

Preparation and characterisation of lime/coal ash sorbents for sequential CO₂ and SO₂ capture at high temperature

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Abstract:

Extensive research has been done on Ca-based sorbents as a promising way to capture CO₂ and SO₂ from power plants. Considerable effort has also been directed toward maintaining sorbent activity by means of sorbent modification to deal with activity decay with repeated CO₂ capture cycles. Based on the principle of “treating waste with waste” and inspired by the idea that a pozzolanic reaction can enhance the surface area, this paper presents a method of hydrothermal synthesis of lime and coal ash. A small amount of CaSO₄ or NaOH was added during the hydration process and the mixture was stirred for several hours at about 90°C. The synthesized samples were then characterised by scanning electron microscopy, nitrogen adsorption/desorption spectroscopy and X-ray diffraction. The activity of the synthesized sorbent for CO₂ and SO₂ capture were then tested in a thermogravimetric analyser. The treated samples demonstrate longer-lasting performance for CO₂ cyclic capture, albeit with a slightly reduced capture ability compared to pure lime in the first few cycles due to their lower CaO content (25~81% versus 98%). The sample with lime/ash mass ratio of 45:5 showed higher CO₂ capture ability after three cycles and much greater stability in terms of their activity. The main product of the

pozzolanic reaction is CaSiO_3 , which has a network structure, whose development is related to the ratio of CaO /coal ash, hydration duration and the amount of CaSO_4 and NaOH additives. After high temperature calcination, a new phase, namely $\text{Ca}_3\text{Al}_2\text{O}_6$ is believed to serve as a skeleton preventing sintering in repeated capture cycles. After experiencing multiple cycles, the synthesized sorbents also have a high SO_2 capture capacity. A small amount of added NaOH decreases the cyclic CO_2 carrying capacity of the synthesized sorbent but enhances SO_2 carrying capacity dramatically. The explanation for this is that the sulphation reaction is controlled not only by gas diffusion but also by solid-state ion diffusion. Na^+ ions generate more crystal lattice defects which can accelerate the ion diffusion rate in the product layer, and consequentially enhance overall SO_2 carrying capacity.

Keywords: Ca-based sorbent, coal ash, pozzolanic reaction, cyclic CO_2 capture, SO_2 retention

Introduction

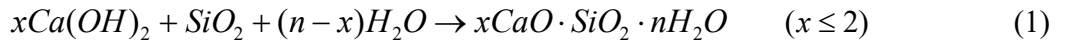
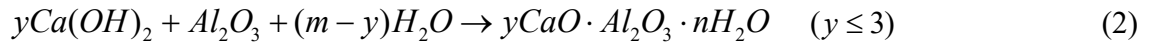
For over a hundred years the combustion of coal has been a major source of power, fueling the industrial revolution, and this situation is unlikely to change in the near future ^[1]. However, the emissions generated from coal combustion have gained increasing attention due to their adverse environmental effects ^[2,3]. To control SO₂ emissions from coal-fired power plants and boilers in industrial processes, effort has been put into developing flue gas desulphurisation (FGD) technologies over the past few decades ^[4]. Recently, research has also increasingly focused on CO₂ capture techniques ^[5,6]. Amine chemical absorption is an effective method and a number of demonstration projects have been developed ^[7]. However, amines have various shortcomings, like high price, solvent instability, low absorption rate, and a high corrosion rate ^[8]. Moreover, amines are expensive and suffer from several potential problems such as an irreversible reaction with SO₂ contaminants, producing non-reclaimable and potentially corrosive salts. Furthermore, amines are also sensitive to O₂ and other flue gas components. In addition, although the wet FGD process is widely used in power plants due to high desulphurisation efficiency and flexibility, it requires a large amount of water and has high capital and operating costs. So, it is desirable to develop dry technologies for both CO₂ and SO₂ capture, especially for the very arid regions throughout the world.

Calcium-looping (CaL) technology is a promising technology for both high-temperature CO₂ and SO₂ capture from flue gas, given the wide availability and low cost of limestone ^[9]. Ca-based sorbent can be carbonated in flue gas and then calcined in oxy-combustion atmosphere to separate CO₂ from flue gas and generate near pure CO₂ stream. The oxy-combustion system is normally used because it not only provides heat for sorbent calcination but its flue gas mainly contains CO₂, so that a near pure CO₂ stream can be collected. Intensive research has been carried out on the single processes of either CO₂ capture or SO₂ retention in terms of reaction mechanisms, sorbent modification, and hydration

reactivation processes ^[10-12]. The main challenge for CO₂ capture is the decay of sorbent activity due to sintering as the number of carbonation/calcination cycles increases and this effect is most pronounced during the initial cycles ^[13]. This generates large amounts of spent sorbent and adversely affects the economic benefits of the technology. A fluidised bed combustion (FBC) system with in situ SO₂ capture by injection of calcium-based sorbents also generates large quantities of solid residue, as a high molar ratio of Ca/S is needed to achieve high levels of desulphurisation. It is therefore necessary to find ways to regenerate sorbent activity and enhance its utilisation. Methods to improve the performance of CaO-based sorbent include thermal pretreatment ^[14], pelletisation ^[15], hydration with steam ^[16] or water ^[17], and addition of inert materials ^[18]. Reactivation of spent sorbent has also been exhaustively investigated for improving SO₂ capture in FBC systems ^[19]. The steam or water hydration method is the most simple and effective way to reactivate spent sorbent, albeit that it weakens the sorbent particles and causes severe attrition ^[20]. Incorporating inert material as supports in Ca-based sorbents is also an efficient method to generate high porosity and prevent severe sintering. These inert support materials can include a wide range of dopants of alkali metals such as Mg, Ce, Ti, and Al^[21-25]. However, a compromise must be made between improving the sorbent performance and increasing its cost. In particular, Al-doped Ca-based sorbents show significantly enhanced durability over multiple cycles and are relatively inexpensive, so they represent a good choice of dopant.

Based on the idea of “Treating the wastes with wastes”, the utilisation of coal ash is attractive both economically and environmentally, as it is the most voluminous by-product of coal-fired power plants. Some research has also focused on synthesizing a Ca-based sorbent by mixing coal fly ash/CaO/CaSO₄ in a hydration process for SO₂ retention ^[26]. The main constituents of coal fly ash are Al₂O₃ and SiO₂ based compounds which can be dissolved in alkaline solutions and then react with Ca²⁺. The reaction between the fly ash and Ca(OH)₂ is known as a pozzolanic reaction and yields hydrated calcium

silico-aluminates which are fibrous gels that can enhance surface area and pore volume ^[27]. In fact, any kind of ash which contains Al_2O_3 and SiO_2 would be effective in the synthesis process. An advantage of using coal ash to synthesize sorbent is that the CaO contained in coal ash could be reused to capture CO_2/SO_2 , especially when the ash contains relatively high content of CaO , like ash from CFB combustion with injection of limestone into furnace for desulphurisation. The pozzolanic reaction can be summarized in terms of following global reactions (1) and (2).



Lee et al ^[28,29], succeeded in synthesizing sorbent with enhanced surface areas of 16.1 to 133.3 m^2/g by varying three factors: the ratio of coal ash to lime, the reaction time and the amount of $CaSO_4$ addition. The synthesized sorbent showed a much better performance for SO_2 retention. However, the pozzolanic reaction rate is very slow at room temperature, so the synthesis process was accelerated by heating and stirring a paste made of a suitable composition. $NaOH$ and $CaSO_4$ are commonly used as activators to accelerate the pozzolanic reaction ^[30], as $NaOH$ increases the pH value of the solution and this helps to dissolve SiO_2 and Al_2O_3 , which promote the formation of Ca-Si-H compounds and thus increases the sorbent sulphation performance ^[31,32]. $CaSO_4$ is also thought to enhance the pozzolanic reaction as it restrains the growth of $Ca(OH)_2$ crystals and promotes the reaction between $Ca(OH)_2$ and SiO_2 dissolved from coal ash ^[26]. However, the enhanced surface area depends strongly on the synthesis conditions and there is research which can be drawn on with respect to improving SO_2 retention at low temperature ^[28]. Inspired by the results from such hydration methods, similar experiments were performed with two kinds of coal ash in deionized water by varying synthesis conditions to see if this approach would work for high temperature capture. The sorbent, after reaction with SO_2 , is then

converted into an eco-friendly product, which can be disposed of easily due to its possible uses, including as a fertilizer or a coagulating agent.

Previous research on simultaneous CO₂ and SO₂ capture with a Ca-based sorbent have shown that SO₂ impedes sorbent carbonation resulting in rapid decay of sorbent activity, while the presence of CO₂ had a beneficial effect on sulphation behavior^[33]. However, our previous work on this subject has confirmed that using a Ca-based sorbent to capture CO₂ and SO₂ sequentially can avoid the detrimental effect of SO₂ on CO₂ capture and enhance resource utilization^[34]. To demonstrate this with our new synthesized sorbents, they were first tested in cyclic CO₂ capture and then for SO₂ retention at high temperature. As the flue gas stream generally contains a considerable amount of steam and this also has a significant influence on sorbent conversion^[35], the tests are conducted in a simulated atmosphere as close as possible to that of a real flue gas.

1. Materials and experimental methods

2.1 Sorbent preparation and analysis

The main raw materials employed in the synthesis process were two kinds of coal ash, lime, CaSO₄ and NaOH. The two coal ashes were fly ash obtained from the bag house of a CFB system and bottom ash from a pulverized coal combustion power plant in the UK. Both were screened to a particle size of less than 200 µm. The chemical composition of the coal ashes is listed in Table 1. This shows some differences between fly ash and bottom ash. The fly ash contains a relatively high percentage of CaO and MgO, as the SO₂ was captured by limestone in a fluidised bed. The major components of bottom ash are SiO₂ and Al₂O₃. The CaO was obtained by calcining a UK limestone (Longcal SP52, with CaCO₃ content of 98%) at 900 °C for two hours in air. The loss on ignition is 43.1%. The analytical reagents used in this work, namely CaSO₄ and NaOH were purchased from Fisher Scientific and were used without further processing as activating agents.

Table 1. Chemical composition of coal ash

Coal ash	SiO ₂ wt%	Al ₂ O ₃ wt%	Fe ₂ O ₃ wt%	CaO wt%	MgO wt%	SO ₃ wt%	K ₂ O wt%	TiO ₂ wt%	Others wt%
CFB fly ash	25.4	9.1	8.6	30.0	9.0	9.5	0.8	0.2	7.4
Bottom ash	48.0	29.5	9.0	3.0	2.5	0.8	3.0	1.0	3.2

To enhance the activity of SiO₂ and Al₂O₃ and accelerate the pozzolanic reaction, the sorbent synthesis procedure was carried out at 90 °C with stirring. CaSO₄ and NaOH were employed as additives as they are believed to influence the formation of pozzolanic reaction product Ca-Si-H compounds ^[27]. The synthesized sorbents with a range of specific surface areas were obtained by varying three key process variables: the ratio of lime and coal ash, the amount of additive, namely CaSO₄ or NaOH, and hydration time. The other conditions such as the amount of water and reaction temperature were kept constant at 600 ml and 90 °C respectively, as it has been shown that they have little influence on sorbent specific surface area ^[28]. The experimental design is shown in Table 2. The synthesized samples are represented using the format of CS or BS N(a/b/c/d/e), where CS or BS means the new sample is synthesized from CFB fly ash or bottom ash; N is the index number given when the samples were prepared; a, b, c and d denote mass(g) of lime, coal ash, CaSO₄ and hydration time, respectively; e denotes the mass of NaOH, if it is present. For example, CS20(35/15/10/8/NaOH 1g) means this sample was synthesized from CFB fly ash; the mass of lime, CFB fly ash and CaSO₄ were 35g, 15g, 10g respectively; hydration time was 8 h and the mass of NaOH was 1g. The procedure used to prepare the sorbents comprised the following sequential steps. The raw materials were measured and then evenly mixed in a beaker, after which 600 ml deionized water was added. The slurry was then heated on a hot plate at approximately 90 °C. The slurry was stirred well throughout the hydration process by means of a magnetic rod. After hydration, the slurry was filtered and then dried in an oven at 80 °C for 48 h. The resulting dried cake is fragile and was easily ground into powder with a mortar and pestle. The synthesized sorbents were then screened with a mesh of 200 µm for TGA experiments. The

samples were then characterised by X-ray diffraction (XRD) analysis, nitrogen intrusion porosimetry (BET/BJH) and scanning electron microscopy (Philips XL30 ESEM) observation.

1.2 Activity test on TGA

The raw limestone and synthesized sorbent were subjected to TGA experiments to determine the CO₂ and SO₂ carrying capacity. The sample mass used in each run was 20mg and the gas flowrate was 100ml/min. The samples were calcinated in high CO₂ concentrations simulating oxy-combustion conditions (86% CO₂ + 10% H₂O + 4% O₂) at 950 °C for 10 min. Carbonation was conducted in atmosphere simulating air combustion flue gas (15% CO₂ + 10% H₂O + 3% O₂ + N₂ balance) at 700 °C for 10 min. It was assumed that the flue gas had previously been scrubbed of SO₂, so there was no SO₂ in the gases experiencing decarbonation. Here, 1200 ppm SO₂ was added into the simulated flue gas atmosphere for sulphation, and the sulphation temperature and time were set at 900 °C and 120 min, respectively. The summary of the run conditions is presented in Table 2.

Table 2 The run conditions in TGA

	Gas composition (%)	Temperature (°C)	Time (min)
Calcination	86%CO ₂ +10%H ₂ O+4%O ₂	950	10
Carbonation	15%CO ₂ +10%H ₂ O+3%O ₂ +N ₂ balance	700	10
Sulphation	0.12%SO ₂ (1200ppm) +15%CO ₂ +6%H ₂ O+3%O ₂ +N ₂ balance	900	120

The sorbent carrying capacity for CO₂ or SO₂ was calculated by Eq. (3)

$$X = \frac{m_{car/sul} - m_{cal}}{m_{cal}} \quad (3)$$

where X is the sorbent carrying capacity for CO₂ or SO₂, m_{car/sul} is the mass of carbonation sorbent or sulphation sorbent(g), and m_{cal} is the mass of the calcined sorbent(g).

3 Results and discussion

3.1 Pore surface area and volume analysis

It is well accepted that specific pore surface area and volume of Ca-based sorbent have significant influence on sorbent CO_2 and SO_2 carrying capacity ^[36]. The general understanding is that chemisorption occurs and a sorbent with a large surface area and porosity has good physical absorption ability, which in turn benefits chemisorption. The molar volume of product (CaSO_4 or CaCO_3) is larger than that of CaO , and the reaction progress is eventually limited by pore blockages. To realize high calcium conversion ratios, many researchers have attempted to develop effective methods to improve the sorbent microstructure, including enhancing the surface area, the pore volume, and the pore-size distribution ^[37]. Here, raw materials and hydrated samples were also tested for surface area and porosity. The results are listed in Table 3. Longcal limestone itself had effectively no porosity and its surface area is only $0.195 \text{ m}^2/\text{g}$. After calcinating, the lime had a surface area of $9.95 \text{ m}^2/\text{g}$, and then after hydration, its surface area was further increased to $14.4 \text{ m}^2/\text{g}$. The surface area for the bottom ash ($8.01 \text{ m}^2/\text{g}$) was slighter higher than that of CFB fly ash ($6.73 \text{ m}^2/\text{g}$), although the CaO content was higher in the CFB fly ash itself, due to CaO -based sorbent sulphation in the CFB system. Given their different background and properties, the two coal ashes hydrated with lime, generated new samples with very different surface area and performance for CO_2 and SO_2 capture.

After hydrothermal reaction, the samples had a range of surface area from $16.96 \text{ m}^2/\text{g}$ to $47.27 \text{ m}^2/\text{g}$, which is much higher than that of the raw materials. Many studies have proven that the hydration conditions have a great influence on surface area. Here, three parameters namely hydration time, ratio of lime/ash and activator, are explored. The optimised conditions obtained by other researchers ^[38] were used and only a limited combination of parameters was examined. From samples of Group (2), it can be seen that when other parameters remained effectively constant, the surface area increased with hydration

time. However, samples of Group (3) show that if the hydration time is long enough (32 h), the pozzolanic reaction reaches equilibrium and the resulting sorbents have a similar surface area regardless of the lime/ash ratio. The average pore size for raw lime and hydrated samples were approximately the same, 15nm, which means the hydration process has little effect on pore size but does generate new pores. When CaSO_4 was added to the hydration process, no obvious enhancement of surface area was observed, as shown by samples from Group (4). There is however, some uncertainty about adding CaSO_4 as it is still disputed whether CaSO_4 benefits pozzolanic reactions^[38-42]. Some researchers have found that CaSO_4 can restrain the growth of $\text{Ca}(\text{OH})_2$ crystals and help the reaction between $\text{Ca}(\text{OH})_2$ and dissolved SiO_2 , whereas others have reported that a small amount of CaSO_4 actually decreases the reaction between $\text{Ca}(\text{OH})_2$ and dissolved SiO_2 . Appropriate amounts of NaOH can promote pozzolanic reaction, and thus slightly increase the surface area and pore volume as SiO_2 and Al_2O_3 can also be dissolved more easily with increased pH, while an excess amount of NaOH reverses that effect dramatically, as higher concentrations of Na^+ decrease Ca^{2+} concentrations due to common ion effect. From samples of Group (5), it can be seen that the surface area of hydrated sorbents decreases dramatically after calcination, but the samples with CaSO_4 additive maintain a higher surface area than raw lime. The surface area of samples with NaOH additive decrease from about $27 \text{ m}^2/\text{g}$ to $5 \text{ m}^2/\text{g}$, which is definitely unfavorable for CO_2 or SO_2 capture, although Na^+ is expected to help ion diffusion. Where the use of such additives has both positive and negative effects, the benefits must be carefully weighed against possible losses.

Table.3 BET pore surface areas and BJH cumulative pore volumes of samples

sample	$S_{\text{BET}} (\text{m}^2/\text{g})$	$V_{\text{BJH}} (\text{cm}^3/\text{g})$	Pore diameter(nm)
Sample of Group (1): samples before carbonation or sulphation			
bottom ash	8.01	0.01	4.94
fly ash	6.73	0.03	10.65
limestone	0.20	0.001	9.52
quick lime	9.95	0.04	14.66

hydrated lime	14.40	0.09	15.19
Sample of Group (2): the influence of slurring time			
CS10(35/15/10/1h)	16.96	0.1	16.55
CS6(35/15/10/4h)	19.76	0.12	17.13
CS14(35/15/10/8h)	21.01	0.12	16.02
CS26(35/15/10/16h)	22.94	0.12	14.79
CS23(35/15/10/32h)	26.37	0.16	15.72
CS11(15/35/10/1h)	13.79	0.07	14.35
CS12(15/35/10/4h)	22.53	0.12	13.81
CS15(15/35/10/8 h)	28.21	0.13	13.38
CS27(15/35/10/16 h)	35.77	0.16	12.83
BS31(35/15/10/8h)	23.95	0.12	14.81
BS32(35/15/10/16h)	32.76	0.16	14.69
BS33(35/15/10/32h)	47.27	0.24	14.44
Sample of Group (3): the influence of ratio of lime to ash			
CS7(15/35/5/4h)	21.78	0.11	13.13
CS9(25/25/5/4h)	23.46	0.11	13.25
CS5(35/15/5/4h)	24.46	0.15	16.13
CS22(15/30/18/32h)	26.87	0.13	13.23
CS23(35/15/10/32h)	26.37	0.16	15.72
CS40(45/5/5/32h)	26.95	0.16	14.93
Sample of Group (4): the influence of activator CaSO ₄ or NaOH			
CS4(35/15/0/4h)	24.79	0.15	15.62
CS6(35/15/10/4h)	19.76	0.12	17.13
CS2(35/15/15/4h)	18.46	0.11	15.71
CS7(15/35/5/4h)	21.78	0.11	13.13
CS12(15/35/10/4h)	22.53	0.12	13.81
CS13(15/35/15/4h)	19.90	0.11	13.99
CS14(35/15/10/8h)	21.014	0.12	16.02
CS20(35/15/10/8h/NaOH 1g)	22.48	0.13	16.42
CS28(35/15/0/8h/NaOH 3g)	17.19	0.10	15.48
CS15(15/35/10/8h)	28.21	0.13	13.38
CS21(15/35/10/8h/NaOH 1g)	32.60	0.14	12.99
CS29(15/35/0/8h/NaOH 3g)	16.42	0.09	14.10
Sample of Group (5): samples after calcination			
CS36(CS23 after calcination)	14.01	0.06	10.75
BS38(BS33 after calcination)	11.14	0.03	7.44
BS39(BS35(35/15/10/8h/NaOH3g) after calcination)	4.89	0.01	6.85

CS or BS N(a/b/c/d/e), where CS or BS means the new sample is synthesized from CFB fly ash or bottom ash; N is the index number given when the samples were prepared; a, b, c, d denote mass(g) of lime, coal ash, CaSO₄ and hydration time, respectively; e denotes the mass of NaOH, if it is present. For example, CS20(35/15/10/8/NaOH 1g) means this sample was synthesized from CFB fly ash; the mass of lime, CFB fly ash and CaSO₄ were 35g, 15g, 10g respectively; hydration time was 8 hours and the mass of NaOH was 1g.

Our previous research verified that the pore size distribution has different effects on CO₂ and SO₂

capture, and that larger pores are more favorable to sulphation than carbonation ^[34] due presumably to different product volume. It is thus necessary to study the pore size distribution of the synthesized sorbents. Representative results are shown in Fig. 1. It can be seen that the main proportion of the pores is found in the range from 10 to 100 nm which are favorable for both carbonation and sulphation. The pores under 10nm have a significant contribution to pore surface area but a small contribution to the total pore volume. These pores provide large surface where reactions can take place but the space provided for product growth is very limited due to their small pore volume. The hydrated samples have a similar pores distribution to raw lime, while the main BJH pore volume distribution peak is much larger and wider. That means the hydration process does not change pore size significantly but it does increase the number of pores. This can be seen in Fig.1, which shows that the sorbent pore structure is improved by this synthesis method. Sample BS33 had the largest pore volume ($0.24 \text{ cm}^3/\text{g}$) and its surface area ($47.27 \text{ m}^2/\text{g}$), is much greater than that of the original lime ($0.04 \text{ cm}^3/\text{g}$ and $9.95 \text{ m}^2/\text{g}$). When the synthesized sample was calcined, its pore volume and surface area were reduced but were still larger than raw lime. As to synthesized samples, a small peak can be seen at around 80 nm in pore area distribution, while it is missed in pore volume distribution. This means the synthesis process enlarge sorbent specific area but not pore volume. This phenomenon can be explained by means of SEM images (Fig. 3) that synthesized sorbents present filamentary and network structure. Given these various effects it is clear that their effect on CO_2 and SO_2 capture still needs further research.

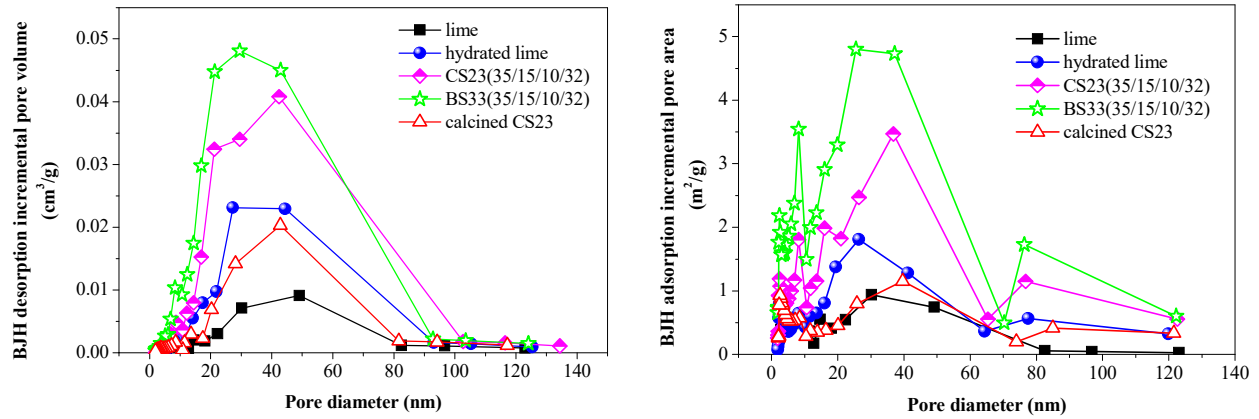
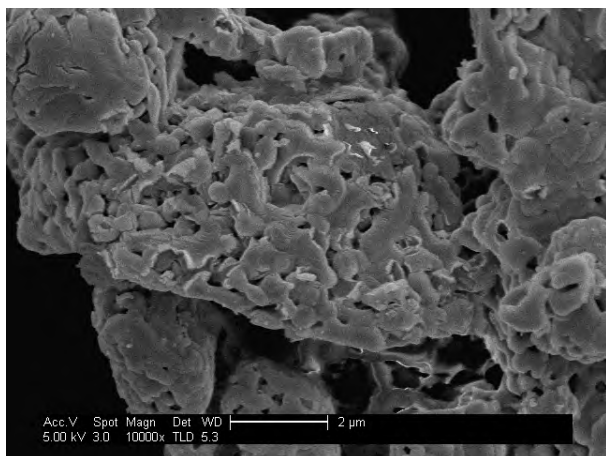


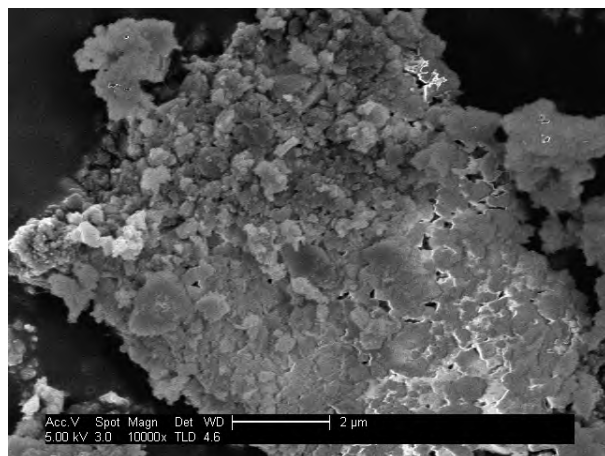
Fig. 1 BJH pore volume and surface area distributions in samples

3.3 Microstructure property

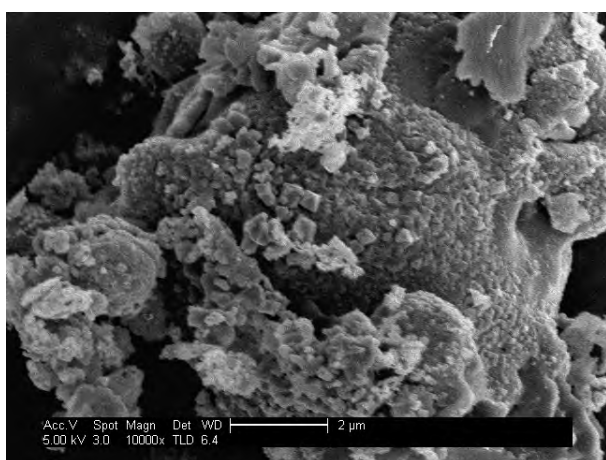
To help to understand the mechanisms of hydration, carbonation and sulphation, the evolution of sorbent surface microstructure was examined. The increase of surface area is illustrated in the following SEM images. Fig. 2 shows the surface structure of lime (a), hydrated lime (b), CFB fly ash (c) and bottom ash from pulverized coal power plant (d). It can be seen that raw lime has irregular shapes and macro pores at the surface. After hydration, there are many small particles adhering to the surface of hydrated lime, making it look like it has a looser structure than lime. This agrees with other experimental observations that the sorbent activated by hydration becomes fragile and results in severe sorbent attrition [43-45]. The explanation for this effect is that the rapid heat release of the lime hydration reaction essentially causes the lime particles to “explode” into smaller Ca(OH)_2 particles. Generally, CFB fly ash particles look fluffy as they are agglomerates from smaller size ash particles. The very small particles adhere on relatively large particles due to electrostatic force. Compared to CFB fly ash, the bottom ash particles have a much smoother surface and are spherical in shape.



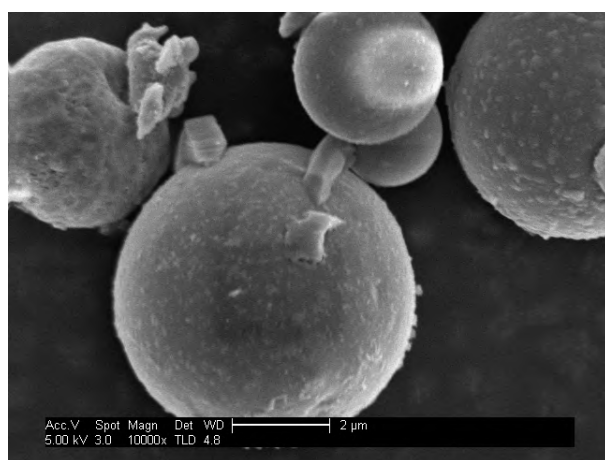
(a)Lime



(b)Hydrated lime



(c)CFB fly ash

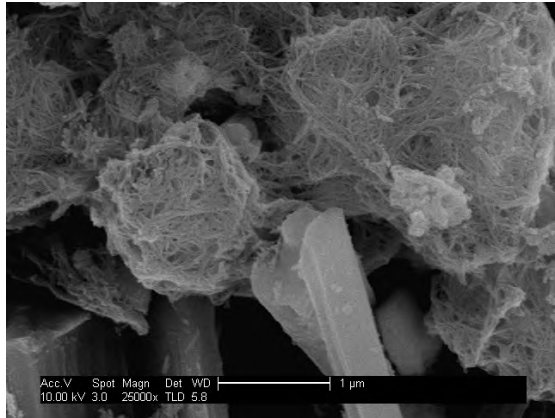


(d) bottom ash

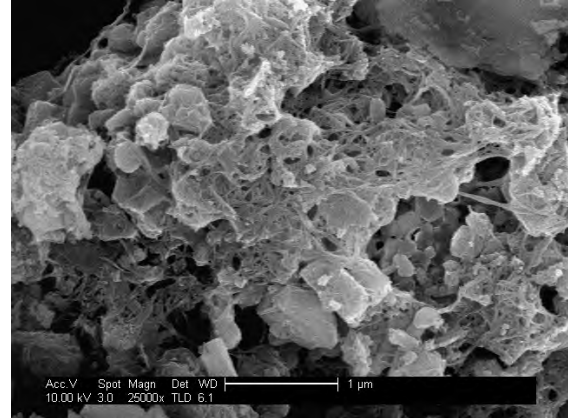
Fig. 2 Surface morphology of raw materials under SEM

The surface morphology of representative sorbents synthesized from CFB fly ash is illustrated in Fig.3. After the $\text{CaO}/\text{fly ash}/\text{CaSO}_4$ was mixed at different ratios and hydrated in hot water for the maximum hydration time (32 h) as illustrated in (a) and (b), a network structure developed on the particle surfaces, which causes an effective increase in surface area. Here, the additive NaOH is expected to promote pozzolanic reaction as it increases solution pH and helps dissolve SiO_2 and Al_2O_3 . Finally, little network structure is found on this kind of sample, as shown in (c). A similar network structure was also found on surface of sorbent synthesized from bottom ash, as shown in (d). When the samples are calcined in a CO_2 -enriched atmosphere however, it is still easy to find particles with developed network structure, as shown in (e) and (f). An easily overlooked phenomenon is that the lines

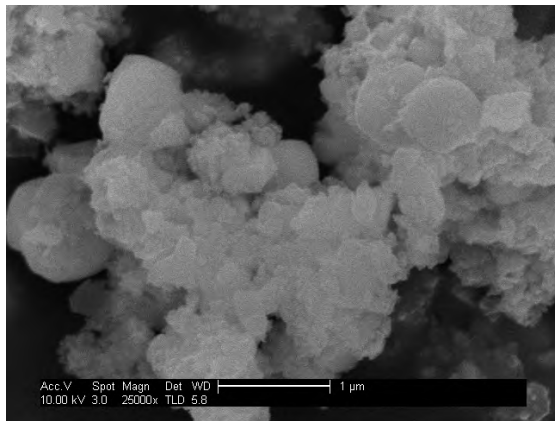
between the network structure are not smooth and appear fragile.



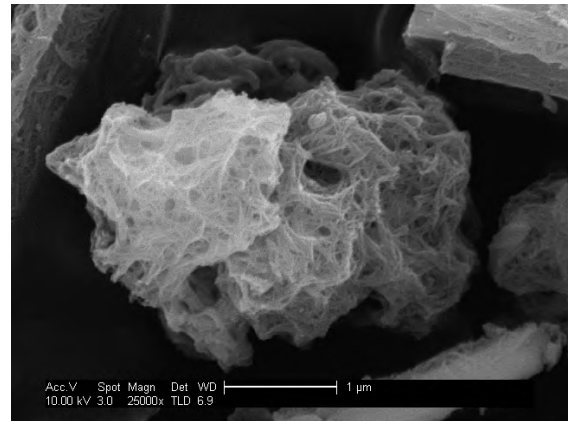
(a) CS22(15/30/18/32)



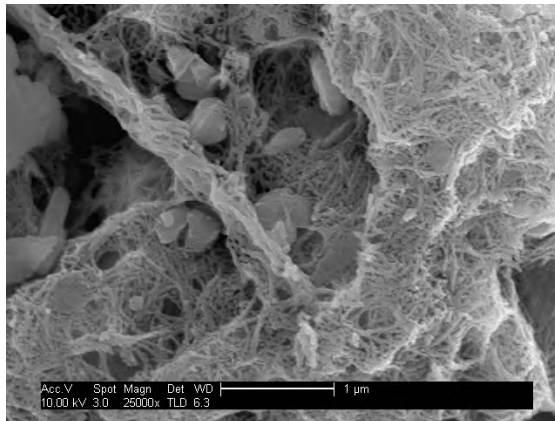
(b) CS23(35/15/10/32)



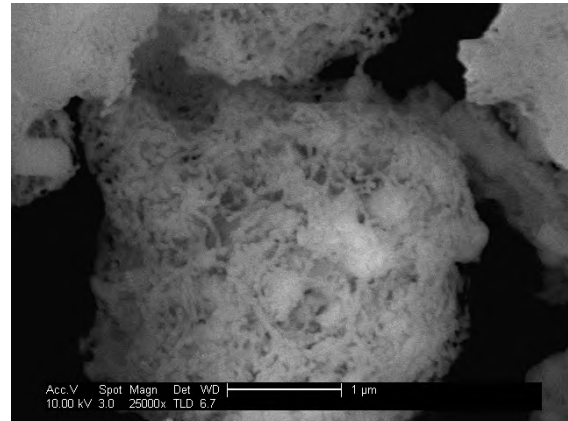
(c) CS28(35/15/0/8/NaOH 3g)



(d) BS43(35/15/10/32)



(e) CS23(35/15/10/32) cal

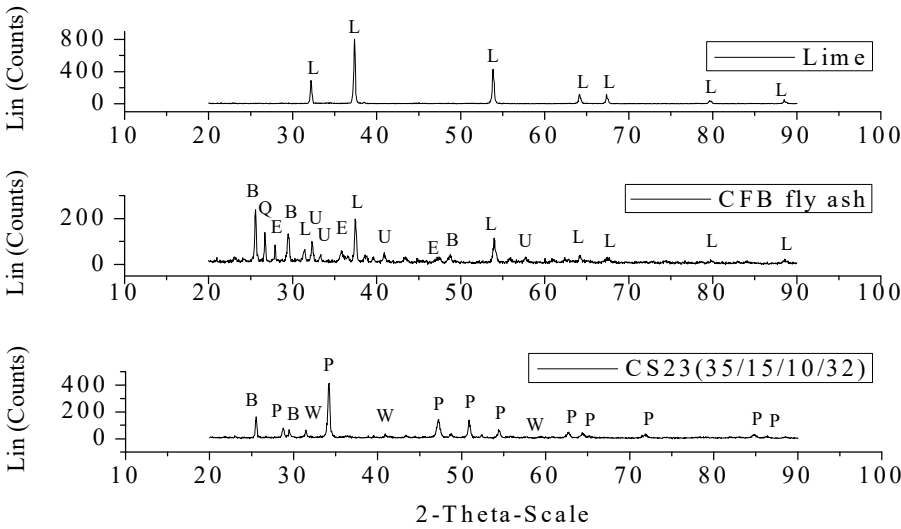


(f) BS43(35/15/10/32) cal

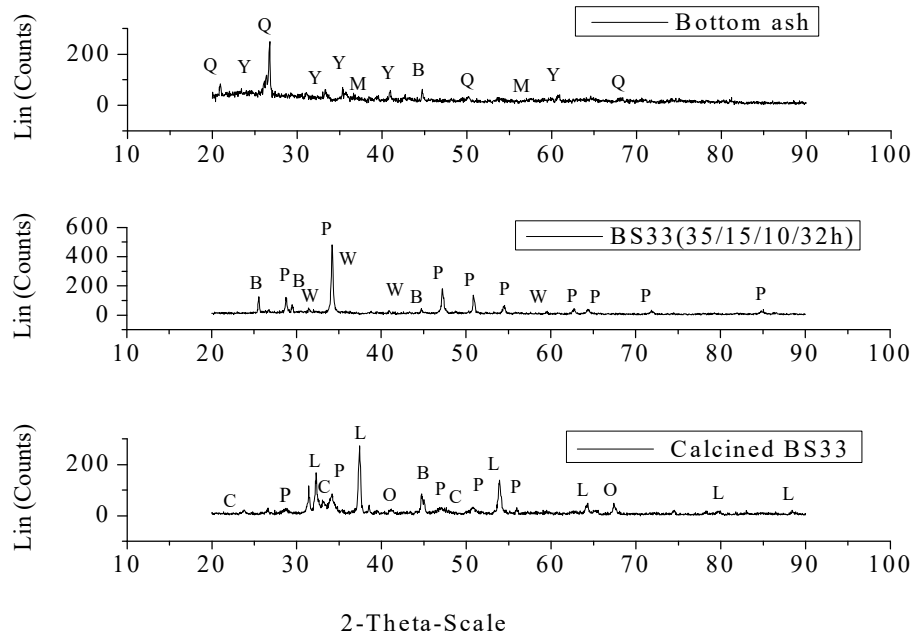
Fig. 3 Surface morphology of sorbents synthesized from CFB fly ash and bottom ash

X-Ray Diffraction (XRD) analysis is an effective way to determine the chemical composition of sorbents, although its ability is limited when the content of any given phase is less than 3%. The XRD spectrum of raw materials and hydrated sorbents is shown in Fig. 4. It can be seen that only one phase,

namely CaO was detected as the calcined Longcal limestone is relatively pure. However, the composition for CFB fly ash is complicated and the main phases are CaO, CaSO₄ and SiO₂. However, some complex compounds containing Na and Al were also detected. After the pozzolanic reaction between lime and CFB fly ash, the main product is calcium silicate (CaSiO₃), which is believed to be the main contributor to the surface area increase. The bottom ash has a very complicated XRD spectrum and it is difficult to identify the compound for each weak peak. The main compositions are salts and oxides of Si, Al, and Fe. The sorbent synthesized from lime and bottom ash is very similar in composition to the sorbent synthesized from lime and CFB fly ash. When synthesized sorbent is calcined, Ca(OH)₂ decomposes into CaO as expected, while CaSiO₃ phase itself is not distinct. A new phase of Ca₃Al₂O₆ formed in the calcination. This is believed to act as a skeleton preventing sintering in the following CO₂ capture cycles and SO₂ retention.



(a) Lime, fly ash and synthesized sorbent



(b) Bottom ash, synthesized sorbent and calcined synthesized sorbent

Note: L: Lime (CaO); B: Calcium Sulphate (CaSO_4); E: Ephesite-2M1($\text{Na}_2\text{Al}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$); U: Calcium Silicate (Ca_2SiO_4); Q: Quartz (SiO_2); P: Portlandite ($\text{Ca}(\text{OH})_2$); Y: Sillimanite (Al_2SiO_5); M: Maghemite-Q(Fe_2O_3); W: Wollastonite-1A^a(CaSiO_3); C: Aluminum Calcium Oxide ($\text{Ca}_3\text{Al}_2\text{O}_6$); O: Aluminum Oxide alumina (Al_2O_3)

Fig. 4 XRD material analysis of lime, coal ash and synthesized sorbents

3.4 Sorbent activity

Cyclic CO_2 capture and sequential SO_2 retention of sorbents were analyzed by TGA. The results are illustrated in Fig. 5 and Fig. 6. From Fig. 5 it can be seen that original limestone shows better activity than the other two hydrated sorbents for the first 40 cycles. The main reason is that hydrated sorbents contain a relatively high content of ash and CaSO_4 , decreasing effective content for CO_2 capture in sorbent. The XRD analysis shows that the purity of original limestone is about 98%, while CaO content for both hydrated sorbents is about 58% when calculated by means of the mixing ratio. The real effective content of CaO in CS23 is higher than BS33 as CFB fly ash contains 30wt% CaO , while

bottom ash contains only 3wt%. It is also found that although the hydrated sorbents have lower CO₂ capture ability in the first few cycles, they show better performance in terms of cycling stability. After 18 cycles, the sorbent hydrated with CFB fly ash has nearly the same performance as the original limestone.

It has been previously demonstrated that following carbonation the spent CaO-based sorbent remains active for SO₂ capture^[33], and some literature indicates that sorbent obtained by hydration between lime and coal ash actually has a high efficiency for SO₂ capture at low temperature (60 °C) ^[39]. Here, the hydrated sorbent was not only tested in cyclic CO₂ capture but also for SO₂ capture at high temperature. The performance of SO₂ capture is shown in Fig.6. The order of SO₂ capture ability for these three sorbents is original limestone>CS23>CS33, in accord with their CaO content. An important result is that the cycled sorbents are still active for SO₂ capture. For original limestone, the SO₂ capture activity is 0.56 g SO₂/g sorbent, 0.54 g SO₂/g sorbent and 0.57 g SO₂/g sorbent for fresh, 10 cycled and 40 cycled sorbents, respectively. The trend for the other two hydrated sorbents is basically the same. This result confirms our previous study that sorbents produced after more cycles have better SO₂ capture activity than those produced after only a few cycles, as sintered pore structure provides greater product growing space for reactions to occur in the pore inner surface.

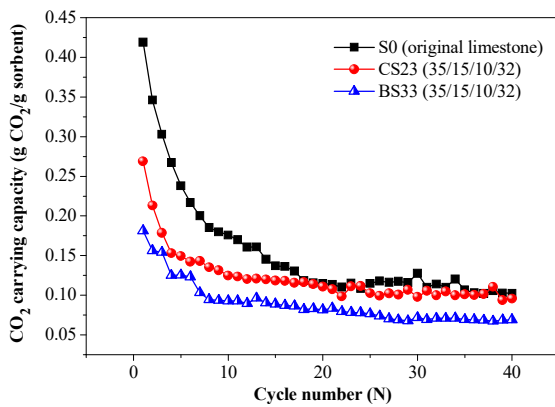


Fig. 5 The CO₂ carrying capacity of original

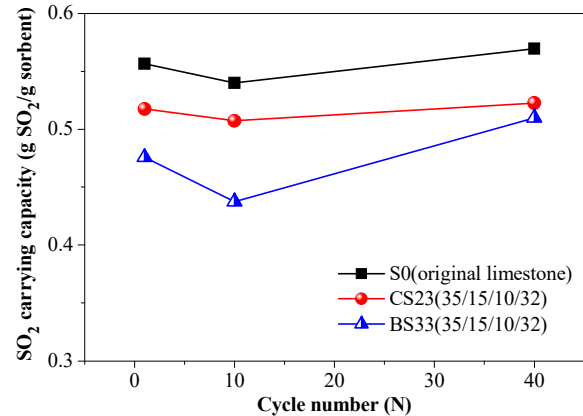


Fig. 6 The influence of CO₂ capture cycle number

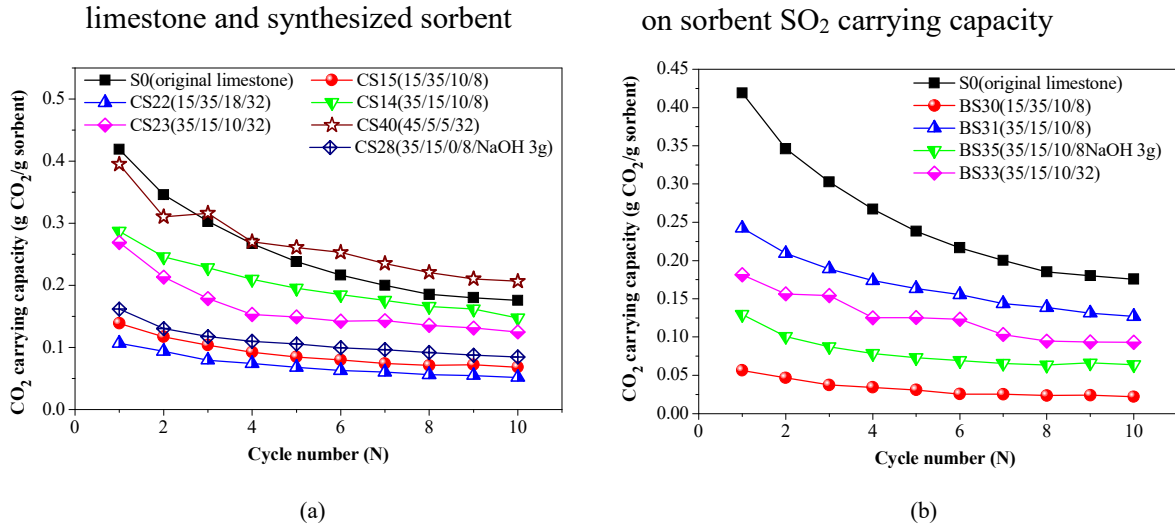


Fig. 7 Cyclic CO₂ carrying capacity of sorbents synthesized with CFB fly ash (a) and bottom ash(b)

The comparison of CO₂ capture for original limestone and hydrated sorbents in the first 10 cycles is illustrated in Fig.7. The CaO content is a major factor influencing CO₂ capture. However, the sorbent CS40 shows better CO₂ capture activity than the original limestone after the third cycle, indicating the hydration process enhances cycling stability of sorbent CO₂ capture. Although the surface area of sorbents increases as hydration time increases, too long a hydration time may result in loss of effective CaO content due to pozzolanic reaction, which thus reduces its CO₂ capture ability. Sorbent CS23 has a larger surface area than CS14, and sorbent BS33 has a larger surface area than BS31, while both CS23 and BS33 showed lower CO₂ capture ability in first 10 cycles. The addition of NaOH is not beneficial for CO₂ capture although it was expected to promote pozzolanic reaction as more Si and Al could be dissolved in an alkaline environment. However, a previous study also reports that the presence of Na⁺ will intensify sorbent sintering at high temperatures [46].

It can be seen from Fig.8 that the hydrated sorbents with different mix ratios have improved SO₂ capture even after 10 cycles of CO₂ capture. It is also obvious that a too low content of CaO is not helpful for CO₂ or SO₂ capture. However, a sorbent with high CaO content, although it has high CO₂ capture ability, doesn't necessarily have a high SO₂ capture ability. The SO₂ capture ability of sorbent

CS40 (CaO/fly ash/CaSO₄=45/5/5) is lower than that of sorbent CS23 (CaO/fly ash/CaSO₄=35/15/10). This suggests that there must be some difference in reaction mechanism between carbonation and sulphation, causing the optimised mix ratio for CO₂ and SO₂ capture to be different. The optimised mix ratio may therefore differ given that different kinds of coal ash have different composition.

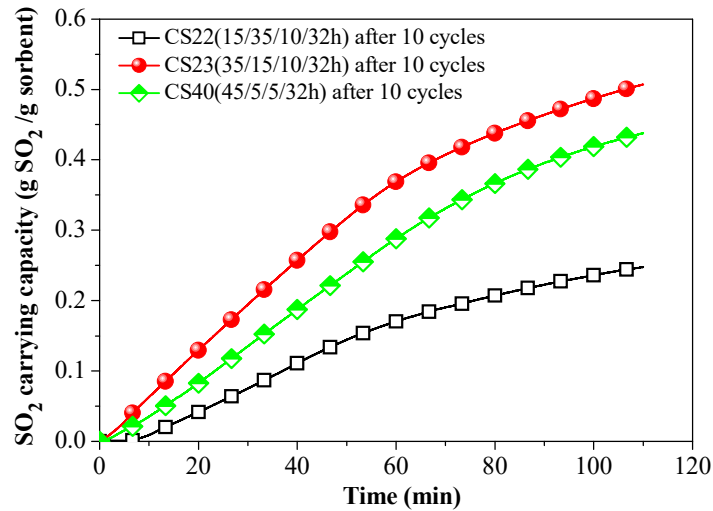


Fig.8 The influence of CaO/coal ash ratio on SO₂ carrying capacity of synthesized sorbents

The effect of NaOH addition on CO₂ capture and SO₂ capture is effectively opposite. A small amount of NaOH reduces CO₂ capture ability, but increases SO₂ capture ability dramatically. As shown in Fig.9, when adding 1g NaOH into the sorbent with CaO/fly ash/CaSO₄ ratio of 35/15/10, its sulphation conversion is maintained at 0.46 g SO₂/g calcined sorbent after 10 cycles, 31% higher than the sample without NaOH addition under the same conditions. In the case of CS28(35/15/0/NaOH 3g), the sulphation conversion of sorbent after 10 cycles is up to 0.62 g SO₂/g calcined sorbent, higher than that of fresh limestone with 0.55 g SO₂/g calcined sorbent. From the process curve, one can see that the kinetic-controlled stage and diffusion-controlled stage with different reaction rates are clear for the original limestone, while it is difficult to differentiate them in the synthesized sorbents, especially for CS28. For the original limestone, the reaction rate in the kinetic-controlled stage is highest after about 60 min and then slows as it is dominated by the diffusion-controlled stage. For synthesized sorbents, the reaction rate is lower in the initial stage but deteriorates more slowly over time. In the case of CS28, the

reaction rate is nearly steady over the test time and the process curve is close to a straight line. If the reaction time were extended, a higher conversion could be expected.

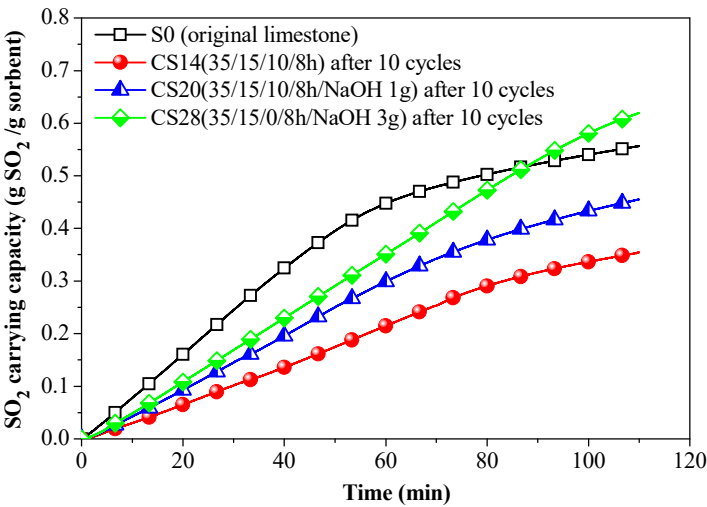


Fig.9 The influence of NaOH on SO₂ carrying capacity of synthesized sorbents

The sorbents hydrated with bottom ash have similar SO₂ capture characteristics to those hydrated with CFB fly ash, as shown in Fig. 10. Sorbent BS30 has the lowest sulphation conversion of about 0.2 g SO₂/g calcined sorbent due to low CaO content. When comparing sorbents BS31 and BS33, it can be seen that the sorbent with longer hydration time (BS33) has a lower reaction rate in the first stage, but this rate continues in the second stage and its final conversion is ultimately higher than that of BS31. The sorbent with NaOH added has a lower initial reaction rate than original limestone, but it maintains this rate for a longer time and the conversion finally exceeds that of the original limestone.

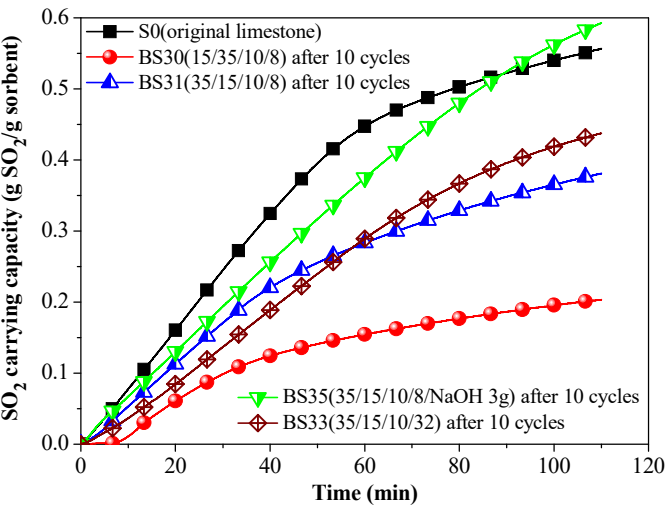


Fig. 10 The influence of NaOH on SO₂ carrying capacity of synthesized sorbents

From Fig.8 to Fig.10, the main characteristic of sulphation can be clearly elucidated: synthesized sorbents have lower reaction rates in the initial stage, but the reaction rates are relatively stable over the whole reaction process and the distinction between a fast and slow reaction stage is not obvious. NaOH additive can increase SO₂ capture ability dramatically but reduces CO₂ capture ability. The reason for this phenomenon is that the reaction mechanisms for carbonation and sulphation are different. Both carbonation and sulphation processes can be divided into fast and slow reaction stages. For carbonation, the reaction is controlled by kinetics in the fast stage while by gas diffusion in the slow stage. Besides kinetic and gas diffusion control, solid ion diffusion plays a significant role in the sulphation process^[47-49]. CaSO₄ is a fast ion conductor as it is an ionic crystal with high ionic conductivity. The conductivity rate of Ca²⁺ in CaSO₄ is up to 1/1000 S/cm^[50]. One ion diffusion mechanism which is confirmed by Hsia et al is that the Ca²⁺ and O²⁻ penetrate the CaSO₄ product layer from inside to outside and then react with SO₂ gas^[51]. When the CaO is modified by Na₂CO₃, Na⁺ will replace Ca²⁺ ions and form vacancy defects due to different ion charge of Na⁺ and Ca²⁺ and solid ions diffuse by means of these vacancy defects^[52]. The more vacancy defects there are, the faster the ion transfer and the reaction is. By contrast, CaCO₃ does not easily allow solid ion transfer in its product layer and this is the reason why the addition of NaOH benefits sulphation significantly.

4 Conclusions

Modifying Ca-based sorbents by using hydrothermal synthesizing lime and coal ash is proposed as a method of improving their capture performance. The pozzolanic reaction is believed to take place in the hydrothermal process and generate CaSiO₃, enhancing the surface area of synthesized samples. TGA tests have verified that the synthesized samples have good performance in CO₂ cyclic capture, although showing lower capture ability than pure lime in first few cycles due to lower effective CaO content(25~81% versus 98%). A sample with lime:ash ratio of 45:5 showed much higher CO₂ capture

ability than lime after three cycles and much better activity stability. The reason for better performance for CO₂ capture is that the microstructure of synthesized samples is improved and a new product Ca₃Al₂O₆ is formed in high temperature calcination, which is believed to serve as a skeleton preventing sintering during cycles.

The synthesized sorbents which experienced multi-carbonation/calcination cycles still maintain a high SO₂ carrying capacity. Adding a small amount of NaOH decreases the CO₂ carrying capacity of synthesized sorbent but enhances its SO₂ carrying capacity dramatically. The reason is that the sulphation reaction is controlled not only by gas diffusion but also by solid-state ion diffusion and Na⁺ ions generate more crystal lattice defects which can accelerate the ion diffusion rate in the product layer, and consequentially enhance the overall SO₂ capture performance.

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Preparation and characterization of lime/coal ash sorbents for sequential CO₂ and SO₂ capture at high temperature

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