

From waste to valuable utilization of spent bleaching clay in synthesizing high-performance calcium-based sorbent for CO₂ capture

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Abstract

A novel calcium looping (CaL) process integrated with a spent bleaching clay (SBC) treatment is proposed whereby fuels and/or heat from regeneration of SBC provide supplemental energy for the calcination process; in addition, the regenerated SBC could be used to synthesize enhanced CaO-based sorbents. Composite samples were prepared with various doping ratios together with the regenerated SBC via a pelletization process. All pellets were subjected to thermogravimetric analysis (TGA) tests employing severe reaction conditions to determine the optimal doping ratios and regeneration method for the SBC-based sorbents. These results demonstrate that pellets containing combustible components showed higher CO₂ uptake, due to the improved pore structure, which was verified by N₂ adsorption measurements. The as-prepared sorbent “L-10PC” (90% CaO/10% pyrolytic SBC) achieved a final CO₂ uptake of 0.164 g(CO₂) g(calcined sorbent)⁻¹ after 20 cycles, which was 67.3% higher than that of natural limestone particles. A new larnite (Ca₂SiO₄) phase was detected by XRD analysis; however, the weak XRD peak associated with it indicated a low content of larnite in the pellets, which produced a smaller effect on performance compared to cement. A synergistic effect was achieved for a sample designated as “L-5PC-10CA” (85% CaO/5% pyrolytic SBC/10% cement), which resulted in the highest final uptake of 0.208 g(CO₂) g(calcined sorbent)⁻¹. Considering the simplicity of the pyrolysis regeneration process and the excellent capture capability of pellets doped with pyrolytic SBC, the proposed system integrating CaL with SBC pyrolysis treatment appears to be promising for further development.

Keywords: Calcium looping, CaO-based sorbents, spent bleaching clay treatment, cement,

pelletization.

1. Introduction

With the Paris agreement, the reduction of anthropogenic CO₂ emission is receiving increasing attention. To achieve the goals of that agreement, CO₂ emissions must decline rapidly after 2030, with global CO₂ from energy- and industry-related sources reaching net-zero levels between 2060 and 2080.¹ Post-combustion carbon capture and storage (PCCS) is an essential part of incorporating existing energy-intensive industries, such as coal-fired power plants, cement and iron-and-steel production into such a strategy, as they remain the top three anthropogenic sources of CO₂ emission.²⁻⁴ Calcium looping (CaL), as one of the newer and promising methods of PCCS, has been studied extensively and appears to be an important, rapidly developing PCCS technology.⁵⁻¹¹ Limestone is a cheap and abundant natural material, making it particularly suitable for the CaL process. However, although 1.7 MWth⁷ and 1.9 MWth⁸ demonstration projects have been successfully tested, the cyclic performance degradation and attrition loss of sorbent are still two major obstacles that need to be overcome. CO₂ capture capacity of limestone decreases rapidly (about 15% decay per cycle) due to thermal sintering related to the lower Tammann temperature of CaCO₃ (533 °C).^{9, 12} Hence lime-based sorbent supported by a stable phase (with high $T_{Tammann}$) improves its performance. Several types of inert material, including Al₂O₃^{6, 10, 13, 14}, MgO^{15, 16}, SiO₂^{5, 11, 17, 18}, ZrO₂¹⁹, and Y₂O₃²⁰ have been shown to effectively improve the cyclic stability of this sorbent. It also appears possible that the spent CaO sorbents from the CaL process can be reused to produce cement,^{2, 3} which offers a decrease by at least half of the CO₂ emissions from that industry, owing to the energy-intensive calcination procedure required when using natural limestone. In view of the requirements of the cement industry, components like Al₂O₃ and/or SiO₂ supported lime-based sorbents are likely to be more suitable for subsequent cement production.

Although CaL has been shown to be more cost-effective than other CO₂ capture methods,²¹ its cost could be dramatically reduced if such sorbents were prepared partially or totally from wastes. Li et al.¹⁰ prepared carbide slag-derived Ca₃Al₂O₆-stabilized sorbents, which exhibited favorable capture performance compared to the original carbide slag itself. Ca₃Al₂O₆ has also been reported

as an inert material in other work.²² Chen et al.¹¹ examined CaO-based sorbents modified by fly ash in a thermogravimetric analyzer, and demonstrated that $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and CaSiO_3 could help sorbents resist sintering. In particular, rice husk ash (containing 93 wt. % SiO_2) was also identified by Li et al.⁵ and Chen et al.²³, as particularly promising in enhancing the cyclic capture performance of synthetic sorbents. Yan et al.¹⁷ first introduced nanosilica derived from photovoltaic waste (SiCl_4) into synthetic lime-based sorbents. The capture performance tests revealed that such sorbents exhibited pronounced improvement in performance, even under severe calcination conditions (e.g., at 920 °C in pure CO_2), in which larnite (Ca_2SiO_4) played a role. Tian et al.⁴ successfully proposed an efficient CO_2 capture process wherein Ca and Fe were recovered from steel slag to prepare high-purity CaO-based sorbents for CO_2 capture and to obtain high-quality iron ores for steel production. It is, therefore, clear that the use of wastes in the PCCS process is an important option.

Because of its high specific surface area, activated bleaching clay is widely used in the process of petroleum refining to remove the coloring and unstable impurities from lubricating base oils. Usually, the spent bleaching clay (SBC) contains as much as 30% or more oil by weight. It has been estimated that around 600,000 tonnes or more SBC are produced yearly worldwide.²⁴ The disposal of SBC causes environmental pollution due to the presence of the waste oil, often requiring expensive remediation of such sites. Currently, several methods have been proposed to recycle this oil and to ensure that SBC disposal is environmentally benign, and these approaches include thermal treatment (calcination in air)^{25, 26} and solvent extraction²⁶⁻²⁹ involving organic solvents,²⁷⁻²⁹ acid solutions²⁵ and hot alkali solutions²⁵. Among these, organic solvent extraction has been repeatedly reported to be an appropriate method for SBC treatment. Wang et al.²⁹ proposed a process whereby step-by-step solvent extraction was used to recover the adsorbed oil from lubricating oil refining clay: first, the spent clay is extracted by petroleum ether; second, this is followed by extraction with petroleum ether and ethanol (95 v%) two or three times; and then the resulting material is extracted with ethanol (95 v%), followed by water washing; finally, the clay is dried at 130 °C to obtain a regenerated clay. Although, more than 99 wt. % of the adsorbed oil can be recovered by these procedures, such sophisticated processes are so complicated that they are economically and commercially unfeasible. Thermal treatment, namely calcination in air, is usually regarded as a substandard albeit cheap method to recover SBC, as it leads to the

destruction of the clay's structure and the release of pollutants.²⁹

All studies on SBC regeneration are aimed at recovering oil and achieving its reuse. It should be noted that the fresh bleaching clays usually come from bentonite activated by acid treatment, the main components of which are SiO_2 and Al_2O_3 , (the same components as in regenerated SBC). As noted above, SiO_2 and Al_2O_3 are good inert phases to mitigate the sintering of lime-based sorbents. As a result, the regenerated SBC can potentially be used for preparing enhanced CO_2 capture sorbents with lime. In general, any CaL CO_2 capture process contains dual reactors, namely the carbonation and calcination reactors. In the calcination reactor, it is necessary to consume extra fuels to achieve and maintain a high reaction temperature of 900 °C. Here, the fuels and heat can serve to supplement the energy consumed in the calcination reactor as part of the regeneration process for the SBC. Furthermore, the residual flammable components in treated SBC will increase the porosity of any synthetic sorbents.

Currently, there is no research on the incorporation of SBC treatment into the CaL process and, hence, we have proposed a potential CO_2 capture system (shown in **Fig. 1**) whereby fuels (oil and combustible gases) and/or heat from various SBC regeneration processes are introduced into the calciner; three types of residue are mixed with calcined lime powder separately and used to prepare sorbent pellets; the fresh sorbents are then introduced into the calciner, while the spent sorbent is utilized for cement production. We have tested the regenerated residues and they behave very well in cement production, the results of which will be published elsewhere. In this paper, different types of synthetic sorbents were prepared with variously regenerated SBC by pelletization. CO_2 capture tests were then carried out to determine the optimal doping ratios and regeneration method of SBC for this system.

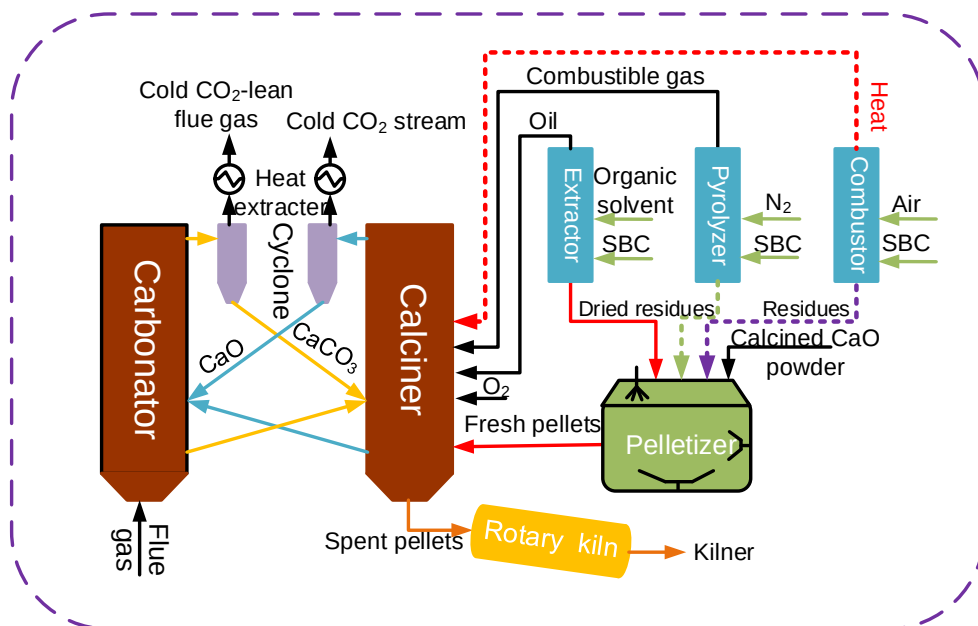


Fig. 1. Scheme of a potential CO₂ capture system integrated with spent bleaching clay treatment.

2. Experimental Section

2.1 Materials

Fresh bleaching clay (FBC) and spent bleaching clay (SBC) studied in this paper were obtained from a Chinese petroleum company. Prior to examination by X-ray fluorescence (XRF), the spent clay was dried overnight in a hot air blast drying oven at 110 °C, and its main components were shown to be SiO₂ and Al₂O₃, (Table S1, Electronic supplementary information, ESI†). Natural limestone containing ~55% CaO was obtained from Omya Fine Chemical Industry Co., Ltd., Nanjing, China.

Determination of oil content in SBC. Firstly, both the FBC and SBC were dried in a hot air blast drying oven at 110 °C, until constant mass was achieved. Then the FBC sample was calcined in a muffle roaster at 900 °C for 2 h, to determine the inert content in the material, and allow the oil content in the SBC to be determined by difference. For each test, 10 g of virgin and spent clay were tested, and three parallel tests were carried out to determine the average content, ensuring an absolute error no more than 0.5% for any random two tests. The results indicated that the average moisture content of virgin and spent clay was 6% and 5%, respectively. The average mass loss (dry basis) of SBC was 34.8%, compared to 8.5% for FBC. Therefore, the average oil content in SBC was determined as 26.3%.

2.2 SBC Regeneration Treatments

It has been reported that the regenerated SBC possessed various textural characteristics after different regeneration processes.³⁰ In order to identify the effect of particular regeneration methods, three different methods were used as described below:

Pyrolysis regeneration. The apparatus for SBC regeneration by pyrolysis is shown in **Fig. S1†**. It has been reported that the major compounds found in the pyrolytic products are carboxylic acids and alkanes with short chains of carbon atoms.³¹ These oils are associated with the production of high levels of monoaromatic compounds as well as carcinogenic polycyclic aromatic hydrocarbons (PAHs). To study these better, an ice-bath device was added to condense these organic compounds. The pyrolysis regeneration was performed in pure N₂ at a given temperature in the range of 500~800 °C for 2 h. The effect of pyrolysis temperature on the performance of regenerated SBC was more significant than the pyrolysis time, and 2 h was enough for the treatment process.²⁷ Finally, the regenerated SBC was removed and stored in a desiccator as soon as the reactor cooled down to ambient temperature.

Calcination regeneration. To treat the noxious flue gas, the calcination process was similarly performed in the device mentioned above. The calcination process was typically carried out in air at 500 °C for 2 h.

Organic solvent regeneration. During each extraction run, 25 g SBC and 250 mL absolute ethanol (solid-to-liquid ratio of 1:10) were added successively into a three-neck flask with an electric stirrer. Then the mixtures were stirred (at an appropriate speed) at room temperature for 30 minutes. After that, the clay and the solvent were separated by vacuum filtration. The oil and solvent were recovered by vaporizing the filtrate. The same process was repeated two or three times. Finally, the regenerated SBC was dried in an air-blower-drier at 120 °C for 24 h, then weighed and stored in a desiccator.

Determination of residual combustible component content in regenerated SBC. Various combustible components (unburned carbon and organics) were found in the regenerated SBC after these different treatments, and their contents were determined by methods discussed above in **section 2.1**.

2.3 Synthetic Sorbent Preparation

Lime-based pellets doped with various materials were prepared in a laboratory high-shear wet

granulator (Xiyite G6, China). Prior to pelletization, raw limestone powder was calcined at 850 °C in air for 2 h. The calcined limestone powder (sieved to <45 μm) and the various regenerated SBC and/or cement powders (sieved to <41 μm) were ground in an agate mortar for 30 mins, then loaded into a 1L pelletizer vessel at different ratios of lime to dopants (~200 g in total for each batch). Then the materials were mixed energetically by means of an agitator and a chopper at a specific rotation speed. To achieve granulation, deionized water was sprayed intermittently through a pressurized atomizing nozzle during the procedure at the end of the pre-mixture process. More details about this pelletization process can be found elsewhere.¹⁴ After that, the pellets were air dried and then sieved to the desired size of 0.1-0.6 mm (see **Fig. 2**).

Five types of sorbent pellets doped with different materials were synthesized, and the compositions of pellets are shown in Table 1. The sorbents pellets were named as follows: L- α PC/CC/OC/CA (for pellets doped with only one material), or L- α PC/CA- β PC/CA (for pellets doped with two types of material), where α and β refer to the weight percent of dopant in pellets. Additionally, PC/CC/OC/CA refer to pyrolytic SBC, calcined SBC, organic-extracted SBC and cement, respectively. For instance, the pellet containing 5 wt.% pyrolytic SBC and 10 wt.% cement is referred to as L-5PC-10CA. Here, raw limestone particle is designated as L and pelletized calcined limestone is designated as LP, which are used to determine the effect of pelletization on sorbent performance.

Table 1: Material compositions of different samples

Sample	Lime (wt.%)	Treated SBC (wt.%)	Cement (wt.%)
L	100	0	0
LP	100	0	0
L-5PC	95	5	0
L-10PC	90	10	0
L-15PC	85	15	0
L-10CC	90	10	0
L-10OC	90	10	0
L-10CA	90	0	10

L-5PC-5CA	90	5	5
L-5PC-10CA	85	5	10
L-10PC-5CA	85	10	5

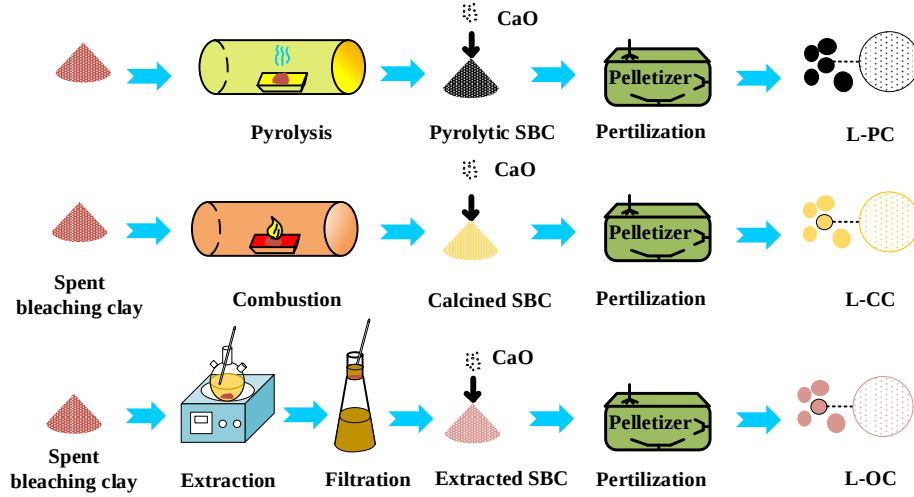


Fig. 2. Preparation procedures of various synthetic sorbent pellets

2.4 TGA Test

The cyclic CO₂ capture tests were performed using a TGA with ~15 mg samples (pellets in size range of 100~350 μm) loaded in a quartz tube (i.d. 20 mm). Prior to testing in the TGA, all sorbents were calcined in a muffle roaster at 900 °C for 2 h. For each run, the sample was heated to 920 °C at a heating rate of 40 °C min⁻¹ in 100% CO₂ for 5 min for calcination, then the temperature was cooled down to 650 °C at a cooling rate of 20 °C min⁻¹, switching to 100% N₂ atmosphere simultaneously to prevent carbonation at this stage. As soon as the temperature reached 650 °C, a gas flow containing 15% CO₂ (N₂ balance) was reintroduced into the reaction chamber to carbonate the sample for 25 min. All gas flow rates throughout these processes were set at 100 mL min⁻¹, which was controlled by mass flowmeters. Subsequently, the chamber temperature was increased to 920 °C to start a new cycle. In total, each sample was subjected to 20 calcination/carbonation cycles. The cyclic CO₂ uptake (X_{1N}) of sorbents is expressed in g(CO₂) g(calcined sorbent)⁻¹, which was calculated according to Eq 1: $X_{1N} = (m_2 - m_1) / m_0$, where m_0 refers to the mass of calcined sorbent; m_1 and m_2 denote the sorbent weight of carbonation and calcination after N cycles, respectively. The carbonation conversions (X_{2N}) were given in partial

results according to Eq 2: $X_{2N} = (m_2 - m_1) * M_{CaO} / m_0 * \chi_{CaO} * M_{CO_2}$, where χ_{CaO} is the corresponding content of CaO in m_0 . Blank runs were performed for accurate calculations.

2.5 Material Characterization

The main elemental compositions of raw limestone, SBC, and synthetic sorbent pellets were determined by XRF analysis (Rigaku ZSX Primus II, Japan), and the results are shown in **Table S1†**. X-ray diffraction (XRD) analysis was performed to determine the phase composition of the materials synthesized using an X-ray diffractometer (Smartlab-9KW, Rigaku, Japan) with a 40 kV/150 mA power generator, using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). An angular range of 5–85° 2 θ was measured, with a step size of 0.02° and counting time of 2 s per step. Particle size distribution of original material powders were measured using a Malvern Mastersizer 2000 instrument by laser diffractometry of samples dispersed in absolute ethyl alcohol, and the results are illustrated in **Fig. S2†**. The pore characteristics of pellets were detected by an accelerated surface area and porosimetry system (Micromeritics ASAP 2020), working at ~-196 °C. Specific surface areas and pore size distributions were calculated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The surface morphology of pellets before and/or after cyclic reaction were observed by a Hitachi S-4800 scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Combustible contents in regenerated SBC

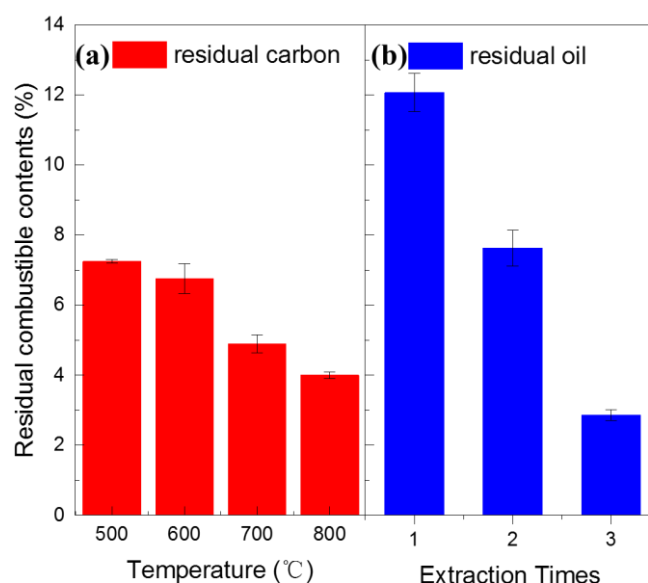


Fig. 3. Residual combustible contents in regenerated SBC: (a) residual carbon contents under various pyrolytic temperatures; (b) residual oil contents after different extraction times.

It is clear that different treatment conditions result in different combustible contents left in regenerated SBC. With respect to the proposed system, higher oils and unburnt carbon in the regenerated SBC might be more positive for sorbent performance, as this leads to a reduced fuel requirement in the calciner. **Fig. 3** is a plot of the residual combustible contents under different regeneration conditions of pyrolysis and organic solvent extraction. As shown in **Fig. 3a**, residual carbon content in regenerated SBC declines following increases in pyrolysis temperature in the range of 500~800 °C. Here, the highest content (7.2%) of carbon was obtained at 500 °C, compared to 4.0% at 800 °C. Interestingly, it has been reported that regenerated SBC exhibited significantly improved performance after being calcined at 500 °C rather than at 600 °C, due to the destruction of the clay structure at higher temperatures (>500 °C).²⁷ As a result, it appears that pyrolytic SBC at 500 °C should be the preferred material to prepare sorbent pellets. **Fig. 3b** shows that residual oil content similarly declined with increased extraction times. After 3 extractions, the oil recovery efficiency was up to 87.6%; however, the presence of 2.9% residual oils in the treated material appears to be less effective for the production of synthetic sorbents. By contrast, although the highest content (12.0%) was achieved after only one extraction, the high stickiness has an adverse effect on the homogeneity of prepared sorbent pellets. In addition, lower oil was extracted.

Twice extracted SBC powder possessed relatively low stickiness, and is more suitable for sorbent preparation. Additionally, its residual oil content (7.6%) was close to that of pyrolytic (500 °C) SBC material. Therefore, it is more reasonable to compare the effect of residual combustible contents on sorbent performance on this basis.

3.2 Results of XRD analysis

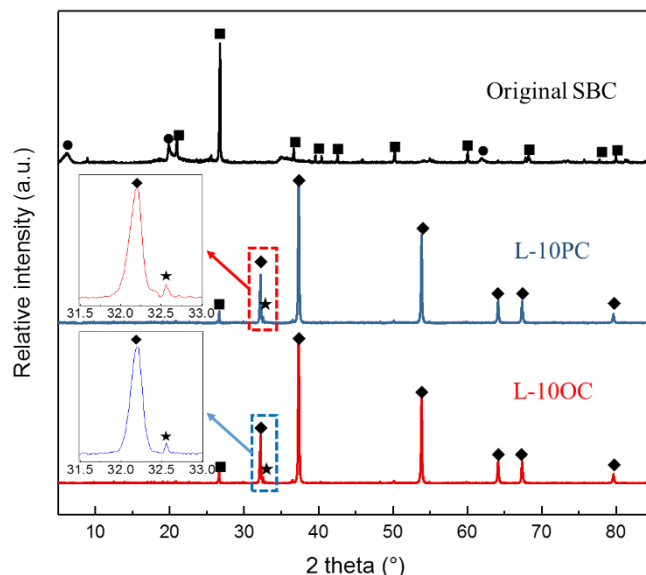


Fig. 4. The crystal phase composition of original SBC and pellet doped with pyrolytic and organic-extracted SBC after pre-treatment. (■) SiO₂, (●) montmorillonite, (◆) CaO, and (★) larnite.

Fig. 4 gives the phase composition of original SBC and prepared sorbents as detected by XRD analysis. It must be noted that the FBC comes from bentonite activated by acid, in which montmorillonite (also called smectites, $(\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{20} \cdot x\text{H}_2\text{O}$) is the main component, followed by crystalline silica. As shown in **Fig. 4**, although the peaks of SiO₂ are dominant in the original SBC, only a small peak due to SiO₂ was detected in “L-10PC” and “L-10OC”. In addition, a weak peak at $2\theta = 32.58^\circ$ was identified as the larnite (Ca_2SiO_4) phase, but two other intensive characteristic peaks of larnite at $2\theta = 32.05, 32.14^\circ$ did not appear. This might be caused by the fact that most of the SiO₂ in clay is found in the form of montmorillonite, and cannot react with CaO to form Ca_2SiO_4 . In consequence, these two characteristic peaks were weak and covered by the more intense CaO peak.

3.3 Porosity characteristics

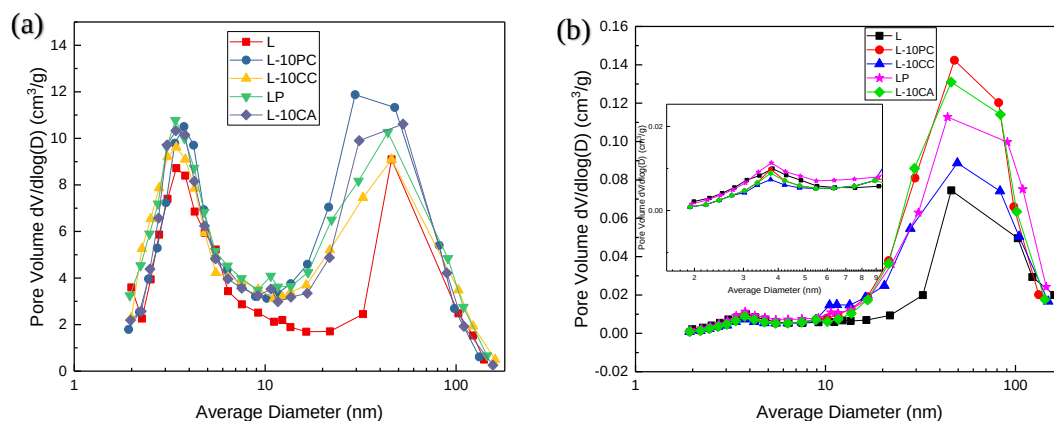


Fig. 5. Porous structure distribution of sorbents; (a) pore area, and (b) pore volume.

The results of N_2 adsorption measurements are provided in **Table 2**, including BET surface area and BJH pore volume. In addition, **Fig. 5** illustrates the porosity characteristics of five typical synthetic pellets. Here these sorbents show a significant number of pores in the 2~200 nm size range, namely mesoporous, which are optimal for sorbent capture performance.³² As can be seen from **Table 2**, all doped samples showed a larger specific surface area and pore volume, compared to natural limestone particles. However, an interesting phenomenon that should be noted is that the BET surface area of “L-10CA” was slightly lower than that of “LP”. Although acid-activated bleaching clay is considered desirable owing to its high specific surface area and excellent porous structure, this would be destroyed under high regeneration temperature (over 600 °C).^{33, 34} As reported by Önal,³⁴ the heated smectites possessed the highest specific surface area and mesopore volume of 90 m² g⁻¹ and 0.115 cm³ g⁻¹ at 400 °C, respectively. Then the values decreased rapidly under higher temperature (> 800 °C), due to collapsing of the crystal structure and interparticle sintering of the smectites. As a result, the positive effect of treated SBC addition on the porous structure of synthetic sorbents would be decimated after pretreatment at 900 °C for 2 h. This can be confirmed by the images of porous structure distribution. In **Fig. 5(a)** and **(b)**, it can be seen that all sorbents presented a bimodal pattern with peaks at 3-5 nm and 30–80 nm. The natural limestone showed fairly narrow distributions in these two pore size ranges, compared to the other synthetic pellets. This appears to be due to the relatively homogeneous composition of natural limestone, in which CaCO₃ is the main component with scant impurities. Similarly, the difference seen in the first peak in the range of 3-5 nm pores is less obvious, and might be

attributed to the release of CO₂ after the sorbents calcined at 850 °C. However, all treated pellets displayed much greater specific surface area in the second range. Cement as a support material has been reported to provide a mesoporous Al₂O₃ phase which contributes to the mesoporosity of sorbents.^{6, 32} The residual combustible components act as template materials and are considered to contribute to the increased porosity of pellets for the second peak, which is similar to the suggested role of biomass in previous work.^{14, 32}

Table 2: Porosity characterization of pellets

Sample	BET Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)
L	9.13	0.055
LP	11.02	0.076
L-10PC	12.47	0.103
L-10CC	10.91	0.081
L-10OC	12.73	0.101
L-5PC-10CA	13.74	0.110
L-10CA	12.62	0.092

3.3 CO₂ Capture Performance of Pellets

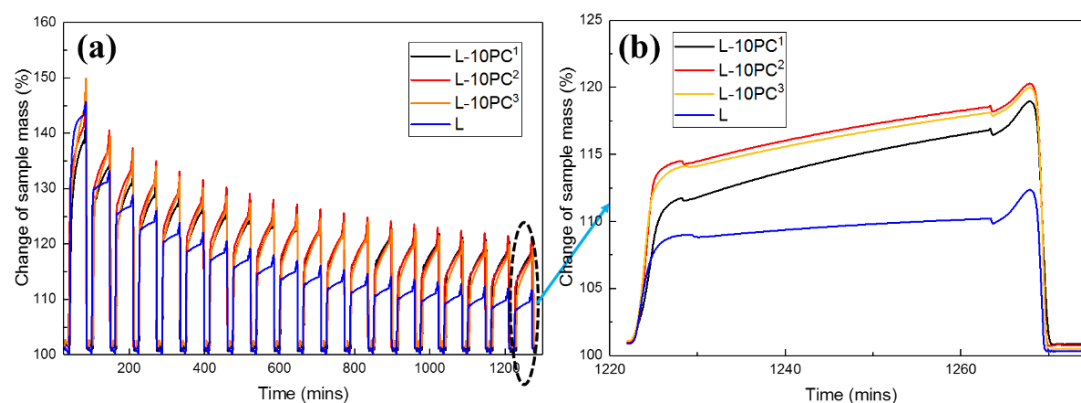


Fig. 6. Changes of sample mass during 20 calcination/carbonation cycles with pellet prepared from calcined limestone and pyrolytic SBC (three parallel runs) vs. natural limestone particles.

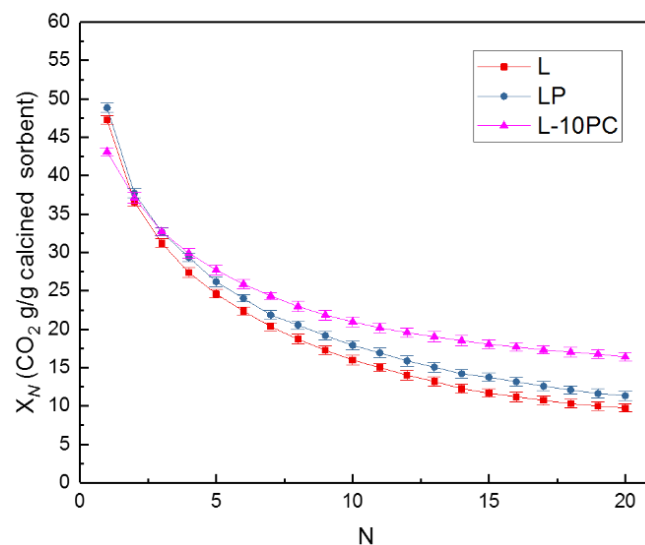


Fig. 7. Carrying capacity of three sorbents through 20 reaction cycles under severe conditions; error bars represent twice standard deviations calculated for three parallel experiments.

Effect of pyrolytic SBC addition. To demonstrate experimental reproducibility, three parallel tests were conducted for each sorbent (L, LP, and L-10PC), and three repeated 20-cycle test runs of L-10PC are plotted in **Fig. 6**; also presented is an image of the 20th cycle. From **Fig. 6b**, it can be seen that the carbonation conversion of sorbent doped by pyrolytic SBC increased for both the “fast stage” and the “slow stage”, when compared to raw limestone particles. The prolonged “fast stage” appears to be due to the enhancement in porosity for L-10PC, which agrees with the findings in our previous work.¹⁴ It should be noted that L exhibited a limited “slow stage”, due to the narrow range of porosity seen in **Fig. 6b**. **Fig. 7** gives the capture performance of three sorbents. Here the error bars represent twice the standard deviation. The natural limestone particles demonstrated a high CO₂ uptake of 0.473 g(CO₂) g(calcined sorbent)⁻¹ in the first cycle, but rapidly decreased to 0.098 g(CO₂) g(calcined sorbent)⁻¹ after 20 cycles, namely, a 79.3% drop. Comparing lines of “L” and “LP”, it is clear that sorbent prepared with calcined limestone powder showed somewhat higher CO₂ uptake than the same size of natural limestone particles. “LP” achieved CO₂ uptake of 0.488 and 0.113 g(CO₂) g(calcined sorbent)⁻¹ in the 1st and 20th cycles, respectively. This is probably caused by the fact that natural limestone granules possess more compact structure through long-term lithification over geological timescales.³⁵ Whereas, pellets prepared by the pelletization process have larger grain gaps and looser structure resulting in improved porosity. This is confirmed by the results shown in **Table 2**. With regard to doped

sorbents, “L-10PC” experienced a comparatively weak decline in capture capacity from 0.431 $\text{g}(\text{CO}_2) \text{ g}(\text{calcined sorbent})^{-1}$ in the initial cycle to 0.164 $\text{g}(\text{CO}_2) \text{ g}(\text{calcined sorbent})^{-1}$ after 20 cycles, namely, a 61.9% drop (3.10% per cycle). This means that synthetic sorbents doped with pyrolytic SBC demonstrated enhanced stability, when compared to natural limestone particles. This is probably caused by the fact that a new, more stable crystalline phase, larnite (Ca_2SiO_4), was formed by the reaction of CaCO_3 and SiO_2 , which was confirmed by the XRD analysis, presented in **Fig. 4**. Due to the high Tammann temperature of 929 °C, larnite has been suggested as a favorable inert phase to alleviate the sintering of sorbents in other work.^{9, 17}

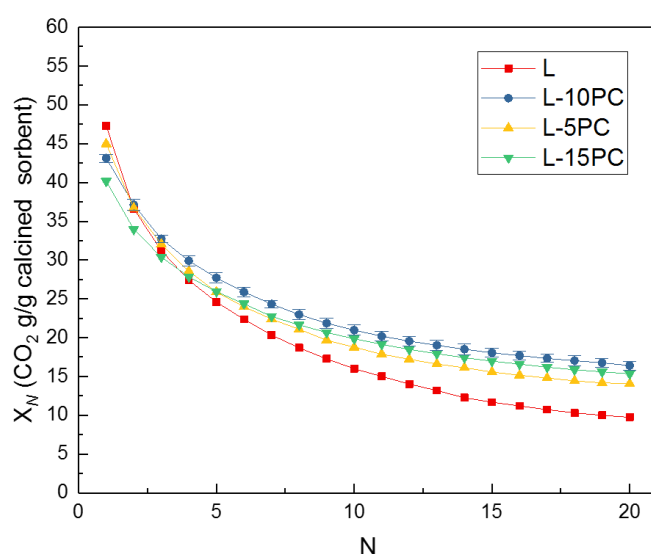


Fig. 8. CO_2 capture performance for synthetic pellets doped with the indicated CaO/PC ratios. For clarity, error bars representing 2 standard deviations are given only for L-10PC.

Effect of different ratios of CaO and pyrolytic SBC. Although addition of pyrolytic SBC improved the specific surface area and pore volume of prepared samples, shown in **Table 2**, it must be noted that “L-10PC” achieved lower CO_2 uptakes than “L” and “LP” during the first several cycles. This is probably caused by the fact that part of the active CaO phase was consumed by the formation of larnite, that is the reduction of active CaO leading to lower uptakes for as-prepared sorbents in the initial cycles. As a result, it is necessary to evaluate the capture capacity of sorbents doped with different contents of pyrolytic SBC to obtain the optimal CaO/PC ratios. Three different ratios were investigated in these tests. From **Fig. 8**, “L-5PC” (mass ratio of lime to pyrolytic SBC of 95:5) exhibited a higher initial CO_2 capture of 0.450 $\text{g}(\text{CO}_2) \text{ g}(\text{calcined sorbent})^{-1}$, but 68.7% of its capture capacity was lost after 20 cycles. As expected, “L-15PC”

achieved a slower decay (61.9%) in CO₂ uptake with repeated cycles, sacrificing more active CaO simultaneously. From **Fig. 8**, it is clear that “L-10PC” exhibited the greatest capture capacity over multiple carbonation/calcination cycles. As a consequence, the most appropriate ratio of lime to pyrolytic SBC is 9:1, and this ratio is used in the subsequent study on CO₂ capture behavior.

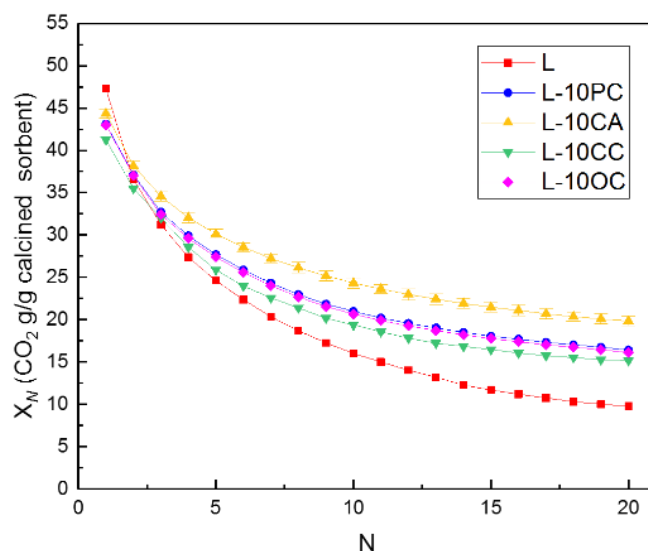


Fig. 9. Carrying capacity for sorbents prepared with different types of additives. For clarity, error bars representing 2 standard deviations are given only for L-10CA.

Effect of different types of additives on CO₂ uptake. Cement, as a promising binder, has been investigated in many early studies.^{6, 14} Additionally, different SBC treatments are expected to result in diverse structural properties, which might cause variation in the capture ability for sorbents. Three regeneration methods were investigated in these tests, including pyrolysis, calcination in air and organic solvent extraction. The results of TGA tests on samples doped with different materials are plotted in **Fig. 9**. Here we can see that all doped sorbents containing support materials displayed more favorable cyclic stability than natural limestone sorbent. Under the same doping ratio, “L-10PC” and “L-10CC” exhibited a similar capacity decay of 61.9% and 63.2%, respectively. However, the average CO₂ uptake of “L-10PC” was 0.234 g(CO₂) g(calcined sorbent)⁻¹, slightly higher than that of “L-10CC” (0.218 g(CO₂) g(calcined sorbent)⁻¹). This can be attributed to the fact that the residual carbon in pyrolytic SBC improved the pore structure of the prepared sorbent. Indeed, “L-10PC” possessed higher specific surface area and pore volume (**Table 2**) compared to “L-10CC”, which contributed to a greater improvement of capacity. By contrast, as has been mentioned previously, “organic regeneration” was the best method to recover

the porous structure of SBC; however, “L-10OC” did not display better capture capacity than “L-10PC”, which might be due to the destruction of montmorillonite crystal structure under high-temperature pretreatment of pellets. Particular emphasis is placed on the fact that cement produced more pronounced improvement on capture behavior. “L-10CA” achieved an initial CO_2 uptake of $0.444 \text{ g}(\text{CO}_2) \text{ g}(\text{calcined sorbent})^{-1}$. This value declined to $0.198 \text{ g}(\text{CO}_2) \text{ g}(\text{calcined sorbent})^{-1}$ after 20 cycles, indicating significantly slower decay of 55.4% (2.77% per cycle). The carbonation conversions of these tests are also given in **Fig. S3†**, which displays a similar tendency related to the CO_2 uptakes in **Fig. 9**. Although the doped regenerated SBC is expected to enhance the stability of sorbents, its inferior effect compared to cement is likely caused by two factors: firstly, only a small diffraction peak of Ca_2SiO_4 was detected by XRD analysis, as shown in **Fig. 4**, which meant only a small amount of Ca_2SiO_4 formed in pellets. This partly accounts for the limited stability of pellets mixed with regenerated SBC. Secondly, it has been reported that final destruction of the montmorillonite lattice, along with interparticle sintering, occurs between 600°C and 900°C . This can be confirmed by the following SEM images (**Fig. 11**). As the mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) formed in pellets mixed with cement is refractory, it can provide a stable framework in pellets to retard the sintering of CaO , and this has been shown elsewhere.^{6, 13}

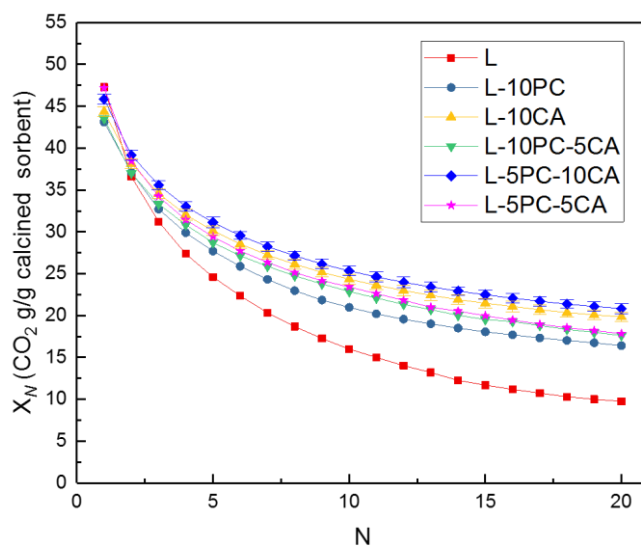


Fig. 10. CO_2 uptake performance of synthetic pellets doped with various pyrolytic SBC and cement contents. For clarity, error bars representing 2 standard deviations are given for L-10CA and L-5PC-10CA.

Synergistic effect of additives on CO_2 uptake. It is clear that although regenerated SBC displays only a weak ability to act as refractory matter, the residual combustible actually plays a role in

improving the pore structure of samples. Considering cement's strong supporting effect, we decided to study the synergistic effect of cement and regenerated SBC. Pyrolytic SBC was chosen as the object of study, because of its relatively simple regeneration process compared to organic extraction. Pellets were prepared with different ratios of calcined CaO to cement and/or pyrolytic SBC, and the CO₂ uptakes were plotted in **Fig. 10**. At the same level of 10% doping, the line of "L-5PC-5CA" was located between the lines of "L-10PC" and "L-10CA", owing to cement's stronger effect. When the content of pyrolytic SBC in pellets was doubled, "L-10PC-5CA" didn't show any improvement on capture performance compared with "L-5PC-5CA"; in fact it showed a slight decay. It can be concluded that 10% content of pyrolytic SBC was unnecessary to achieve the desired sample capacity. "L-5PC-10CA" demonstrated a CO₂ uptake of 0.208 g(CO₂)/g(calcined sorbent)⁻¹ which is slightly higher than that of "L-10CA". Consequently, the results of these tests revealed that cement and pyrolytic SBC were able to produce a synergistic effect to some extent, although the latter exhibited a limited ability to produce such an effect. As mentioned above, lattice collapse and interparticle sintering take place inside clay, which leads to the reduced effect seen here. In other words, the doped SBC could be regarded as relatively pure due to too high levels of impurity. It is evident that excess doping of the regenerated SBC material would damage the capacity of samples.

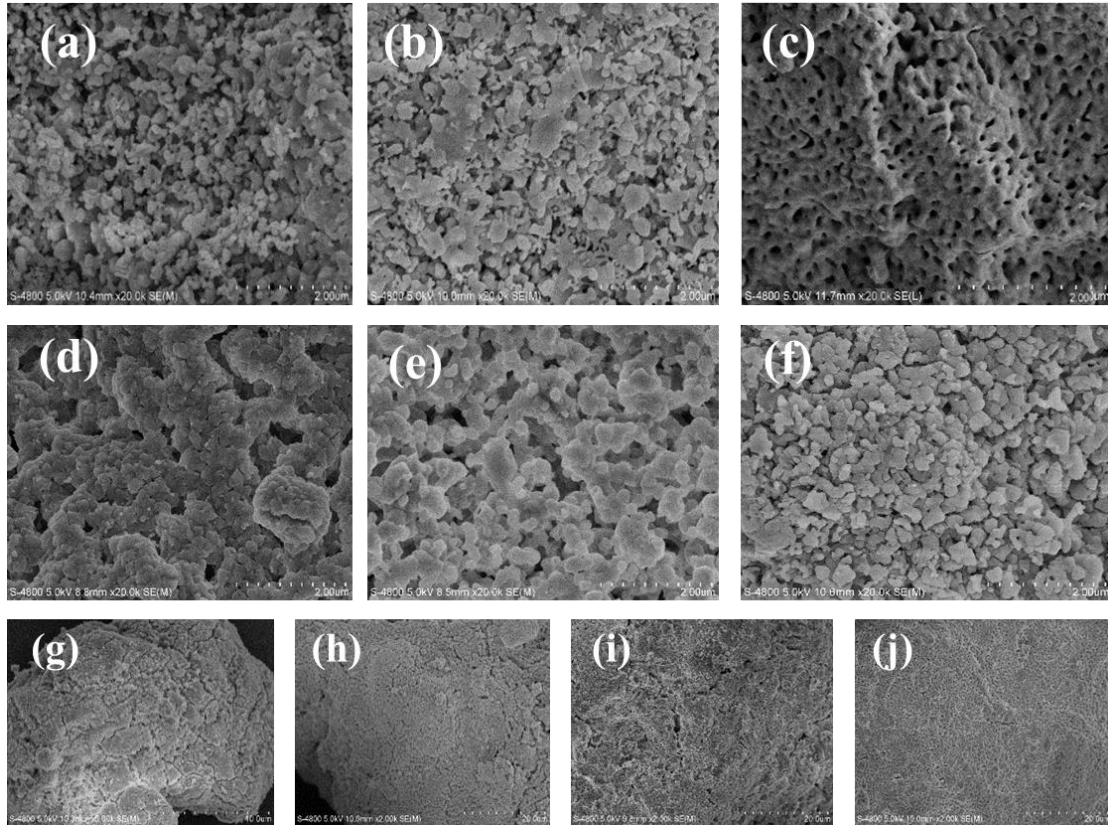


Fig. 11. SEM images of samples before and/or after 20 carbonation/calcination cycles in TGA tests, before cyclic reaction: (a), (b), and (c) for L-10CA, L-10PC, and LP, respectively; after 20 cycles: (d) and (j) for LP, (e) and (g) for L-10PC, (f) and (h) for L-10CA, (i) for L-5PC-10CA.

The images of partial synthetic samples before and/or after multiple cycles are displayed in **Fig. 11**. It is clear that the addition of treated SBC and cement exhibited more complex surface structure with much of the pores <200 nm, comparing **Fig. 11a, b** with **c**. The addition of pyrolytic SBC and cement binder played roles in the increase of mesopores. Obvious sintering occurred when “LP” sample underwent rigorous calcination condition (920 °C, 100% CO₂), confirmed by **Fig. 11d**. As shown in **Fig. 11e** and **f**, synthetic sorbents doped with pyrolytic SBC and cement displayed subdued sintering levels, due to the presence of inert phases. It should be noted that much more macropores (> 200 nm) were formed in “L-10PC” than in “L-10CA”. This indicated that pyrolytic SBC, as an additive, showed a poorer ability to resist sintering of lime-based sorbent, when compared to cement. As mentioned above, this might be caused by the fact that a low content of inert Ca₂SiO₄ phases formed in sorbents and smectites lattices collapsed under high temperature. It has also been reported by Wang et al.³⁶ that Ca₂SiO₄ could absorb CO₂ over a broad temperature range of 500 °C to 800 °C, based on the reaction of $\text{Ca}_2\text{SiO}_4 + 2\text{CO}_2 \rightarrow 2\text{CaCO}_3 + \text{SiO}_2$. So,

it can be inferred that this reaction happened during the carbonation stage (at 15% CO₂, N₂ balance, for 25 min), which resulted in the consumption of Ca₂SiO₄ to generate CaCO₃ and SiO₂ phases. Obviously, sintering is likely for this CaCO₃. Also, the SiO₂ appears to combine with the surrounding free CaO to form new Ca₂SiO₄. The instability of smectites under high temperature means that they display poor performance when subjected to thermal stress, as can be confirmed by **Fig. 11f-j**, illustrating the surface morphology of representative synthetic pellets after 20 cycles. In particular, many cracks emerged on the surface of “L-10PC” after repeated cycles, whereas only a few were observed on “L-10CA”, which shows that cement performed better than regenerated SBC in terms of resistance to thermal stresses. Further evidence for these conclusions can be seen in **Fig. 11j** about “L-5PC-10CA”. In particular, the surface of “LP” was flat and unbroken despite the severe sintering of CaCO₃ shell after many reaction cycles.

4. Conclusion

Here we propose a potential CO₂ capture system integrated with reuse of spent bleaching clay whereby efficient lime-based sorbents are prepared with regenerated SBC and, at the same time, fuel and heat from SBC regeneration could serve as supplemental energy for the calcination process. Three regeneration methods were investigated, including pyrolysis, calcination, and organic solvent extraction. CO₂ capture tests were carried out to determine the optimal doping ratios and regeneration method of SBC for this system. N₂ adsorption measurements revealed that pellets containing combustible components showed higher specific surface area and pore volume, which resulted in higher CO₂ uptakes. The as-prepared sorbent “L-10PC” achieved a final CO₂ uptake of 0.164 g(CO₂) g(calcined sorbent)⁻¹ after 20 cycles, which is significantly higher than that of “L-10CC”. By contrast, “L-10OC” didn’t display a significantly better capture capacity than “L-10PC”, which might be due to the destruction of montmorillonite crystal structure under high-temperature pretreatment of pellets. A new larnite (Ca₂SiO₄) phase was detected by XRD analysis, but the weak XRD peak indicated a low content of larnite in the pellets, leading to a poorer result when compared to cement doping. A synergistic effect was seen for “L-5PC-10CA”, which resulted in the highest final uptake of 0.208 g(CO₂) g(calcined sorbent)⁻¹. Considering the simplicity of the pyrolysis regeneration process and the superior capture capability of pellets doped with pyrolytic SBC, the proposed system integrating CaL with SBC pyrolysis treatment

appears to be promising and should be further developed.

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Notes

The authors declare no competing financial interest.

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