

# CO<sub>2</sub> Capture Performance Using Biomass-templated Cement-supported Limestone Pellets

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## Abstract

Synthetic biomass-templated cement-supported CaO-based sorbents were produced by granulation process for high-temperature post-combustion CO<sub>2</sub> capture. Commercial flour was used as the biomass and served as a templating agent. The investigation of porosity showed that the pellets with biomass or cement resulted in enhancement of porosity. Four types of sorbents containing varying proportions of biomass and cement were subject to 20 cycles in a TGA under different calcination conditions. After first series of tests calcined at 850 °C in 100% N<sub>2</sub>, all composite sorbents clearly exhibited higher CO<sub>2</sub> capture activity compared to untreated limestone with exception of sorbents doped by seawater. The biomass-templated cement-supported pellets exhibited the highest CO<sub>2</sub> capture level of 46.5% relative to 20.8% for raw limestone after 20 cycles. However, the observed enhancement in performance was substantially reduced under 950 °C calcination condition. Considering the fact that both sorbents supported by cement exhibited relatively high conversion with a maximum value of 19.5%, cement promoted sorbents appear to be better at resisting of harsh calcination conditions. Although flour as biomass-templated material generated significantly enhancement in CO<sub>2</sub> capture capacity, further exploration must be carried out to find the way of maintaining outstanding performance for CaO-based sorbents under severe reaction conditions.

**Keywords:** Calcium looping; CO<sub>2</sub> capture; Granulation; Limestone; Biomass; Cement;

## 1. Introduction

Anthropogenic CO<sub>2</sub> emissions are widely considered as one main contributor to climate change, in particular power plants consuming fossil fuels produce ~40% of global CO<sub>2</sub> emissions.<sup>1</sup> Carbon

capture and storage (CCS) technology is one promising and emerging way to mitigate CO<sub>2</sub> emissions effectively.<sup>2, 3</sup> However, the cost of the CO<sub>2</sub> capture step contributes to ~80% of the whole cost associated with CCS.<sup>4</sup> Hence, it is of great importance to develop efficient and cost-effective CO<sub>2</sub> capture technologies. Several relatively mature CO<sub>2</sub> capture technologies, however, exhibit specific drawbacks, respectively. In the case of amine scrubbing, the degradation and regeneration of expensive solvents cause large economic and efficiency penalties.<sup>4</sup> While in the case of oxy-fuel combustion, the air-separation unit (ASU) required is energy intensive, and incurs large costs.<sup>2</sup> Therefore, the majority of research in this area aims to develop novel and potential better carbon capture technology such as calcium looping (CaL) using solid CO<sub>2</sub> sorbents.

The CaL process is based on two reverse reactions for the formation and decomposition of CaCO<sub>3</sub>, where CaO-based sorbents capture CO<sub>2</sub> (i.e. from flue gas) in carbonation reactor, followed by regeneration of sorbents in calcination reactor to fulfill a cycle. Natural limestone is regarded as one of the most suitable candidates for large scale CO<sub>2</sub> capture, due to its abundance and low cost as well as its potentially high CO<sub>2</sub> capture capacity of 0.786 g CO<sub>2</sub>/g CaO. However, two major challenges associated with this technology should be addressed: (1) the sorbent reactivity decays rapidly with increasing number of reaction cycles because of sintering; and (2) the attrition of the particles in an actual working environment can be excessive. As a result, a high make-up flow is required to compensate for the deactivation and elutriation of raw limestone to maintain desired CO<sub>2</sub> capture efficiency, but this damages the economics of the process. Thus, considerable research efforts have been focused on improving CO<sub>2</sub> capture performance of natural CaO-based sorbents and developing more stable ones over multiple cycles.

Several techniques have been proposed in previous works such as precipitation methods,<sup>5, 6</sup> organic acid treatments,<sup>7-11</sup> chemical doping,<sup>12, 13</sup> hydration,<sup>12, 14-17</sup> and synthesis techniques of highly efficient sorbents, i.e. sol-gel method,<sup>18-21</sup> carbon template,<sup>19, 22</sup> and biomass template.<sup>23</sup> In terms of chemical doping method, different techniques and dopants have been used in recent work. Work carried out by González et al. demonstrated that 0.5M solution of KCl enhanced long-term activity of limestone in both fluidized bed and TGA tests, in spite of decreasing reactivity for the initial cycle.<sup>24</sup> Other dopants were also investigated, such as NaCl, CaBr<sub>2</sub>,<sup>12, 26</sup> MgCl and Mg(NO<sub>3</sub>)<sub>2</sub>.<sup>27</sup> Various synthetic CO<sub>2</sub> sorbents have proved highly efficient. Ridha et al.<sup>23</sup> examined four types of biomass-templated CaO-based sorbents, and noted that biomass materials improved the porosity of sorbents and biomass

ash contributed to the enhancement of stabilization of pellets. Inert  $\text{Al}_2\text{O}_3$  is now widely used as additive to form inert support materials, i.e.  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  or  $\text{Ca}_9\text{Al}_6\text{O}_{18}$  ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ),<sup>17, 18, 28</sup> which improves the stability of sorbents over multicycles. However, it should be noted that these modifications appear to be cost-ineffective because of the correspondingly high cost of materials and complex procedures, as well as potential problems for further scale up for commercialization. Granulation<sup>10, 12, 15, 16, 29-32</sup> has been proposed recently as a promising method, which allows the addition of various dopants and using kaolin<sup>30, 33</sup> and/or cement<sup>34</sup> as binders to support sorbents.

Given that multiple  $\text{CO}_2$  capture performance tests about synthetic sorbents, especially doped with biomass were carried out under correspondingly mild calcination condition (i.e.  $850\text{ }^\circ\text{C}$ ). In this work, synthetic sorbents were produced through pelletization process, which were supported by calcium aluminate cement, templated by biomass, and also doped by seawater. Then  $\text{CO}_2$  capture tests were performed in a TGA under mild and harsh conditions to compare the difference between observed characteristics.

## 2. Experimental section

### 2.1 Materials and Pelletization

In this work, a batch of powdered Longcal limestone was used as the source of CaO precursor. Commercial calcium aluminate cement, CA-14(73%  $\text{Al}_2\text{O}_3$ , 27% CaO), from Almatris Inc. was chosen as the binder for pelletization; >80% of the powders were <45  $\mu\text{m}$  in diameter. The biomass-templated material used was commercial flour. Artificial seawater (Complete Aquatics treated with moderate NaClO) was served for doping purposes.

The biomass-templated cement-supported limestone pellets were prepared by using TMG Tabletop granulator (Glatt HmGb). Raw limestone was calcined at  $850\text{ }^\circ\text{C}$  in air for 2 hours before preparation. A batch of powdered materials (~800 g in total) was loaded into the pelletiser vessel (4 L). The pelletization process was achieved by the agitator and the chopper attached to the vessel with velocities of 500 rpm and 2500 rpm respectively. Water (~400 ml) was sprayed intermittently through a pressurized atomizing nozzle during the procedure, namely spraying for 1s at intervals of 4s. Usually, the amount of spraying water and the speed of two rotor blades play critical roles on controlling the final pellet size, it must be noted here that visual inspection of the mixture should be

continuously performed accordingly, to ensure moderate water and desired particle size. More details about this pelletization can be found elsewhere.<sup>15,31</sup> After pelletization, the pellets were air dried and then the desired size particles of 0.1-0.6 mm were sieved out to storage. Four kinds of pellets were prepared with varying proportions of different dopants and calcined limestone. Combinations of the first letter of different materials were used to denote pellets, as seen in Table 1. Raw limestone was designated as LS for comparison.

Table 1: Compositions of materials used in different preparation of samples

<b>Sample</b>	<b>Lime (wt %)</b>	<b>Cement (wt %)</b>	<b>Flour (wt %)</b>	<b>Type of water used</b>
<b>LC*</b>	90	10	0	Deionized water
<b>LF*</b>	90	0	10	Deionized water
<b>LCF*</b>	80	10	10	Deionized water
<b>LCFSW*</b>	80	10	10	Sea water

\*LC: lime and cement

\*LF: lime and flour

\*LCF: lime, cement and flour

\*LCFSW: lime, cement and flour doped by seawater

## 2.2 Sorbents characterization

Elementary analysis of the samples was performed using ICP-OES (inductively coupled plasma optical emission spectrometry) and the composition is given in Table 2. Prior to N<sub>2</sub> adsorption-desorption measurement using an accelerated surface area and porosimetry system (Micromeritics ASAP 2020), sorbents were decomposed into CaO in a muffle furnace at 850 °C in air for 15 mins which also allowed the complete combustion of biomass. The BET surface area and BJH pore size distribution were derived from N<sub>2</sub> adsorption isotherms obtained at ~-196 °C. BET surface area distribution was derived from adsorption data, while BJH pore volume distribution was derived from the corresponding desorption data. The surface morphology of pellets was observed by a Hitachi S-4800 scanning electron microscopy (SEM).

Table 2: Elementary analysis of all sorbents

Component (wt %)	LS	LC	LF	LCF	LCFSW
Al <sub>2</sub> O <sub>3</sub>	0.082	5.63	0.218	4.73	5.22
BaO	0.007	0.007	0.007	0.005	0.015
CaO	53.9	58.4	58.2	52.4	57.3
Fe <sub>2</sub> O <sub>3</sub>	0.015	0.033	0.040	0.027	0.030
K <sub>2</sub> O	0.007	0.006	0.037	0.023	0.051
MgO	0.185	0.208	0.210	0.197	0.335
MnO <sub>2</sub>	0.008	0.008	0.009	0.008	0.010
Na <sub>2</sub> O	0.053	0.071	0.052	0.056	0.806
P <sub>2</sub> O <sub>5</sub>	0.007	0.011	0.035	0.022	0.012
SO <sub>3</sub>	0.034	0.039	0.122	0.055	0.234
SiO <sub>2</sub>	0.701	1.20	0.770	0.267	0.292
SrO	0.017	0.018	0.018	0.017	0.018
TiO <sub>2</sub>	0.006	0.015	0.013	0.006	0.007
Total oxides	55.1	65.7	59.7	57.8	64.4
TC (Total Carbon)	42.7	12.8	28.1	25.6	15.4
Water at 105°C	0.10	0.10	0.10	0.10	0.10
Water at 950°C	0.10	22.3	15.9	20.5	23.1
Total	98.0	100.8	103.8	103.9	102.9

### 2.3 TGA Test

The CO<sub>2</sub> capture tests were performed using a thermogravimetric analyser (TGA) with ~15 mg samples (particles size of <180 μm) loaded in a quartz tube (i.d. 20 mm). The gas flow rate was set at 100 mL min<sup>-1</sup>, which was controlled by mass flowmeters. The heating rate and cooling rate were 40 °C min<sup>-1</sup> and 20 °C min<sup>-1</sup>, respectively. Two major conditions were studied in these tests: firstly, the samples were calcined at 850 °C in 100% N<sub>2</sub> (except for the initial cycle in air) for 5 min, then were carbonated at 650 °C under 15% CO<sub>2</sub> (N<sub>2</sub> balance) for 35 mins. Secondly, the calcination process was carried out at 950 °C under 100% CO<sub>2</sub> (except for the initial cycle in air) for 5 mins, and then the carbonation step was performed at 650 °C under 15% CO<sub>2</sub> (N<sub>2</sub> balance) for 35 mins. All the sorbents were subject to 20 cycles. Here, the atmosphere was switched from 100% CO<sub>2</sub> to 100% N<sub>2</sub> below 900 °C during the transition between calcination and carbonation to avoid carbonation ahead of time. In addition, the initial cycle under both calcination conditions was in air to ensure the complete combustion of biomass.

### 3. Results and discussion

#### 3.1 Porosity characterization.

The results of N<sub>2</sub> adsorption measurements are presented in Table 3. As can be seen, all the synthetic pellets presented larger BET surface area and BJH pore volume relative to untreated limestone except for LCFSW. Pellets containing flour and cement showed the highest pore surface area of 14.11 m<sup>2</sup> g<sup>-1</sup> and pore volume of 0.110 cm<sup>3</sup> g<sup>-1</sup> in comparison to 9.00 m<sup>2</sup> g<sup>-1</sup> and 0.061 cm<sup>3</sup> g<sup>-1</sup> for raw materials respectively. This result can be attributed to the enhancement effect on porosity by biomass and cement, consistent with previous works.<sup>12,23</sup> Surprisingly, although LCFSW also contained these two types of additives, it exhibited inferior pore structure, actually far less than that of raw limestone. It is possible that the doping with too high levels of seawater produced an excess of Na<sup>+</sup> ion in the sorbent, which led to more pronounced sintering owing to the presence of the lower melting point of Na<sub>2</sub>O. Additionally, as noted by Manovic et al.,<sup>13</sup> Na<sub>2</sub>O might react with CaO and CO<sub>2</sub> to form lower melting point compounds (Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>/Na<sub>2</sub>Ca<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>), as a result, active CaO declined and sintering enhanced. This finding agrees with the previous work of Xu et al.<sup>35</sup> who found that calcined limestone doped by sea salt (main component is NaCl) experienced severe sintering during the cycles.

Table 3: Porosity characterization of five type pellets

Sample	BET Surface Area ( m <sup>2</sup> /g )	BJH Pore Volume ( cm <sup>3</sup> /g )	Av. Pore width,( nm )
LC	11.54	0.086	29.34
LF	12.60	0.093	30.93
LCF	14.11	0.110	28.30
LCFSW	4.03	0.017	16.32
LS	9.00	0.061	31.50

Fig. 1. displays pore surface area and pore volume distribution of sorbent pellets. It can be seen in Fig. 1a. that all samples showed a bimodal pattern with peaks at 3-4 nm and 30-70 nm. The phenomenon revealed pores (< 100 nm in diameter), especially mesopores, were mainly contributors to surface area, which is consistent with previous work.<sup>23</sup> The pore surface area profiles demonstrate that the additives used improved pore properties markedly. Similarly, there are two peaks in pore volume

distribution, as can be seen in Fig. 1b. However, given that the first peak at ~4 nm is much small, it is obvious that the significant increase in pore volume is attributed to the development of pores with size range of 30 nm~100 nm. As expected, LCF exhibited the highest pore volume of  $0.110 \text{ cm}^3 \text{ g}^{-1}$ , corresponding to 83.3% higher than that of LS followed by LF and LC except for LCFSW. Accordingly, the addition of biomass and cement enables to enhance the porous structure of limestone.

### *3.2 CO<sub>2</sub> capture performance*

In order to compare these results with early studies, a typical reaction condition (calcination at  $850 \text{ }^\circ\text{C}$  in 100% vol.  $\text{N}_2$ ) was carried out in TGA, and the carbonation conversion curves of four sorbents during the first two cycles are presented in Fig. 2. There is a similar tendency in all treated pellets, which displays typically carbonation patterns with fast and slow reaction stages. On the fast stage, the reaction achieved a considerable conversion quickly controlled by chemical kinetics, followed by a slower stage controlled by diffusion. It is clear that biomass and cement doped prolonged the slow reaction stage. Moreover, compared two profiles of LC and LCF, it is also notable that biomass doped in sorbents had effect on the fast reaction stage, which agrees with the finding by Ridha et al.<sup>23</sup> These results are ascribed to the enhancement in porosity, as shown in Table 3. Whereas, the shift between two reaction stages was so abrupt that the slow stage was hardly recognized in the profile of LS. This appears to be connected with the closure of most of small pores in rapid reaction stage, given relatively narrow range of porosity seen in Fig. 1b. In addition, Fig. 5(a) displayed smooth and solid surface porous structure for LS, which is easy to be covered by layer of  $\text{CaCO}_3$ .<sup>20, 36</sup> As a result, the resistance of  $\text{CO}_2$  diffusion increased rapidly to retard the slower reaction.

The  $\text{CO}_2$  capture performance of four synthetic pellets together with raw limestone is shown in Fig. 3. All sorbents showed monotonically declined profiles with multiple reaction cycles. In the first cycle, LF exhibited the highest conversion of 88.2%, compared to about 73.4% for LS. This can be explained by the fact that LF produced a surface area of  $12.60 \text{ m}^2 \text{ g}^{-1}$ , higher than that of  $9.00 \text{ m}^2 \text{ g}^{-1}$  for LS, which was attributed to the addition of biomass. Usually, higher surface area in sorbent means better  $\text{CO}_2$  carrying capacity. LC realized a conversion of 70.5% after initial carbonation reaction, slightly lower than that of LS. It was proposed that  $\text{Al}_2\text{O}_3$  in the binder reacts with  $\text{CaO}$  to form mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ), however, this part of the “ $\text{CaO}$ ” cannot be used to capture  $\text{CO}_2$ .<sup>28</sup> After 20 capture cycles, LC showed a capture rate of 40.4%, compared to 20.8% of LS, corresponding to 57.3% and

28.3% of their initial conversion, respectively. It is apparent that cement can stabilize CaO-based sorbent over multiple reaction cycles, which is also likely due to the formation of inert mayenite. This result agrees with the finding in other studies that the inert material enables to maintain sorbents a stable capture capacity.<sup>12, 16</sup> Interestingly, it should be noted that the final conversion of LF was 41.4%, slightly over that of LC, which appears to result from the presence of some small amount of residue (ash) in the sorbent after biomass combustion. As was reported earlier, treating CaO-based sorbents with aqueous solution of lower concentration of different mineral salts, such as KCl and  $K_2CO_3$ ,<sup>24</sup> can improve the cyclic performances of the sorbents. It has been shown in Table 2 that the content of potassium salt in LF is five times as many as that in LC. Accordingly, this probably accounts for the somewhat higher  $CO_2$  uptake for LF. As was expected, LCF, containing flour and cement, possessed the best  $CO_2$  capture capacity, with the final conversion reaching 46.5%. By contrast, LCFSW showed rather poor capacity compared to other sorbents. This must be attributed to excessively inferior pore structure seen in Table 3. The later SEM images showed that quantities of cracks on the surface of LCFSW pellet, which means much severer sintering.

Usually, it is relatively reasonable to explore the process of  $CO_2$  looping cycles under mild calcination conditions in laboratory, if the goal is to collect sufficient experimental data for carrying out fundamental studies. However, to simulate industrial conditions, further experiments using realistic conditions need to be carried out. Fig. 4. shows conversion of sorbent synthesized in carbonation/calcination cycles, operated under harsh calcination conditions. In Fig. 4, it is evident that the impact on capture capacity of synthesized sorbents clearly diminishes, although all synthesized sorbents exhibited higher  $CO_2$  uptakes than their counterparts, if we exclude the initial cycle. This agrees with the result under prior calcination condition. However, harsh condition impaired the performance of sorbents. Conversion of LC was 55.3% in the first cycle, which decreased by 21.6% compared to that under 850 °C calcination condition. In a similar fashion, LF, LCF and LS declined by 32.2%, 19.4% and 17.2%, respectively. It is noticeable that these harsh conditions cause reduced  $CO_2$  uptake. This is because severe calcination conditions cause more serious sintering, which was noted in previous studies.<sup>33-35</sup> It is also clear that the presence of cement is beneficial as compared to biomass under severe conditions. Thus, the optimized porosity structure produced by adding biomass is strongly affected by severe temperature conditions. After 20 cycles, the conversion of LS sharply



dropped to 13.5%, equivalent to 22.2% of its initial value. This was close to the residual conversion noted in previous work.<sup>37</sup> Additionally, LC and LCF achieved almost the same conversion, 19.5% for LCF, as compared to 18.5% for LC, due presumably to the presence of an inert aluminate phase ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ). However, it should be pointed out that these levels were no match to a residual activity of 28% for cement supported pellets obtained under 800°C isothermally by Manovic and Anthony.<sup>38</sup> Clearly, severe calcination conditions account for the excessively reduced activity. By contrast, although LF still obtained a conversion of 16.0%, this was just 2.5% over that of LS, which is not a significant advantage when compared to the much better performance than LC after 20 cycles under milder condition. Except for the much serious sintering under this harsh condition, as mentioned above, the ash remaining (especially the content of potassium salt) in sorbents may partially account for the satisfactory capacity of LF. Moderate potassium salt concentrations present in sorbent particles have proved to have positive impact on performance. Nevertheless, it must be noted here that the melting point of potassium carbonate is about 900 °C. Moreover, González et al.<sup>24</sup> found that potassium carbonate would vaporize above 900 °C by comparing the concentration of potassium ions before and after cycling. Therefore, vaporization of potassium carbonate under 950 °C might partly account for the decline of capacity by a large margin for LF. Unfortunately, for TGA test, the low amounts of material produced containing potassium salts are insufficient for further chemical analysis, and a series of tests on lab-scale bubbling fluidized bed (BFB) will be performed in the future study. In addition, LCFSW showed rather poor capacity in both calcination conditions, which is set beyond the comparison of pellets capture capability.

Considering the various results observed under different calcination conditions, further explorations are necessary to examine the effect of high calcination temperature and high concentration  $\text{CO}_2$  atmosphere on the performance of additives. Subsequent tests at 900 °C in 100%  $\text{CO}_2$  and at 950 °C in 100%  $\text{N}_2$  were carried out, respectively. The experimental results obtained have been plotted in Fig. 5. Fig. 5a. demonstrates different conversion profiles for LC. As can be seen, tests at 900 °C showed almost the same conversion with that at 950 °C in 100%  $\text{CO}_2$  atmosphere, except for somewhat superiority in the first seven cycles. It can be concluded that the  $\text{CO}_2$  uptake of cement-supported sorbent was clearly reduced at 900 °C which is identical to that at 950 °C under pure  $\text{CO}_2$  flows. LF exhibited a similar trend as shown in Fig. 5b. It has been reported that the high concentration of  $\text{CO}_2$  during calcination may cause dramatically decline on the reactivity of CaO-based sorbents.<sup>39, 40</sup> To

investigate the influence of different calcination atmosphere, LC and LF sorbents were subjected to reaction cycles at 950 °C in 100% N<sub>2</sub> for comparing. It is evident that the inert atmosphere plays a secondary role at high calcination temperature of 950 °C, owing to the fact that the conversion of LC increased over ~3% averagely throughout 20 cycles under pure N<sub>2</sub> gas flow compared with pure CO<sub>2</sub> atmosphere, as showed in Fig. 5a. By contrast, three almost overlapping curves (seen in Fig. 5b.) indicate that high temperature takes up the predominant position for LF compared rather than the calcination atmosphere. Switching to pure inert calcination gas cannot increase CO<sub>2</sub> conversion at all. Accordingly, 900 °C can be regarded as extremely severe condition of damaging the reactivity of sorbents containing biomass. These results reveal that biomass-templated sorbents are more sensitive to high temperature than those supported by cement.

### *3.3 Surface morphology*

Fig. 6. shows partially surface morphology images of LS, LC, LF, LCF and LCFSW following 20 cycles after calcination at 850 °C or 950 °C. It is clear that the sintering of LS is much severer under 950 °C conditions, given the obvious decline of mesopores seen in Fig. (b). On the other hand, Fig. (c), (e), and (g) represented the morphology of LC, LF, LCF after calcination at 850 °C. These images demonstrated the positive effect of doping sorbents with biomass and cement on porous structure transformation. LF (only containing biomass) shows an obviously sintered structure under severe temperature as can be seen by comparing images (e) and (f), where much long and narrow textures were found because of the coalescence of small pores. The enhanced sintering seen here confirms the reduced impact on improving performance of sorbents by adding biomass like flour, when examined in TGA under 950 °C. In contrast, cement (Al<sub>2</sub>O<sub>3</sub> actually) exhibited great durability and resisted damage from these harsh temperature conditions, as can be seen from Fig. (g) and (h). Furthermore, the structure from LCFSW suggests that the formations of compounds from the sea salts are detrimental for the structure of the pores. It is suggested that pores are replaced by the multiple cracks seen here as a result of formation of lower melting point compounds (Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>/Na<sub>2</sub>Ca<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>).

## **4. Conclusion**

In this work, four types of sorbents containing varying proportions of biomass and cement were synthesized by pelletization process. Relative to the untreated limestone, both additives caused

improvement on porous structure. In particular, biomass-templated cement-supported pellets exhibited the greatest porosity with high pore surface area and pore volume up to  $14.11 \text{ m}^2 \text{ g}^{-1}$  and  $0.110 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Whereas the sorbents doped by seawater decreased significantly in porosity, here it is possible that the lower melting point of  $\text{Na}_2\text{O}$  caused pronounced sintering owing to the excess of  $\text{Na}^+$  ion in this sorbent. A finding from TGA test under calcination temperature of  $850 \text{ }^\circ\text{C}$  in  $\text{N}_2$  demonstrated that all synthetic sorbents exhibited significant increase in  $\text{CO}_2$  uptake in comparison to raw limestone. Wherein the biomass-templated cement-supported pellets represented the highest  $\text{CO}_2$  capture rate of 46.5% relative to 20.8% for raw limestone after 20 cycles. This promising result was attributed to the enhancement of developed porosity and cyclic stability from the addition of biomass and calcium aluminate cement, respectively. However, this positive effect of biomass is substantially reduced for  $950 \text{ }^\circ\text{C}$  calcinations after multicycles. This appears to be the result of pronounced sintering in this situation. Additionally, the vaporization of potassium carbonate under  $950 \text{ }^\circ\text{C}$  may influence on the reduction of activity, given that it is noted that moderate potassium salt existing in pellets proved to have positive impact on performance. Further exploration to find more effective biomass dopants and/or enhancing the biomass-templated pellets will be carried out in subsequent studies.

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### Notes

The authors declare no competing financial interest.

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## Figure captions

**Fig. 1.** Porous structure distribution of all sorbents used; (a) pore area, and (b) pore volume.

**Fig. 2.** Conversion profiles during the first two cycles in TGA. Conditions: 10 mins calcination at 850 °C in 100% vol. N<sub>2</sub> and 20 mins carbonation at 650 °C in 15% vol. CO<sub>2</sub>, N<sub>2</sub> balance.

**Fig. 3.** Conversion of the sorbent synthesized, tested 20 cycles of carbonation and calcination in TGA (10 mins calcination at 850 °C in 100% vol. N<sub>2</sub> and 20 mins carbonation at 650 °C in 15% vol. CO<sub>2</sub>, N<sub>2</sub> balance).

**Fig. 4.** Conversion of the sorbent synthesized, tested 20 cycles of carbonation and calcination in TGA (10 mins calcination at 950 °C in 100% vol. CO<sub>2</sub> and 20 mins carbonation at 650 °C in 15% vol. CO<sub>2</sub>, N<sub>2</sub> balance).

**Fig. 5.** Effects of high temperature and high CO<sub>2</sub> concentration on reactivity of two synthetic sorbents: (a) LC; (b) LF.

**Fig. 6.** SEM images of samples after 20 carbonation/calcination cycles in TGA under different calcination conditions; under 850 °C: (a), (c), (d), (e) and (g) for LS, LC, LCFSW, LF and LCF, respectively; under 950 °C: (b) LS, (f) LF and (h) LCF.



# Figures

Figure 1

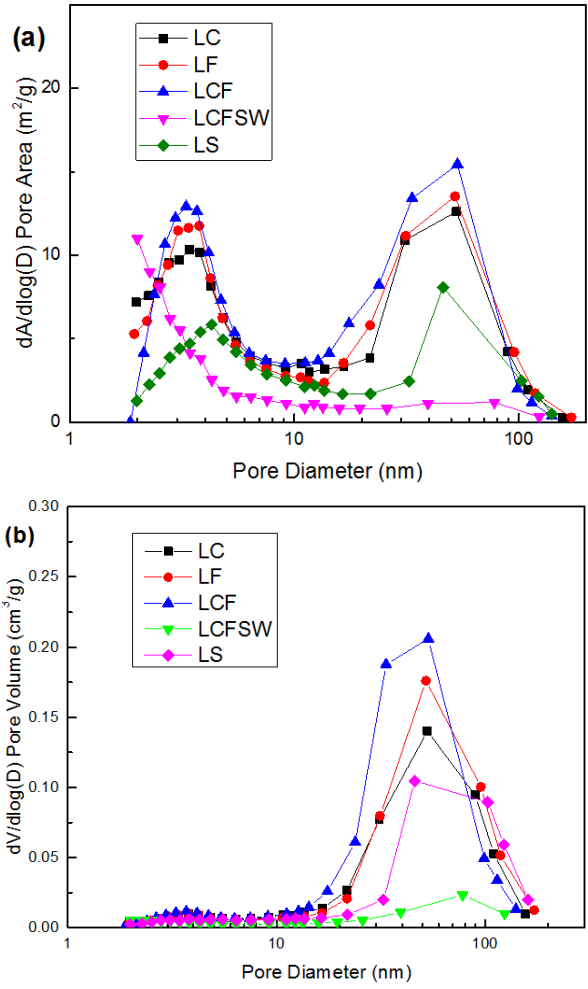


Figure 2

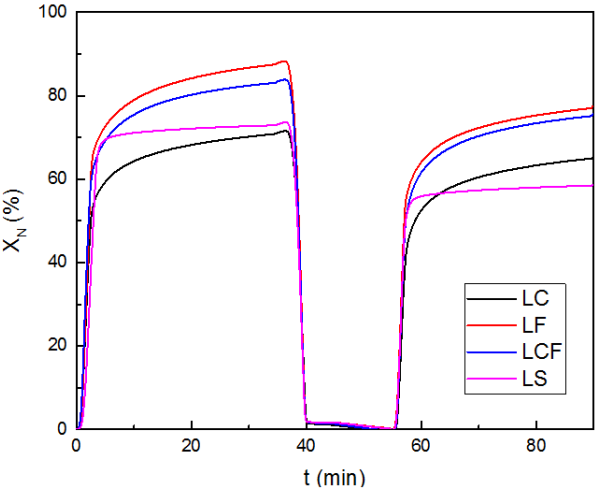


Figure 3

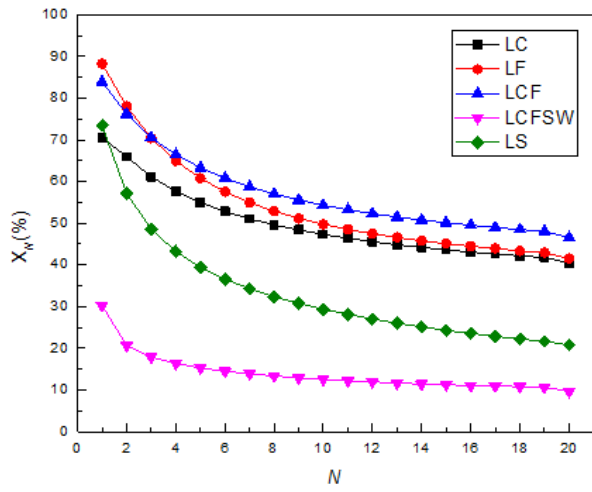


Figure 4

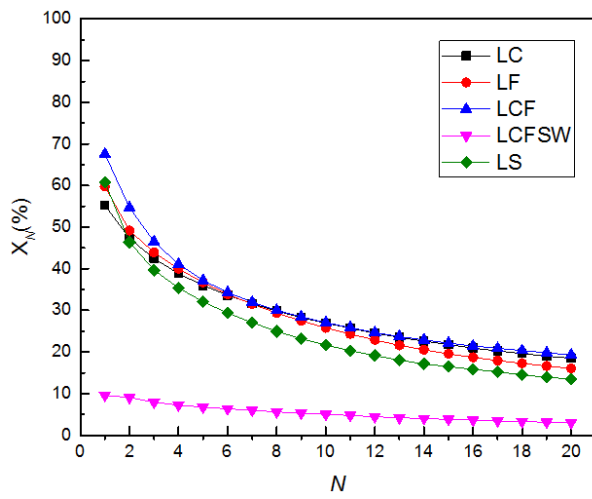


Figure 5

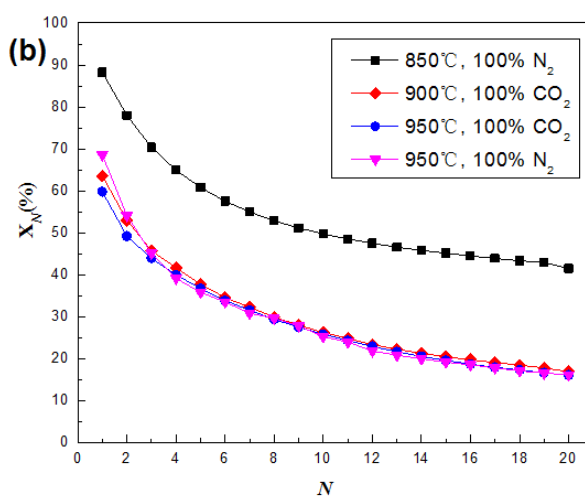
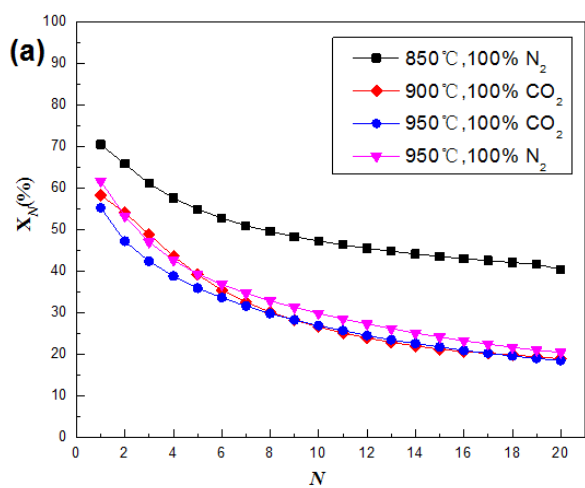
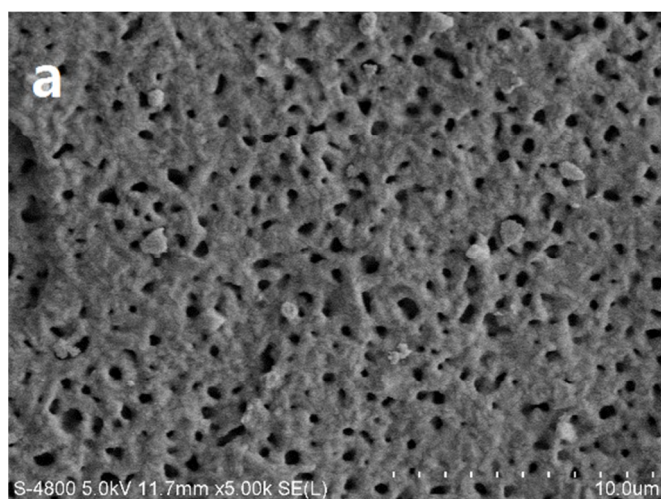
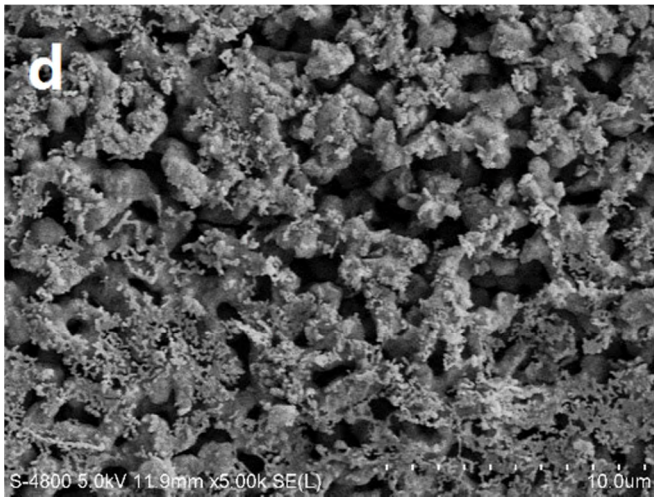
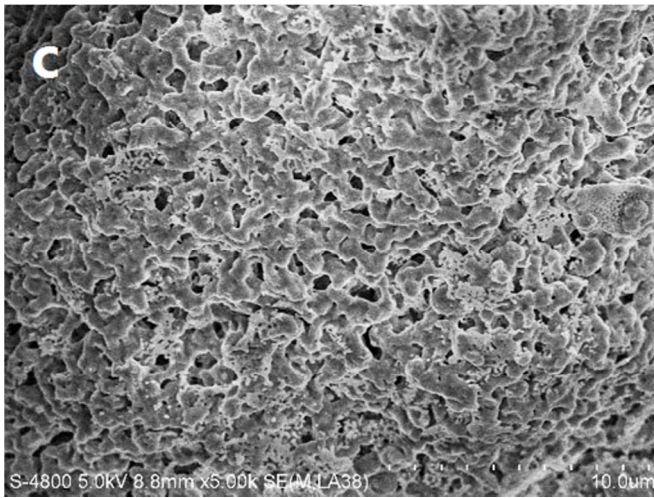
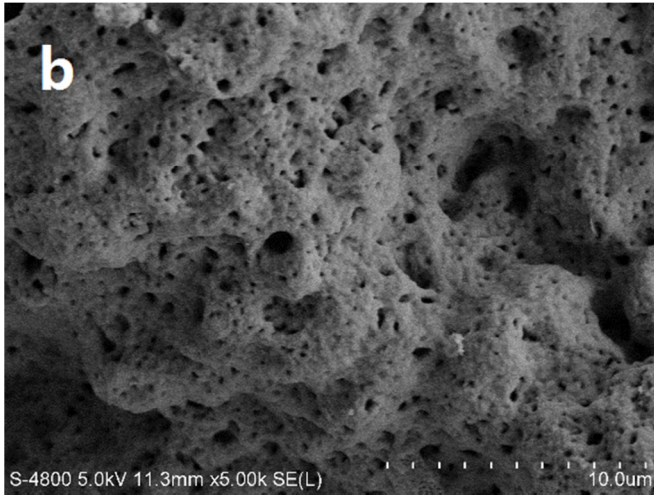
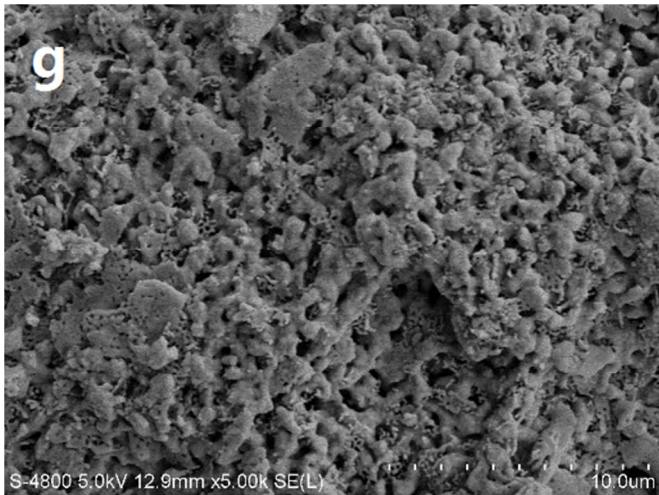
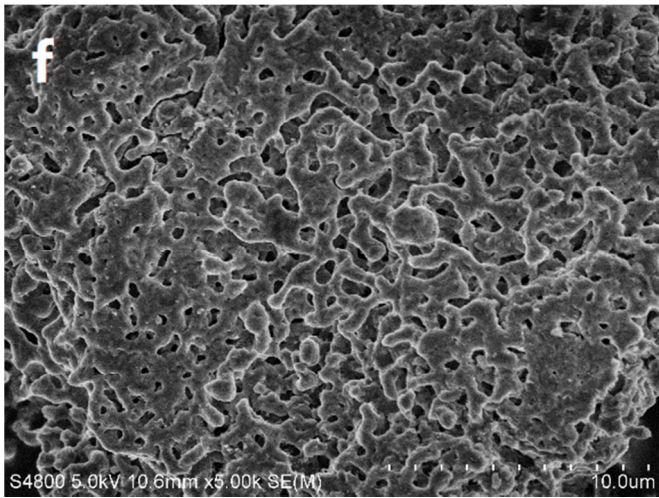
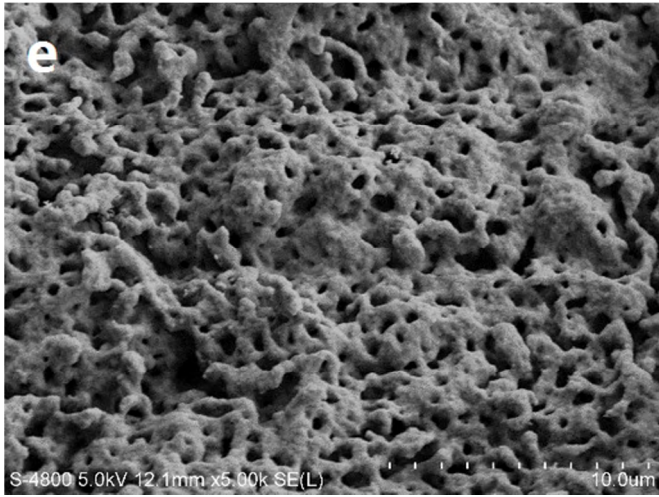
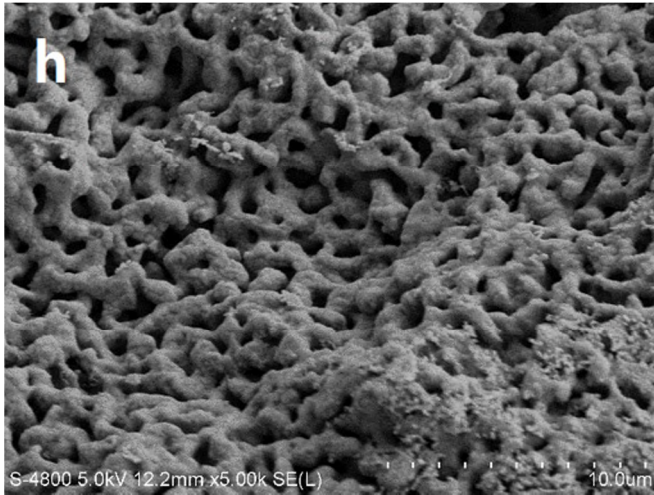


Figure 6









## Table of Contents

