperature(°C)	Duration (min)
<i>Dry condition</i>	20	0	80	0	100				
<i>Carbonation_10 %</i>	20	10	70	0	100				
<i>Carbonation_20 %</i>	20	20	60	0	100				
<i>Carbonation_40 %</i>	20	40	40	0	100				
<i>Calcination_10 %</i>	20	0	80	10	90				
<i>Calcination_20 %</i>	20	0	80	20	80				
<i>Calcination_40 %</i>	20	0	80	40	60				
<i>Hydration_10 %</i>	20	0	80	0	100	10	90	300	10
<i>Hydration_20 %</i>	20	0	80	0	100	20	80	300	10
<i>Hydration_40 %</i>	20	0	80	0	100	40	60	300	10
<i>Hydration_200C</i>	20	0	80	0	100	20	80	200	10
<i>Hydration_400C</i>	20	0	80	0	100	20	80	400	10
<i>Hydration_20min</i>	20	0	80	0	100	20	80	300	20
<i>Hydration_30min</i>	20	0	80	0	100	20	80	300	30

Table 2

BET surface area and BJH pore volume of the CaO sorbent under different dry conditions.

Sample	Reaction condition			BET surface area, m ² /g	BJH pore volume, cm ³ /g
	Carbonation	Calcination	Number of cycles		
<i>Fresh CaO</i>	–	–	–	2.37	n.d. ^b
<i>DryCycle_5</i>	650 °C, 20 vol.% CO ₂ (N ₂ balance), 30 min	900 °C, 100 vol.% N ₂ , 10 min	5	3.24	2.22 × 10 ^{−2}
<i>DryCycle_10^a</i>			10	3.04	1.75 × 10 ^{−2}
<i>DryCycle_20</i>			20	2.09	1.48 × 10 ^{−2}
<i>Calcination_1000C</i>		1000 °C, 100 vol.% N ₂ , 2 h	1	2.02	n.d. ^b

^a The *DryCycle_10* sample refers to the same sample of *Dry condition* in Table 1.^b The pore volume of the *Fresh CaO* and *Calcination_1000C* samples cannot be detected with the equipment used, which is likely due to the existence of very large pores (macropores) in these samples.

hydration process after each CaL cycle. The furnace was cooled to target temperature (200/300/400 °C) using 100 vol.% N₂ after the last calcination stage, and then maintained for 10/20/30 min under a given steam concentration (0/10/20/40 vol.% steam and N₂ balance). Thereafter the furnace was reheated to 650 °C in N₂, prepared for the next CaL cycle.

2.3. Product characterization

A thermogravimetric analyser (TGA, LABSYS T6 Evo) measured the CO₂ capture capacity of different spent CaO samples. The experimental procedures for the TGA test were kept consistent as in the BFB reactor: the reactor was heated at a rate of 20 °C/min (100 vol.% N₂) to 650 °C for carbonation for 30 min (20 vol.% CO₂, N₂ balance). This was followed by heating the reactor to 900 °C (100 vol.% N₂) for calcination for 10 min (100 vol.% N₂) before cooling down to room temperature. The weight variation of the CaO sorbent was recorded. Carbonation conversion efficiency (CCE, %) was used to determine the reactivity of the sorbent, which was defined as the number of molar of CO₂ captured per molar of CaO loaded in the reactor, according to Eq. 3:

$$\text{CCE (\%)} = \frac{m_1 - m_0}{m_0} \frac{M_{\text{CaO}}}{M_{\text{CO}_2}} \times 100 \quad (3)$$

where, m_1 and m_0 stands for the mass of the sample after carbonation in TGA and the initial mass of the loaded sample, respectively; M_{CaO} and M_{CO_2} is the molar mass of CaO and CO₂, respectively. For each sample, the CCE value was measured after 10 CaL cycles in the BFB reactor. A few experiments also extracted the CaO samples after the 2nd, 4th, 6th and 8th CaL cycle, the aim was to examine the variation of CCE as a function of the number of CaL cycles.

The sorbent morphology was measured by scanning electron microscope (SEM). The specific surface area, pore volume and pore size

distribution of the samples were determined via nitrogen adsorption/desorption analysis using a Micromeritics analyser (ASAP 2010 type).

3. Results

3.1. Course of cyclic carbonation/calcination under dry conditions

A number of preliminary tests without steam addition were performed to identify main mechanisms responsible for CaO decay, in particular, as benchmark to examine different steam addition alternatives. Two types of tests were conducted in the BFB reactor: a longer series of CaL cycles (up to 20 cycles), and a deeper sintered sorbent (calcination at a higher temperature and longer duration). The experimental setup was the same as that of the *Dry condition* sample described in Table 1. This was except for the *Calcination_1000C* sample, of which the CaL was conducted for only one cycle, with calcination at 1000 °C for 2 h (100 vol.% N₂).

The structural properties of the sorbent associated with BET and BJH measurement are shown in Table 2. It is noted that the non-detectable of pore volume for the *Fresh CaO* and *Calcination_1000C* samples were due to the limitation of equipment used, which was likely due to the existence of very large pores (macropores) in these samples. The surface area and pore volume of CaO after 5 cycles (*DryCycle_5*) were higher compared to the fresh sorbent. This indicated that pores were created upon CO₂ release during calcination, which led to structural rearrangement of particles during initial CaL cycles [5,13,33]. Both the surface area and pore volume of the sorbent then experienced a continuous reduction with increasing CaL cycles up to 20 times. This indicated that the closure of reactive pores, which occurred during cyclic CaL and did not re-open, should be an important reason responsible for the decay of CaO. The morphological study with SEM supported this phenomenon (Fig. 3). The fresh CaO particles exhibited irregular

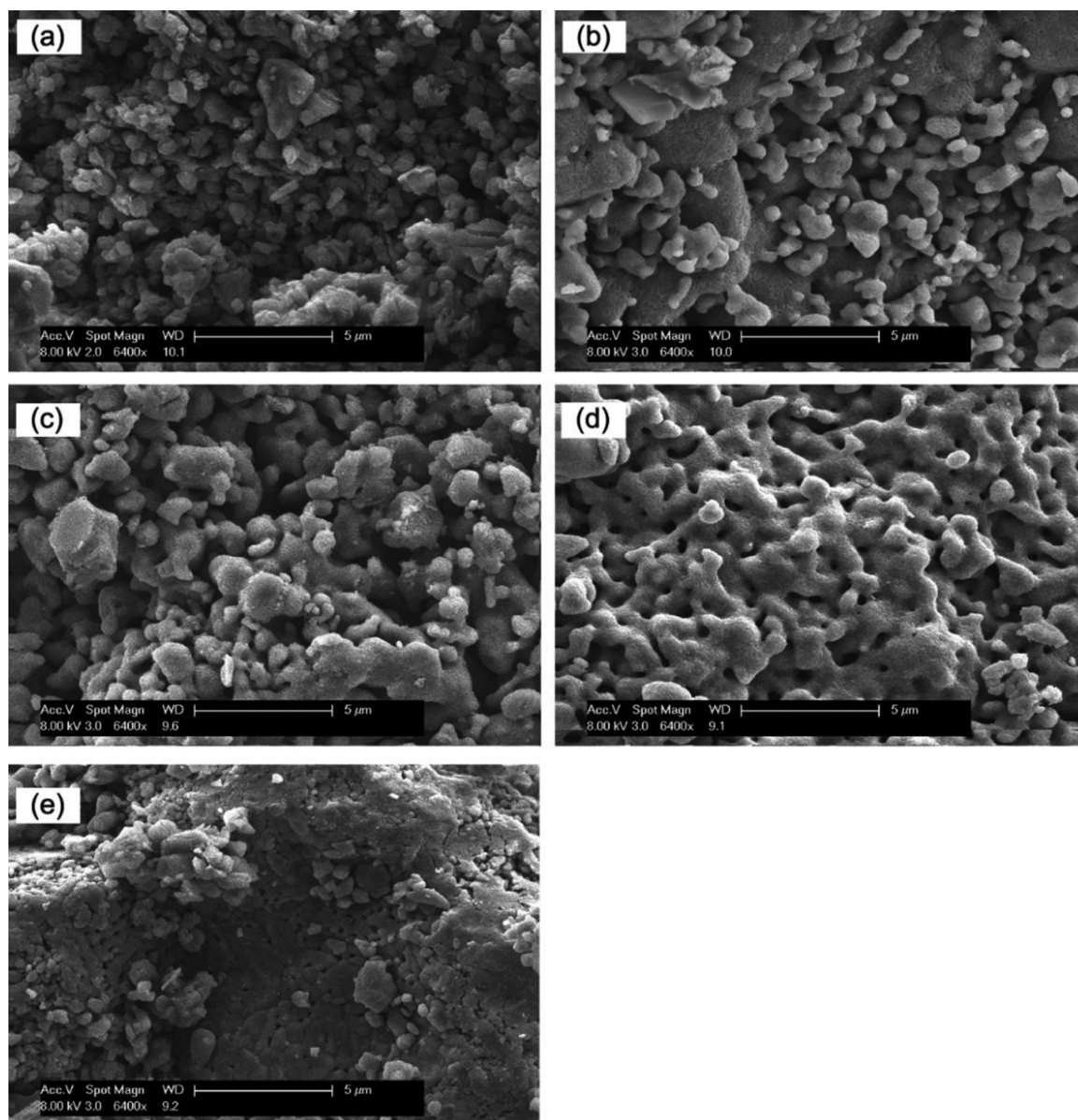


Fig. 3. SEM images of (a) *Fresh CaO* sample; (b) *DryCycle_5* sample; (c) *DryCycle_10* sample; (d) *DryCycle_20* sample; (e) *Calcination_1000C* sample.

shapes, their active surfaces were quite porous and rough. Fig. 3(b) showed that the surface of particles after 5 repeated cycles (*DryCycle_5*) appeared smoother. With increasing number of CaL cycles, some particles were agglomerated, indicating a loss of fine structure and decrease of sorbent reactivity. Only a number of large pores were observable on the outer surface of the *DryCycle_20* sample (Fig. 3(d)). The results were explained by Lysikov et al. [34] as the CaO degradation mechanism. Over the course of cyclic adsorption and decomposition reactions, the necks between adjacent CaO grains become thick and reinforced, which lead to pore blocking and a decreased conversion of the subsequent carbonation reaction. The amount of unreacted CaO increases with repeated cycles, finally a rigid unreactive outer layer of the CaO sorbent is formed.

Table 2 also shows that increasing the calcination temperature to 1000 °C for 2 h (*Calcination_1000C*) seriously deteriorated the structure of sorbent. Despite that the CaL was repeated for only once for this sample, its surface area and pore volume were even lower than the *DryCycle_20* case. SEM picture (Fig. 3(e)) confirmed a relatively compact and flat surface of this sample, while visible pores were not found. The aggregation of particles indicated severe sintering of the sorbent,

which clearly showed that sintering was also a significant cause of CaO decay. Given that CaCO_3 has a lower Tammann temperature of 524 °C and is more readily sintered than CaO (Tammann temperature of 1170 °C), sintering occurs mainly during the calcination process [35]. A higher calcination temperature and longer calcination duration thus would accelerate sintering, which lead to sharp decrease in the surface area and porosity of the CaO sorbent.

3.2. Effect of steam addition during cyclic carbonation/calcination

Experiments were conducted for three steam addition options: injecting steam during carbonation step, during calcination step, or intermediate steam hydration after each CaL cycle. Fig. 4 compares the effect of steam addition (20 vol.%) on the CCE of CaO through 10 CaL cycles. Based on the results the addition of steam showed a positive effect in enhancing the sorbent reactivity for the *Carbonation_20 %* and *Hydration_20 %* samples. When steam was added during carbonation a significant 43 % increase in CCE was observed after the 2nd carbonation in comparison to the base-case (*Dry condition*). The final CCE reached 18.6 % after 10th cycle, about 25 % higher than that of the *Dry*

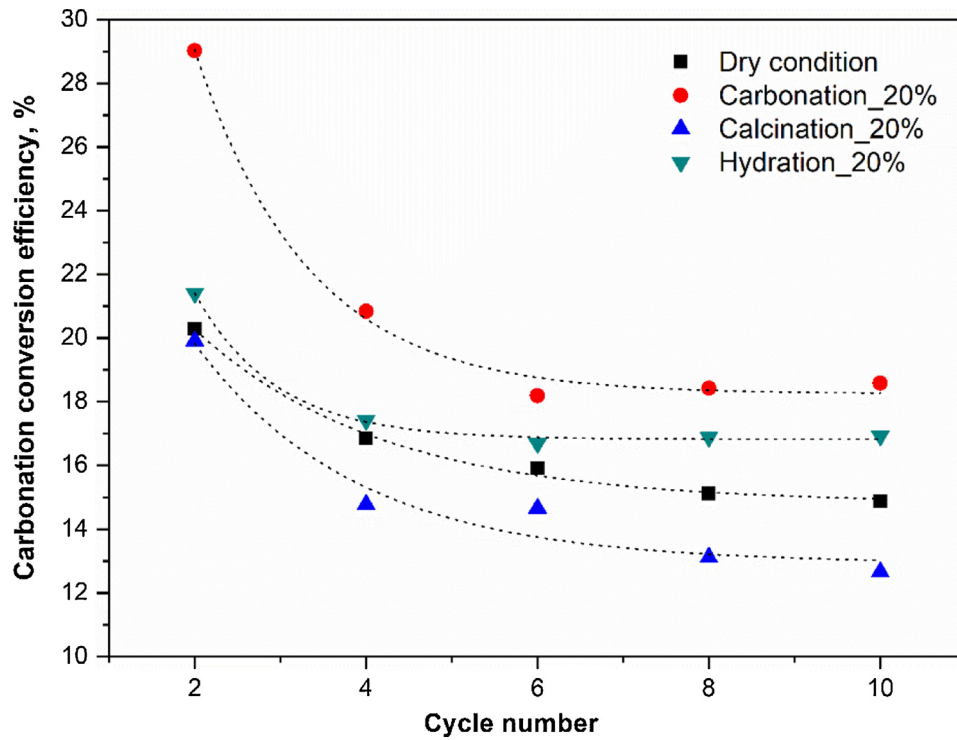


Fig. 4. Carbonation conversion efficiency of CaO sorbent as a function of the number of CaL cycles under different steam addition options.

condition sample. A similar trend was found for the *Hydration_20 %* case. The decay of sorbent was effectively restrained after the 6th cycle and the conversion was then stabilised at around 17 %, which was 14 % higher than the *Dry condition*. On the contrary, the CCE of the *Calcination_20 %* case dropped rapidly from 19.9 % after the 2nd cycle to 12.7 % after the 10th cycle, the final conversion was 15 % lower than the *Dry condition*.

Fig. 5 demonstrates the CCE of the sorbent after 10 CaL cycles under various steam addition conditions. The results extended the findings in Fig. 4 that the positive effect of steam injection during carbonation or steam hydration increased with steam concentrations. Compared to the *Dry condition* case, the CCE was increased by 12 %, 25 % and 38 %, for respectively 10, 20 and 40 vol.% of steam addition during carbonation. The effect of intermediate steam hydration was less pronounced; a higher CCE among these samples was found for the *Carbonation_40 %* sample, reaching 20.5 %. On the contrary, the sorbent reactivity was considerably decreased with increasing steam addition during calcination. The CCE of the *Calcination_10 %* sample experienced an increment to 16.8 %, however, further increase in steam resulted in a rapid drop of CCE. The CCE of the *Calcination_40 %* sample reached only 10.7 %, which was 28 % lower than the *Dry condition*.

Within the steam hydration temperature range of 200–400 °C in this experiment, the reactivity of CaO enhanced monotonously with increasing hydration temperature. The CCE of the *Hydration_400C* sample reached 19.5 %, which was 13 % and 16 % higher than the samples hydrated at 300 °C (*Hydration_20 %*) and 200 °C (*Hydration_200C*), respectively. The effect of steam hydration duration was marginal, as the samples hydrated for 10, 20 and 30 min showed quite comparable CCE values of 16.8–16.9 %.

3.3. Analysis of CaO reactivity under different steam addition conditions

Based on the results it is clearly that steam has an either positive or negative effect on the CaL process, depending on how it is added into the system. To better understand the mechanisms of steam, the evolution of carbonation reaction profile, pore structure, and surface morphology of the sorbent were analysed. The results are detailed as

following.

3.3.1. Effect of steam addition during carbonation

Fig. 6 presents the carbonation conversion profile versus reaction time performed on CaO sorbent after the 10th cycle in the BFB reactor, which was detected by the TGA tests. The relative performance was consistent throughout all 10 cycles so that other cycles are not shown here.

As well discussed in the literature [18,36,37], the reaction between CaO and CO₂ proceeds along two principal rate controlling stages: an initial fast carbonation stage controlled by kinetics of heterogeneous surface reaction, followed by a diffusion stage, which is much slower due to the formation of CaCO₃ product layer on the outer surface of the CaO particles. Fig. 6(a) shows the condition when steam was added during carbonation. The curves indicated that compared to the *Dry condition* case, both the duration and extent of fast-kinetic stage were higher when steam was present during carbonation, and, this effect was more pronounced with an increased steam concentration up to 40 vol. %. The prolonged fast-kinetic stage can conclude an improved morphology of the sorbent to retain more “reactive” surface area [32,36]. This was confirmed by comparing the BET surface area and BJH pore volume of different samples (Table 3). Both the sorbent surface area and pore volume were significantly increased when steam was added during carbonation. The increased sorbent pore volume was effective in retarding carbonation into the diffusion-controlled reaction regime [21]. Siriruang et al. [38] and Liu et al. [39] reported that the enhanced reactivity of CaO by steam during carbonation was mainly ascribed to the formation of Ca(OH)₂, as the reactivity of Ca(OH)₂ is much higher than CaO. According to the thermodynamic equilibrium [40] (Eq. 4), the equilibrium partial pressure of steam at 650 °C equals to 1.14 MPa. Although Ca(OH)₂ would not be stable at current temperature and steam partial pressure, it may react as an important intermediate to enhance carbonation reaction through Eqs. 5 and 6. The transient formation and decomposition of Ca(OH)₂ may also promote the structural rearrangement of the sorbent [13], leading to the development of a higher pore volume.

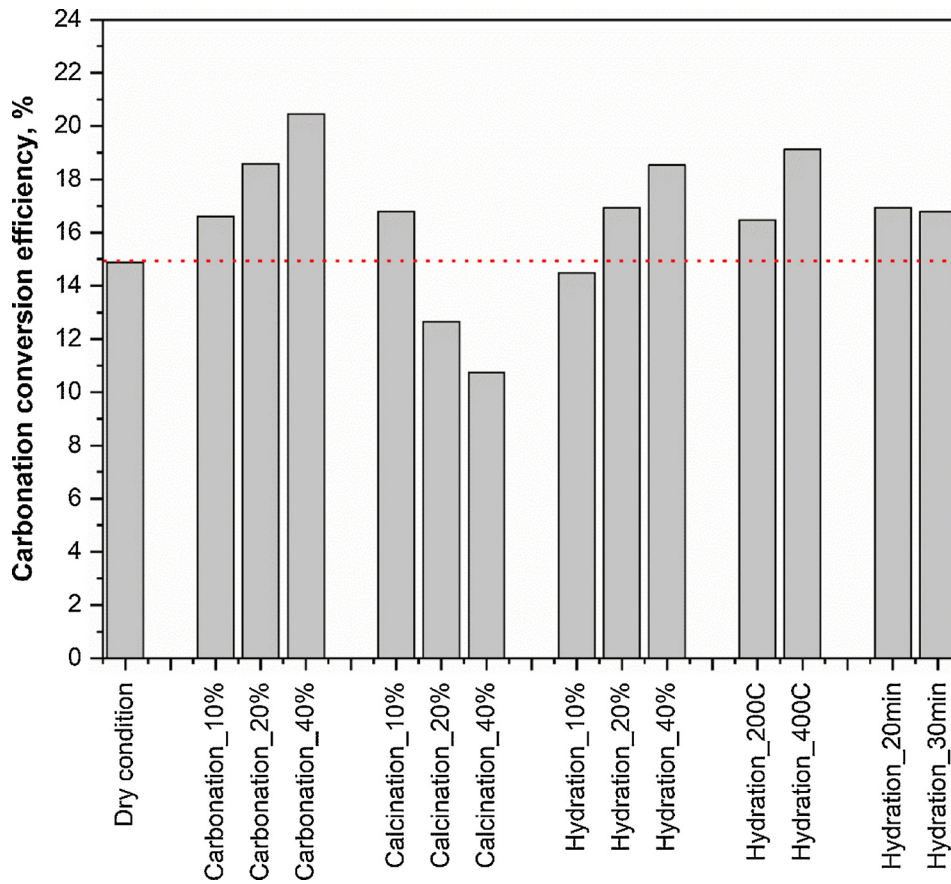


Fig. 5. Carbonation conversion efficiency of CaO sorbent under various steam addition conditions after 10 CaL cycles. Definition of each sample was detailed in Table 1.

$$P_{\text{H}_2\text{O}}^* = 9 \times 10^{11} \times \exp(-12531.5/T) \text{ Pa} \quad (4)$$



Fig. 6(a) also revealed that the presence of steam during carbonation had no influence on the fast carbonation reaction rate. This result was inconsistent with Yancheshmeh et al. [13], who found an increased fast-kinetic rate with the addition of 2.3–9.5 % steam during carbonation due to the steam catalysis effect. In addition, Liu et al. [39] and Manovic and Anthony [41] reported an enhanced solid-state diffusion, which was not seen in this study. A possible explanation may be due to the difference in experimental setup. In our study, steam was added during cyclic CaL in the BFB reactor, while its effect on the reactivity of the spent sorbent was determined by subsequent TGA tests. No steam was added in the TGA apparatus. This indicated that steam addition during carbonation may influence the kinetic rate and/or diffusion resistance; however, these findings could not be observed here. The overall effect of steam during carbonation had resulted in an increased surface area and pore volume, thus improving the CCE of the CaO sorbent with growing steam concentrations.

3.3.2. Effect of steam addition during calcination

The effect of steam addition during calcination with varying concentrations is shown in Fig. 6(b). The results indicated that steam addition during calcination mainly influenced the sorption kinetics. 10 vol.% steam showed an elevated reaction rate of the fast-kinetic stage, and thus, an increased overall CCE. By contrast, the rate and duration of fast carbonation reaction were both decreased at steam concentrations of 20 and 40 vol.%. By comparing the morphological changes of the sorbent, it is clear that an increasing steam during

calcination led to a significant loss of pore volume (Table 3) and an enlarged average pore size (Fig. 7) over the *Dry condition* sample. Previous studies [6,32] revealed that a higher partial pressure of steam in the calcinator would accelerate sorbent sintering. The agglomeration of particles and collapse of pore structure probably enhanced with an increasing steam concentration, as the pore size of the *Calcination_40 %* sample seemed to become relatively large (macropores) that beyond the thresholds of the analysing equipment.

Pores with a diameter of > 50 nm were relatively stable and less susceptible to pore blockage [8]. As reported by Champagne et al. [32], large pores facilitated the diffusion of CO₂ through the CaCO₃ product layers, where reactive CaO sites still existed, allowing for a higher carbonation conversion. According to our results, the addition of 10 vol. % steam during calcination did not affect significantly the sorbent surface area. The fast carbonation could thus proceed at a higher rate and the sorption capacity was improved. However, if continuously increasing the steam concentration, this positive effect of enhanced CO₂ diffusion brought by larger pores could not compensate the negative effect of reduced surface area under serious sintering [8,13]. Therefore, the CCE was decreased for the *Carbonation_20 %* and *Carbonation_40 %* cases.

3.3.3. Effect of steam addition during intermediate steam hydration

The effects of intermediate steam hydration were analysed by considering three aspects: steam concentration, hydration temperature, and hydration duration. The carbonation curves for sorbents hydrated at varying steam concentrations are compared in Fig. 6(c). Steam hydration exhibited a positive influence on increasing the diffusion reaction rate. The transition between the first, fast stage and the subsequent, diffusion stage was not obvious; however, the extent of the fast-kinetic stage was decreased compared to the *Dry condition* sample.

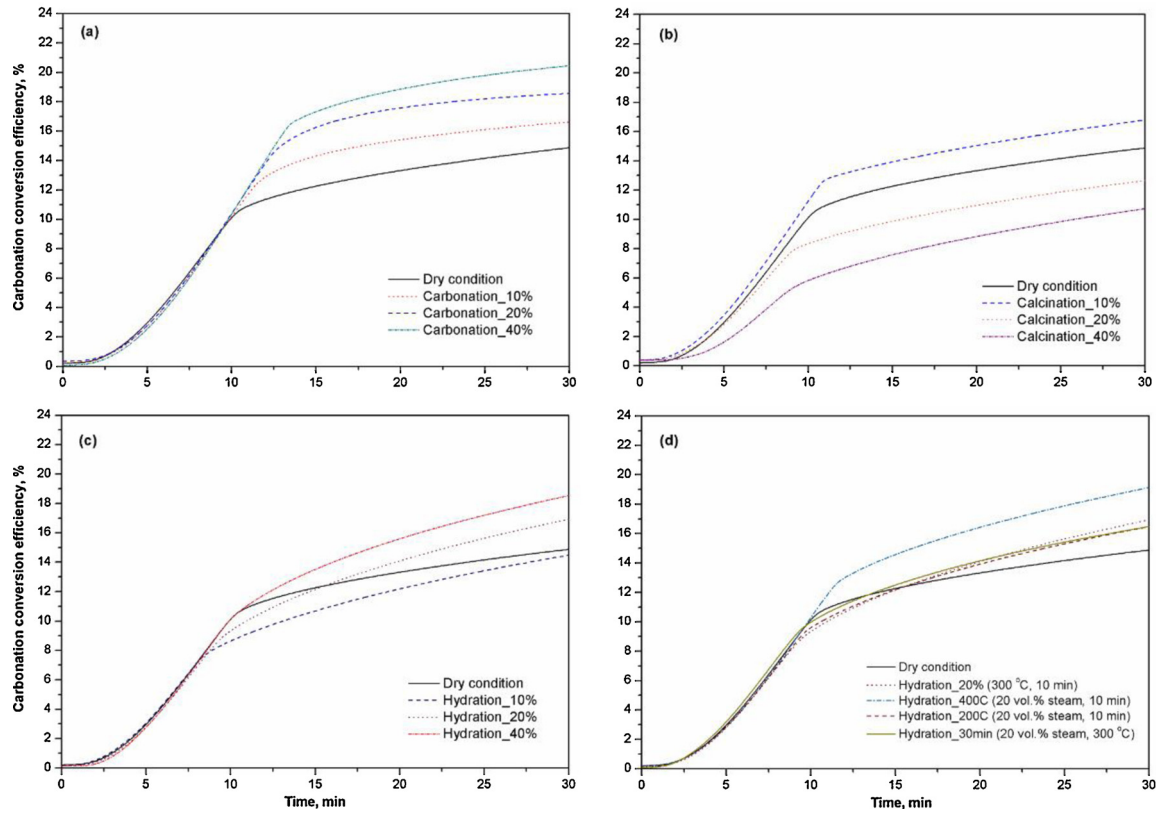


Fig. 6. Carbonation conversion efficiency versus reaction time performed on CaO sorbent after 10 CaL cycle in BFB reactor. The analysis was detected by TGA: (a) steam addition during carbonation with varying steam concentrations; (b) steam addition during calcination with varying steam concentrations; (c) intermediate steam hydration after each CaL cycle at 300 °C for 10 min with varying steam concentrations; (d) intermediate steam hydration after each CaL cycle at varying temperatures or durations.

Table 3

BET surface area and BJH pore volume of the CaO sorbent under different steam addition conditions.

Sample	BET surface area, m ² /g	BJH pore volume, cm ³ /g
Dry condition	3.04	1.75×10^{-2}
Carbonation_10 %	5.98	5.34×10^{-2}
Carbonation_20 %	7.13	7.99×10^{-2}
Carbonation_40 %	7.24	7.55×10^{-2}
Calcination_10 %	3.37	1.40×10^{-2}
Calcination_20 %	2.18	1.01×10^{-2}
Calcination_40 %	1.48	n.d. ^a
Hydration_10 %	4.31	1.54×10^{-2}
Hydration_20 %	7.58	3.03×10^{-2}
Hydration_40 %	17.56	4.94×10^{-2}
Hydration_200C	7.04	2.79×10^{-2}
Hydration_400C	13.40	1.86×10^{-2}
Hydration_20min	8.95	3.53×10^{-2}
Hydration_30min	7.96	3.10×10^{-2}

^a The pore volume of the *Calcination_40 %* sample cannot be detected with the equipment used, which is likely due to the existence of very large pores (macropores) in the sample.

The enhanced diffusion rate can be seen as a result of cracking, fissuring and other phenomena responsible for structure rearrangement of the sorbent [25], as inferred from the inspection of the SEM micrographs in Fig. 9(d). According to Eq. 4 mentioned previously, the formation of Ca(OH)₂ would be favoured when low temperature steam (200–400 °C) was added. The molar volume of Ca(OH)₂ and CaO is 33.7 and 16.9 cm³/mol, respectively; the larger value of the former would cause swelling of CaO particles during hydration. Subsequently during dehydration (i.e. heating to carbonation temperature), Ca(OH)₂ is decomposed to CaO and the recrystallisation of the sorbent has the

potential to maintain the reaction surfaces [24]. This was supported by the evolution of the particle pore structure (Table 3). The BET surface area of the hydrated samples was remarkably increased by 1.4–5.8 times than the *Dry condition* sample. Notably, steam hydration did not show great effect to develop “fine structure”, as the pore volume of the hydrated samples was 7–81 % lower than the cases when steam was added during carbonation. This indicated that the pore structure developed by hydration treatment was quite “external”. It is probably reasonable to assume that the increased sorbent surface area was mainly ascribed to the formation of those wider and deeper cracks, which led to an easier diffusion channel of CO₂ through the CaCO₃ layer, accelerating the diffusion rate of carbonation and finally a higher CCE value at 20 and 40 vol.% steam concentrations.

Contrarily, the CCE for the case of 10 vol.% steam hydration was slightly lower than the case without steam addition. This might be due to the sintering of sorbent during the cooling stage, that is, the sorbent needed to cool from 900 to 300 °C, which took ~55 min, before hydration treatment. As a result, the extent of fast-kinetic carbonation stage was decreased for all hydrated samples. This negative effect was in particular relevant to the *Hydration_10 %* case, which could not be compensated by the positive effect of enhanced CO₂ diffusion and finally the overall carbonation conversion of this sample was decreased.

Fig. 6(d) shows the effects of hydration temperature and duration on carbonation. When comparing *Hydration_200C*, *Hydration_20 %* (i.e. hydration at 300 °C) and *Hydration_400C* samples, one could observe that 400 °C hydration was more effective in maintaining the CO₂ capture capacity; while 200 °C and 300 °C showed a quite comparable performance with the latter being slightly better. The result was inconsistent with Rong et al. [24], who found that in the range of 300–500 °C a higher hydration temperature was detrimental to carbonation due to Ca(OH)₂ sintering. However in our experiment, it is

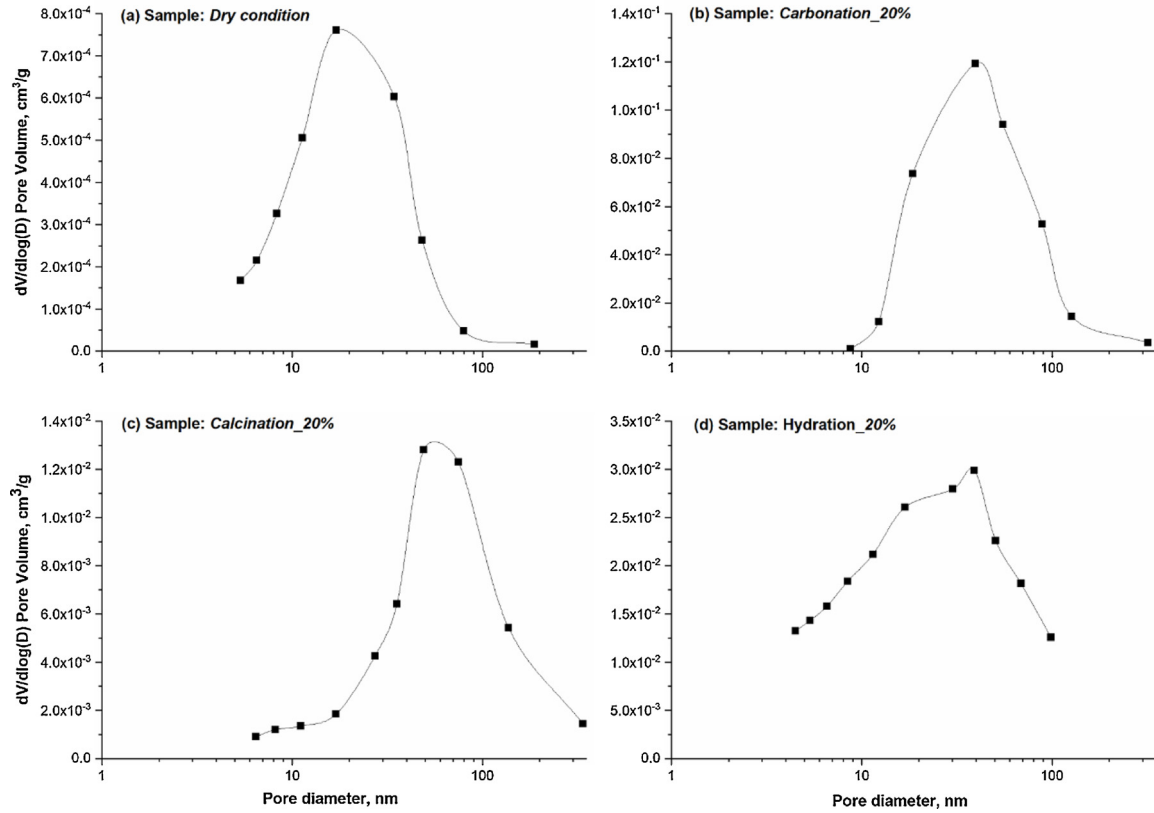


Fig. 7. Pore size distribution of CaO sorbent after 10 CaL cycles in BFB reactor: (a) *Dry condition* sample; (b) *Carbonation_20 %* sample; (c) *Calcination_20 %* sample; (d) *Hydration_20 %* sample.

more likely that the sintering of sorbent upon cooling, which took place prior to hydration treatment, had dominated the decay of sorbent. It took around 30 min for the BFB reactor to cool from 900 to 400 °C, which nearly one-half that time from 900 to 300 °C as mentioned previously. The findings were supported by structural evolution of the sorbent. As shown in Fig. 6(d), the extent of fast-kinetic stage of the *Hydration_400C* sample was higher than that of the *Hydration_20 %* and *Hydration_200C* samples, which indicated a larger surface area for carbonation. Table 3 confirmed higher surface area and pore volume of the *Hydration_400C* sample over those hydrated at lower temperatures (200 and 300 °C).

Fig. 6(d) also compares the cases of 10 min hydration (*Hydration_20 %*) and 30 min hydration (*Hydration_30min*). Results showed an insignificant difference between their CCE values, as well as the shape of the carbonation curves. As reported by Coppola et al. [25], competition effect existed between swelling/fissuring phenomena and cold sintering/molecular cramming. Both effects tended to increase with hydration duration. It is thus reasonable to assume that these two effects were equal-important and finally led to a comparable carbonation performance under varying hydration durations.

3.3.4. Sorbent structure and morphology changes

Fig. 8 shows the relations between the CCE of different sorbents and their pore structure. For samples that injecting steam during carbonation, the surface area and pore volume showed a correlation coefficient R^2 of 0.65 and 0.23, respectively, suggesting that both factors had a synergetic influence on the sorbent reactivity. For samples that injecting steam during calcination, the surface area was mostly responsible for the change of CCE ($R^2 = 0.99$), however, the pore volume also affected sorbent reactivity ($R^2 = 0.60$). On the contrary, the CCE of the steam hydrated samples was found only dependent on the surface area, while the correlation of pore volume was insignificant ($R^2 = 0.01$). The results accorded well with our previous deductions.

The surface morphologies of sorbent under different steam addition conditions were examined, with typical SEM images displayed in Fig. 9. The spent sorbent after 10 cycles with steam addition during carbonation (Fig. 9(a) and (b)) maintained higher porosity. The particle surface showed analogous morphology as the fresh sorbent (Fig. 3(a)), which verified the positive effect of steam during carbonation to improve the sorbent pore structure. As comparison, more sintered surface was observed in Fig. 9(c) when steam was added during calcination. The particles congregated severely to form aggregates, the morphologies were similar as Fig. 3(e). The transition from a rugged surface of the fresh sorbent to a smoother structure indicated the loss of surface area for CO₂ adsorption, which was consistent with the lower CCE of the *Calcination_20 %* sample presented in Fig. 5.

The morphologies of the sorbent experiencing hydration treatment are shown in Fig. 9(d)–(h). Fig. 9(d) observed several wide and deep cracks on the surface of *Hydration_20 %* sample, however this was not seen in Fig. 9(a). This morphology change might contribute to the reduced diffusion resistance of the *Hydration_20 %* sample as discussed previously. Fig. 9(e) further illustrated a porous structure of the *Hydration_20 %* sample, which proved the positive effect of steam hydration to maintain sorbent reactivity. However, Fig. 9(e) showed a smoother and aggregated surface than Fig. 9(b), which was consistent with their relevant CCE values. When comparing different hydration temperatures (Fig. 9(e), (f) and (g)), it is found that sorbent sintering in Fig. 9(f) (*Hydration_200C*) was more serious than Fig. 9(g) (*Hydration_400C*). This again supported that a longer cooling time was a principle cause of the decreased sorbent reactivity. Fig. 9(h) illustrated similar surface appearance as Fig. 9(e); this similarity of morphologies was also verified by relatively comparable CCE values (16.8 % vs. 16.9 %) of these two samples.

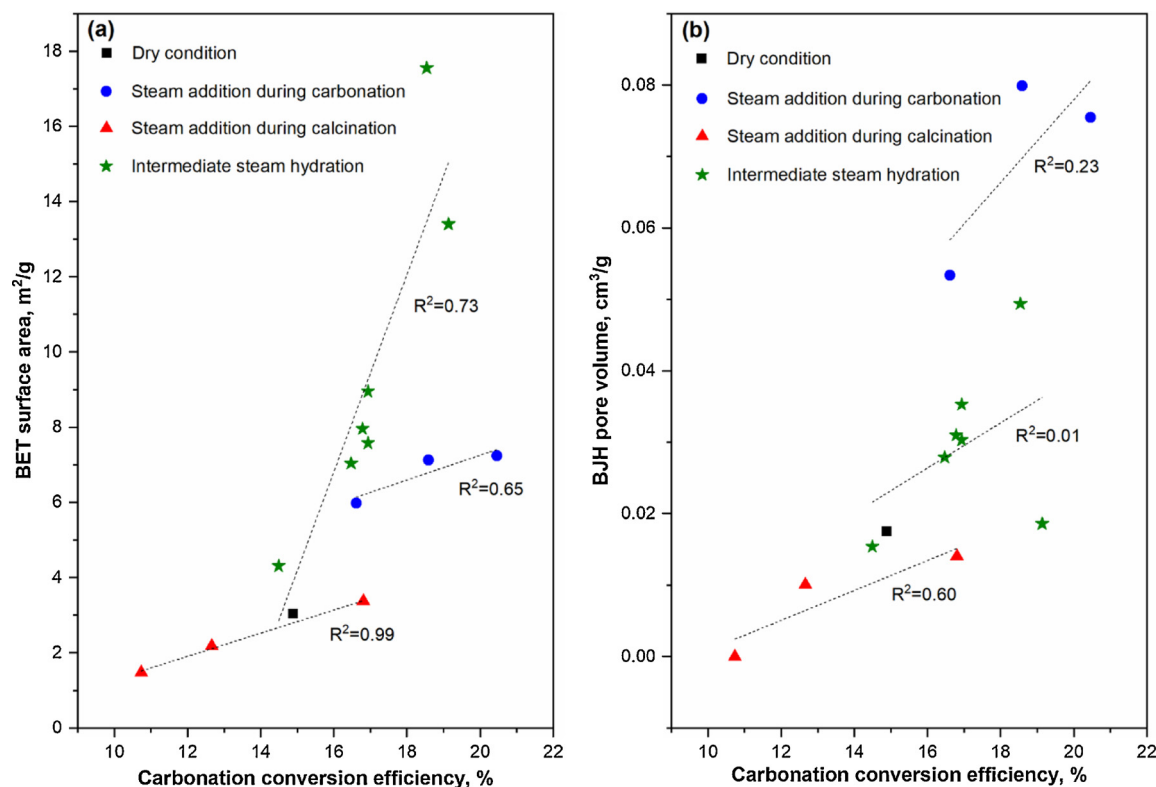


Fig. 8. Relations between carbonation conversion efficiency and (a) BET surface area; (b) BJH pore volume, for CaO sorbent under different steam addition conditions.

3.4. Discussions

In this work, the effectiveness of three steam addition options as a means to re-activate the CaO sorbent was compared. Based on the results, it is important to recommend a feasible approach for future scaled-up CaL application.

Experiments performed with steam addition during calcination were generally detrimental to the sorbent reactivity. Under such conditions, steam has been shown to significantly change the morphology of the sorbent, mainly as a result of sintering. Existing literature reported that the sintering of CaO-based sorbents mainly takes place via two mechanisms: thermal sintering and atmosphere-induced sintering [22]. It is therefore reasonable to infer that the sintering of CaO will be accelerated in the presence of high-temperature steam, relative to N₂. According to our results, the addition of steam during calcination is not recommended for CaO re-activation. In commercial operation, careful process control in the calcinator is necessary. Feasible strategies may include limiting steam concentration in the calcinator, limiting calcination temperature, etc., thus to avoid both thermal and atmosphere-induced sintering on sorbent reactivity.

The addition of steam during carbonation and intermediate steam hydration were both found effective for CaO re-activation. When the two options were compared, the former showed more remarkable enhancement in CO₂ capture. The improved sorbent reactivity was mainly achieved in the fast-kinetic carbonation stage (Fig. 6), which is of great significance for industrial applications. In contrast, steam hydration is less practical, as its positive effect was mainly in the diffusion-controlled stage. Particle fragility would be another challenge of the hydration treatment. Fig. 9(d) indicated that steam hydration was more prone to develop large and deep cracks. Existing literature [42,43] reported that these cracks tended to transform the re-activated sorbent into fines. This was verified by a comparison of the particle size distribution of different samples, which was conducted using mechanical sieving. Fig. 10 shows that the fractional mass of fine particles

(< 430 μm) for hydration treated samples (*Hydration_20 %* and *Hydration_30min*) was higher than the *Carbonation_20 %* and *Calcination_20 %* samples. This fragmentation tendency was enhanced with increasing hydration duration. The particle size distribution of the *Hydration_30min* sample was changed into a bimodal structure with an additional peak of fragments finer than 250 μm. Even if undesired, the results indicated difficulties for the use of hydrated sorbent, in particular for fluidised bed furnaces.

By considering the trade-off among sorbent reactivity, pore structure, fragmentation tendency, and simplicity of CaL process design, the addition of steam during carbonation is recommended for CaO re-activation based on this work. The sorbent reactivity increased monotonically with steam addition, reaching a maximum at 40 vol.% concentration. However, it cannot be concluded that 40 vol.% of steam is the optimal point. It is reasonable to infer that further increase in steam may continue to improve the reactivity of the sorbent or peak it somewhere. However, excessive steam feed may not be cost-effective in practical applications. The increase in steam flow can potentially cause difficulty in controlling the reaction temperature. In addition, given the energy required to generate high temperature steam, increasing steam supply may be detrimental to the overall process efficiency [44]. Overall, future work remains crucial to determine an optimal steam concentration, which can eventually strike a balance between sorbent reactivity and steam consumption.

The CaL technology is currently being developed with successful demonstrations up to 10 MW_{th} [45]. Therefore, a final consideration of this work is relating to the techno-economic performance of CaL process which is crucial to its future commercial deployment. It has been estimated that the CaL process imposes an efficiency penalty of 5–8 %, which is significantly lower than that of amine scrubbing (9.5–12.5 %), oxy-fuel combustion (8–12 %), or other commercially viable CCS technologies [46]. The CaL process also shows a preferable economic performance in terms of leveled cost of electricity (54.3–96 €/MW_{el}h), compared to chemical solvent scrubbing (65–89 €/MW_{el}h),

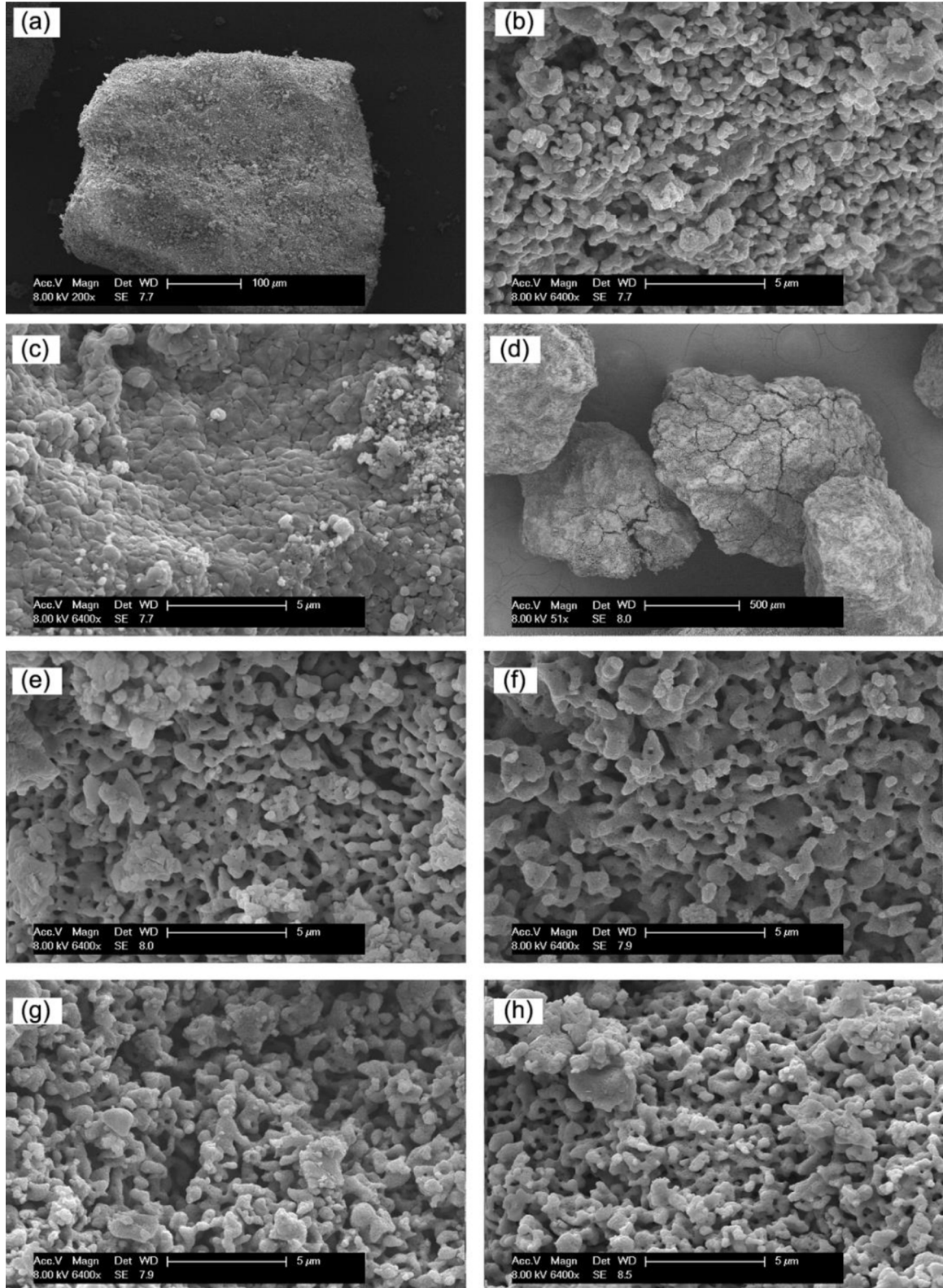


Fig. 9. SEM images of CaO sorbent after 10 CaL cycles under different steam addition conditions: (a) and (b) *Carbonation_20 %* sample; (c) *Calcination_20 %* sample; (d) and (e) *Hydration_20 %* sample; (f) *Hydration_200C* sample; (g) *Hydration_400C* sample; (h) *Hydration_30min* sample.

and oxy-fuel combustion (55–75 €/MW_eh). The industrial competitiveness of CaL process has been proven, hence, further developments of this technology will have to address the reduction of energy and cost penalties. Some of these possibilities have been proposed, such as:

- Recovering the high-quality heat available in CaL to increase power output [47]. The high operating temperature of both carbonator and calcinator, as well as the sensible heat of the output gas streams, enable significant heat recovery for electricity generation through a secondary steam cycle;

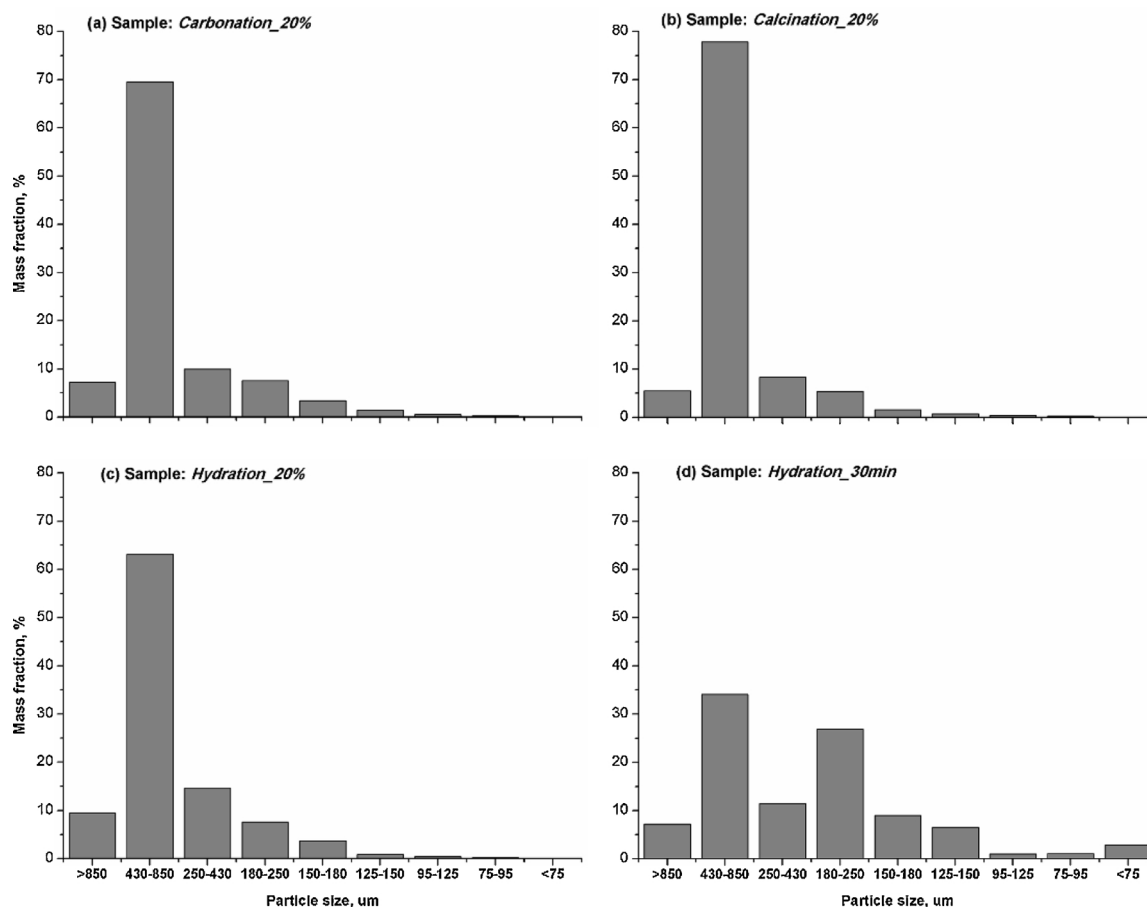


Fig. 10. Particle size distribution of CaO sorbent after 10 CaL cycles in BFB reactor: (a) *Carbonation_20 %* sample; (b) *Calcination_20 %* sample; (c) *Hydration_20 %* sample; (d) *Hydration_30min* sample.

- Increasing internal heat integration to minimise energy demand in the calcinator. An alternative is to exchange heat from the calcinator outlet to the carbonator outlet particles, thus to raise temperature of the sorbent fed to the calcinator and, consequently, reducing fuel and oxygen consumptions [48]; and
- Application of more durable sorbents to decrease efficiency and cost penalties [49]. Sorbents with higher average reactivity can diminish the solid circulation rate between the reactors, leading to a decrease in the heat penalty of the calcinator and a reduction in CO₂ removal cost.

The implementation of steam for sorbent re-activation can easily match these targets. Importantly, the required steam can be extracted from the secondary steam cycle with relatively low complexity and cost. This is verified by the study of Wang et al. [50,51] and Hanak et al. [52], who proved that CaL operates with a hydrator could reduce an efficiency penalty of 0.3–22.2 % than that of the conventional CaL process. Overall, steam re-activation is a viable option to improve sorbent performance. Yet there is still the potential to further reduce its efficiency penalty to below 5% points [45], as well as to improve the economic feasibility and attractiveness to the market.

4. Conclusion

The effect of introducing steam into CaL process on the reactivity of a CaO sorbent for CO₂ capture has been investigated in a fluidised bed reactor. The following conclusions were drawn from this study:

- (1) Carbonation in the presence of steam improved the reactivity of the

sorbent via enhancing the extent of the kinetic-controlled carbonation reaction. The carbonation conversion efficiency of CaO increased with steam concentration. The improved sorbent performance was mainly associated with the development of particle pore structural properties such as surface area and pore volume.

- (2) The effect of steam during calcination was influenced by the steam concentration. While the carbonation conversion efficiency increased with 10 vol.% steam addition after 10 CaL cycles, a concentration of 20 and 40 vol.% led to a negative effect on sorbent reactivity, due to the acceleration of sintering leading to lower surface area and larger pore size.
- (3) Intermediate steam hydration was generally effective on CaO re-activation, attributed to the formation/decomposition of Ca(OH)₂ for an improved diffusion rate of carbonation. The sorbent reactivity was decreased at lower hydration temperatures (e.g. 200 °C), because of the more severe sintering upon cooling. Hydration duration showed an insignificant effect on the sorbent reactivity.
- (4) For the given CaO sorbent, the addition of steam during carbonation is recommended as a more favourable CaO re-activation approach for the CaL process.

CRediT authorship contribution statement

Jun Dong: Methodology, Investigation, Writing - original draft. **Yuanjun Tang:** Validation, Writing - review & editing. **Ange Nzihou:** Supervision, Funding acquisition. **Elsa Weiss-Hortala:** Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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