

# CO<sub>2</sub> Capture by Calcium Aluminate Pellets in a Small Fluidized Bed

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## Abstract

Synthetic pellets made using calcium aluminate cement and quicklime have been examined in a small fluidized bed reactor to determine their performance in cyclic CO<sub>2</sub> capture for up to 20 calcination/capture cycles. Two batches were examined one a “fresh” batch, and the second an “aged” batch of pellets and their performance was compared with the original parent limestone. Carbonation was carried out at 650 °C and calcination at 900 °C, both with 15 % CO<sub>2</sub>, balance N<sub>2</sub>, as a synthetic flue gas. Experiments were also performed with and without steam in the flue gas and showed that steam always improved capture performance. In addition, there was no major attrition associated with the pellets, and pellets tended to perform better in terms of carbon capture than the parent limestone.

## 1 Introduction

Calcium looping (CaL) is a high-temperature solids looping cycle that can be used for carbon capture from power or industrial source [1], with particular synergies with cement manufacture. In typical post-combustion CaL processes, CaO-containing sorbent is cycled between a carbonator, where it reacts with CO<sub>2</sub> in a flue gas to form CaCO<sub>3</sub>, and a calciner, where CaO is reformed releasing a pure stream of CO<sub>2</sub> for compression and storage. CaL can also be adapted to pre-combustion processes.

The carbonation process is exothermic and can, therefore, be used to generate steam. The calcination reaction is endothermic and, therefore, requires heat, with in-situ oxy-combustion of a low-sulphur and low-ash fuel typically proposed. One potential advantage of CaL is the use of limestone, which is abundant in nature and relatively inexpensive. In addition, spent (or unreactive) sorbent, can be used in the cement industry. However, sorbent derived from natural limestone has been found to become less reactive to CO<sub>2</sub> upon repeated cycling. This is the result of a combination of high temperature and reactive sintering processes, side reactions with sulphurous gases and ash, as well as loss from reaction systems (typically fluidized beds) through attrition. As a result, several methods of sorbent enhancement, including synthetic sorbents, have been proposed [2-4], which may offer reduced decay rates in reactivity or increased resistance to attrition. Use of synthetic sorbents may have an initial energy penalty in production, with long-term benefits in terms of reduction of sorbent requirement.

Broda et al. [3] have suggested that there are two general approaches to synthetic sorbents: (i) unsupported CaO derived from the calcination of complex calcium precursors; and (ii) supported CaO, stabilized with a material where the onset of sintering occurs at an elevated temperature. They add that the supports can be divided into three classes: (i) supports that form a mixed metal oxide with CaO that is inert to carbonation; (ii) supports that do not form a mixed metal oxide with CaO and are inert; and (iii) supports that react with CO<sub>2</sub>.

Synthetic sorbents without support attempt to increase the reactivity by increasing the initial porosity or surface area. Typically, the first step in the generation of synthetic sorbent from limestone is the calcination of CaCO<sub>3</sub> to form the more reactive CaO. However, limestone can also be reacted directly with acids stronger than carbonic acid to form the precursors directly [5]. The most simple precursor is Ca(OH)<sub>2</sub> [6]; however, numerous other precursors have been investigated, such as calcium acetate, calcium formate, calcium nitrate [7], amongst others. These precursors have been shown to give a CaO of a very high porosity and surface area [8, 9]. Grasa et al. [10] reported that the benefit of many of these type of sorbents was significantly reduced under realistic conditions, i.e., higher temperatures and CO<sub>2</sub> concentration in the calcination

stage, over many cycles. This is likely a result of a very rapid reduction in surface area and porosity, as CaO sinters significantly more rapidly above 900 °C [11].

As a result, researchers have investigated the use of reactive or unreactive supports in an attempt to increase resistance to sintering, which will often have an additional benefit in increasing resistance to attrition. One of the most studied supports is Al<sub>2</sub>O<sub>3</sub>, which thermodynamically will form the inert-to-CO<sub>2</sub> mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) upon reaction with CaO [12, 13], though there are kinetic reasons why this may not form rapidly – or, e.g., in the first few cycles of carbonation and calcination [14]. Other proposed supports include: MgO [15, 16], in analogy with enhancements seen with natural dolomite over natural limestone [17], which does not form mixed metal oxides with CaO [3]; SiO<sub>2</sub>, which forms mixed metal oxides with CaO [18], has a relatively low sintering temperature, but phase change materials have the potential to increase the porosity upon calcination [19]; amongst others such as ZrO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>/CaTiO<sub>3</sub>, CuO, CoO, BaO and Cr<sub>2</sub>O<sub>3</sub> [3, 4].

The generation of supported synthetic sorbent often uses non-carbonate calcium precursors, as well as using techniques such as sol-gel [20, 21], which can be energy intensive and expensive. As a result, alternative methods of incorporating supports have been sought. One simple method is the pelletization of CaO powder using calcium aluminate cement and water spray [22, 23]. Calcium aluminate pellets have been shown to work effectively over a long series of calcinations and carbonations [24] and with elevated temperatures and concentrations of CO<sub>2</sub> expected in the calciner [25]. In addition, it has been estimated that the pellets (at \$200/t for the calcined pellets, 2009 estimate) should give a competitive cost for avoided CO<sub>2</sub> over 60 cycles [22].

The main focus of this work is to investigate the CO<sub>2</sub>-capture capacity of the calcium aluminate pellets, which showed the greatest CO<sub>2</sub> uptake efficiency in cycling experiments in a thermogravimetric analyzer (TGA) [23, 24], using a small fluidized bed (FB) over an extended series of carbonation and calcination cycles. A wide range of conditions have been investigated and the results obtained have been compared with the corresponding natural limestone (Cadomin). A major advantage of using a FB, besides introducing more realistic hydrodynamic conditions with attrition [26-28],

is that the pellet samples used in the FB were significantly larger than that used in a TGA experiment allowing the recovery of sufficient material after each experiment to enable various analytical techniques (e.g., N<sub>2</sub> adsorption analysis to determine Brunauer-Emmett-Teller (BET) surface area) to be used. Resistance of pelletized materials to attrition behaviour has been tested previously in FB reactors [29, 30]; however, not for an extended series of carbonation and calcination cycles. Here, cycling experiments with and without steam present have been investigated; steam having been shown to significantly enhance the long-term CO<sub>2</sub> capture efficiency of sorbents [31] and recently verified in a larger pilot plant [32].

## **2 Experimental**

Here, pellets were formed of a mixture of calcined Cadomin limestone and calcium aluminate cement. The primary focus was to investigate the behaviour of pellets upon simulated CO<sub>2</sub> capture cycling experiments in a fluidized bed under a range of conditions. The testing was performed in two stages separated by a year, during which time pellets were found to have reacted slowly with H<sub>2</sub>O and CO<sub>2</sub> in the atmosphere; resulting in different performance upon cycling. As such, here two batches of pellets are referred to: the 'Original' batch and an 'Aged' batch.

### **2.1 Pellet Fabrication.**

Pellets were prepared using a previously reported method [30]. Pellets were prepared using calcined limestone mixed with a binder. The limestone used was Cadomin (95.5 % CaO, calcined basis), crushed to < 1 mm and calcined for 6 h in a muffle furnace at 850 °C. The binder used was a commercial refractory calcium aluminate cement, CA-14, (71 % Al<sub>2</sub>O<sub>3</sub> and 28 % CaO), produced by Almatix Inc., which was supplied as a very fine powder with > 80 % of the particles < 45 µm. The sorbent-to-cement weight ratio used was 9:1. The pellets were prepared in batch mode using a mechanical pelletizer (Glatt GmbH). The powdered material (~ 300 g in total) was mixed in the desired proportions in the pelletization vessel (1 L). Water was sprayed intermittently during pelletization, with a nozzle which can produce micron-sized water droplets (< 300 µm at about 25 mL water per minute under an excess pressure of 700 kPa) required for the pelletization process. The water droplet size and the total amount

of water added affected the final size of the pellets being made. In addition, the pellet size was also affected by the speed of a pair of rotor blades attached to the vessel, *i.e.*, one agitator (operated at 500 rpm) located on the bottom and one chopper (operated at 2500 rpm) on the side. Typically one batch of pellets was produced in 20-30 min.

Pellets were sieved to the size fraction 500-710  $\mu\text{m}$  for the fluidized bed experiments. As a result of contact with water spray in the pelletization process, all of the pellets were partially hydrated. In addition, some carbonation occurred as a result of reaction with  $\text{CO}_2$  in the atmosphere during the pelletization process. Further hydration and carbonation can be expected from further exposure to the air, and these are in fact a potential reactivation method for spent natural sorbent [2, 33, 34], although it is much less clear what they might do to pellets produced by a partial hydration method.

## 2.2 Fluidized Bed Experiments.

Fluidized bed experiments were carried out using a small (21 mm internal diameter) fluidized bed reactor. A more detailed description of the reactor and the experimental procedure has been presented elsewhere [31, 35]. Cadomin limestone or pellets derived from Cadomin were used in these experiments. Briefly, these were conducted using  $4 \pm 0.1$  g limestone (or equivalent to 4 g  $\text{CaCO}_3$  for the pellets, which was  $\sim 3.12$  g) and  $12 \pm 0.1$  g of sand (sieved to 355-425  $\mu\text{m}$ ). The dilution of the bed using sand reduces ramping times and temperature overshoot upon temperature cycling. Two types of experiments were performed: (i) dry, without steam and (ii) with  $\sim 10$  % v/v steam. The flow-rate of gas into the fluidized bed for dry experiments was 47.5  $\text{cm}^3/\text{s}$ , with 15 % v/v  $\text{CO}_2$ , balance  $\text{N}_2$ . Very similar fluidization behaviour is expected of sand and calcined limestone of the size fractions used.  $U/U_{\text{mf}}$  values were typically within 25% of each other in the range of temperatures investigated: 7.2 and 5.8 at 700  $^\circ\text{C}$  and 9.8 and 7.9 at 900  $^\circ\text{C}$  for 355-425  $\mu\text{m}$  sand and 500-710  $\mu\text{m}$  calcined limestone, respectively (minimum fluidization velocity calculated using correlation provided by Wen and Yu [36]). Given the size of the internal diameter of the bed, there is a small amount of slugging behaviour. The flow-rate of gas for 10 % v/v steam experiments was 52.8  $\text{cm}^3/\text{s}$ , with 13.5 % v/v  $\text{CO}_2$ , 10 % v/v steam, balance  $\text{N}_2$ . The gas flow-rates were kept the same in both calcination and carbonation; therefore, calcinations and

carbonations were effected by switching temperature. The heating and cooling rates were 1 K/s and heating and cooling times are included in the overall calcination and carbonation times, with the bed continuously fluidized. This heating rate is lower than it would be in a “real” process, which could result in reduced particle fracture through thermal shock and, therefore, reduced mass loss from the system. It should also be noted that another implication of the heating rate is that calcination starts below the calcination temperature and the carbonation starts above the carbonation temperature. The concentration of CO<sub>2</sub> in the calcination stage was chosen to be 15 % in order to allow easy estimation of the CO<sub>2</sub> uptake and release using the CO<sub>2</sub> analyzer; a higher concentration would be expected in a real environment, which is likely to have a deleterious effect on sorbent performance through accelerated CaO sintering [37]. The temperatures of calcination and carbonation were 900 and 650 °C, respectively, and the typical time at setpoint was 600 s. Some additional experiments were performed with an extended carbonation time of 1200 s. Alternative carbonation temperatures of 600 °C and 700 °C were also used. The experiments were conducted for 20 cycles, prior to termination upon calcination. The molar uptake of CO<sub>2</sub> ( $n_{\text{CO}_2,\text{carb}}$ ) by the sorbent during carbonation was calculated using the formula shown in Equation 1, where  $t$  signifies the time of carbonation,  $X_{\text{in}}$  the inlet fraction of CO<sub>2</sub>,  $X_{\text{out}}$  the outlet fraction of CO<sub>2</sub> and  $\dot{n}_{\text{in}}$  the total molar flow-rate of gas into the reactor. The molar release of CO<sub>2</sub> during calcination was calculated in a similar manner. The carrying capacity is presented as the mass of CO<sub>2</sub> captured in cycle  $N$ ,  $a_N$ , as shown in Equation 2, where  $M_{\text{CO}_2}$  is the molar mass of CO<sub>2</sub> and  $m_c$  the original mass of limestone added calcined.

$$n_{\text{CO}_2,\text{carb}} = \int_0^t \left( \frac{\dot{n}_{\text{in}}(X_{\text{in}} - X_{\text{out}})}{(1 - X_{\text{out}})} \right) dt \quad \text{Equation 1}$$

$$a_N = \frac{M_{\text{CO}_2}(n_{\text{CO}_2,\text{carb},N} + n_{\text{CO}_2,\text{calc},N})}{2m_c} \quad \text{Equation 2}$$

Finally, mass loss at the end of the experiment was also calculated. Mass measurements of the limestone added ( $m_0$ ), the sand added ( $m_s$ ) and the final calcined material at the end of the experiment ( $m_f + m_s$ ) were taken. Then the mass

loss ( $\Delta m_{\text{exp}}$ ), expressed as a percentage, was calculated as shown in Equation 3, where  $m_t$  is the maximum theoretical carbonated weight of the sample. The assumptions are (i) that there is no re-hydration or re-carbonation of the calcined material and (ii) that the mass of sand remained constant throughout the experiment.

$$\Delta m_{\text{exp}} = 100 \left[ 1 - \frac{m_f}{m_t} \right] \quad \text{Equation 3}$$

### 2.3 Analytical Techniques

A thermogravimetric analyzer (TGA), TA Instruments Q500, was used to determine hydration and carbonation extents of the pellets. This was performed by heating the pellets from 50 °C to 450°C, at 50 °C/min, before holding under isothermal conditions for 5 min; the pellets were then heated up to 900 °C, at ramp 50 °C/min, and then held under isothermal conditions for 10 min. The whole experiment was performed with a sample gas flow-rate of 100 cm<sup>3</sup>/min of N<sub>2</sub>. The TGA plot shows four characteristic steps of mass loss: the first step at 100 °C related to loss of chemically unbound water; the second step is around 200 °C and is likely to correspond to decomposition of calcium aluminium hydroxide hydrates (see, for example, Packter and Khaw [38]); the third step leading into 450 °C relates to decomposition of any calcium hydroxide; and the fourth step leading into 900 °C relates to calcination of any calcium carbonate. Therefore, the mass decrease before 450 °C was assumed to be due to H<sub>2</sub>O release, and the subsequent mass decrease was assumed to be due to CO<sub>2</sub> release.

Elemental analysis was established by X-ray fluorescence (XRF), using a Bruker AXS S4 Explorer. Nitrogen adsorption (Micromeritics Tristar 3000 N<sub>2</sub> Sorption Analyzer) analyses were performed to establish the BET pore surface area and the Barrett-Joyner-Halenda (BJH) pore size distribution. The physisorption measurements were performed using calcined samples after cycling.

### 3 Results and Discussion

#### 3.1 Sorbent Characterization

The composition of the pellets and the original Cadomin limestone are summarized and compared in Table 1. From the point of view of CO<sub>2</sub> capture the main difference between the original and pelletized material is the CaO and Al<sub>2</sub>O<sub>3</sub> content. The reduced CaO content in pellets, 86.51 %, results in lower CO<sub>2</sub> carrying capacity (mass basis) for the same conversion, but it is compensated on a longer series of cycles due to a sintering mitigation effect by mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) [22].

*Table 1 Chemical Composition of Parent Limestone and Produced Pellets (mass fraction)*

<b>Species</b>	<b>Original Cadomin</b>	<b>Pellets</b>
<b>CaO</b>	0.9547	0.8651
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.0077	0.0692
<b>MgO</b>	0.0103	0.0294
<b>SiO<sub>2</sub></b>	0.0161	0.0171
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.0061	0.0129
<b>K<sub>2</sub>O</b>	0.0008	0.0019
<b>SO<sub>3</sub></b>	0.0007	0.0017
<b>CuO</b>	n/a	0.0012
<b>Cr<sub>2</sub>O<sub>3</sub></b>	n/a	0.0007
<b>SrO</b>	0.0005	0.0006
<b>NiO</b>	n/a	0.0002
<b>MnO</b>	0.0031	n/a

The hydration and carbonation extents of the Original and Aged pellets were calculated, using data collected from a TGA, and are presented in Table 2. Note that the mass reduction upon dehydration is caused by three phenomena combined: (i) release of any chemically unbound H<sub>2</sub>O; (ii) decomposition of calcium aluminium hydroxide hydrates; and (iii) decomposition of calcium hydroxide. These three



phenomena were not separated since in practice all of these effects will occur rapidly in a FBC environment at high temperatures. The Aged pellets are carbonated to greater extents than the Original pellets; whereas their hydration extents are similar. The additional carbonation is likely to have occurred through a hydroxide intermediate, suggesting that some additional calcium oxide may have hydrated to retain a similar fraction of hydrated material.

*Table 2 Hydration and Carbonation extents of Pellets*

	<b>Hydration extent (g H<sub>2</sub>O/g calcined sorbent)</b>	<b>Carbonation extent (g CO<sub>2</sub>/g calcined sorbent)</b>
<b>Original pellet batch</b>	0.243	0.139
<b>Aged pellet batch</b>	0.239	0.187

### **3.2 Fluidized Bed Experiments**

Fluidized bed experiments were performed to investigate maximum uptake of CO<sub>2</sub> upon cycling and to give an insight into sorbent resistance to attrition. These were carried out with the following aims: (i) to compare the performance of synthetic sorbents with that of natural limestone and to investigate the effect of aging; (ii) to investigate the effect of carbonation temperature; (iii) to investigate the effect of carbonation time; and (iv) to investigate the effect of steam. Note that, if there are no error bars, data from single experiments are presented, and, if there are error bars, two experiments were performed (excluding aged pellets, carbonated at 700 °C for 600 s, with steam, where four experiments were performed). In each case, the mean is plotted with a single standard deviation.

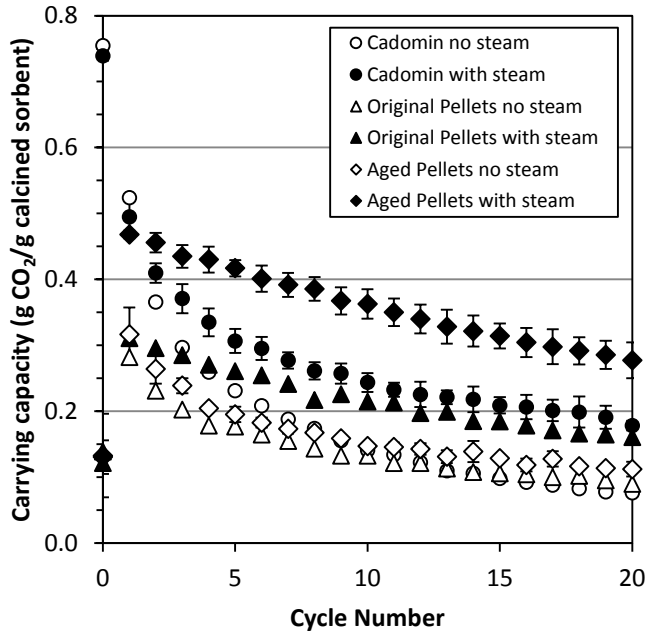


Figure 1  $\text{CO}_2$  uptake by pellets at various stages of aging against original limestone; carbonation at  $650\text{ }^\circ\text{C}$  for 600 s; with 10 % steam or without steam; error bars show 1 standard deviation

Figure 1 shows that without steam present during carbonation, original and aged pellets behaved similarly, with aged pellets showing slightly improved behaviour. This improved behaviour is likely to be a result of the increase in carbonation conversion of the pellets upon aging. Increased carbonation conversion (often by extending carbonation times) has been shown as a useful method of increasing the reactivity of particles to subsequent carbonation [39, 40]. A similar process will have this occurred here upon aging; though the carbonation mechanism would be different, likely going through a  $\text{Ca}(\text{OH})_2$  intermediate, which has also been shown to increase sorbent reactivity [33, 34]. However, once steam is introduced a marked improvement in reactivity was observed for aged pellets over the original pellets. It is also clear that without steam, Cadomin limestone remained competitive with both sets of pellets after 20 cycles; while with steam, Cadomin limestone showed consistently higher reactivity than the original pellets and lower reactivity than the aged pellets. A critical difference, however, is that with and without steam, Cadomin limestone showed a much higher rate of decay in reactivity upon cycling than both sets of pellets – a trend expected to continue after 20 cycles.

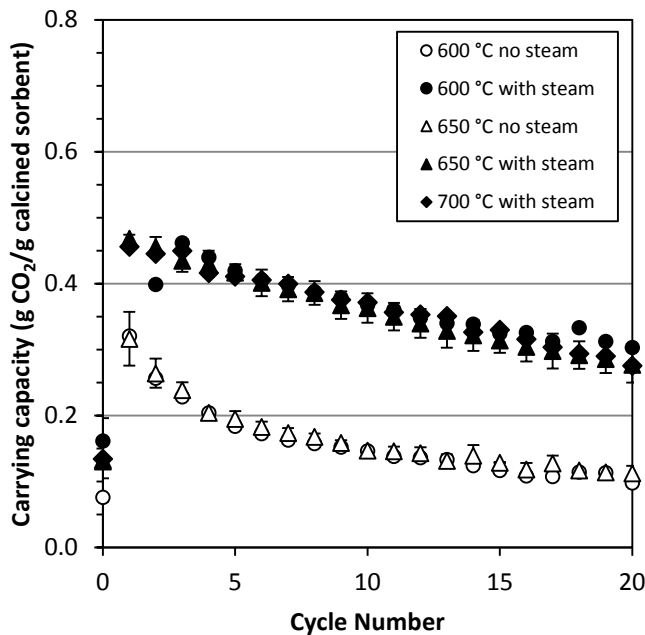


Figure 2 CO<sub>2</sub> uptake for aged pellets at a variety of different carbonation temperatures; carbonation at 600, 650 or 700 °C for 600 s with 10 % steam or without steam; error bars show 1 standard deviation

Figure 2 shows that there is a large enhancement in CO<sub>2</sub> uptake by the aged pellets through the use of steam during the carbonation stages; but interestingly the experimental data show a very similar effect across the range of carbonation temperatures. It is in agreement with earlier work, which found that steam is more beneficial under conditions when product layer diffusion becomes reaction-rate limiting at an earlier stage during carbonation, characteristic for lower temperatures [41]. In other words, the effect of steam is more pronounced at lower temperatures, diminishing the effect of the temperature on product layer diffusion and consequently CO<sub>2</sub> uptake.

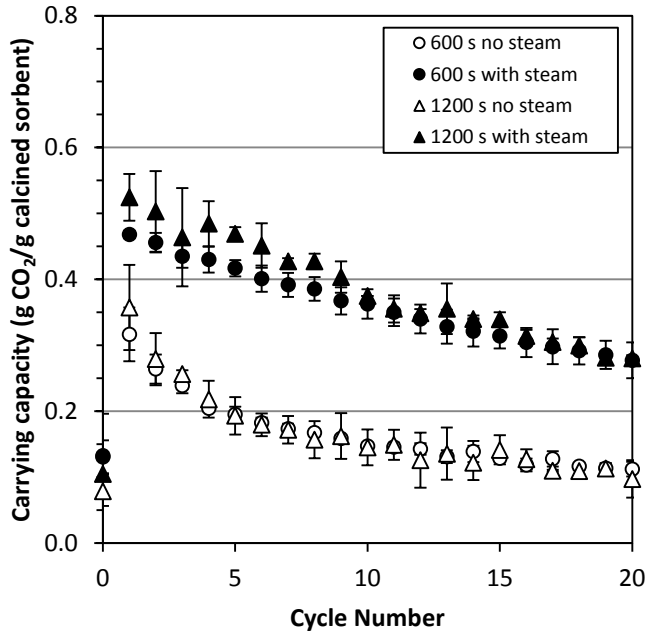


Figure 3 CO<sub>2</sub> uptake for aged pellets under a variety of different carbonation times; carbonation 650°C for 600 and 1200 s; experiments performed with 10 % steam or without steam; error bars show 1 standard deviation

In addition, Figure 3 shows that extended carbonation time does not have a significant effect on the carrying capacity of the pellets; however, it is possible that it is having a positive effect for low cycle numbers upon addition of steam. The similar carrying capacities of the pellets are most likely the consequence of carbonation reaction profiles which means that the fast reaction stage occurs in a relatively short period reaching the “maximum” conversion, and the further conversion during the diffusion-controlled slow reaction stage is relatively small [42]. However, the decay of activity during cycling is faster in the case of prolonged carbonation, a phenomenon which has also been observed in the case of natural sorbents [43, 44].

Finally, collected experimental data from aged pellets and the original limestone are summarized in Table 3. The attrition resistance of the pellets is improved in comparison to the parent limestone (excluding one experiment at 600 °C, without steam), and there is no obvious trend associated with the use of steam. One possible explanation for this fairly good attrition behaviour, which is not in line with the observations of Knight et al. [29], is that higher temperatures sinter and harden the material in the pellets. This suggestion has been offered by Coppola et al. [26] to

explain a beneficial result of higher temperatures on attrition of lime-based particles being used for Ca looping experiments in a small fluidized bed. It may also be that pellets offer less resistance to CO<sub>2</sub> release during calcination, which is the negative aspect of operating at higher temperatures as noted by Coppola et al. [27]

This table also includes calculated coefficients for the Grasa and Abanades [45] equation, see *Equation 5*, where  $C_N$  is the carrying capacity in cycle  $N$ , expressed in moles CO<sub>2</sub> per mole of CaO,  $k_G$  is the Grasa decay constant and  $C_\infty$  is the residual carrying capacity.  $C_N$  can be readily calculated from  $a_N$ , using *Equation 4*, where  $F_{CaO}$  is the fraction of CaO in the original material as determined by XRF (see Table 1). Data were fit to *Equation 5* using a least squares minimization. The residual capacity is also given in mass of CO<sub>2</sub>/mass of calcined sorbent ( $a_\infty$ ), and a comparison to the average capacity in cycles 18-20 ( $a_{N=18-20}$ ) is given.

$$C_N = \frac{a_N M_{CaO}}{F_{CaO} M_{CO_2}} \quad \text{Equation 4}$$

$$C_N (\text{mol}_{CO_2} / \text{mol}_{CaO}) = \frac{1}{\left(\frac{1}{1 - C_\infty}\right) + k_G} + C_\infty \quad \text{Equation 5}$$

*Table 3 Summary of experimental measurements and conditions of Cadomin and aged pellets with different condition; constants from Equation 5; average carrying capacity between 18 and 20 cycles; BET surface area for calcined material after the 20<sup>th</sup> cycle*

<b>Sorbent</b>	<b>10 % Stea m</b>	<b>Carb. temp. (°C)</b>	<b>Carb time (s)</b>	<b><math>k_G</math></b>	<b><math>C_\infty</math> (mol CO<sub>2</sub>/mol CaO)</b>	<b><math>a_\infty</math> (g CO<sub>2</sub>/g calcined sorbent)</b>	<b>Mean <math>a_{N=18-20}</math> (g CO<sub>2</sub>/g calcined sorbent)</b>	<b>Mass loss <math>\Delta m</math> (%) (<math>\pm</math> s.d.)*</b>	<b>BET surface area (m<sup>2</sup>/g)</b>
<b>Cad-</b>	No	650	600	0.49	0.016	0.012	0.076	5.7	2.42
<b>omin</b>	Yes	650	600	0.78	0.207	0.155	0.178	8.4	5.61
<b>Pellets</b>	No	650	600	1.62	0.158	0.108	0.113	7.9 ( $\pm$ 4.6)	2.97

Yes	650	600	0.85	0.405	0.275	0.277	7.1	4.32
							(± 4.8)	
No	600	600	1.54	0.143	0.097	0.098	12.2	5.12
Yes	600	600	0.93	0.433	0.294	0.303	5.6	5.37
Yes	700	600	1.09	0.433	0.294	0.275	7.0	5.12
No	650	1200	1.18	0.134	0.091	0.097	9.3	4.25
							(± 3.4)	
Yes	650	1200	0.30	0.318	0.216	0.280	8.3	5.12

\*Mass measurements for single experiments were available for most data points; where standard deviation is indicated, data from two experiments were available

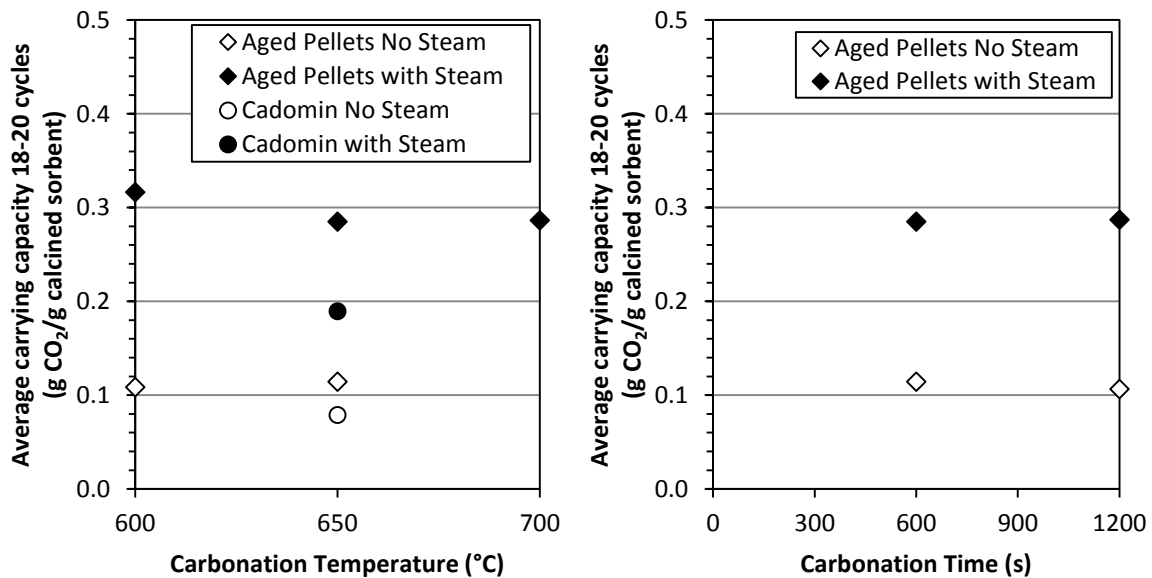


Figure 4 Mean carrying capacity of aged pellets and Cadomin limestone in cycles 18 to 20

The mean carrying capacity of aged pellets and Cadomin limestone between cycles 18 and 20 ( $a_{\infty}$ ) has been chosen as the best indicator of long-term carrying capacity and has been plotted in Figure 4. Trends in  $a_{\infty}$  largely follow the trends in residual capacity for the Grasa equation (Equation 5). However, the projection of the Grasa equation from 20 cycles to an infinite number can give unusual data, such as the artificially low residual capacity of 1.6% for Cadomin limestone without steam. All data strongly confirm an increase in long-term capacity with addition of steam and much improved capacities of pellets in comparison to the original limestone, which was

shown to improve further on aging. However, the trends with temperature and time are harder to ascribe.

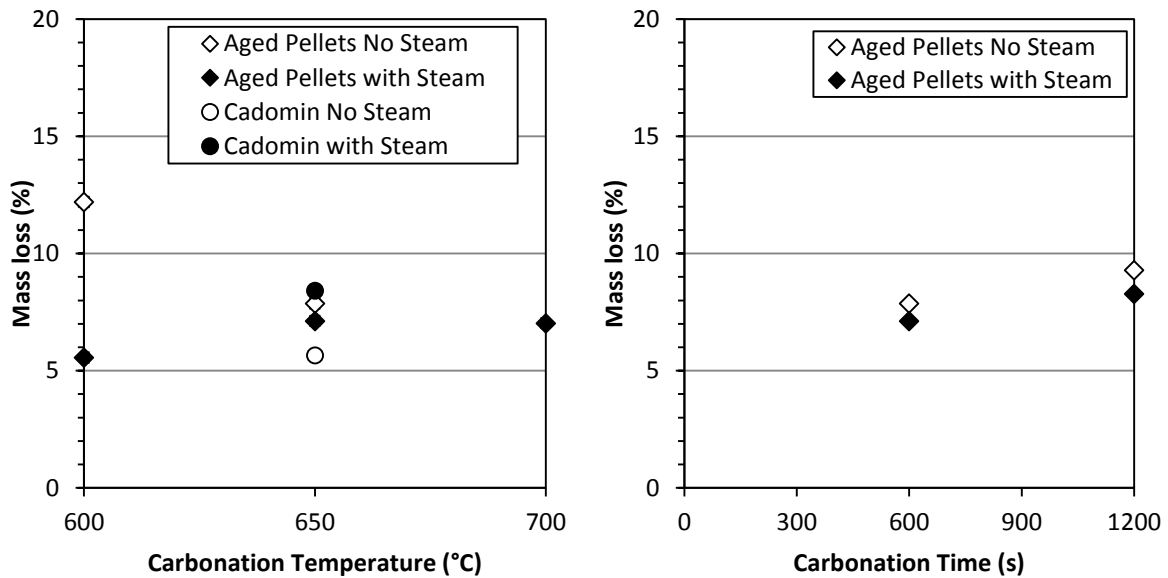


Figure 5 Mass loss during the 20 cycle fluidized bed experiments for aged pellets and Cadomin limestone

Data for mass loss during the experiments are plotted in Figure 5; note from Table 3 that the error in mass loss measurement is relatively high in comparison with the variation between data points. As such, it is difficult to conclude that there is a reduction in mass loss upon generation of the pellets, as may be desired.

A critical issue in the CaL FBC systems is mass loss [26] and Figure 5 shows that generally there is a reduced mass loss for pellets than Cadomin limestone. What is clear is that there is no major mass loss associated with the use of pellets, although there is a noticeable spread in the mass loss measurements. These results are in agreement with tests done by the University of British Columbia, which showed better resistance of pellets than the parent limestone in a bubbling bed attrition test [29]. However, in other tests, pellets were found to be worse; unfortunately, the work done at UBC was with unrealistically low temperatures, but it does highlight the need to test with such materials in fully operational Ca looping pilot plants and if the attrition performance is insufficient, to change the formulation of the pellets.

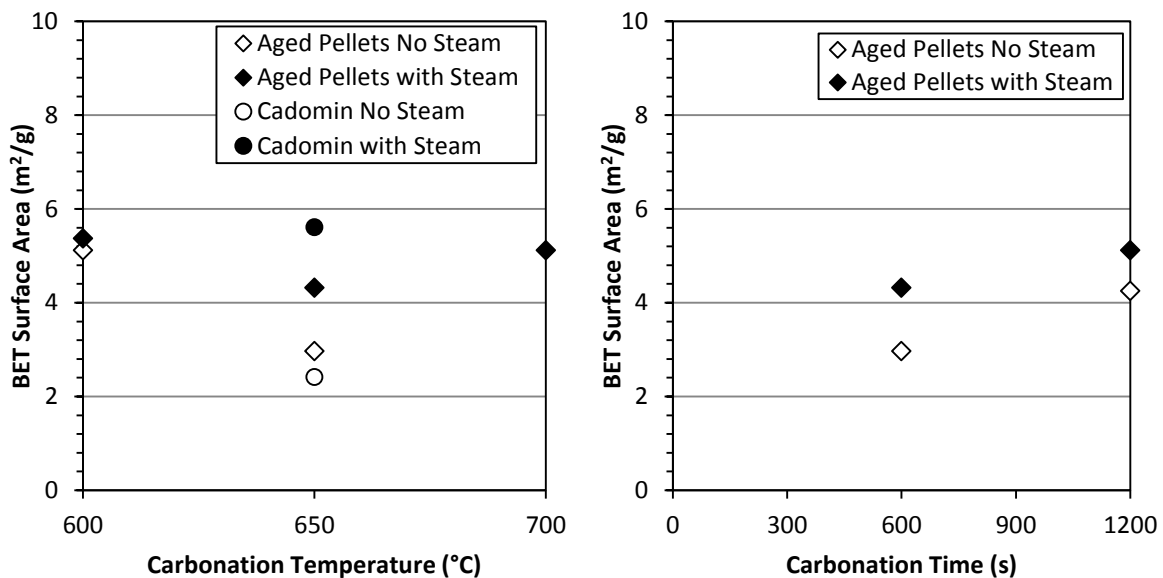


Figure 6 BET Surface Areas for aged pellets and Cadomin limestone

Figure 6 shows that steam increases BET surface area, although there is some scatter in these data. Interestingly, Cadomin with steam shows the highest surface area, though less reactive than pellets. It is also clear that increasing time of carbonation increases surface area (despite the use of the Grasa and Abanades equation [45] suggesting reduced residual capacity). Finally, aging has a marked effect on reactivity of pellets; hydration and carbonation extents should be monitored in future studies of hydrated pellets.

Pelletization, as it comes with a cost in production, ought to produce clearly superior sorbents, and these must be at least as attrition resistant as the parent sorbent. That said, pelletization would offer a method of re-using spent lime [46], if lime were not easily available in a given location, or the attrition resistance of a particular limestone was very poor. In addition, it offers the potential ability to use cheap additives which TGA tests have suggested are particularly effective in producing extremely reactive sorbents [47, 48]. However, such tests must be done at the pilot plant level under realistic fluidizing velocities and temperatures if they are to provide the evidence that these approaches represent an advantage over using untreated lime-based sorbents and this represents the next goal of our research.



## 4 Conclusions

Bubbling bed tests have been done for up to 20 CO<sub>2</sub> capture cycles on lime-based pellets produced using calcium aluminate as a binder. These tests show that the pellets exhibit similar behavior in terms of attrition resistance to the parent limestone, and that they generally show superior CO<sub>2</sub> capture performance, with Aged pellets performing better than the original pellets when carbonated under realistic conditions. An additional benefit is the very favorable effect of steam at levels typical of that associated with the conversion of a hydrocarbon fuel. Finally, it is strongly evident from this work that TGA and other tests when done without steam addition will produce unrealistic results and that tests in a fluidized bed environment are highly desirable for all new or treated sorbents. The research presented in this study is a step forward to full demonstration at pilot scale of the Ca looping process with calcium aluminate pellets produced by the granulation technique.

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