

The Extent of Sorbent Attrition and Degradation of Ethanol Treated CaO Sorbents for CO₂ Capture within a Fluidised Bed Reactor

Peter T. Clough^a, Gianluca Greco^{a,b}, Maria Erans^a, Antonio Coppola^c,
Fabio Montagnaro^{d*}, Edward Anthony^{a*}

Abstract

The application of an ethanol pre-treatment step on biomass templated calcium looping sorbents resulting in an improved pore structure for cyclic CO₂ capture was investigated. Three ethanol solutions of varying concentrations were used and an improved pore and particle structure, and thermogravimetric analyser CO₂ carrying capacity arising with the 70 vol.% ethanol solution. The extent of attrition of these sorbents was tested within a fluidised bed reactor and compared against an untreated sorbent and a limestone base case. It found that despite the ethanol treated sorbents displaying an admirable CO₂ carrying capacity within the thermogravimetric analyser even under realistic post-combustion conditions, this was not translated equivalently in the fluidised bed. Attrition and elutriation of the biomass templated sorbents was a significant issue and the ethanol pre-treatment step appeared to worsen the situation due to the roughened surface and mechanically weaker structure.

Affiliations

^a Energy and Resource Technology Centre, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK.

^b Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy.

^c Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Piazzale Tecchio 80, 80125 Napoli, Italy.

^d Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, 80126 Napoli, Italy.

* Corresponding authors: Email addresses - fabio.montagnaro@unina.it, b.j.anthony@cranfield.ac.uk.

Keywords: Ethanol pre-treatment, Attrition, Fluidised bed, Calcium looping, CCS

1. Introduction

Climate change is forcing the global community to rethink the way energy and industrial products are generated. Carbon Capture and Storage (CCS) is one method of preventing CO₂ emissions from carbon intensive industries, whereby the CO₂ is collected, transported and safely stored underground thus preventing its action as greenhouse gas in the atmosphere. CCS is also well regarded as being essential to cost-effectively combatting climate change [1, 2].

Calcium looping (CaL) is one form of CCS and can be operated as a post- or pre-combustion system [3]. The most familiar is a post-combustion setting consisting of two reactors: a carbonator - where CO₂ is absorbed onto a CaO sorbent to form CaCO₃, and a calciner – where CO₂ is released from the sorbent generating a nearly pure stream of CO₂ [4]. Typically, the CO₂ sorbent used is CaO derived from natural limestone although many synthetic sorbents have also been manufactured with varying suitability for commercial application [5].

A major technical limitation to the full market deployment CaL is the degradation in the sorbents ability to cyclically capture and release CO₂. Pure CaO has a maximum CO₂ carrying capacity of 1 mole CO₂ per 1 mole CaO, however due to high-temperature CO₂/H₂O sintering [6], attrition [7] and competitive sulphation reactions [8] this CO₂ carrying capacity can decrease to just 0.1-0.2 mol/mol in a matter of a few cycles. Some previously demonstrated effective methods for minimising the degradation in the carrying capacity are the incorporation of a support structure within the particle (such as a calcium aluminate cement [9], polymorphic dicalcium silicate [10], or many others [11-13]), doping with HBr [14], steam or water hydration [15], thermal pre-activation [16], biomass templating [17], acid treatment [18-20] and ethanol treatment [21].

Ethanol treatment is where a solution of ethanol and water are allowed to soak a sorbent (whilst in its calcined form). The water then begins to react with the CaO to form disassociated Ca²⁺ and OH⁻ ions, in doing so opening up the pores [22]. The extent of the hydration reaction is limited by a high ethanol concentration and the strong polar bonds experienced between the water and ethanol molecules. Upon drying the sorbent to remove the solution the dissolved ions reform at the surface of the particle to form Ca(OH)₂ leaving behind particle with increased porosity and a high surface area. This method has been demonstrated to be quite effective at increasing the long-term CO₂ carrying capacity of the sorbent over multiple cycles, even under realistic calcination conditions [21].

Attrition in particular has been ignored in much of the research efforts in trying to maintain the original carrying capacity. Nevertheless, attrition is an important factor to consider as a sorbent that easily attrites will require a higher make-up rate of fresh sorbent thus increasing the operating cost [23]. Attrition is known to be caused by three main routes: [24]

- Primary fragmentation – Thermal shocks and over-pressurisation (due to near instantaneous reactions occurring within the particle) causing the particle to splinter/crack and break apart into finer particles
- Secondary fragmentation – Crushing and mechanical weakening of particles caused by mechanical contact between other particles and a reactor's internal features
- Abrasion – The rubbing of particles against other particles and a reactor's internals providing a shear force at the exterior of the particles, gradually wearing away the surface

The aim of this investigation was to examine the extent of attrition on a simply manufactured sorbent with an additional ethanol pre-treatment step for pore structure enhancement. The sorbents tested within this work also benefited from an enhanced macro-pore structure due to biomass templating with wheat flour and the pores were developed further by the application of ethanol pre-treatment. Additional structural rigidity was given to the particles from the inclusion of a calcium aluminate cement support structure. The ethanol treated sorbents were tested within a TGA and a fluidised bed reactor to determine their ability to resist attrition.

2. Materials and Methods

2.1. Sorbent preparation

To produce the sorbents utilised within this work Longcliffe limestone (supplied by Longcliffe Quarries Ltd, UK) was first calcined in a muffle furnace at 850 °C for 2 h under an air purge gas. The produced lime was transferred into a mixing vessel (Glatt TMG 1/6 granulator) in which a commercial calcium aluminate cement (CA-14, 73 % Al_2O_3 and 27 % CaO) and flour was added in order to form a powdered mixture of 80 wt.% CaO, 10 wt.% calcium aluminate cement and 10 wt.% flour. After thoroughly dry mixing the powders, de-ionised water was gradually sprayed into the vessel whilst the mixture continued to stir, thus forming aggregated particles. After observing the particles forming in sufficient quantities the material was dried for 24 h in air and then screened using a vibratory sieve shaker to obtain particles in the range of 300 – 500 μm . These particles were then calcined in air in a muffle furnace for 2 h at 850 °C before being pre-treated with the ethanol solutions.

Three ethanol/water solutions were prepared, which were (in terms of ethanol concentration) 70 vol.%, 80 vol.% and 90 vol.%; the pre-treated samples were named according to these concentrations. 10 mg aliquots of raw calcined particles were mixed with 10 ml of ethanol (EtOH)/water solution for about 30 seconds, after which the samples were placed in an oven at 100 °C for 3 h.

2.2. Sorbent analysis

The EtOH/water pre-treated sorbents were assessed for their ability to resist sintering degradation over multiple calcium looping cycles. This cycling was conducted within an atmospheric pressure TGA (TA Instruments Q5000IR) and utilised industrially representative post-combustion calcination conditions, which has been shown to be vital in determining the actual potential of a sorbents carrying capacity [25]. The sorbents were carbonated at 650 °C for 20 minutes in 15 vol.% CO₂ balanced with N₂ and were calcined at 950 °C for 1 minute in 100 vol.% CO₂. To delay premature calcination whilst increasing the samples temperature from 650 to 950 °C between the carbonation and calcination, the CO₂ partial pressure was also increased and the N₂ partial pressure decreased corresponding to the furnace temperature. The temperature was ramped at 50 °C/min and the CO₂ concentration was ramped up at a rate such that the sample remained slightly above the equilibrium position (until about 890 °C at which point a partial pressure greater than 1 bar was required to prevent calcination). A detailed explanation of this temperature linked CO₂ partial pressure ramping system is given by Clough et al. [25]. A constant flow rate of 110 cm³/min was utilised throughout these runs. At the end of the calcination period, the gas mixture was switched directly to N₂ and the sample was cooled to the carbonation temperature. The sample was cycled through carbonation and calcination 20 times. The BET surface area was determined utilising a Micromeritics TriStar N₂ adsorption surface area analyser after degassing at 110 °C for 2 h. A scanning electron microscope (SEM, FEI/Philips XL-30 Field Emission ESEM) was utilised to study the surface morphology of the produced sorbents.

The extent of sorbent attrition was studied within a fluidised bed reactor located at Università degli Studi di Napoli Federico II, Italy. The reactor (a schematic is presented as Figure 1) is constructed of stainless steel, with an internal diameter of 40 mm, a wall thickness of 3 mm and a total height of ~1.60 m (~1 m fluidisation column). The fluidisation gases (controlled by mass flow controllers) entered from the bottom of the reactor where it was preheated and mixed within a ceramic packing material, before passing through a distribution plate which supported the bed material. The reactor was heated by two 2.4 kW electric furnaces and was controlled via type K thermocouples linked to a PID controller. The reactor was insulated with an alumina-silicate mineral wool material. At the exit of the reactor, a sample of the gas flow was extracted, cooled to condense any water and further filtered through a glass wool filter to remove any remaining fine solids before continuing onto a gas analyser (ABB AO2020) which measured the CO₂ concentration by infrared. All data from the reactor was recorded using LabVIEW.

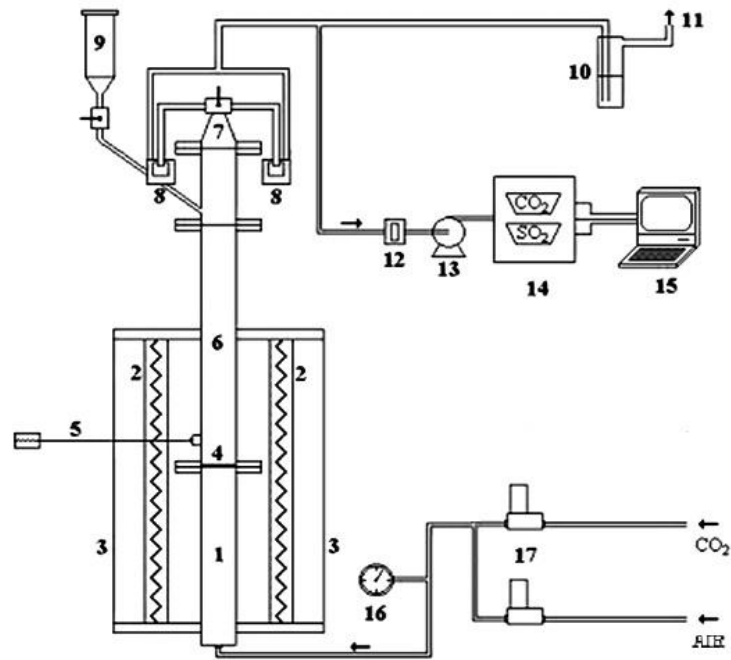


Figure 1 – Schematic outline of the fluidised bed reactor employed: 1) pre-heating and mixing area, 2) electric furnaces, 3) Insulation, 4) distribution plate, 5) type K thermocouple, 6) fluidisation column, 7) reactor head (removable), 8) two cylindrical, sintered brass filters for fine solids, 9) raw material hopper, 10) flue gas rock wool filtration, 11) flue gases outlet to extraction hood, 12) fixed bed filter of glass wool, 13) membrane pump, 14) gas analysers, 15) computer, 16) pressure gauge, 17) mass flow controllers.

Each calcium looping experiment consisted of a zeroth calcination of the original material and then four complete carbonation/calcination cycles. Firstly, 150 g of silica sand (0.9-1 mm) was loaded into the reactor and heated to the calcination conditions, then 20 g of sorbent (0.4–0.6 mm) was added. The fluidised bed reactor served as both a calciner and a carbonator: at the end of each cycle phase the bed material was retrieved from the reactor via a vacuum pump. Sand was then separated from the sorbent by gentle sieving (to avoid further particle fragmentation). Effective separation of the sand/sorbent mixture was accomplished due to the coarser sand particles together with their negligible attrition tendency. Subsequently, sand was reinjected into the bed and the operating conditions for the next cycle phase were set up. After having reached stable conditions, the sorbent was added again to the reactor and the cycle phase began, this process was repeated for each carbonation and calcination.

In more detail, calcination was carried out isothermally at 940 °C with a fluidising velocity of 0.7 m/s consisting of 70 vol.% CO₂ (balanced with air), while carbonation was carried out isothermally at 650 °C with a fluidising velocity of 0.6 m s⁻¹ consisting of 15 vol.% CO₂ (balanced with air). Superficial gas velocities were set at 2–2.5 times the minimum fluidisation velocity to ensure effective mixing within the bed. The duration of each cycle phase (20 and 15 minutes for calcination and carbonation, respectively) was such that the relevant chemical reactions went to practical completion, this was verified by flue gas

analysis. For each carbonation stage, the CO₂ capture capacity was calculated on the basis of the flue gas analysis as the mass of CO₂ cumulatively captured divided by the mass of sorbent initially fed to the system.

The system was equipped with filters that acted as collection vessels that enabled the time-resolved collection of elutriated fines at the exit of the reactor (Figure 1, item No. 8). The fines collected in these filters which were then weighed at the end of each cycle phase to determine the mass of sample elutriated. The rate of fines generated by attrition, here also termed rate of elutriation, was measured as a function of time during each stage; defined as the mass of elutriated fines collected divided by the time interval that filter was in operation and by the initial mass of sorbent. Again, the negligible attrition tendency of sand meant it was safe to assume that only sorbent fines were collected in filters.

3. Results and Discussion

3.1. TGA carrying capacity study

The results of the calcium looping cycling conducted within the TGA are displayed as Figure 2. The CaO conversion displayed in Figure 2 was calculated based on the mass change between the sample mass after the zeroth calcination and the sample mass at the end of each carbonation period. These mass changes were converted into moles by dividing by the relative molecular masses of each respective species, as shown in Equation 1. The value of CaO purity utilised in Equation 1 was determined through XRF and was found to be ≈80.8 wt.%.

Equation 1 – CO₂ carrying capacity:

$$CO_2 \text{ carrying capacity (mol } CO_2/\text{mol } CaO) = \frac{\left(\frac{\Delta Mass_{carb}}{M_{W \text{ } CO_2}}\right)}{\left(\frac{Mass_0 \cdot Purity_{CaO}}{M_{W \text{ } CaO}}\right)}$$

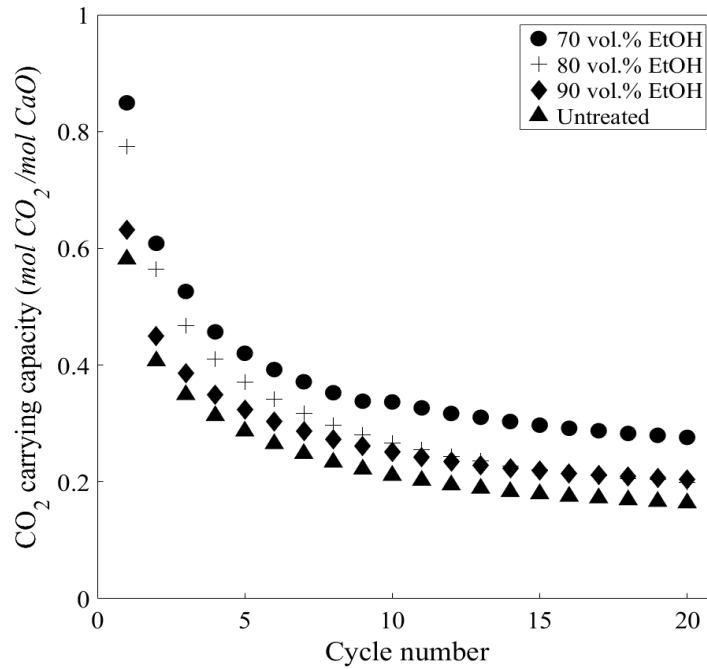


Figure 2 – CO₂ carrying capacity over 20 calcium looping cycles, of EtOH/water pre-treated particles (300 – 500 μm) with a calcium aluminate cementitious binder and flour as a biomass pore forming spacer. Conducted within an atmospheric TGA, carbonation performed at 650 °C for 20 minutes and calcination at 950 °C for 1 minute. The CO₂ partial pressure was ramped between the carbonation and calcination conditions to prevent undesired early calcination [25].

It can be observed from the results displayed in Figure 2, that the particles treated with 70 vol.% EtOH solution outperformed all the other samples in terms of its CO₂ carrying capacity over 20 cycles. The sample treated with 70 vol.% EtOH solution had an initial CO₂ carrying capacity of 0.84 mol CO₂/mol CaO which decreased to 0.27 mol CO₂/mol CaO, thereby presenting a 67.5 % decrease. This compares favourably to the untreated, raw sample which showed a 71.8 % decrease in carrying capacity (starting at 0.58 mol CO₂/mol CaO and finishing at 0.16 mol CO₂/mol CaO). The sample treated with the 70 vol.% EtOH solution therefore showed a ~68.8 % improvement in long-term CO₂ carrying capacity.

The reason for the lower degree of carrying capacity retention when increasing the ethanol concentration, was likely because of the small quantity of water in the pre-treatment solution. It has been shown previously that the ethanol molecules within the solution enhance the water molecules affinity and penetrability within the CaO matrix. However, it is the interaction between the controlled reaction of the water and CaO molecules, which forms small amounts of Ca(OH)₂, that leads to the enlarged/enhanced pore structure [21]. Therefore by decreasing the amount of water available within the solution (i.e. at 90 vol.% EtOH) less Ca(OH)₂ is formed and the influence on the pore structure was diminished. It has been further noted by Li et al., that Ca(OH)₂ is slightly soluble in EtOH/water solutions and therefore as the solution with the dissolved Ca(OH)₂ evaporated the recombination of Ca²⁺ and OH⁻ ions at the surface of the particle and along the pore walls would have altered the pore structure and particle size further [21].

Contrary to the work of Li et al. [21], a lower CO₂ carrying capacity was observed when the sample was treated with a solution containing a higher ethanol concentration, this could be due to high temperature CO₂ sintering during the calcination phase at the commercially applicable conditions utilised in this work. The observed trend could also be explained by noting the BET surface areas in Table 1, which show that the sample treated with the 70 vol.% EtOH solution had the highest surface area whereas the untreated sample had the lowest surface area. It can therefore be stated that the lower 70 vol.% EtOH treatment solution considerably altered the pore structure by redistribution of Ca²⁺ ions from the internal pores to the external surface thus enlarging the pores and developing a skeleton structure that was able to resist sintering.

Table 1 – BET surface areas of samples treated with various EtOH/water solutions.

Sample name and ethanol solution treatment	BET surface area (m²/g)
Raw, untreated limestone	9.02
70 vol.%	10.96
80 vol.%	10.75
90 vol.%	9.54

The surface morphology of the samples can be observed within the SEM images displayed as Figure 3a-d. It can be observed from these figures that the surface roughness increased with decreasing ethanol concentration, this was likely because of Ca(OH)₂ that formed at the surface of the particle after the Ca²⁺ and OH⁻ ions had previously dissolved in the EtOH/water solution [21]. The sample treated with the 90 vol.% EtOH solution appeared visibly smoother than even the raw, untreated sample, which could have been because of the high ethanol concentration suppressing the action of the water due to the constraining intermolecular polar bonding of the water and ethanol.

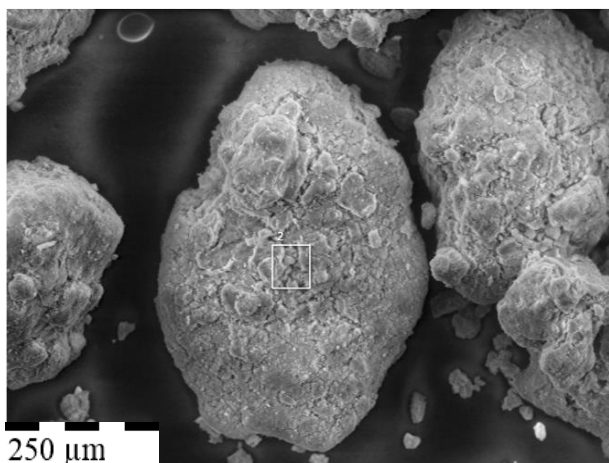


Figure 3a – SEM image of the untreated sample.

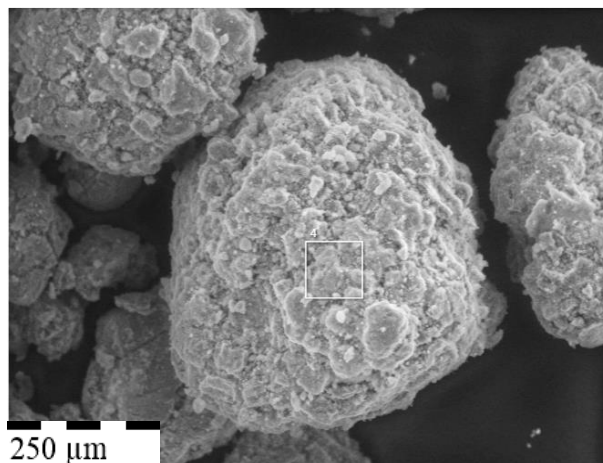


Figure 3b – SEM image of the sample treated with 70 vol.% EtOH solution.

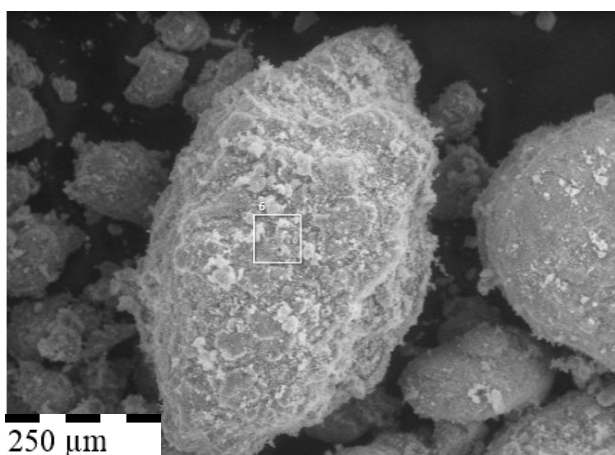


Figure 3c – SEM image of the sample treated with 80 vol.% EtOH solution.

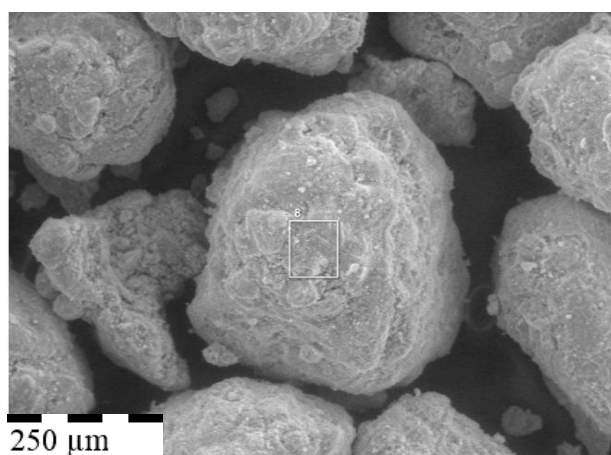


Figure 3d – SEM image of the sample treated with 90 vol.% EtOH solution.

3.2. Fluidised bed attrition study

To investigate the extent of sorbent degradation due to attrition, a set of experiments were conducted utilising the fluidised bed reactor described earlier. It was decided to conduct this study with only the sample treated with 70 vol.% EtOH, due to the superior CO₂ carrying capacity performance observed within the TGA. Four CaL cycles were conducted within the fluidised bed, as minimal attrition was expected beyond this point; it is widely known that the majority of attrition (for natural untreated limestone) occurs within the first cycle [4, 24, 26]. These CaL cycling experiments were also conducted with untreated, natural Longcliffe limestone and a sample of the untreated manufactured particles (with the cementitious binder and flour but no ethanol treatment) which provided comparable reference materials. A typical system response of the CO₂ concentration with time during the first four carbonations is displayed in the supporting information appendix; observed temperature deviations with

time were negligible due to effective fluidisation and mixing within the bed. The CO₂ carrying capacities were determined via the same method outlined in previous work [27].

The CO₂ carrying capacities of the two sorbents (70 vol.% EtOH/water treated and natural limestone) are displayed in Figure 4 in terms of moles CO₂ captured per mole of CaO. The reported carrying capacities of the EtOH treated sorbent were considerably lower than that of the limestone sample, this was likely due to attrition during the zeroth calcination thus leaving little reactive sorbent for subsequent carbonations. Unlike the data presented in Figure 2 (TGA carrying capacities comparing untreated and EtOH treated sorbents) the carrying capacities of the untreated and EtOH treated sorbents were quite similar; both were significantly lower than the natural limestone. The increased surface roughness of the EtOH treated particles (observable in the SEM images - Figure 3a-d) was in all probability eroded by secondary mechanical attrition (collisions with other particles and the reactor walls) and abrasion produced by the fluidised bed environment rather than primary attrition (thermal shocks). Consequently, it can be stated that attrition was the leading cause for the observed discrepancy between the carrying capacities achieved within the TGA and the fluidised bed. The loss in surface roughness due to attrition would have also impacted on the available surface area for carbonation thereby decreasing the CO₂ carrying capacity further.

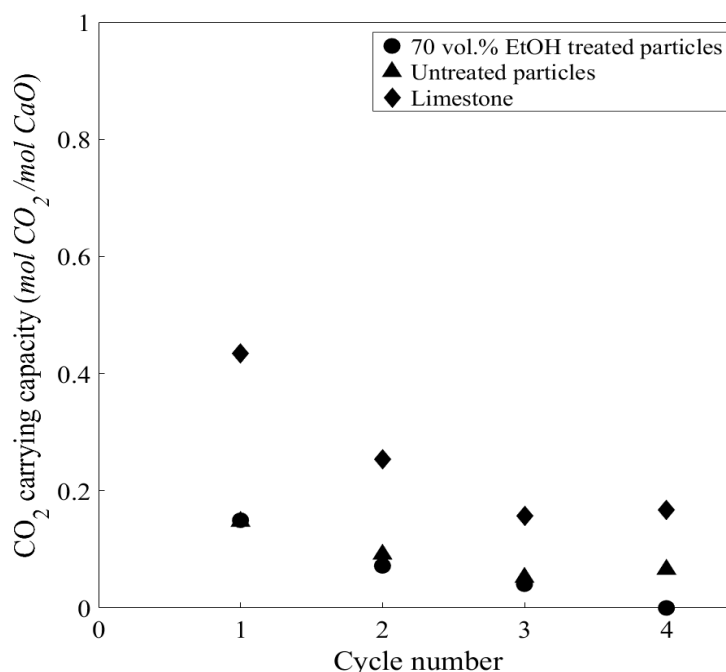


Figure 4 – CO₂ carbonation carrying capacity over 4 calcium looping cycles, of 70 vol.% EtOH/water treated and untreated particles (400 – 600 μm) which were composed of calcined limestone, a calcium aluminate cementitious binder and flour as a pore forming spacer, and natural limestone for baseline comparison. Conducted within fluidised bed reactor, carbonation performed in 15 vol.% CO₂ and 85

vol.% air at 650 °C for 15 minutes and calcination used 70 vol.% CO₂ and 30 vol.% air at 940 °C for 20 minutes.

The elutriation rate of fines normalised for the initial starting mass during the zeroth calcination is displayed in Figure 5. During this calcination, little CO₂ was released from the EtOH treated and the untreated sorbents as the materials were mostly in a hydrated/calcined form due to the manufacturing method. The EtOH treated sorbent displayed the greatest rate of elutriation during the zeroth calcination, almost an order of magnitude above the samples of untreated sorbent and natural limestone. Attrition of the rough treated particle surface was thought to be the cause of the higher rate of elutriation compared to the other samples during this calcination.

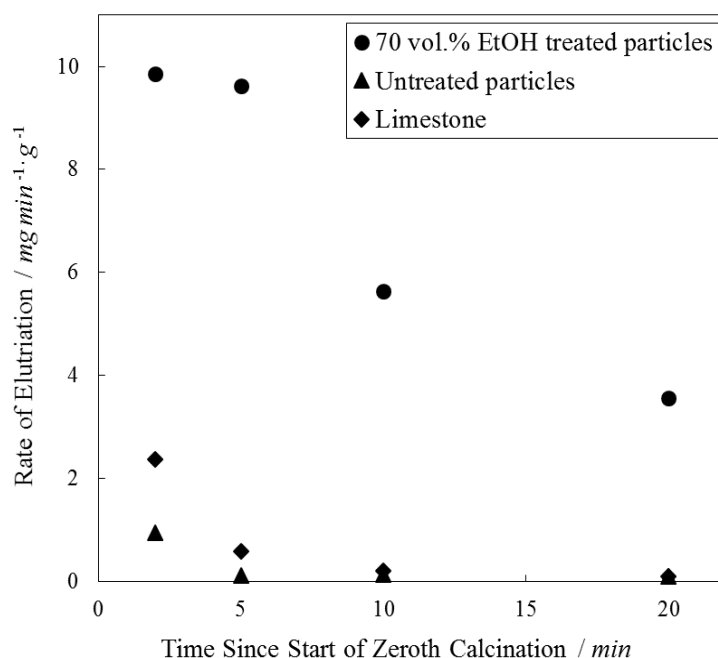


Figure 5 – Rate of elutriation during the zeroth calcination of 70 vol.% EtOH/water treated and untreated particles which were composed of calcined limestone, a calcium aluminate cementitious binder and flour as a pore forming spacer, and natural limestone for baseline comparison. Conducted within fluidised bed reactor with particles of size fraction 0.4 – 0.6 mm in a gas composed of 70 vol.% CO₂ and 30 vol.% air at 940 °C for 20 minutes.

The rates of elutriation normalised for initial starting mass, during each carbonation and calcination phase are displayed in Figure 6 and Figure 7 respectively. The rate of elutriation can be seen to be significantly higher for the carbonation cycle phases, the cause of which was identified in previous work to be down to the rapid elutriation of produced fines when the softer, porous and frailer calcined material was added into the hot reactor [24, 28]. This calcined material was also likely weakened by partial

hydration when it came in contact with atmospheric moisture. Primary attrition (thermal shock) at the beginning of the carbonation period in this work is unlikely to occur in a commercial CaL system as the sorbent would ordinarily be cooling from the calcination temperature rather than heating from atmospheric temperature. It should also be noted that the extent of attrition observed could be higher than that of a commercial system, as the particles were heated from room temperature at the start of each cycle phase, therefore their thermal history was not representative of expected CaL operation.

In both the carbonation and calcination phases the rates of elutriation were greatest when the samples were first added into the reactor (first two minutes) which implies that primary attrition was the leading cause of sorbent mass loss. The rates of elutriation gradually tailed off towards zero by the end of the carbonation and calcination time periods, which demonstrates that the intrinsic particle strength (provided by the calcium aluminate cement structure) was suitable for fluidised bed usage and was eventually comparable to natural limestone. The rate of elutriation was consistently higher for the manufactured sorbents compared to limestone, which combined with the carrying capacity data in Figure 4, thereby demonstrates that the remaining bed material after four CaL cycles was probably only the calcium aluminate cement with small amounts of sintered/trapped CaO. The addition of the biomass for templating purposes also likely affected the rate and extent of attrition. It has been demonstrated previously in multiple studies that the use of biomass for templating purposes leads to more attrition prone sorbents that degrade rapidly within a fluidised bed environment [29-31]. Some research has suggested that the extent of attrition can be minimised effectively by the addition of a calcium aluminate binder, which in their case reduced the mass loss to <0.5 % of the starting mass [17, 32, 33], but by utilising the same cement in this work didn't seem to prevent the attrition observed. Although it must be stated that in the work by Sun et al. [33], the particles were only rotated in a drum at atmospheric temperature which could be an explanation for the low levels of attrition compared to the work in a hot fluidised bed here. Nevertheless, considering the evidence gathered across the available literature and the experiments conducted in this study it can be suggested that a sorbents' (produced by the method in this work) propensity to attrite is dependant more on the extent of CaO hydration during manufacturing, than the incorporation of the cementitious binder to the particles matrix.

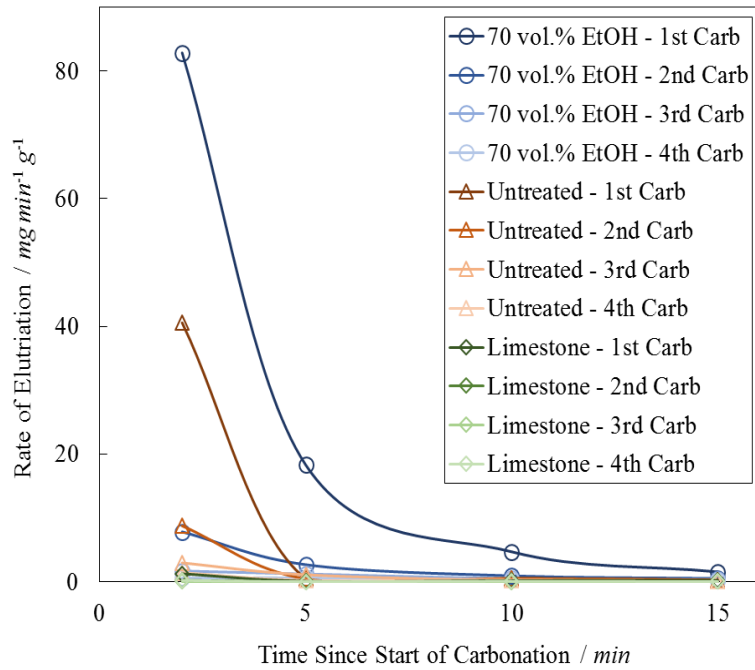


Figure 6 – Rate of elutriation during the first four carbonation phases, of 70 vol.% EtOH/water treated and untreated particles which were composed of calcined limestone, a calcium aluminate cementitious binder and flour as a pore forming spacer, and natural limestone for baseline comparison. Conducted within fluidised bed reactor with particles of size fraction 0.4 – 0.6 mm in a gas composed of 15 vol.% CO₂ and 85 vol.% air at 650 °C for 15 minutes.

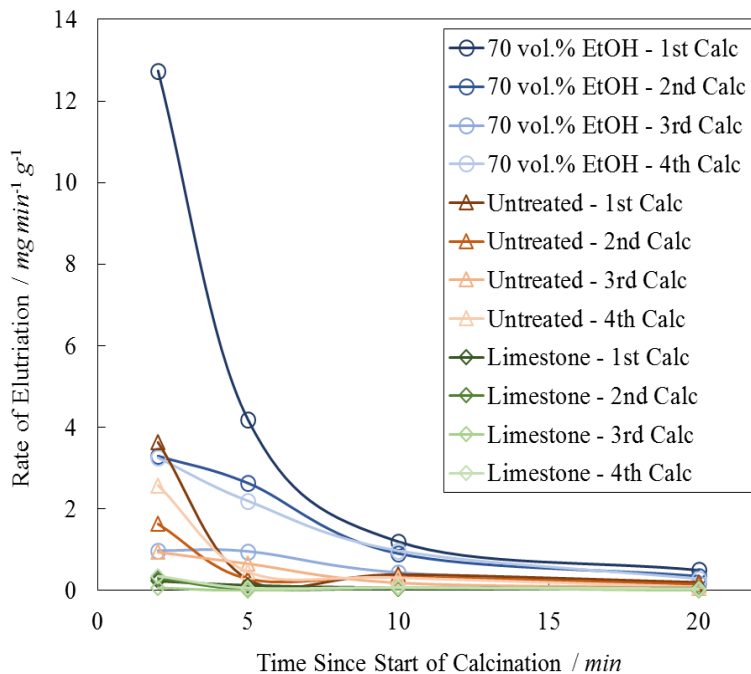


Figure 7 – Rate of elutriation during the first four calcination phases, of 70 vol.% EtOH/water treated and untreated particles which were composed of calcined limestone, a calcium aluminate cementitious binder and flour as a pore forming spacer, and natural limestone for baseline comparison. Conducted within fluidised bed reactor with particles of size fraction 0.4 – 0.6 mm in a gas composed of 70 vol.% CO₂ and 30 vol.% air at 940 °C for 20 minutes.

The fluidisation conditions were assumed to be approximately the same between the carbonation and calcination phases as the hot gas velocities and the U/U_{mf} 's were within 14.5 % of each other. The amount of attrition observed within any system will of course be highly dependent upon the operating conditions, type of limestone/sorbent used and reactor design/solids transportation methods applied [34].

The total mass lost during all carbonations and calcinations for the limestone sample was ~0.42 g which represented about 2.9 % of the initial mass. The total mass lost was higher for the untreated sample of synthetic sorbent (~3.3 g representing 16.4 % of the initial mass) and significantly higher for the EtOH treated sample (~9.3 g representing 51.4 % of the initial mass). The extent of attrition over the ~3 h of cycling for these synthetic sorbents was far greater than literature values for limestone in a large pilot scale rigs 2-5 wt.%/hour [35] [36], however one study did report attrition degradation of ~30 % of the initial mass but this was thought to be due to the limestone type utilised [37]. The sorbent mass losses due to attrition reported in this study were very comparable with another set of work also using lime and cement based sorbents [30].

4. Conclusions

The aim of this investigation was to examine the extent of attrition of an easy to manufacture sorbent with an enhanced macro-pore structure due to sacrificial biomass (flour) templating and the application of an ethanol pre-treatment step. Additional structural rigidity was provided by the incorporation of a calcium aluminate cementitious support structure. The sorbents were tested within a TGA and a fluidised bed reactor to determine their ability to resist attrition.

This work has highlighted the importance of fluidised bed CaL studies and the impact of attrition on a synthetic sorbent. The multicycle CaL experiments conducted within the TGA showed the synthetic sorbents treated with a 70 vol.% EtOH solution performed admirably relative to the untreated sample, even under realistic conditions. The 20th cycle CO₂ carrying capacity for the sample treated with 70 vol.% EtOH was found to be 0.27 mol CO₂/mol CaO which was ~68.8 % greater than the untreated sample. An optimal EtOH concentration may lie at a lower value as only solutions in the range of 70-90 vol.% EtOH were investigated here.

These experiments provided an example of the possible rates of attrition and elutriation that could be expected within a commercially operated fluidised bed CaL system for these sorbents. It should however be noted that due to the method of operating the fluidised bed the thermal history may not be completely representative. The total masses lost during the first four CaL cycles within the fluidised bed as a percentage of the initial sample masses were 2.9 %, 16.4 % and 51.4 % for the raw, untreated limestone sample, untreated synthetic sorbent and 70 vol.% EtOH treated synthetic sorbent respectively. The EtOH treated sample appeared to fair quite badly within the fluidised bed reactor, which appears to be due to the erosion of the roughened surface and weakening of the internal pore structure brought about by the EtOH pre-treatment method.

5. Acknowledgements

The research leading to these results has received funding from the European Community's Research Fund for Coal and Steel (RFCS) under grant agreement n° RFCR-CT-2014-00007.

6. References

1. Global CCS Institute, The costs of CCS and other low-carbon technologies in the United States - 2015 update. 2015.
2. Boot-Handford, M.E., et al., Carbon capture and storage update. *Energy & Environmental Science*, 2014. 7(1): p. 130-189.
3. Shimizu, T., et al., A Twin Fluid-Bed Reactor for Removal of CO₂ from Combustion Processes. *Chemical Engineering Research and Design*, 1999. 77(1): p. 62-68.
4. Blamey, J., et al., The calcium looping cycle for large-scale CO₂ capture. *Progress in Energy and Combustion Science*, 2010. 36(2): p. 260-279.
5. Erans, M., V. Manovic, and E.J. Anthony, Calcium looping sorbents for CO₂ capture. *Applied Energy*, 2016. 180: p. 722-742.
6. Borgwardt, R.H., Calcium oxide sintering in atmospheres containing water and carbon dioxide. *Industrial & Engineering Chemistry Research*, 1989. 28(4): p. 493-500.
7. Jia, L., et al., Attrition of Calcining Limestones in Circulating Fluidized-Bed Systems. *Industrial & Engineering Chemistry Research*, 2007. 46(15): p. 5199-5209.
8. Chu, C.Y. and S.J. Hwang, Attrition and sulfation of calcium sorbent and solids circulation rate in an internally circulating fluidized bed. *Powder Technology*, 2002. 127(3): p. 185-195.
9. Manovic, V. and E.J. Anthony, CaO-Based Pellets Supported by Calcium Aluminate Cements for High-Temperature CO₂ Capture. *Environmental Science & Technology*, 2009. 43(18): p. 7117-7122.
10. Zhao, M., et al., A novel calcium looping absorbent incorporated with polymorphic spacers for hydrogen production and CO₂ capture. *Energy & Environmental Science*, 2014. 7(10): p. 3291-3295.
11. Sanchez-Jimenez, P.E., L.A. Perez-Maqueda, and J.M. Valverde, Nanosilica supported CaO: A regenerable and mechanically hard CO₂ sorbent at Ca-looping conditions. *Applied Energy*, 2014. 118: p. 92-99.
12. Jing, J.-y., et al., Enhanced CO₂ sorption performance of CaO/Ca₃Al₂O₆ sorbents and its sintering-resistance mechanism. *Applied Energy*, 2017. 199: p. 225-233.
13. Hu, Y., et al., High Temperature CO₂ Capture on Novel Yb₂O₃-Supported CaO-Based Sorbents. *Energy & Fuels*, 2016. 30(8): p. 6606-6613.

14. González, B., et al., Additive effects of steam addition and HBr doping for CaO-based sorbents for CO₂ capture. *Chemical Engineering and Processing: Process Intensification*, 2016. 103: p. 21-26.
15. Coppola, A., et al., Hydration-induced reactivation of spent sorbents for fluidized bed calcium looping (double looping). *Fuel Processing Technology*, 2014. 120(0): p. 71-78.
16. Manovic, V. and E.J. Anthony, Thermal activation of CaO-based sorbent and self-reactivation during CO₂ capture looping cycles. *Environ Sci Technol*, 2008. 42(11): p. 4170-4.
17. Sun, J., et al., CO₂ Sorption Enhancement of Extruded-Spheronized CaO-Based Pellets by Sacrificial Biomass Templating Technique. *Energy & Fuels*, 2016. 30(11): p. 9605-9612.
18. Al-Jeboori, M.J., et al., Improvement of Limestone-Based CO₂ Sorbents for Ca Looping by HBr and Other Mineral Acids. *Industrial & Engineering Chemistry Research*, 2013. 52(4): p. 1426-1433.
19. Hu, Y., et al., Structurally improved CaO-based sorbent by organic acids for high temperature CO₂ capture. *Fuel*, 2016. 167: p. 17-24.
20. Sun, R., et al., Enhancement of CO₂ capture capacity by modifying limestone with propionic acid. *Powder Technology*, 2013. 233: p. 8-14.
21. Li, Y.J., et al., CO₂ Capture Using CaO Modified with Ethanol/Water Solution during Cyclic Calcination/Carbonation. *Chemical Engineering & Technology*, 2008. 31(2): p. 237-244.
22. Wang, S., et al., Enhanced CO₂ adsorption capacity and stability using CaO-based adsorbents treated by hydration. *AIChE Journal*, 2013. 59(10): p. 3586-3593.
23. Diego, M.E., et al., Calcium Looping with Enhanced Sorbent Performance: Experimental Testing in A Large Pilot Plant. *Energy Procedia*, 2014. 63: p. 2060-2069.
24. Coppola, A., et al., Attrition of Limestone During Fluidized Bed Calcium Looping Cycles for CO₂ Capture. *Combustion Science and Technology*, 2012. 184(7-8): p. 929-941.
25. Clough, P.T., et al., Degradation study of a novel polymorphic sorbent under realistic post-combustion conditions. *Fuel*, 2016. 186: p. 708-713.
26. Fennell, P.S., et al., 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): p. 2072-2081.
27. Coppola, A., et al., Fluidized bed calcium looping cycles for CO₂ capture under oxy-firing calcination conditions: Part 1. Assessment of six limestones. *Chemical Engineering Journal*, 2013. 231: p. 537-543.
28. Coppola, A., et al., Fluidized bed calcium looping: The effect of SO₂ on sorbent attrition and CO₂ capture capacity. *Chemical Engineering Journal*, 2012. 207-208(0): p. 445-449.
29. Erans, M., et al., Effect of SO₂ and steam on CO₂ capture performance of biomass-templated calcium aluminate pellets. *Faraday Discussions*, 2016. 192(0): p. 97-111.
30. Erans, M., et al., Fragmentation of biomass-templated CaO-based pellets. *Fuel*, 2017. 187: p. 388-397.

31. Duan, L., et al., Attrition Study of Cement-Supported Biomass-Activated Calcium Sorbents for CO₂ Capture. *Industrial & Engineering Chemistry Research*, 2016. 55(35): p. 9476-9484.
32. Sun, J., et al., Enhanced performance of extruded–spheronized carbide slag pellets for high temperature CO₂ capture. *Chemical Engineering Journal*, 2016. 285: p. 293-303.
33. Sun, J., et al., Stabilized CO₂ capture performance of extruded–spheronized CaO-based pellets by microalgae templating. *Proceedings of the Combustion Institute*, 2017. 36(3): p. 3977-3984.
34. Arias, B., et al., Demonstration of steady state CO₂ capture in a 1.7 MW_{th} calcium looping pilot. *International Journal of Greenhouse Gas Control*, 2013. 18(0): p. 237-245.
35. Charitos, A., et al., Parametric investigation of the calcium looping process for CO₂ capture in a 10 kW_{th} dual fluidized bed. *International Journal of Greenhouse Gas Control*, 2010. 4(5): p. 776-784.
36. Dieter, H., et al., Progress in Calcium Looping Post Combustion CO₂ Capture: Successful Pilot Scale Demonstration. *Energy Procedia*, 2013. 37: p. 48-56.
37. Lu, D.Y., R.W. Hughes, and E.J. Anthony, Ca-based sorbent looping combustion for CO₂ capture in pilot-scale dual fluidized beds. *Fuel Processing Technology*, 2008. 89(12): p. 1386-1395.