



# Effect of steam on CaO regeneration, carbonation and hydration reactions for CO<sub>2</sub> capture



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## ABSTRACT

CaO sorbent is one of the most promising sorbents for CO<sub>2</sub> capture. However, the reactivity of CaO sorbent decreased rapidly with carbonation–calcination cycles. Steam activation is a feasible approach to improve the sorbent reactivity. In this study, the effects of steam on CaCO<sub>3</sub> calcination (CaO regeneration), CaO carbonation and CaO hydration were both investigated. Compared with pure CO<sub>2</sub> calcination atmosphere, introducing steam into calcination atmosphere enhanced CaCO<sub>3</sub> decomposition rate, which was because that (1) the partial pressure of CO<sub>2</sub> decreased; (2) the absorption of H<sub>2</sub>O by active site CaO\* weakened the binding ability between CO<sub>2</sub> and CaO\*; (3) the amount of heat-transfer between steam and CaCO<sub>3</sub> was higher. Lower decomposition temperature in steam/CO<sub>2</sub> calcination atmosphere resulted in lower sorbent sintering and higher sorbent reactivity. Besides, the carbonation reactivity of CaO sorbent was over doubled when steam was introduced into carbonation atmosphere, which was due to the formation of OH<sup>-</sup>. In CaO hydration reaction, sorbent particle pore structure was also developed by hydration treatment. The hydrated Ca(OH)<sub>2</sub> sorbent reactivity as well as cyclic reactivity of CaO sorbent was therefore enhanced.

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## 1. Introduction

An increase in the emission of greenhouse gas CO<sub>2</sub> from fossil fuel utilization intensifies global warming [1,2]. The emission of CO<sub>2</sub> mainly comes from coal-fired power plants [3]. The methods for CO<sub>2</sub> capture mainly contain pre-combustion capture, post-combustion capture, oxy-combustion capture and calcium chemical looping. Post-combustion capture is the most applicable method to be applied in current power plants reformation. CO<sub>2</sub> is usually absorbed from flue gas by chemical sorbents during post-combustion capture [4]. Among all potential sorbents, CaO-based sorbent can be used to cyclic capture CO<sub>2</sub> (Eq. (1)) [5,6], because of its wide sources, low-cost and relatively high CO<sub>2</sub> absorption efficiency [5,7].



However, the reactivity of CaO sorbent decreases with calcination–carbonation cycles [8]. Many researchers developed methods to enhance the CaO sorbent reactivity. Chen et al. [9] declared that sorbent had relatively high reactivity after several carbonation and calcination cycles when the sorbent was preheat treated. Li et al. [10] discovered that dolomite also produced CaO-based sorbent with high reactivity after acetic acid treatment. Besides, other researchers developed

methods to enhance sorbent reactivity by dispersing CaO on solid particle skeleton. For example, Li et al. [11] used this method to obtain Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorbent; Alfe et al. [12] used carbon–magnetite composites as CO<sub>2</sub> adsorbent and it showed a very high CO<sub>2</sub> uptake capacity.

Importantly, steam activation is also a good method to activate CaO-based sorbents [13–16]. In calcination step, introducing steam into calcination atmosphere can enhance the reactivity of CaO sorbent [17]. In carbonation step, even a small addition of 0.02 atm of steam could have a significant effect on the reactivity of CaO sorbent [18]. CaO can be used to capture CO<sub>2</sub> directly, or firstly hydrated to Ca(OH)<sub>2</sub> and absorbed CO<sub>2</sub> indirectly. The Ca(OH)<sub>2</sub> sorbent had a better performance for CO<sub>2</sub> capture [19,20].

However, both studies about steam activation just simply owed the reactivity enhancement to the developed sorbent pore structure through SEM analysis. Actual mechanism of the reactivity enhancement isn't clarified and there are still some arguments and different conclusions. It still needs to be deeply investigated how steam influence the sorbent reactivity both in CaO regeneration, carbonation and hydration processes. Firstly, heat and mass transfer in steam atmosphere may also influence the calcination or carbonation reaction, and its mechanism was investigated in this study. Secondly, we previously found that Ca(OH)<sub>2</sub> sorbent had a higher strength when it was generated from hydration reaction under high steam partial pressure [21]; in addition to the high strength, the reactivity (especially cyclic reactivity) of Ca(OH)<sub>2</sub> sorbent had great influence on CO<sub>2</sub> absorption efficiency, and it was also investigated in this study.

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## 2. Material and method

### 2.1. Material

In this study, CaCO<sub>3</sub> sample was used in calcination and carbonation experiments. Limestone sample was used in hydration and cyclic calcination-carbonation experiments. Chemical composition of limestone was shown in Table 1. CaCO<sub>3</sub> sample was ground and sieved to 38–45 μm. Limestone was ground and sieved to 0.25–0.355 mm.

### 2.2. Calcination experiment

CaCO<sub>3</sub> calcination (CaO regeneration) experiment was operated on a thermogravimetric apparatus. The inner diameter and length of the reactor are 70 and 500 mm, respectively. The steam line is heated by a heater until it is introduced into the reactor. The temperature was first heated (20 K/min) to 1223 K and then kept stable. N<sub>2</sub>/CO<sub>2</sub> or steam/CO<sub>2</sub> flow was introduced into reactor after temperature stabilized. Experimental conditions were shown in Table 2. CaCO<sub>3</sub> sample (1.0 g) was spread on the sample basket, and then it was dropped to a fixed height to start CaCO<sub>3</sub> decomposition.

The decomposition rate ( $X_1$ ) of CaCO<sub>3</sub> can be calculated as follow:

$$X_1 = \frac{(M_1 - M_2)/M_{CO_2}}{M_1/M_{CaCO_3}} \quad (2)$$

where  $M_1$  is the initial weight of CaCO<sub>3</sub> sample and  $M_2$  is the sample weight during calcination.  $M_{CO_2}$  and  $M_{CaCO_3}$  are the molecular weights (in units of kg/kmol) of CO<sub>2</sub> and CaCO<sub>3</sub>.

### 2.3. Carbonation experiment

Carbonation experiment was conducted by using a horizontal fixed bed reactor. The temperature was first rose to 923 K. CO<sub>2</sub> (3 L/min) or CO<sub>2</sub>/steam (1 L/min of steam and 2 L/min of CO<sub>2</sub>) flow was introduced into the reactor. CaO sample (about 0.3 g), which was obtained in calcination experiment, was spread in the porcelain boat and sent into the reactor to start carbonation reaction. After 40 min, sample was taken out of the reactor and weighted after cooling to room temperature.

The reactivity ( $X_2$ ) of CaO sorbent can be calculated as follow:

$$X_2 = \frac{(M_2 - M_1)/M_{CO_2}}{M_1/M_{CaO}} \quad (3)$$

where  $M_1$  is the initial weight of CaO;  $M_2$  is the sample weight after carbonation;  $M_{CO_2}$  and  $M_{CaO}$  are the molecular weights (in units of kg/kmol) of CO<sub>2</sub> and CaO.

### 2.4. Hydration and cyclic CO<sub>2</sub> capture

Ca(OH)<sub>2</sub> was produced on a high-pressure thermogravimetric apparatus. The detailed description of the thermogravimetric apparatus was presented in our previous paper [21]. Ca(OH)<sub>2</sub> was generated during hydration reaction. The reactivity of CaO decomposed from Ca(OH)<sub>2</sub> was measured and compared with that of CaO decomposed from CaCO<sub>3</sub>. The carbonation atmosphere was under 923 K and 0.1 MPa partial pressure of CO<sub>2</sub> (total pressure, 3.0 MPa) [22].

**Table 1**  
Chemical analysis of limestone.

Composition [wt.%]				
CaO	MgO	SiO <sub>2</sub>	LOF	Other
51.62	3.70	0.45	43.49	0.74

LOF: loss on fusion.

**Table 2**  
CaCO<sub>3</sub> calcination experimental conditions.

No.	Flow rate (L/min)		
	Steam	N <sub>2</sub>	CO <sub>2</sub>
1	–	–	3.0
2	–	0.6	2.4
3	–	1.2	1.8
4	–	1.8	1.2
5	–	3.0	–
6	0.6	–	2.4
7	1.2	–	1.8
8	1.8	–	1.2

During cyclic CO<sub>2</sub> capture, limestone was first mixed with coal powder (supplying coal combustion heat for limestone decomposition) and then decomposed to CaO. Some of CaO sorbents were hydrated with steam while the other weren't. All sorbents were used to cyclic absorb CO<sub>2</sub>. Carbonation was carried out for 20 min under 923 K with CO<sub>2</sub> flow of 9 mL/min (total 60 mL/min, N<sub>2</sub> balance). Calcination was carried out for 10 min under 1193 K with pure CO<sub>2</sub> flow (60 mL/min). The carbonation-calcination cycle was conducted 17 times for each sample.

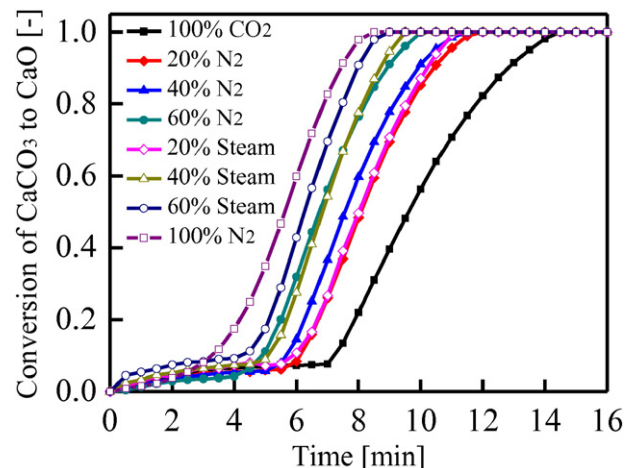
## 3. Results and discussion

### 3.1. Effect of steam on CaO regeneration

The calcination reaction was conducted in CO<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>/CO<sub>2</sub> and steam/CO<sub>2</sub> calcination atmospheres with different gas mixture ratios. As shown in Fig. 1, the decomposition reaction of CaCO<sub>3</sub> started at the 3rd minute and finished at the 8th minute in 100% N<sub>2</sub> atmosphere, while it started at the 7th minute and finished at the 15th minute in 100% CO<sub>2</sub> atmosphere. CaCO<sub>3</sub> was decomposed obviously slower in CO<sub>2</sub> atmosphere than N<sub>2</sub> atmosphere. When CO<sub>2</sub> calcination atmosphere was diluted by N<sub>2</sub> or steam with the dilution ratio varying from 20%, 40% to 60% in the experiments, the required time for CaCO<sub>3</sub> completely decomposition was different. CaCO<sub>3</sub> was decomposed quicker in the diluted (N<sub>2</sub> or steam) atmosphere than pure CO<sub>2</sub> atmosphere. Moreover, the decomposition rate was increased with dilution ratio. The results can be explained by the difference of CO<sub>2</sub> partial pressure and the heat-transfer.

#### 3.1.1. CO<sub>2</sub> partial pressure

High CO<sub>2</sub> partial pressure restrained the decomposition reaction of CaCO<sub>3</sub> (Eq. (1)). CaCO<sub>3</sub> decomposition rate ( $R_r$ ) depends on the differential pressure between the balanced pressure of CO<sub>2</sub> ( $P^*$ ) and the experimental partial pressure of CO<sub>2</sub> ( $P_{CO_2}$ ) [23], which can be described



**Fig. 1.** Effect of N<sub>2</sub> and steam dilution ratios on CaCO<sub>3</sub> decomposition.

as:

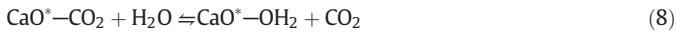
$$R_r = K_D(P^* - P_{CO_2}) = A[\exp(-E/RT)](P^* - P_{CO_2}) \quad (4)$$

$$P^* = 4.192 * 10^9 \exp(-20,474/T) \quad (kPa) \quad (5)$$

where  $P^*$  is the balanced pressure of  $CO_2$ ;  $P_{CO_2}$  is the partial pressure of  $CO_2$ ;  $A$  is frequency factor ( $0.012 \text{ mol.m}^{-2}.\text{s}^{-1}.\text{kPa}^{-1}$ );  $E$  is activation energy ( $33.47 \text{ kJ.mol}^{-1}$ ) [23].

In calcination experiment, the temperature was 1223 K.  $P^*$  and  $K_D$  were both constant value according to Eqs. (4) and (5).  $CaCO_3$  decomposition rate ( $R_r$ ) only depends on  $P_{CO_2}$ . Therefore, the decomposition rate in  $CO_2$  atmosphere was lower than  $N_2$  atmosphere;  $N_2$  or steam dilution reduced  $P_{CO_2}$ , so  $CaCO_3$  decomposition rate was also increased.

Furthermore,  $CaCO_3$  is decomposed to  $CaO$  and  $CO_2$ , but  $CO_2$  is firstly absorbed by the active site of  $CaO^*$  instead of being released into calcination atmosphere, as shown in Eq. (6). The binding ability between  $H_2O$  and  $O^*$  was stronger than that between  $CO_2$  and  $O^*$  [24]. Therefore, when steam was introduced into calcination atmosphere, the absorption of  $H_2O$  by  $CaO^*$  weakened the binding ability between  $CO_2$  and  $CaO^*$ .  $CO_2$  molecule was replaced by  $H_2O$  molecule and  $CO_2$  was then released into calcination atmosphere. The actual decomposition reaction of  $CaCO_3$  under steam/ $CO_2$  calcination atmosphere can be described as Eqs. (7) and (8).  $CaCO_3$  is first decomposed to  $CaO^* - CO_2$ , and then  $CaO^* - CO_2$  absorbs  $H_2O$  molecule to generate  $CaO^* - OH_2$  and  $CO_2$  gas. The partial pressure of  $H_2O$  ( $P_{H_2O}$ ) increased while partial pressure of  $CO_2$  ( $P_{CO_2}$ ) decreased after introducing steam into calcination atmosphere, which accelerated the reaction (8). Therefore,  $CaCO_3$  decomposition reaction was then promoted.



### 3.1.2. Heat-transfer

As shown in Fig. 1, it could also be found that  $CaCO_3$  decomposition rate in steam dilution atmosphere was higher than  $N_2$  dilution atmosphere at the same dilution ratio. This result couldn't be explained by the difference of  $CO_2$  partial pressure, because  $P_{CO_2}$  was the same in  $N_2/CO_2$  and steam/ $CO_2$  atmospheres under the condition of the same dilution ratio. The thermal properties between steam and  $N_2$  are different, and it may be the reason for the difference of decomposition rate. In our previous study, the heat transfer rate ( $Q_T$ ) between gas and particle and the heat for  $CaCO_3$  particle decomposition ( $Q_R$ ) were both calculated [25], as shown in Eqs. (9) and (10).

$$Q_T = 0.03(d_p u \rho_g / \mu_g)^{1.3} \pi d_p k_g (T_b - T_p) \quad (9)$$

$$Q_R = \pi d_p \Delta H [A \exp(-E/(RT_p))] (P^* - P_{CO_2}) \quad (10)$$

where  $d_p$  is the diameter of  $CaCO_3$  particle;  $u$ ,  $\rho_g$ ,  $\mu_g$ ,  $k_g$  are the velocity, density, viscosity coefficient and heat conductivity coefficient, respectively;  $T_b$  and  $T_p$  are the bed temperature and  $CaCO_3$  particle temperature, respectively;  $\Delta H$  is the enthalpy change of the decomposition reaction.

The calculation parameters of  $Q_T$  and  $Q_R$  were shown in Table 3. The curves of  $Q_T$  and  $Q_R$  with the particle temperature were shown in Fig. 2. The thermal conductivity of steam is higher than  $N_2$ , which resulted that  $Q_T$  was higher in steam/ $CO_2$  atmosphere than  $N_2/CO_2$  atmosphere. Besides,  $Q_R$  was increased with  $P_{CO_2}$  decreasing. Only one intersection point was found between the curves of  $Q_R$  and  $Q_T$ .  $CaCO_3$  particle started to be decomposed at the intersection point. Decomposition reaction became faster with  $Q_T$  increasing. The same result was also obtained in our

**Table 3**

The parameters required for calculation of  $Q_T$  and  $Q_R$  (1, 223 K; 0.1 MPa).

Atmosphere	$\rho_g [10^{-1}(\text{kg.m}^{-3})]$	$\mu_g [10^{-5}(\text{Pa.s})]$	$k_g [10^{-1}(\text{W.m}^{-1}.\text{K}^{-1})]$
100% $CO_2$	4.38	5.00	0.86
80% $CO_2$ + 20%steam	3.87	4.80	0.94
60% $CO_2$ + 40%steam	3.35	4.60	1.02
40% $CO_2$ + 60%steam	2.84	4.40	1.11
80% $CO_2$ + 20% $N_2$	4.08	4.94	0.83
60% $CO_2$ + 40% $N_2$	3.77	4.88	0.80
40% $CO_2$ + 60% $N_2$	3.47	4.82	0.77
100% $N_2$	2.86	4.70	0.71
	$d_p [10^{-5}(\text{m})]$	$u$ [ $10^{-2}(\text{m.s}^{-1})]$	$\Delta H_{1223K} [\text{kJ.mol}^{-1}]$
	4.15	1.30	166.20

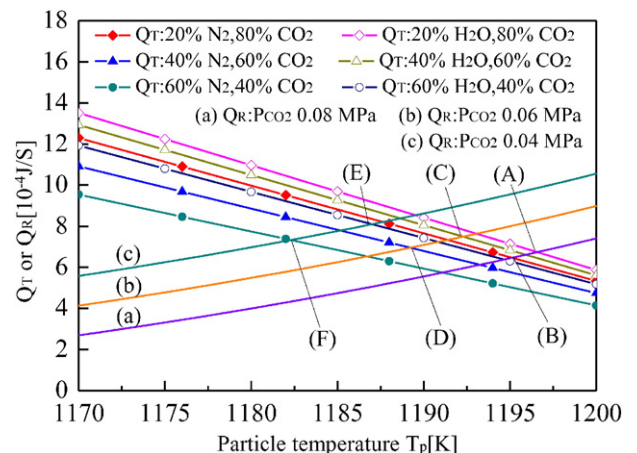
previous work in fluidized bed reactor [25]. The amount of  $Q_T$  at the intersection point was ranked in order  $E > C > F > D > A > B$  in different  $P_{CO_2}$  atmospheres. This result corresponded well to the experiment result in Fig. 1. For example, Fig. 1 showed that the decomposition rates in 40%  $N_2$  and 60%  $CO_2$  atmospheres were higher than 20% steam and 80%  $CO_2$  atmospheres. Similarly as shown in Fig. 2,  $Q_T$  at point D was larger than point A, which proved that  $Q_T$  in 40%  $N_2$  and 60%  $CO_2$  atmospheres were higher than 20% steam and 80%  $CO_2$  atmospheres. Higher  $Q_T$  resulted in higher  $CaCO_3$  particle decomposition rate.

### 3.2. Effect of steam on CaO reactivity

#### 3.2.1. Steam in calcination atmosphere

$CaO$  sorbent was obtained in calcination experiment. Its reactivity was tested in carbonation experiment. Two carbonation atmospheres were conducted:  $CO_2$  and steam/ $CO_2$  carbonation atmospheres. Fig. 3 showed that the reactivity of  $CaO$  sorbent, which was generated in different dilution calcination atmospheres, was much higher than that generated in pure  $CO_2$  calcination atmosphere. It means that the reactivity of  $CaO$  was increased when steam (or  $N_2$ ) was introduced into calcination atmosphere. Further, the reactivity of  $CaO$  gradually increased when the dilution ratio of steam or  $N_2$  increased ( $P_{CO_2}$  decreased), and it was higher in  $N_2/CO_2$  than steam/ $CO_2$  calcination atmosphere.

Firstly, the required particle temperature for  $CaCO_3$  decomposition was lower in low  $P_{CO_2}$  calcination atmosphere (Fig. 2), which resulted in lower sintering and reactivity increasing in the atmosphere of higher steam or  $N_2$  dilution ratio. Secondly, particle temperature in  $N_2/CO_2$  atmosphere was lower than steam/ $CO_2$  atmosphere (Fig. 2), which also resulted in higher sorbent reactivity. In practical application,  $CaCO_3$



**Fig. 2.**  $Q_T$  and  $Q_R$  curves with particle temperature  $T_p$  in different calcination atmospheres.

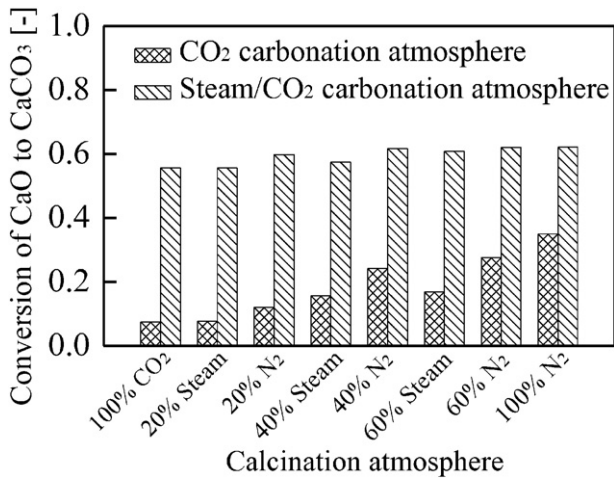


Fig. 3. Effect of calcination and carbonation atmospheres on the reactivity of CaO sorbent.

should be decomposed in steam/CO<sub>2</sub> other than N<sub>2</sub>/CO<sub>2</sub> atmosphere to obtain pure CO<sub>2</sub> exhaust gas for utilization or compression. It is because that steam is easily to be condensed from steam/CO<sub>2</sub> exhaust gas while N<sub>2</sub> is difficult to be separated from N<sub>2</sub>/CO<sub>2</sub> exhaust gas. Therefore, introducing steam into calcination atmosphere is a good choice and it improves not only the decomposition rate of CaCO<sub>3</sub> particle, but also the reactivity of the produced CaO sorbent.

### 3.2.2. Steam in carbonation atmosphere

The reactivity of CaO sorbent in two different carbonation atmospheres was also compared in Fig. 3. Obviously, the reactivity of CaO in steam/CO<sub>2</sub> carbonation atmosphere was over doubled the CaO reactivity in CO<sub>2</sub> carbonation atmosphere. Particularly, when CaCO<sub>3</sub> was decomposed in high CO<sub>2</sub> concentration calcination atmosphere (e.g. 100% CO<sub>2</sub>), the reactivity of CaO in CO<sub>2</sub> carbonation atmosphere was only about 10%, while it was increased to about 56% in steam/CO<sub>2</sub> carbonation atmosphere. CaO sorbent occurred sintering in high CO<sub>2</sub> concentration calcination atmosphere. Steam in carbonation atmosphere may improve the sintering and then increased sorbent reactivity. This result indicated that introducing steam into carbonation atmosphere could also improve the reactivity of CaO sorbent.

Sorbent reactivity was enhanced by 1 ~ 4 times when ~33% steam was introduced carbonation atmosphere (compared with CO<sub>2</sub> carbonation atmosphere). However, even if 40% steam was introduced into calcination atmosphere, sorbent reactivity was only enhanced by 1.1 times. Introducing steam into both calcination and carbonation atmospheres can enhance sorbent reactivity, but the enhancement extent by introducing steam into carbonation atmosphere was much higher than introducing steam into calcination atmosphere.

### 3.2.3. Model description

Symonds et al. [26] and Dou et al. [27] reported that the reactivity enhancement by steam introducing into carbonation atmosphere was mainly because of the formation of transient Ca(OH)<sub>2</sub>, and the reactivity of transient Ca(OH)<sub>2</sub> was much higher than normal CaO sorbent. Anthony et al. [28] considered the reactivity enhancement by steam accelerating the solid-state diffusion. However, the effect and actual mechanism of how steam influences carbonation reaction is still not completely understood, and there are some arguments between different authors.

Ion diffusion was analyzed in this study to investigate the effect of steam on carbonation reaction. When H<sub>2</sub>O molecule is absorbed on the surface of CaO, both chemical absorption and dissociative chemical absorption may occur. The total energy for the dissociative absorption is smaller than the energy needed to absorb H<sub>2</sub>O molecule [29], which means H<sub>2</sub>O molecule is easily dissociated on CaO particle surface. Oxygen vacancies (V<sub>O</sub>) on the surface layer are shown to dissociate H<sub>2</sub>O

molecule by transferring one proton (H<sup>+</sup>) to nearby oxygen atoms (O<sup>2-</sup>), forming two hydroxyl groups (OH<sup>-</sup>) for every vacancy [30], as shown in Eq. (11).



Model description of CaO carbonation under steam/CO<sub>2</sub> was shown in Fig. 4. During diffusion controlled stage, CaCO<sub>3</sub> product was generated on CaO particle surface and blocked the direct contact between CaO and CO<sub>2</sub>. In CO<sub>2</sub> carbonation atmosphere, CO<sub>3</sub><sup>2-</sup> diffuses from CaCO<sub>3</sub> surface to CaO surface, and reacts with Ca<sup>2+</sup> to form CaCO<sub>3</sub>. Conversely, O<sup>2-</sup> diffuses from CaO surface to CaCO<sub>3</sub> surface, and reacts with CO<sub>2</sub> to form CO<sub>3</sub><sup>2-</sup>. The diffusion rate of O<sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> in the solid phase is slow in CO<sub>2</sub> carbonation atmosphere. However, when steam is introduced into carbonation atmosphere, H<sub>2</sub>O is dissociated to H<sup>+</sup> and OH<sup>-</sup>. H<sup>+</sup> has a small radius, so it diffuses more easily from CaCO<sub>3</sub> surface to CaO surface, and reacts with O<sup>2-</sup> to form OH<sup>-</sup>. Besides, Kronenberg et al. [31] reported that oxygen diffusion is accelerated markedly by the steam partial pressure increasing. Therefore, oxygen vacancy (V<sub>O</sub>) is quickly formed due to oxygen diffusion, which accelerated the formation of OH<sup>-</sup> (Eq. (11)). The quickly formed OH<sup>-</sup> diffuses from CaO surface to CaCO<sub>3</sub> surface, and reacts with CO<sub>2</sub> to form CO<sub>3</sub><sup>2-</sup>, which then also promoted the carbonation reaction.

### 3.3. Effect of steam on CaO hydration

Limestone was first decomposed to CaO, and CaO was then hydrated with steam. The particle strength of generated Ca(OH)<sub>2</sub> particle was relatively high, which was reported in our previous study [21]. The

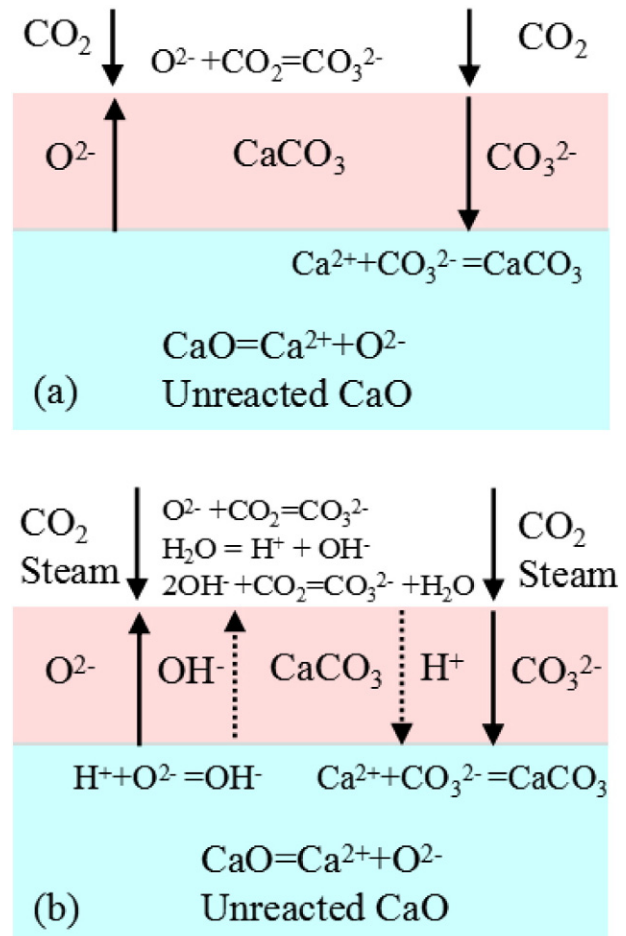


Fig. 4. Model description of the effect of steam on CaO carbonation.

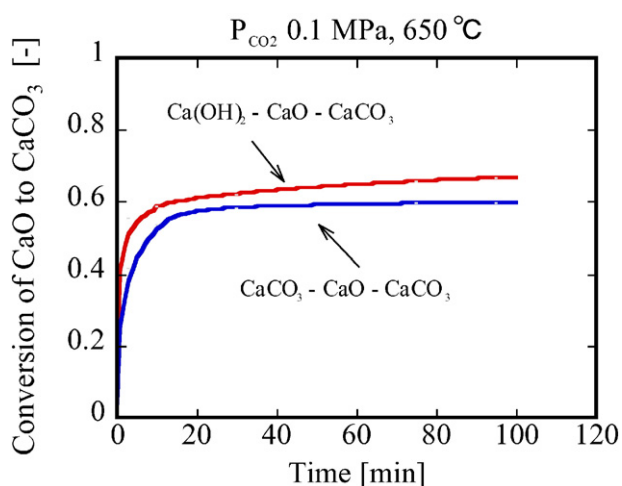


Fig. 5. Comparison of carbonation reactivity of CaO produced from Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>.

carbonation reactivities of CaO sorbents generated from CaCO<sub>3</sub> and high-strength Ca(OH)<sub>2</sub> were compared in Fig. 5. The reactivity of CaO sorbent decomposed from high-strength Ca(OH)<sub>2</sub> particle was also higher than that decomposed from CaCO<sub>3</sub>. It means that the generated Ca(OH)<sub>2</sub> particle gained not only high strength but also high reactivity after steam hydration treatment. Then, Ca(OH)<sub>2</sub> sorbent is used to cyclic capture CO<sub>2</sub> to improve absorption efficiency.

The cyclic reactivity of sorbent was also tested and the result was shown in Fig. 6. Sorbent reactivity decreased with cycles. In the 1st cycle, the reactivity of CaO was relatively high, which was 0.366 (hydration treatment) or 0.253 (no hydration treatment) g-CO<sub>2</sub>/g-sorbent. Then, the reactivity decreased rapidly to 0.147 or 0.120 g-CO<sub>2</sub>/g-sorbent after sorbent suffering high calcination temperature (1, 193 K) in the 2nd cycle. Therefore, sorbent reactivity was at relatively low value after the 2nd cycle. Sorbent particle remained porous in the 1st cycle (Fig. 7a), allowing reactant gas diffusion into the particles. However, it lost pores after 17 cycles (Fig. 7b), which resulted in the decrease of sorbent reactivity. Fortunately, hydration treatment was conducted in the 1st cycle in this study. It can be seen that sorbent reactivity was enhanced by hydration treatment (especially in the 1st cycle) (Fig. 6), which was mainly because particle pore structure was developed by hydration treatment (Fig. 7c). Accordingly in practical application, hydration treatment could be conducted in each cycle (not only the 1st cycle), we can infer that sorbent reactivity between the 2nd and 17th cycle would be higher. Moreover, the carbonation reaction detail of the 2nd cycle was also shown in Fig. 6. A fast carbonation reaction stage was first observed, followed by a slow carbonation stage. It can be seen

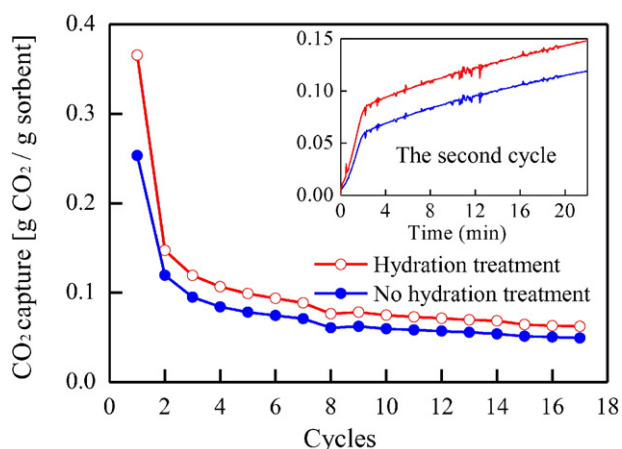


Fig. 6. Effect of steam activation on the cyclic reactivity of sorbent for CO<sub>2</sub> capture.

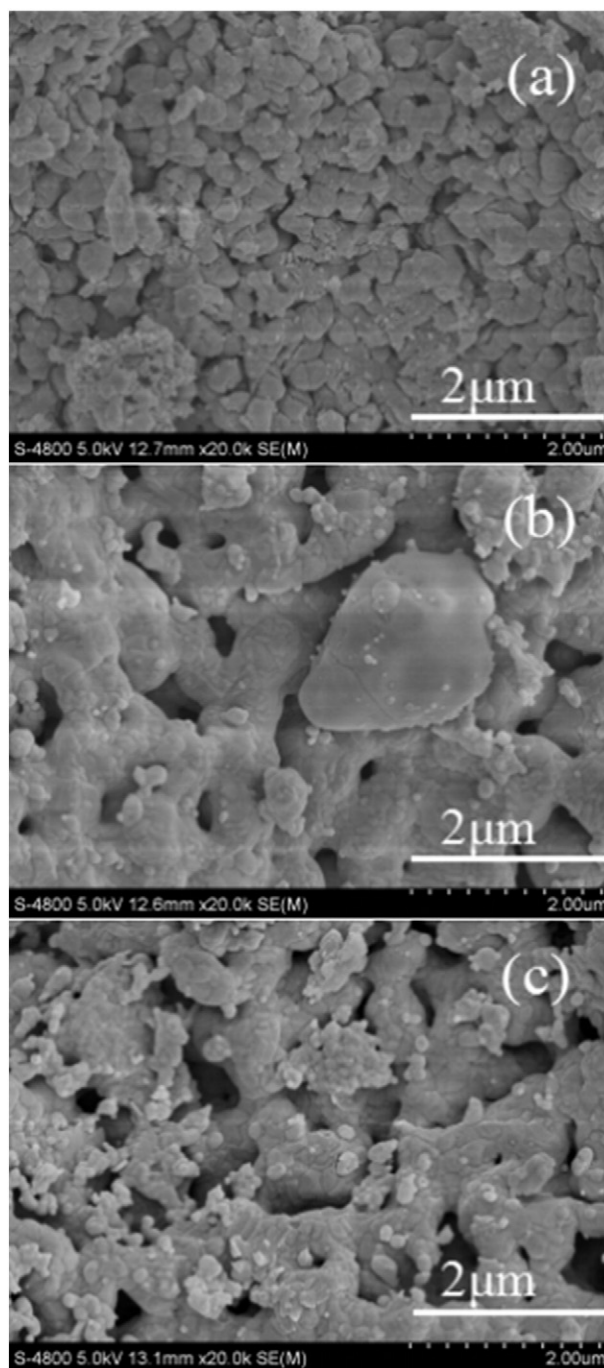


Fig. 7. SEM images of the sorbents: (a) 1st cycle; (b) 17th cycle; and (c) 17th cycle with hydration treatment.

that hydration treatment mainly influenced the fast carbonation stage. Particle pores were developed by hydration treatment, which resulted in a larger pore surface for fast carbonation.

#### 3.4. CaO regeneration, carbonation and hydration for CO<sub>2</sub> capture by steam treatment

As shown in Fig. 8, an effective approach is developed for CO<sub>2</sub> capture. Steam plays an important role in this approach. In CaO regeneration step, CaO is generated from CaCO<sub>3</sub> decomposition. Fuel combustion heat is supplied for CaCO<sub>3</sub> decomposition in steam/O<sub>2</sub>/CO<sub>2</sub> atmosphere. Steam is introduced into calcination atmosphere to improve CaCO<sub>3</sub> decomposition rate and CaO reactivity, as discussed

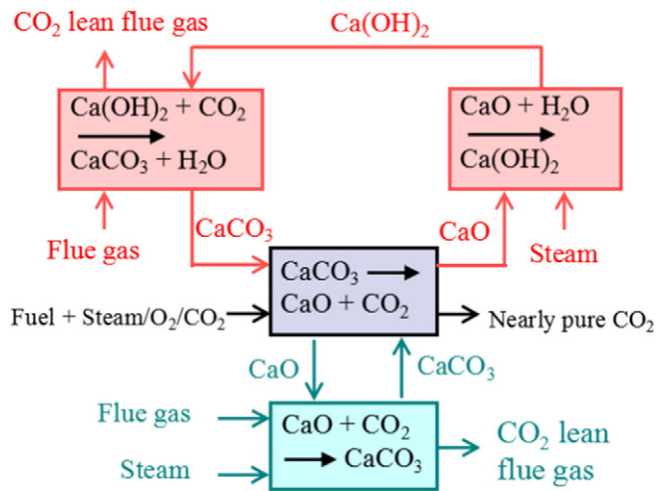


Fig. 8. Schema of CaO regeneration, carbonation and hydration for CO<sub>2</sub> capture with steam treatment.

above. Then, high reactivity CaO sorbent and nearly pure CO<sub>2</sub> exhaust gas is obtained. On the one hand, CaO is directly used to absorb CO<sub>2</sub> in high temperature flue gas. High temperature steam is introduced into carbonation atmosphere to improve absorption efficiency. On the other hand, CaO is first hydrated to generate Ca(OH)<sub>2</sub> and then used to absorb CO<sub>2</sub> indirectly. High partial pressure steam is introduced into hydration atmosphere to improve the sorbent strength and reactivity.

Calcium looping process is usually used for post-combustion CO<sub>2</sub> capture. The main problem of calcium looping process is that the sorbent reactivity decreases with calcination-carbonation cycles. This paper proposed an effective approach to enhance the reactivity of CO<sub>2</sub> sorbent (CaO-based sorbent). Three ways, including steam activation in calcination/carbonation process and hydration treatment, were proved to improve sorbent reactivity effectively in this new calcium looping process. However, when coal combustion heat is supplied for CaCO<sub>3</sub> calcination in steam/O<sub>2</sub>/CO<sub>2</sub> atmosphere (Fig. 8), coal sulfur may react with CaCO<sub>3</sub> to form CaSO<sub>4</sub>. Besides, when CaO or Ca(OH)<sub>2</sub> is used to absorb CO<sub>2</sub>, it may also react with SO<sub>2</sub> in flue gas. Sulfuration reaction is also accelerated by steam in our study, which will be reported in later work.

#### 4. Conclusions

Steam plays an important role in CaO regeneration, carbonation and hydration processes for CO<sub>2</sub> capture. Introducing steam into CaO regeneration atmosphere enhanced CaCO<sub>3</sub> decomposition rate and CaO reactivity. It was because that CO<sub>2</sub> partial pressure was reduced; the heat-transfer rate was enhanced; and the absorption of H<sub>2</sub>O by CaO\* weakened the binding ability between CO<sub>2</sub> and CaO\*. Introducing steam into CaO carbonation atmosphere also enhanced the sorbent reactivity, which was due to the formation of OH<sup>-</sup>. Further, the enhancement by introducing steam into carbonation atmosphere was much higher than introducing steam into calcination atmosphere. Introducing steam into CaO hydration atmosphere enhanced both the reactivity of Ca(OH)<sub>2</sub> and cyclic reactivity of CaO, because that particle pore structure was developed by hydration treatment. Thus, an effective approach through steam activation of CaO sorbent for CO<sub>2</sub> capture was proposed, which mainly contained CaO regeneration, carbonation and hydration processes.

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