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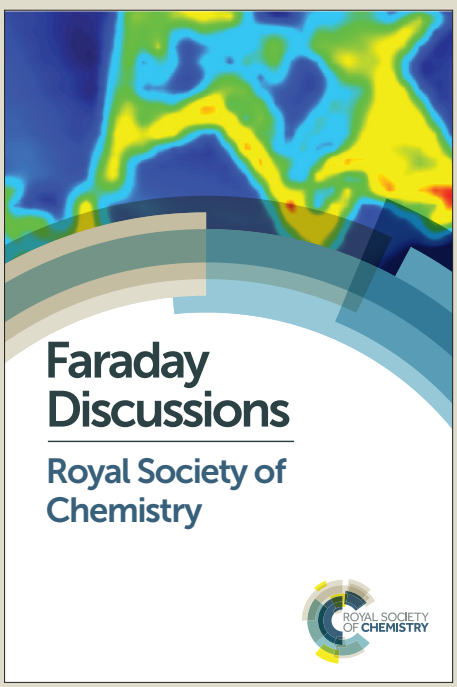
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ARTICLE

Effect of SO_2 and steam on CO_2 capture performance of biomass-templated calcium aluminate pellets

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Four types of synthetic sorbents were developed for high-temperature post-combustion calcium looping CO_2 capture using Longcal limestone. Pellets were prepared with: lime and cement (LC); lime and flour (LF); lime, cement and flour (LCF); and lime, cement and flour, doped with seawater (LCFSW). Flour was used as a templating material. All samples underwent 20 cycles in a TGA under two different calcination conditions. Moreover, the prepared sorbents were tested for 10 carbonation/calcination cycles in a 68-mm-internal-diameter bubbling fluidized bed (BFB) under three environments: with no sulphur and no steam; in the presence of sulfur; and with steam. When compared to limestone, all the synthetic sorbents exhibited enhanced CO_2 capture performance in both a TGA and BFB, with the exception of the sample doped with seawater. In the BFB tests, the addition of cement binder during the pelletisation process resulted in the increase of CO_2 capture capacity from 0.08 gCO_2/gsorbent (LF) to 0.15 gCO_2/gsorbent (LCF) by the 10th cycle. The CO_2 uptake in the presence of SO_2 dramatically declined by the 10th cycle; for example, from 0.22 gCO_2/gsorbent to 0.05 gCO_2/gsorbent in the case of the untemplated material (LC). However, as expected all samples showed improved performance in the presence of steam and the decay of reactivity during the cycles was less pronounced. Nevertheless, in the BFB environment, the templated pellets showed poorer CO_2 capture performance. This is presumably because of material loss due to attrition under the FB conditions. Namely, by contrast, the templated materials performed better than untemplated materials under TGA conditions. This indicates that reduction in attrition is critical in the case of employment of templated materials in realistic systems with FB reactors.

1 Introduction

It is widely accepted that CO_2 emissions are the most contributing factor affecting climate change. Decreasing the anthropogenic CO_2 emissions, especially from the power sector, which accounts for at least one third of the total greenhouse gas emissions in 2010,[1] is one of the main goals of climate change mitigation strategies. Carbon capture and storage (CCS) has been proposed to mitigate CO_2 emission from power plants. [2-5] Currently, the carbon capture technology that is the closest to the market is amine scrubbing[4] with its first commercial-scale plant opened in October 2014 in Canada.[6] However, there are many problems associated with this technology such as degradation of the expensive solvent and the corrosive nature of typical solvents such as monoethanolamide (MEA).[7-13] Due to these challenges other options are being increasingly explored for CO_2 capture such as calcium looping (CaL).[14]

The CaL systems comprises of two interconnected fluidised beds which function as a carbonator and calciner respectively. The CO2 is captured by a lime-based sorbent in the carbonator at 600-700°C, and a high-purity CO_2 stream is produced in the calciner at 850-950°C. This process has many advantages; such as, the use of a cheap natural sorbent[15, 16] and a low energy penalty.[17] However, there are two major challenges associated with this technology: the sorbent reactivity decay over reaction cycles, and the attrition of the particles due to mechanical and thermal stresses experience in a fluidized bed environment. These challenges demand increasing sorbent makeup (i.e. the use of fresh sorbent).[18]

Considerable research effort has been made to develop new sorbents that have a more stable reactivity over many cycles, using techniques such as sol-gel combustion,[19-27] organic/acid modifications,[28-34] calcium carbonate precipitation[33,35,36] and granulation[37-44] among others. Most of these methods have proven to produce materials that have higher capture capacity than natural sorbents. However, although these modifications can result in a better sorbent performance, they are potentially expensive due to the cost of the materials required and the use of multiple process steps.[45, 46]

Granulation is a promising technique for the preparation of sorbents; it allows the chemical doping and also the improvement of mechanical strength using binders such as bentonites, kaolin, alumina and calcium aluminate cements and it appears to be easily scalable. Recently, Ridha et al.[43] explored the templating of pellets using cheap biomass sources; the

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resulting sorbent displayed a higher pore volume and CO_2 capture than biomass-free pellets.

Doping has also been previously explored as a mean to reduce the decay of activity of natural materials. Salvador et al.[47] demonstrated that NaCl improved the relative capture capacity by maintaining it at 40% after 10 cycles due to resulting changes in the pore structure for TGA tests. However, NaCl markedly decreased the CO_2 capture of the treated lime when tested in a FBC compared to the untreated material. Other materials such as KCl and K_2CO_3,[48] manganese salts,[49] MgCl and $Mg(NO_3)_2$,[50] and $CaBr_2$[51,52] have also produced improvement in pore structure, pore volume and pore size. However, in some cases, alkali-metal precursors used as dopants, such as, lithium chloride produced poorer performance in the treated sample than for natural limestone.[53]

The reduction in reactivity over many cycles is aggravated by the presence of SO_2, due to the irreversible reaction between CaO and SO_2 to form $CaSO_4$.[54-56] Unfortunately, Calcium sulphate is stable at the typical CaL temperatures, which leads to a dramatic decay in carbonation conversions during the cycling due to the formation of a $CaSO_4$ layer. Pacciani et al.[57] discovered that sulfation is enhanced in carbonation/calcination cycles for synthetic sorbents. Stanmore and Gilot[58] reviewed that the simultaneous capture of CO_2 and SO_2 causes more sintering than SO_2 capture alone.

The use of pelletised material in the presence of SO_2 has been studied by Manovic and Anthony.[59] They found the particles composed of lime and calcium aluminate cement exhibited a higher sulfation rate (89%) than that of natural limestone (30%). Ridha et al.[60] also studied the effect of sulfation in pelletised particles prepared using kaolin as a binder; and the results showed strong deactivation of all sorbents tested, but it was more pronounced in the case of the pelletised material, which is in agreement with previous results from the same group.[59]

Steam is always present in flue gas due to the combustion process and it was experimentally simulated by, for example, 15%vol steam addition during the carbonation stages of the CO_2 capture experiments.[61,62] These studies show that the presence of steam increased the CO_2 uptake substantially in a bench-scale FBC possibly due to enhanced solid-state diffusion in the product layer.[63]

This work explores the effect of SO_2 and steam on calcium aluminate pellets, as cheap synthetic CaL sorbents templated by biomass and doped by seawater. CO_2 uptake was measured during the carbonation/calcination cycling of the sorbent performed using a TGA, and a bubbling FB to provide realistic test conditions and allow us to study the effects of attrition.

2 Experimental

2.1 Materials

Longcal limestone from United Kingdom was used as a lime precursor. Commercial calcium aluminate cement, CA-14, manufactured by Almantis, was used as a binder in the pelletisation process and as a source of Al_2O_3. Commercial flour was used as the biomass templating material. Artificial seawater (Complete Aquatics) was used for doping purposes; this water is treated with NaOCl, to leave only a small additional amount of Na and Cl.

2.2 Pellet preparation procedure

Four types of materials were prepared: (i) 10% calcium alumina cement and 90% calcined limestone (LC) (ii) 10% flour and 90% calcined limestone (LF), (iii) 10% flour, 10% calcium alumina cement and 80% calcined limestone (LCF), and (iv) 10% flour, 10% calcium aluminate cement and 80% calcined lime doped with seawater (LCFSW). The pellets were prepared in Glatt TMG 1/6 granulator. The desired powder proportional quantities (1 kg batches) were introduced into the pelletizer vessel (6 L) and mixed. The mixing was carried out inside the vessel by two sets of blades (the chopper and the agitator) while continuously spraying water (ca. 1 L during the procedure) for pelletisation. A more detailed explanation of this procedure can be found in the work done by Manovic et al.[64] The particles were then sieved and the size fraction 0.3-0.6 mm was collected. The material was air dried for 24 h before storage and the samples produced are described in Table 1.

2.3 CO_2 capture cycles

A Perkin Elmer Diamond TG/DTA thermogravimetic analyser (TGA) was used for repeated carbonation/calcination cycles. The samples were tested under two conditions; in the first one, carbonation was performed during 20 min at 650°C under 15% CO_2, while the calcination was done for 10 min at 850°C under 100% N_2. In the second round of tests, the carbonation was performed during 20 min at 650°C under 15% CO_2, and the calcination was carried out for 10 min at 950°C under 100% CO_2. Under the later conditions, during the transition between calcination and carbonation, the atmosphere was switched to 100% N_2 below 900°C to avoid carbonation at non-desired conditions. The heating ramp was set to 40°C/min for the heating stage and 20°C/min for the cooling stage. All the sorbents underwent 20 cycles.

In addition to the TGA, a lab-scale bubbling fluidised bed (BFB) was used for testing carbonation/calcination cycles to ensure testing under more realistic conditions.[65] The BFB is 68 mm ID; it was operated at atmospheric pressure and heated to the desired temperature by means of an external electric furnace. The distributor plate consists of four bubble cups and a cyclone downstream of the fluidised bed is used to avoid excessive particle concentration in the flue gas. After the cyclone, the gas

Table 1: Materials used in the preparation of samples

Sample	Lime (wt %)	Calcium aluminate cement (wt%)	Flour (wt%)	Type of water used for pelletisation process
LC	90	10	0	Deionized water
LF	90	0	10	Deionized water

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LCF	80	10	10	Deionized water
LCFSW	80	10	10	Sea water

was filtered and cooled. A fraction of the exhaust gas was continuously sampled to measure CO_2 and SO_2 concentration with ABB EL3020 with infrared (CO_2 and SO_2) photometers in order to monitor the progress of the reactions. The layout of the experimental equipment used is exhibited in Figure 1.

For the BFB tests, 100 g of sorbents were diluted in 1.5 kg of silica sand to avoid excessive increase of temperature in the bed during carbonation. Due to the temperature change limitations caused by the thermal inertia of the BFB, all the experiments were performed isothermally at 850°C with 90% vol. CO_2 during the carbonation and 20% vol. CO_2 during the calcination. The duration of both calcination and carbonation was 15 min.

The effects of sulfur and steam were also investigated in the BFB following the same procedure as above with a sand-diluted bed and isothermal conditions for carbonation/calcination at 850°C. To measure the effect of SO_2 a new series of experiments were performed. For these tests, the concentration of CO_2 was maintained the same as in experiments with no SO_2. The SO_2 concentration was set to 1500 ppm for both carbonation and calcination, simulating not desulfurized flue gas from high-sulphur-coal combustion entering the carbonator and burning high-sulphur coal in the oxy-fuel calciner.[66] A high impact on the carbonation degree and the CO_2 uptake is expected. The concentration of oxygen during carbonation and calcination was maintained constant and at 3% vol.

The effect of steam was also studied in the BFB. The steam is normally present both in the calciner and carbonator due to the moisture content in fuels and due to steam formation during combustion. The selected steam content was 15% vol. during the carbonation and the calcination in accordance to previously published article.[63] The CO_2 concentration during calcination conditions was maintained to 20% vol. on a wet basis and,

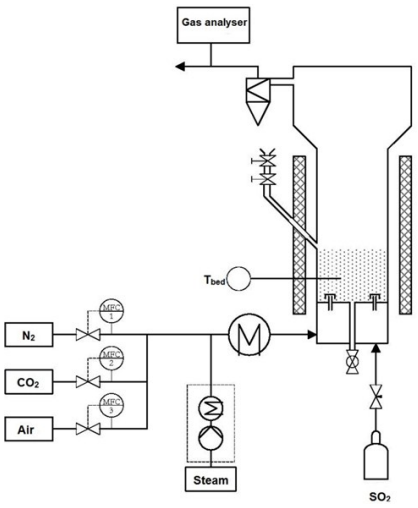


Figure 1: Overview of laboratory-scale fluidised-bed system

during the carbonation, the CO_2 concentration was set to 80% vol. on wet basis.

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For all the fluidised-bed experiments, 10 cycles were performed while maintaining the bed velocity at 0.5 m/s (bubbling regime) during the whole duration of each experiment.

2.4 Sample characterization

Elementary analysis of the samples was performed using ICP-OES (inductively coupled plasma optical emission spectrometry). Compression strength tests were performed using the FGE-5XY Digital Force Gauge. For each sample, 31 measurements were made to ensure the validity of the data for raw material. Mercury porosimetry was performed using the AutoPore IV 9500 for analyses of the total pore area and porosity.

3. Results and discussion

3.1 Sorbent characterization

The ICP-OES (inductively coupled plasma optical emission spectrometry) and carbon analyses of the limestone and the samples are given in Table 2.

Raw pellets made from calcined limestone and 10% alumina cement (LC) show the highest crushing strength resistance (Figure 2). It was expected that cement-containing pellets (LC and LCF) would have higher crushing strength than non-cement containing particles (LF) due to the presence of cement. However, LCFSW was also prepared with a cement containing mixture and its crushing strength is very low. It is possible that the lower crushing strength is due to negative effects of the seawater doping, probably caused by the excess of NaCl in the dopant media.[67] Limestone was not tested for crushing strength due to the small particle size (average size of 180 µm) when compared to the size range of materials produced (300-600µm).

Table 2: Elementary analysis of the sorbents used

Component (wt %)	Limestone	LC	LF	LCF	LCFSW
Al_2O_3	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_2O_3	0.015	0.033	0.040	0.027	0.030
K_2O	0.007	0.006	0.037	0.023	0.051
MgO	0.185	0.208	0.210	0.197	0.335
MnO_2	0.008	0.008	0.009	0.008	0.010
Na_2O	0.053	0.071	0.052	0.056	0.806
P_2O_5	0.007	0.011	0.035	0.022	0.012
SO_3	0.034	0.039	0.122	0.055	0.234
SiO2	0.701	1.20	0.770	0.267	0.292
SrO	0.017	0.018	0.018	0.017	0.018
TiO_2	0.006	0.015	0.013	0.006	0.007
Total oxides	55.1	65.7	59.7	57.8	64.4

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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

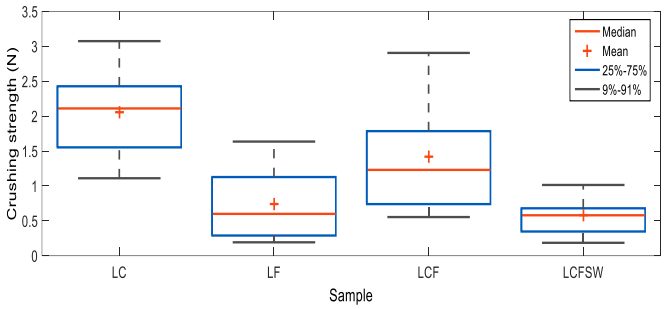


Figure 2: Crushing strength of non-calcined samples

In Table 3, the results for the mercury porosimetry for LC and LCF are shown in order to compare the effect that the addition of flour has on the sorbent pore size. As expected the addition of flour has a positive effect increasing both the porosity and the total pore area of the resulting material.

3.2 Reactivity test

3.2.1 TGA tests

The final TGA results during 20 cycles under the previously mentioned conditions are shown in Figure 3 (samples calcined at 850°C in pure N_2) and Figure 4 (samples calcined at 950°C in pure CO_2). The main aim of these tests was to compare the synthetic sorbents prepared using the pelletisation method in order to assess if flour or any similar material used as a biomass-templating material would be suitable for calcium looping processes.

The carbonation conversion of all pellets was higher, when they were calcined at 950°C in pure CO_2 (Figure 4) compared to the first case (calcination at 850°C in pure N_2; Figure 3). The use of seawater (LCFSW) instead of deionized water (LCF) during the pelletisation process had a very dramatic effect in terms of decreasing the carbonation conversion from 21% to less than 5% in the 20th cycle (and from 41% to 10% in the case of calcination with pure CO_2 in Figure 4). The other samples showed quite uniform behaviour for the calcination in pure N_2

Table 3: Mercury porosimetry for LC and LCF

Sample	Porosity (%)	Total pore area (m^2/g)
LC	**53.3%**	**14.95**
LCF	**68.4%**	**17.173**

(Figure 3). In the tests performed under more realistic conditions (calcination at 950°C in pure CO_2; Figure 4), the biomass-templated pellets (both LF and LCF) showed better carbonation conversion than LC in the first ten cycles, but afterwards their (LF and LCF) conversion remained only slightly higher than the conversion of LC.

3.2.2 BFB tests

The behaviour of the pellets compared to the original limestone in a real BFB during 10 cycles is given in Figure 5. It can be seen that all of the pellets performed better than the initial limestone after the third cycle. The sorbent performance was increased from 0.03 $gCO_2/gsorbent$ for the limestone to 0.22 $gCO_2/gsorbent$ for LC, 0.07 $gCO_2/gsorbent$ for LF, 0.12 $gCO_2/gsorbent$ for LCF and 0.05 $gCO_2/gsorbent$ for LCFSW in the 10th cycle.

It can be observed that the addition of calcium aluminate cement has a clear effect on the biomass-doped pellets increasing their CO_2 uptake by 71% (LCF compared to LF). This phenomenon can be attributed to the presence of the mesoporous Al_2O_3 phase, which increases the porosity of the sample,[68] and to the increased attrition resistance and decreased elutriation rate.

LCFSW pellets exhibited only a marginal improvement of 0.02 $gCO_2/gsorbent$ by the 10th cycle (compared to the limestone),

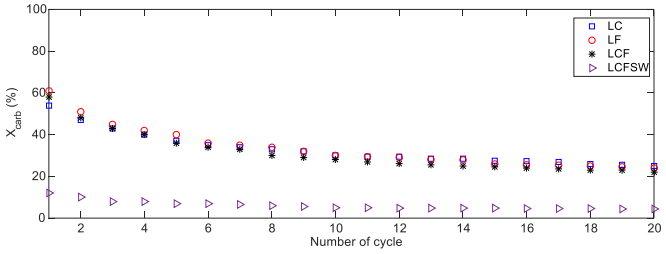


Figure 3: TGA Carbonation conversion of sorbents calcined under N_2 atmosphere (10 min calcination at 850 °C in 100% vol. N_2 and carbonation during 20 min at 650 °C in 15% vol. CO_2)

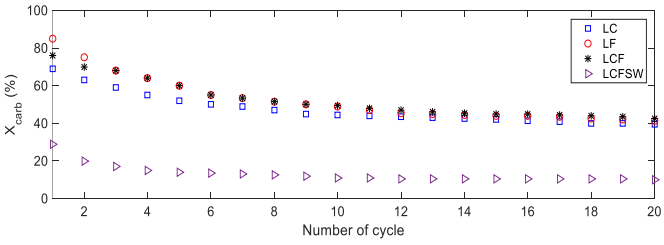


Figure 4: TGA Carbonation conversion of sorbents calcined under CO_2 atmosphere (10 min calcination at 950 °C in 100% vol. CO_2 and carbonation during 20 min at 650 °C in 15% vol. CO_2)

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indicating that doping with seawater did not increase the performance of the sorbent. It was also apparent that the addition of biomass to LC reduced the CO_2 uptake from 0.22 gCO_2/gsorbent to 0.12 gCO_2/gsorbent by the 10th cycle. This suggests that flour templating of the pellets did not improve the resistance towards degradation experienced over the carbonation-calcination cycles.

Figure 6 shows how the sorbents behaved under high SO_2 concentration conditions (1500 ppm). Here, all sorbents behaved poorly when compared to the results without SO_2 addition (Figure 5). Even in the case of the best sorbent, LC there was significant loss of activity. Thus, in this case, the CO_2 capture capacity declined from 0.22 gCO_2/gsorbent to 0.05 gCO_2/gsorbent by the 10th cycle. This highlights the need to desulfurizing flue gas specially when dealing with synthetic sorbents.

For the biomass-containing materials (LF, LCF and LCFSW) the capacity after 10 cycles was found to be very similar at around 5% carbonation, which also represents (when compared to Figure 5) a very dramatic decline especially in LCF that had 31% carbonation degree in the 10th cycle without SO_2 addition. These results can be explained by the progressive build-up of a sulfate layer that reduces CO_2 diffusion in the pores of the pellets and limestone particles.[69]

The effect of steam addition to the X_{carb} is shown in Figure 7. The addition of steam increased the degree of carbonation of all the sorbents. In accordance with previous observations, such as Ridha et al.,[40] the drastic decline observed in the first cycle when cycling without steam is no longer observed when the steam is introduced.

In the 10th cycle LC had a CO_2 uptake of 0.25 gCO_2/gsorbent, which is 14% more than in the case without steam. LCF adsorbed 25% more of CO2 (0.12 gCO_2/gsorbent to 0.15 gCO_2/gsorbent) in the 10th cycle. The other sorbents (Limestone, LF and LCFSW) also improved their capture capacity but their CO2 uptake is still below 0.1 gCO_2/gsorbent.

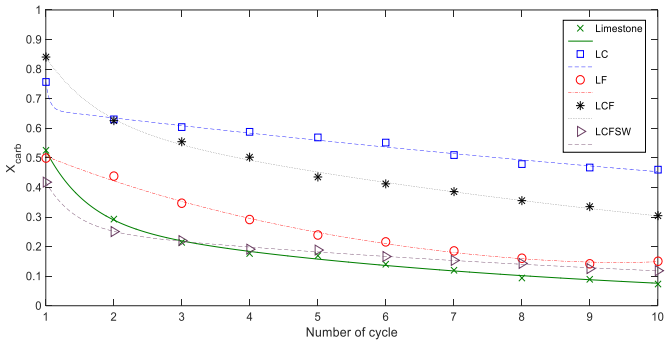


Figure 5: Carbonation conversion of the prepared pellets and original limestone in BFB; carbonation 850°C for 15 min; calcination 850°C for 15 min

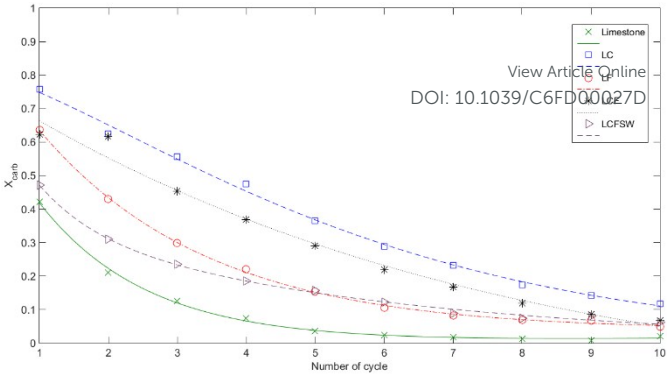


Figure 6: Carbonation conversion of pellets and original limestone with 1500 ppm SO_2; carbonation 850°C for 15 min; calcination 850°C for 15 min in BFB

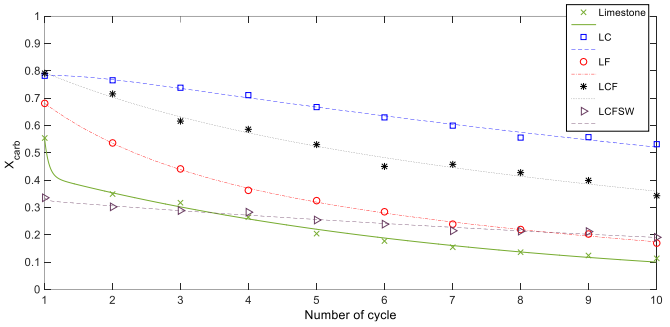


Figure 7: Carbonation conversion of pellets and original limestone with 15% steam in BFB; carbonation 850°C for 15 min; calcination 850°C for 15 min

Conclusions

This work examined the CO_2 capture performance of CaO-based sorbents (limestone, calcium aluminate pellets, biomass-doped pellets with and without binder, and biomass-templated pellets doped with seawater). All of the biomass-containing pellets were made from flour chosen as a cheap biomass source to enhance the CO_2 uptake.

The biomass-free pellets showed superior capture capacity compared with the biomass-containing pellets when cycles were performed in a BFB; and the non-biomass-containing sample (LC) had the highest capacity in all cases. However, when pellets were tested in a TGA (calcination 950°C 100% CO_2), the biomass and cement-containing pellets (LCF) had the highest conversion. It appears that the biomass-containing pellets are more subjected to attrition, so their mechanic strength needs to be improved during the preparation process. This increased attrition agrees with the crushing strength results where the biomass-containing particles showed markedly lower results than biomass-free particles.

The CO_2 uptake by the biomass-free pellets (LC) in the 10th cycle was of 0.22 gCO_2/gsorbent under normal conditions, 0.25 gCO_2/gsorbent with 15% vol of steam and 0.05 gCO_2/gsorbent

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under 1500 ppm of SO_2 in carbonation and calcination, indicating a very dramatic effect with sulfur addition.

It most important difference between the biomass-containing material (LF) and the biomass and cement containing material (LCF) is the presence of a binder (10% calcium aluminate cement in LCF), which has a great impact with a 71.4% higher CO_2 uptake for the cement-containing sample under normal conditions and a 87.5% increase of CO_2 uptake for the same pellets with a 15% vol and around the same conversion for the high sulphur conditions. Although biomass-templating for pelletising Ca-based sorbents could be a beneficial technique to improve reactivity, it is clear that a way of increasing mechanical strength is required and that attrition for these systems needs to be better understood.

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References

1 UNEP, *The Emissions Gap Report 2012*, United Nations Environment Programme (UNEP), Nairobi, Kenya, 2012.

2 N.S Siefert and S. Litster, Exergy and economic analyses of advanced IGCC–CCS and IGFC–CCS power plants, *Appl. Energy,* 2013, **107**, 315–328.

3 M.E. Boot-Handford, J.C. Abanades, E.J. Anthony, M.J. Blunt, S. Brandani, N. Mac Dowell, J.R. Fernandez, M.C. Ferrari, R. Gross, J.P. Hallett, R.S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R.T.J. Porter, M. Pourkashanian, G.T Rochelle, N. Shah, J.G. Yao and P. Fennel, Carbon capture and storage update, *Energy Environ. Sci.*, 2014, **7**, 130–189.

4 L.S. Fan. *Chemical looping systems for fossil energy conversions*. John Wiley & Sons. 2011

5 H. Herzog, B. Eliasson and O. Kaarstad , Capturing greenhouse gases. *Scientif. Am.*, 2000, **282**, 72–79.

6 R. Idem, M. Wilson, P. Tontiwachwuthikul, A. Chakma, A. Veawab, A. Aroonwilas and D. Gelowitz, Pilot plant studies of the CO_2 capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO2 capture technology development plant and the boundary dam CO2 capture demonstration plant, *Ind. Eng. Chem. Res*., 2006, **45**, 2414–2420.

7 T. Supap, R. Idem, P. Tontiwachwuthikul and C. Saiwan, Analysis of monoethanolamine and its oxidative degradation products during CO_2 absorption from flue gases: A comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations, *Ind. Eng. Chem. Res.*, 2006, **45**, 2437–2451.

8 A. Veawab, P. Tontiwachwuthikul and A. Chakma, Investigation of low-toxic organic corrosion inhibitors for CO_2 separation process using aqueous MEA solvent, *Ind. Eng. Chem. Res.*, 2001, **40**, 4771–4777..

9 D. Aaron and C. Tsouris, Separation of CO_2 from flue gas: A review, *Sep. Sci. Technol.*, 2005, **40**, 321–348.

10 S. Chi and G. Rochelle, Oxidative degradation of monoethanolamine, *Ind. Eng. Chem. Res.*, 2002, **41**, 4178–4786.

11 G.S. Goff and G. Rochelle, Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions, *Ind. Eng. Chem. Res.*, 2004, **43**, 6400–6408.

12 G. Fytianos, S. Ucar, A. Grimstvedt, A. Hyldbakk, H.F. Svendsen and H.K. Knuutila, Corrosion and degradation in MEA based post-combustion CO_2 capture, *Int. J. Greenh. Gas Control*, 2016, **46**, 48–56.

13 K. Li, W. Leigh, P. Feron, H. Yu and M. Tade, Systematic study of aqueous monoethanolamine (MEA)-based CO_2 capture process: Techno-economic assessment of the MEA process and its improvements, *Appl. Energy*, 2016, **165**, 648–59.

14 J. Blamey, E.J. Anthony, J. Wang and P.S. Fennell, The calcium looping cycle for large-scale CO_2 capture*, Prog. Energy Combust. Sci.*, 2010, **36**, 260–279.

15 A. Lasheras, J. Ströhle, A. Galloy and B. Epple. Carbonate looping process simulation using a 1D fluidized bed model for the carbonator*, Int. J. Greenh. Gas Control*, 2011, **5**, 686–693.

16 C.C. Dean, J. Blamey, N.H. Florin, M.J. Al-Jeboori and P.S. Fennell, The calcium looping cycle for CO_2 capture from power generation, cement manufacture and hydrogen production, *Chem. Eng. Res. Des*., 2011, **89**, 836–855.

17 M.C. Romano, Modeling the carbonator of a Ca-looping process for CO_2 capture from power plant flue gas, *Chem. Eng. Sci.*, 2012, **69**, 257–269.

18 D.Y. Lu, R.W. Hughes and E.J. Anthony, Ca-based sorbent looping combustion for CO_2 capture in pilot-scale dual fluidized bed, *Fuel Process. Technol*., 2008, **89**, 1386–1395.

19 C. Luo, Y. Zheng, N. Ding and C. Zheng. Enhanced cyclic stability of CO_2 adsorption capacity of CaO-based sorbents using La_2O_3 or $Ca_{12}Al_{14}O_{33}$ as additives, *Korean J. Chem. Eng*., 2011, **28**, 1042–1046.

20 C. Luo, Y. Zheng, N. Ding, Q. Wu, G. Bian and C. Zheng, Development and performance of CaO/La_2O_3 sorbents during calcium looping cycles for CO_2 capture, *Ind. Eng. Chem. Res*., 2010, **49**, 11778–17784.

21 C. Luo, Y. Zheng, C. Zheng, J. Yin, C. Qin and B. Feng, Manufacture of calcium-based sorbents for high temperature cyclic CO_2 capture via a sol-gel process, *Int. J. Greenh. Gas Control*, 2013, **12**, 193–199.

22 H.R. Radfarnia and A. Sayari, A highly efficient CaO-based CO_2 sorbent prepared by a citrate-assisted sol – gel technique, *Chem. Eng. J.*, 2015, **262**, 913–20.

23 S.D Angeli, C.S. Martavaltzi and A.A. Lemonidou, Development of a novel-synthesized Ca-based CO_2 sorbent for multicycle operation: Parametric study of sorption, *Fuel* 2014, **127**, 62–69.

24 B. Wang, R. Yan, D.H. Lee, Y. Zheng, H. Zhao and C. Zheng, Characterization and evaluation of Fe_2O_3/Al_2O_3 oxygen carrier prepared by sol-gel combustion synthesis, *J. Anal. Appl. Pyrolysis*, 2011, **91**, 105–113.

25 B. Wang, X. Song, Z. Wang and C. Zheng. Preparation and application of the Sol – Gel combustion synthesis-made $CaO/CaZrO_3$ sorbent for cyclic CO_2 capture through the severe calcination condition, *Chinese J. Chem. Eng*., 2014, **22**, 991–999.

26 M. Broda and C.R Müller, Sol-gel-derived, CaO-based, ZrO_2-stabilized CO_2 sorbents, *Fuel*, 2014, **127**, 94–100.

27 C. Luo, Y. Zheng, Y. Xu, H. Ding, C. Zheng, C. Qin and B. Feng, Cyclic CO2 capture characteristics of a pellet derived from sol-gel CaO powder with $Ca_{12}Al_{14}O_{33}$ support, *Korean J. Chem. Eng.*, 2015, **31**, 1–5.

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28 M. Zhang, Y. Peng, Y. Sun, P. Li and J. Yu, Preparation of CaO-Al_2O_3 sorbent and CO_2 capture performance at high temperature, *Fuel*, 2013, **111**, 636–642.
29 Y. Li, L. Shi, C. Liu, Z. He and S. Wu, Studies on CO_2 uptake by $CaO/Ca_3Al_2O_6$ sorbent in calcium looping cycles, *J. Therm. Anal. Calorim.*, 2015, **120**, 1519-1528.
30 Y. Li, M. Su, X. Xie, S. Wu and C. Liu, CO_2 capture performance of synthetic sorbent prepared from carbide slag and aluminum nitrate hydrate by combustion synthesis, *Appl. Energy*, 2015, **145**, 60–68.
31 K. Wang, X. Guo, P. Zhao and C. Zheng, Cyclic CO_2 capture of CaO-based sorbent in the presence of metakaolin and aluminum hydroxides, *Appl. Clay Sci*., 2010, **50**, 41–46.
32 C.C. Li, U.T. Wu and H.P. Lin, Cyclic performance of $CaCO_3$@$mSiO_2$ for CO_2 capture in a calcium looping cycle, *J. Mater. Chem. A*, 2014, **2**, 8252-8257.
33 L. Li, D.L. King, Z. Nie and C. Howard, Magnesia-stabilized calcium oxide absorbents with improved durability for high temperature CO_2 capture, *Ind. Eng. Chem. Res*., 2009, **48**, 10604–10613.
34 M. Zhao, M. Bilton, A.P. Brown, A.M. Cunliffe, E. Dvininov, V. Dupont, T.P. Comyn and S.J. Milne, Durability of CaO–$CaZrO_3$ sorbents for high-temperature CO_2 capture prepared by a wet chemical method, *Energy & Fuels*, 2014, **28**, 1275–1283.
35 H. Gupta and L.S. Fan, Carbonation−calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas, *Ind. Eng. Chem. Res*., 2002, **41**, 4035–4042.
36 N. Florin and P. Fennell. Synthetic CaO-based sorbent for CO_2 capture, *Energy Procedia*, 2011, **4**, 830–838.
37 V. Manovic and E.J. Anthony, Screening of binders for pelletization of CaO-based sorbents for CO_2 capture, *Energy & Fuels*, 2009, **23**, 4797–4804.
38 Y. Wu, V. Manovic, I. He and E.J. Anthony, Modified lime-based pellet sorbents for high-temperature CO_2 capture: Reactivity and attrition behaviour, *Fuel*, 2012, **96**, 454–461.
39 F.N. Ridha, V. Manovic, Y. Wu, A. Macchi and E.J. Anthony, Pelletized CaO-based sorbents treated with organic acids for enhanced CO_2 capture in Ca-looping cycles, *Int. J. Greenh. Gas Control*, 2013, **17**, 357–365.
40 F.N. Ridha, V. Manovic, A. Macchi and E.J. Anthony, High-temperature CO_2 capture cycles for CaO-based pellets with kaolin-based binders, *Int. J. Greenh. Gas Control*, 2012, **6**, 164–170.
41 C. Qin, J. Yin, H. An, W. Liu and B. Feng, Performance of extruded particles from calcium hydroxide and cement for CO_2 capture, *Energy & Fuels*, 2012, **26**, 154–161.
42 A. Knight, N. Ellis, J.R. Grace and C.J. Lim, CO_2 sorbent attrition testing for fluidized bed systems, *Powder Technol*., 2014, **266**, 412–423.
43 F.N. Ridha, Y. Wu, V. Manovic, A. Macchi and E.J. Anthony, Enhanced CO_2 capture by biomass-templated $Ca(OH)_2$-based pellets, *Chem. Eng. J*., 2015, **274**, 69–75.
44 V. Manovic and E.J. Anthony, CaO-based pellets with oxygen carriers and catalysts, *Energy & Fuels*, 2011, **25**, 4846–4853.
45 P. Sun, J.R. Grace, C.J. Lim and E.J. Anthony, Investigation of attempts to improve cyclic CO_2 capture by sorbent hydration and modification, *Ind. Eng. Chem. Res*., 2008, **47**, 2024–2032.
46 F.N. Ridha, V. Manovic, A. Macchi, M.A. Anthony and E.J. Anthony, Assessment of limestone treatment with organic acids for CO_2 capture in Ca-looping cycles, *Fuel Process. Technol.*, 2013, **116**, 284–291.
47 C. Salvador, D. Lu, E.J. Anthony and J.C. Abanades, Enhancement of CaO for CO_2 capture in an FBC environment, *Chem. Eng. J.,* 2003, **96**, 187–195.
48 B. González, J. Blamey, M. McBride-Wrigh, N. Carter, D. Dugwell, P. Fennell and J.C. Abanades. Calcium looping for CO_2 capture: Sorbent enhancement through doping, *Energy Procedia*, 2011, **4**, 402–409.
49 R. Sun, Y. Li, H. Liu, S. Wu and C. Lu, CO_2 capture performance of calcium-based sorbent doped with manganese salts during calcium looping cycle, *Appl. Energy*, 2012, **89**, 368–373.
50 M.J. Al-Jeboori, P.S. Fennell, M. Nguyen and K. Feng, Effects of different dopants and doping procedures on the reactivity of CaO-based sorbents for CO_2 capture, *Energy & Fuels*, 2012, **26**, 6584–6594.
51 V. Manovic, P.S. Fennell, M.J. Al-Jeboori and E.J. Anthony, Steam-enhanced calcium looping cycles with calcium aluminate pellets doped with bromides, *Ind. Eng. Chem. Res.*, 2013, **52**, 7677–7683.
52 M.J. Al-Jeboori, M. Nguyen, C. Dean and P.S. Fennell, Improvement of limestone-based CO_2 sorbents for Ca looping by HBr and other mineral acids, *Ind. Eng. Chem. Res*., 2013, **52**, 1426–1433.
53 E.P. Reddy and P.G. Smirniotis, High-temperature sorbents for CO_2 made of alkali metals doped on CaO supports, *J. Phys. Chem. B*, 2004, **108**, 7794–7800.
54 G.S. Grasa, M. Alonso and J.C. Abanades JC, Sulfation of CaO particles in a carbonation/calcination loop to capture CO_2, *Ind. Eng. Chem. Res*., 2008, **47**, 1630-1635.
55 V. Manovic and E.J. Anthony, Competition of sulphation and carbonation reactions during looping cycles for CO_2 capture by CaO-based sorbents, *J. Phys. Chem. A*, 2010, **114**, 3997-4002.
56 Y. Wu, C. Wang, Y. Tan, L. Jia and E.J. Anthony, Characterization of ashes from a $100kW_{th}$ pilot-scale circulating fluidized bed with oxy-fuel combustion, *Appl. Energy*, 2011, **88**, 2940-2948.
57 R. Pacciani, C.R. Müller, J.F. Davidson, J.S. Dennis and A.N. Hayhurst, Performance of a novel synthetic Ca-based solid sorbent suitable for desulfurizing flue gases in a fluidized bed, *Ind. Eng. Chem. Res*., 2009, **48**, 7016-7024.
58 B.R. Stanmore and P. Gilot, Review—calcination and carbonation of limestone during thermal cycling for CO_2 sequestration, *Fuel Process. Technol*., 2005, **86**, 1707-1743.
59 V. Manovic, E.J. Anthony and D. Loncarevic, SO_2 retention by CaO-based sorbent spent in CO_2 looping cycles, *Ind. Eng. Chem. Res*., 2009, **48**, 6627-6632.
60 F.N. Ridha, V. Manovic, A. Macchi and E.J. Anthony. The effect of SO_2 on CO_2 capture by CaO-based pellets prepared with a kaolin derived $Al(OH)_3$ binder, *Appl. Energy*, 2012, **92**, 415-420.
61 F. Donat, N.H. Florin, E.J. Anthony and P.S. Fennell, Influence of high temperature steam on the reactivity of CaO sorbent for CO_2 capture, *Environ. Sci. Technol*., 2012, **46**, 1262–1269.
62 B. Arias, G. Grasa, J.C. Abanades, V. Manovic and E.J. Anthony, The effect of steam on the fast carbonation reaction rates of CaO, *Ind. Eng. Chem. Res*., 2012, **51**, 2478–2482.
63 V. Manovic and E.J. Anthony, Carbonation of CaO-based sorbents enhanced by steam addition, *Ind. Eng. Chem. Res.*, 2010, **49**, 9105–9110.
64 V. Manovic, Y. Wu, I. He and E.J. Anthony, Spray water reactivation/pelletization of spent CaO-based sorbent from calcium looping cycles, *Environ. Sci. Technol*., 2012, **46**(22), 12720-12725.
65 M. Alonso, Y.A. Criado, J.C. Abanades and G. Grasa , Undesired effects in the determination of CO_2 carrying capacities of CaO during TG testing, *Fuel*, 2014, **127**, 52–61.
66 A. Coppola, F. Montagnaro, P. Salatino and F. Scala, Fluidized bed calcium looping: the effect of SO_2 on sorbent attrition and CO_2 capture capacity, *Chem. Eng. J*., 2012, **207**, 445-449.
67 P.S. Fennell, R. Pacciani, J.S. Dennis and J.F. Davidson, The effects of repeated cycles of calcination and carbonation on a variety of different limestones, as measured in a hot fluidized bed of sand, *Energy & Fuels*, 2007, **21**(4), 2072-2081.

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68 V. Manovic and E.J. Anthony, CaO-based pellets supported by calcium aluminate cements for high-temperature CO_2 capture, *Environ. Sci. Technol.*, 2009, **43**, 7117–7122.
69 S.V. Krishnan and S.V. Sotirchos, Effective diffusivity changes during calcination, carbonation, recalcination, and sulfation of limestones, *Chem. Eng. Sci*., 1994, **49**(8), 1195-1208.

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