# Degradation Study of a Novel Polymorphic Sorbent under Realistic Post-Combustion Conditions

Peter T. Clough [a], Matthew E. Boot-Handford [a], Ming Zhao [a, b], Paul S. Fennell [a]*

Abstract:

Calcium looping is a Carbon Capture and Storage (CCS) technology which has the potential to be applied to both power generation plants and some industrial emission sources. The main problem with the use of calcium oxide-based sorbents is their characteristic decay in carrying capacity. This is caused by sintering and is made worse during multiple cycles of $CO_2$ absorption (carbonation) and release (calcination). This paper provides an investigation into the degradation of a novel type of sorbent that is able to regenerate porosity during the temperature cycling of calcium looping. The porosity regeneration of this sorbent is a result of a dicalcium silicate additive undergoing a reliable phase change ($\alpha' \leftrightarrow \beta$), which consequently has a useful volume change associated with it. The sorbent here, has been tested for the first time under reasonably realistic conditions within a TGA for multiple cycles. The results demonstrated that the sorbent displays the characteristic decline in carrying capacity when calcined in the presence of $CO_2$, but not when calcined in the absence of $CO_2$ in the fluidising gas. This paper also presents an improved method to conduct TGA carrying capacity measurements of $CO_2$ sorbents which minimises the over carbonation between cycles.

Keywords: calcium looping, $CO_2$ capture, polymorphic, TGA, $CO_2$ sorbent

Affiliations:

[a] Chemical and Process Engineering Department, Imperial College London, South Kensington, London, UK, SW7 2AZ.

[b] School of Environment, Tsinghua University, Beijing 100084, China

* Corresponding Author: p.fennell@imperial.ac.uk,+44 (0)20 7594 6637

# 1. Introduction:

The earth's climate is predicted to change because of the release of anthropogenic greenhouse gases; it is paramount that emissions are significantly reduced without delay. Carbon Capture and Storage (CCS) has been identified as an important tool for the reduction of anthropogenic $CO_2$ emissions from the combustion of fossil fuels for electricity production and carbon intensive industrial processes such as cement manufacture and iron and steel processing [1]. One of the most promising CCS technologies is calcium looping [2]. The calcium looping process utilises calcium oxide to absorb and release $CO_2$; the calcium oxide is cycled between a carbonator where $CO_2$ is absorbed (eqn 1) and a calciner where $CO_2$ is released (eqn 2) [3]. In a post-combustion capture setting, the carbonator will typically operate around 650 °C with a $CO_2$ concentration of ~15 vol.%, whereas the calciner is likely to have a high $CO_2$ concentration, >80 vol.%, owing to the release of $CO_2$ from the sorbent and from the combustion of fuel for heating the reactor. To overcome the endothermic calcination reaction and to increase the reaction rate a high temperature of around 900-950 °C is required.

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H = \text{-178 kJ/mol} \quad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta H = \text{+178 kJ/mol} \quad (2)$$

Compared to other solid sorbents, such as hydrotalcites and zirconates, CaO has a significant advantage as its typical initial absorption capacity is ~0.79 g$CO_2$/g sorbent (or carrying capacity [4]). CaO can be readily obtained in its carbonated form as limestone, a cheap, abundant and non-toxic material, which is the basic feedstock for the calcium looping process. However, the carrying capacity of limestone derived sorbents degrades over multiple reaction cycles, eventually leading to a carrying capacity of approximately 0.1 – 0.2 g$CO_2$/gCaO (this value can be reached in as few as 20 cycles) [5] [6]. The cause of this loss of carrying capacity is primarily due to sintering, which has been shown to occur by reactive and thermal sintering, thermal softening and the coalescence of smaller grains into larger grains, this results in the loss of a fine pore structure and a shift from smaller micro- and meso-pores to larger macro-pores which are less useful for the capture of $CO_2$ [7] [8].

Calcium looping also offers the further benefit in that when the sorbent particles have lost the majority of their reactivity, the spent material can be used as a de-carbonised feedstock in the cement industry [9].

A range of different approaches have been investigated with the aim of overcoming the issue of sintering of CaO-based sorbents and related decay in the carrying capacity with repeated cycling. These approaches include: the use of dopants [10] [11] [12]; hydration and steam reactivation [13] [14] [15]; thermal pre-sintering [16] [17]; spacer molecule incorporation [18] and sintering resistant internal supports [19] [20]. Recently, Zhao et al. [21] has reported a CaO-based sorbent incorporating a supporting structure composed of dicalcium silicate ($Ca_2SiO_4$, from here on referred to as $C_2S$ which is common notation of this compound in the cement industry) which enabled the sorbent to retain a very high proportion of its carrying capacity throughout many cycles. The authors attributed this to phase transitions that the $C_2S$ underwent during the normal temperature swings of a calcium looping process.

The phase transition exploited within the study by Zhao et al. [21] was the α' ↔ β $C_2S$ transition, which represents ca. 2 % volumetric expansion. The formation of the α' $C_2S$ phase begins to occur at temperatures greater than 690 °C whereas the β $C_2S$ phase begins to form when the material is already in the α' $C_2S$ phase and the temperature reduces below 680 °C [22]. Upon the first calcination of this material the α' $C_2S$ phase will develop, thereby forming microporous channels, which the authors proposed provided an accessible pathway for $CO_2$ to diffuse into the sample, where it could react with free CaO. This reversible phase change leads to predictable and repeatable volumetric changes within the sorbent particles, enabling the microporous channels formed during calcination to be reopened, thereby resisting the effects of sintering. Additionally, a $C_2S$ support is comprised of elements already found in cement and at similar concentrations, which enables the spent sorbent to retain significant value to the cement industry [23] [9] unlike the addition of other typical supports such as $Al_2O_3$ or $ZrO_2$.

Previous work [21] on this type of $C_2S$ supported sorbent attempted to evaluate its performance using a TGA operating at conditions that were not a suitable representation of expected industrial operating

conditions. Calcination was carried out at a temperature of 850 °C under an atmosphere of 100% $N_2$ for an extended time period of 30 minutes. These conditions were not representative of a commercial scale $CO_2$ capture operation where the goal is to produce a concentrated stream of $CO_2$ ready for transportation and storage.
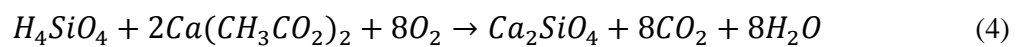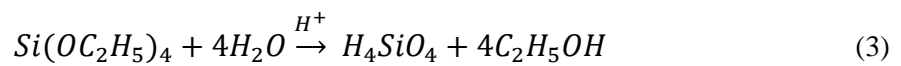
The use of unrealistic conditions, particularly with new sorbent materials is common [24] [25] [26] [27] [28] [29] (This is only a small selection of articles where unrealistic conditions were utilised for cycling experiments in a TGA) and the effect of doing so can lead to unrealistically good findings. More representative operating conditions were first comparatively investigated in this context by Manovic et al [30] where limestone samples were calcined in 100% $CO_2$ at 950 °C; showing that harsh conditions during the calcination stage leads to significantly lower carrying capacities. Some synthetic sorbents and natural limestone derived sorbents, have been comparatively tested under realistic operating conditions, the synthetic sorbents showed a greater ability to resist sintering degradation but decayed similarly to the natural sorbents when calcination occurred under the harshest of conditions [31]. Limestone-derived sorbents have also been calcined under realistic conditions in the presence of $SO_2$ whilst at high partial pressures of $CO_2$ [32]. It was found that the $SO_2$ irreversibly reacted to form $CaSO_4$ [33] which in addition to the enhanced sintering caused by high temperature and high partial pressures of $CO_2$ led to the characteristic decay in carrying capacity.

Here we attempt to address some of the limitations identified in the previous work [21] involving the $C_2S$ supported CaO by testing the resilience of the polymorphic, pore-reforming nature of this support and its ability to preserve the reactivity of the sorbent over repeated cycling at conditions more similar to those of a commercial post-combustion capture calcium looping system. Principally, the calcination conditions have been modified, as the influence of high temperature $CO_2$ on the rate and extent of sintering has been shown to be the most significant parameter on the sorbents longevity [30]. The carbonation time was also shortened to 5 minutes since it is not realistic to have such long carbonation times in an industrial setting, although the authors accept that even 5 minutes could be considered a long time period for carbonation. We also introduce a novel gas switching method that was developed to minimise, as much as possible, any additional carbonation as the temperature was

ramped between carbonation and calcination conditions. This gas switching concept involved ramping the $CO_2$ concentration from 15 % to 100 % $CO_2$ as the temperature was ramped from the carbonation to the calcination phase in line with the thermodynamic equilibrium position of the system.

## 2. Material and Methods:

A detailed description of the sorbent preparation method used in this work was provided by Zhao et al [21]; only a brief outline of the procedure is provided here. A solution consisting of tetraethyl orthosilicate (TEOS, *Sigma Aldrich*) and nitric acid (*VWR*) was prepared and stirred for 1 hour. The nitric acid performed the role of a protonating agent to allow the hydrolysis reaction to go to completion (eqn 3). This solution was then added to a second solution prepared by dissolving calcium acetate (*Sigma Aldrich*) in deionised water. The resulting mixture was stirred thoroughly before the water was removed by freeze drying or heat drying. The freeze dried sample was frozen before it was freeze dried (*VirTis, SP Scientific BenchTop Pro* freeze dryer) at approximately -44 °C and ~0.005 kPa (this sample will be referred to as FD-$C_2$S-CaO). The heat dried sample was dried on a hot plate at 75 °C with a magnetic stirring bar until a thick paste was formed (this sample will be known as HD-$C_2$S-CaO). At this stage, the mixture consisted of a well-mixed fine powder of calcium acetate and hydrolysed orthosilicate; the precursor powder was heated in a Lenton horizontal tube furnace to 950 °C (ramp 20 °C/min) and held for 1 hour under air which acted as an oxidising gas. This ensured that the remaining carbonaceous compounds were completely combusted and removed from the sample, and most importantly, the crystalline $C_2$S compound was formed (eqn 4). The $C_2$S was formed by a solid-solid reaction that is more commonly associated with the manufacture of cement clinker.

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{H^+} H_4SiO_4 + 4C_2H_5OH \tag{3}$$

$$H_4SiO_4 + 2Ca(CH_3CO_2)_2 + 8O_2 \rightarrow Ca_2SiO_4 + 8CO_2 + 8H_2O \tag{4}$$

The molar ratio of Ca to Si was maintained at 9:1 throughout all experiments so that the results were directly comparable with the sorbent reported previously [21]. Analysis with an X-ray Diffractometer (XRD) utilising $CuK\alpha$ radiation (PANalytical, Almelo) was carried out to assess whether the phase formations had occurred in the correct proportions during the sorbent preparation stages. To quantify the intensity of the XRD peaks and thus derive the proportions of each phase, a quantitative phase analysis via Rietveld refinement was performed on the XRD data using the open source GSAS-II program [34].

Initially, the temperature of the tube furnace was set to 850 °C for 1 hour to match the conditions of the original paper by Zhao et al. [21], however the XRD results showed an amorphous mix with no distinguishable peaks for any $C_2S$ phases. The temperature setpoint was subsequently altered to produce samples thermally treated at 900 °C and 950 °C (each held for 1 hour), however, it was not until 950 °C that the peaks became apparent in the predicted quantities. The difference here is likely to be in the work by Zhao et al. [21], the samples' thermal transition step was undertaken in a box furnace where the temperature control was not as accurately calibrated as the tube furnace that was used in this work.

## 2.1. TGA Setup and Gas Control

The multi-cycle performances of the sorbents for $CO_2$ capture was investigated using a TGA (TA Q5000IR). The operating conditions for the TGA cycling experiments are presented in Table 1.

| Parameter | Value |
|---|---|
| Carbonation temperature / °C | 650 |
| Carbonation time / min | 5 & 30 |
| Carbonation, $CO_2$ gas percent / % | 15 |
| Calcination temperature / °C | 850 & 950 |
| Calcination time / min | 1 |
| Calcination, $CO_2$ gas percent / % | 0 & 100 |
| Total gas flow rate / $cm^3$/min at 20 °C | 110 |
| Number of cycles | 15 |

Table 1 – Operating Conditions.

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The mass of sample loaded into the TGA was maintained at a constant value of $4 \pm 1$ mg. Mass transfer effects were investigated by varying the sample size, however no significant effect on the kinetics or extent of reaction was determined for sample masses below 10mg. Samples were pre-calcined in the TGA (not shown in figure 1) under 100% $N_2$ at 950 °C for consistency and to ensure the samples were completely calcined before beginning the cycling experiments.

Nitrogen (99.9% purity, BOC) was utilised as the balance gas for all concentrations of $CO_2$ (99.9% purity, BOC) specified. The gas flow rates were controlled using an external mass flow controller (Brooks) set-up which was controlled via a separate program (the code was written in-house) using Agilent VEE. The TGA and MFC control programs were synchronised using the TGAs' output signal function and a USB data acquisition (DAQ) module (Measurement Computing USB-1208FS). A $CO_2$ concentration of 15 % was used during the carbonation phase of the cycling experiments to simulate the flue gas from a typical coal combustion power plant [35].
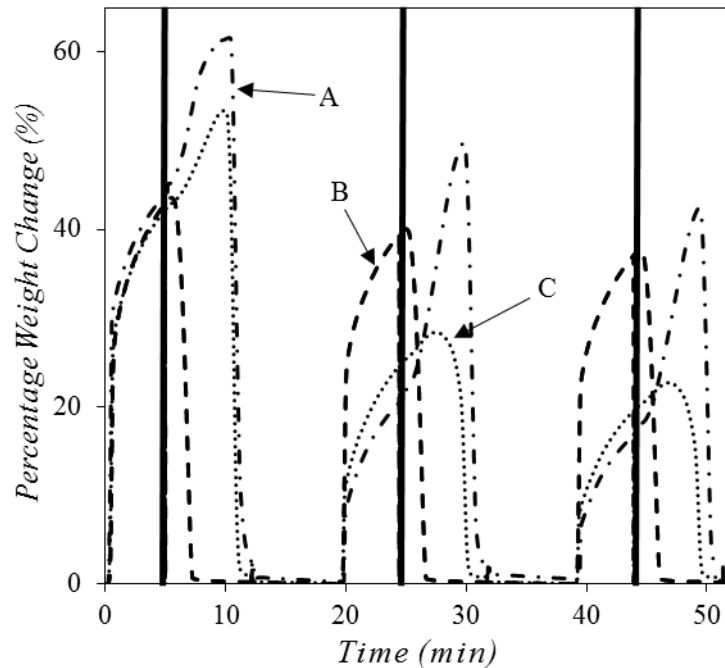


Figure 1: Percentage weight change during the initial 3 carbonation/calcination cycles of the freeze dried CaO-$C_2$S-CaO sorbent when subjected to different gas switching methods. For calcination: profile A switched directly to 100% $CO_2$ after carbonation, profile B switched to 0% $CO_2$ after carbonation, profile C uses the temperature programmed ramping of $CO_2$ after carbonation. Calcination set conditions were: 950 °C for 1 minute. Carbonation set conditions were: 15% $CO_2$,

650 °C for 5 minutes. Constant total flow rate of 110 $cm^3$/min (at 20 °C). The thick vertical lines represent the points of gas switching, i.e. end of carbonation, start of calcination.

To switch between the carbonation conditions and calcination conditions specified, the $CO_2$ gas concentration had to be carefully adjusted. If a direct switch between 15% and 100% $CO_2$ (profile A in figure 1) was used after the 5 minutes of carbonation then the temperature would still be well in the carbonation regime and thus the sample would over carbonate leading to erroneous results. This additional over-carbonation is similar to that described by Arias et al [36]. Nor could the gas be switched to 100% $N_2$ at the end of the 5 minutes as the sample would begin calcination before the setpoint temperature was reached and it would defeat the purpose of operating at realistic conditions (profile B in figure 1).

Consequently, to overcome this problem, the $CO_2$ gas concentration was increased at a rate set by the TGA's heating rate (profile C in figure 1); later on, this is referred to as 'temperature programmed $CO_2$ partial pressure ramping'. Here, the equilibrium thermodynamics of the $CaCO_3$/CaO system were taken into account to produce a best fit third order polynomial for the rate of heating with the rate of $CO_2$ partial pressure increase. During the temperature programmed $CO_2$ ramping, the $CO_2$ partial pressure was kept above the equilibrium partial pressure by an average of $2.4 \pm 0.2$ kPa, this ensured the sample stayed in the carbonation phase and did not begin calcining before the desired $CO_2$ concentration was reached. Figure S1 within the supporting information displays a plot of $CO_2$ partial pressure (from the valve output) and time during this ramping period. By keeping the sample in the carbonation phase, there was some unavoidable over carbonation, but this was significantly lower than the case where the $CO_2$ partial pressure was directly switched, as can be seen in figure 1. The flow of $N_2$ was adaptively modified to maintain a constant total flow rate throughout.

## 3. Results and Discussion:

For comparison, figure 1 displays the effect of changing the gas concentration via the different approaches discussed above is presented for the first 3 cycles. All trials displayed in figure

1 utilised the FD-$C_2$S-CaO sorbent and were carbonated at 650 °C for 5 minutes, under 15% $CO_2$ with $N_2$ as the balance gas. The zeroth calcinations (i.e. the calcination of the original sample) of all samples were conducted under 100% $N_2$ at 950 °C for consistency. All subsequent calcinations were programmed to take place at 950 °C for 1 minute under 0% $CO_2$ (profile B) or 100% $CO_2$ (profiles A & C).

An important detail to notice in figure 1 is the increase in mass at the end of carbonation and start of calcination period (marked by the thick vertical lines). Profile A of figure 1 shows a significant over-carbonation as the gas was switched to 100 % $CO_2$, as a result of this there was a greater carbonation driving force ($P_{CO_2}$ - $P_{eq}$) that led to the rapid reaction with $CO_2$ in the period of time leading up to the temperature at which the equilibrium position of the system transitioned from carbonation to calcination. Profile B of figure 1 illustrates the immediate onset of calcination, occurring directly after the carbonation period, as the gas was switched to 100% $N_2$. The lower temperature calcination will have limited the extent and rate of both thermal and reactive sintering of the sorbent material resulting in the less severe decay observed in carrying capacity (measured after 5 minutes at the end of the carbonation period) compared with the samples calcined under 100% $CO_2$. Profile C of figure 1 shows the benefit of the temperature programmed $CO_2$ partial pressure ramping system, where there was less over carbonation. The first cycle in profile C does show considerable over-carbonation compared to the following cycles. This was mostly likely because of highly reactive nascent CaO in the raw material that carbonated even with only a mild driving force. This was much less evident in the subsequent cycles and is thought to be due to the sintering of the sample which also explains why the rate of carbonation was lower during the temperature ramping stage.

The temperature set point for the calcination was evaluated based on the equilibrium line between CaO and $CO_2$, and the expected $CO_2$ partial pressure within a commercial calciner. This equilibrium line was calculated using equation 5 [37] and was supported with thermodynamic modelling using the ThermoVader excel add-in [38]. From application of equation 5 and the thermodynamic data, it was calculated that the temperature required for calcination under 100% $CO_2$ at atmospheric pressure is at least 898 ± 4 °C. This means that despite setting the calcination temperature to 950 °C, the

calcination actually started before this temperature was reached and the rate of calcination increased as the temperature rose further from this value.

$$K_{eq} = 4.137 \times 10^{12} exp\left(\frac{-20474}{T}\right) \tag{5}$$

Here, $K_{eq}$ is the equilibrium constant for the reaction described by equations 1 and 2 and $T$ is the temperature (K).

The TGA cycling data was analysed in a Matlab routine that amongst other processes applied equation 6 to calculate the carrying capacities of the novel sorbent (as presented in figure 2).

$$C = n_{CO_2}\frac{RMM_{CaCO_3}}{M_{CaCO_3}P_{CaCO_3}} \times 100\% \tag{6}$$

Here $C$ is the carrying capacity, also referred to as CaO conversion, mol $CO_2$ / mol $CaCO_3$, $n_{CO_2}$ is the total number of moles of $CO_2$ released during the calcination reaction, calculated from the mass change and the relative molecular mass (RMM), $RMM_{CaCO_3}$ is the relative molecular mass of $CaCO_3$, $M_{CaCO_3}$ is the mass of $CaCO_3$ equivalent in the original material and $P_{CaCO_3}$ is the purity of $CaCO_3$ equivalent in the original material, %.

Three repeats of all experiments were carried out and the standard deviation at each cycle was calculated to provide an estimation of error, this error can be seen as error bars in figure 2.

The sorbents calcined in atmospheres containing no $CO_2$ (▲ & △) displayed a significantly higher carrying capacity than those that were calcined under more realistic conditions i.e. 100% $CO_2$ (● & ○). Calcining the sorbents at higher temperatures and high partial pressures of $CO_2$ is well known to enhance sorbent sintering mechanisms [32] [37] [39] [40] [41] [42]. The mechanism for the $CO_2$ sintering is thought to be grain boundary diffusion and a surface diffusion of catalytic $CO_2$, this results in an enlargement of the grain size and a reduction in the reactive surface area. The sintering leads to a loss of surface area and reduction of the porosity, leading to a transition from fast, surface-controlled reaction to slow solid state diffusion-controlled process within the lattice of the material [43]. The decay in carrying capacity, of the samples calcined in 100% $CO_2$ (shown in figure 2) display a decline that is consistent with that of all CaO based sorbents, including natural limestone.

On further examination it can be seen that the temperature of calcination had a significant effect on the long term carrying capacity (figure 2), which is consistent with the work of Manovic et al, [30]. This can be observed in figure 2 by comparing the sorbents that were each calcined in 0% $CO_2$ at both the higher temperature of 950 °C (▲ & △) and at the lower temperature of 850 °C (◇ & ◆). The samples (◇ & ◆) calcined at 850 °C were aimed to replicate the conditions utilised by Zhao et al, [21], i.e. carbonation under 15% $CO_2$ balanced with $N_2$ for 30 minutes at 650 °C and Calcination under 100% $N_2$ at 850 °C no dwell time. The carrying capacity results for the replicated samples shows a more substantial decline with increasing cycle number than was observed in the original work. All of the experiments were checked and repeated; the results indicate that there was potentially a difference caused by the different production methodology of the $C_2S$ (though it should be noted that the decay in reactivity was still very low).
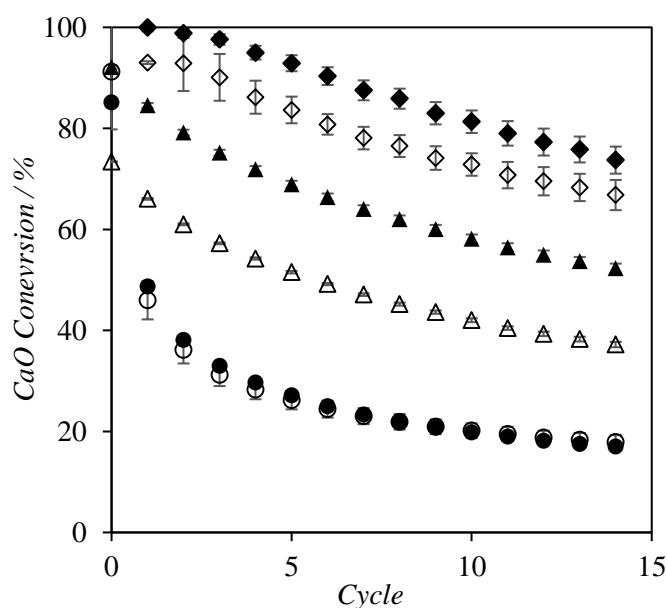
Figure 2: Carrying capacities of the novel sorbent produced by different methods and subjected to either 0% or 100% $CO_2$ during the calcination step; all other conditions are listed in table 1. For comparison, two replicate samples were created and examined under the same conditions specified in the paper by Zhao et al [21]. FD = Freeze dried, HD = Heat dried. (▲) FD-$C_2$S-CaO 0% $CO_2$ calcination, (△) HD-$C_2$S-CaO 0% $CO_2$ calcination, (●) FD-$C_2$S-CaO 100% $CO_2$ calcination, (○) HD-$C_2$S-CaO 100% $CO_2$ calcination, (◆) FD-$C_2$S-CaO Matches the conditions by Zhao et al [21], (◇) HD-$C_2$S-CaO Matches the conditions by Zhao et al [21].

Figure 2 displays evidence that the method of production did influence the trend in carrying capacity decay. The two production methods utilised for the production of the novel sorbent were heat drying and freeze drying; the freeze dried precursor material took longer to produce because the rate of water loss was lower. It has been previously suggested [21] that by freezing the samples, large dendritic ice crystals were formed which left enlarged pores when the water sublimated away. As such, an increased pore volume and an interlinked pore structure was produced which may have improved the diffusion of $CO_2$ during carbonation. The freeze dried sorbents tended to present a higher initial carrying capacity than the heat dried sorbents under all scenarios investigated, but the relative loss of each sample's carrying capacity over 15 cycles was irrespective of the production method used. The final carrying capacities, after 15 cycles, for the freeze dried samples calcined in 0% and 100% $CO_2$ were 0.23 and 0.08 $gCO_2/gCaO$, respectively. For the equivalent heat dried samples, the final carrying capacities, were 0.16 and 0.07 $gCO_2/gCaO$, respectively. The sorbent investigated under identical conditions to those used by Zhao et al [21] presented a much higher 15th cycle carrying capacity; 0.39 $gCO_2/gCaO$ (or a conversion of 74 %) was achieved for the freeze dried sorbent and 0.34 $gCO_2/gCaO$ for a heat dried sorbent. It can thus be shown that using harsh but reasonably realistic calcination conditions led to ~80% drop in 15th cycle carrying capacity.

3.1. $C_2$S sorbent vs limestone sorbent

The reason that this type of sorbent was capable of minimising the extent of deactivation, under certain conditions, was as a result of the $C_2$S phase changes that took place when the

temperature was cycled. During the heating up period to the calcination temperature, the $C_2S$ formed the α' phase and the density increased to 3.38 g/cm³, then as the samples cooled to the carbonation temperature, the $C_2S$ formed the β phase and its density decreased to 3.31g/cm³ [22]. As such, these phase changes produced a small force inside the particle which aided the reformation and reopening of the pore channels. This suggests that more of the CaO was available for carbonation in the following cycle; this was the main advantage for this type of novel sorbent compared to natural limestone. Of course, the phase change, by producing micro-cracks, could change the mechanical stability of the particle, though the powdered nature of the sorbent means that these experiments cannot be used to determine whether or not this is an issue.
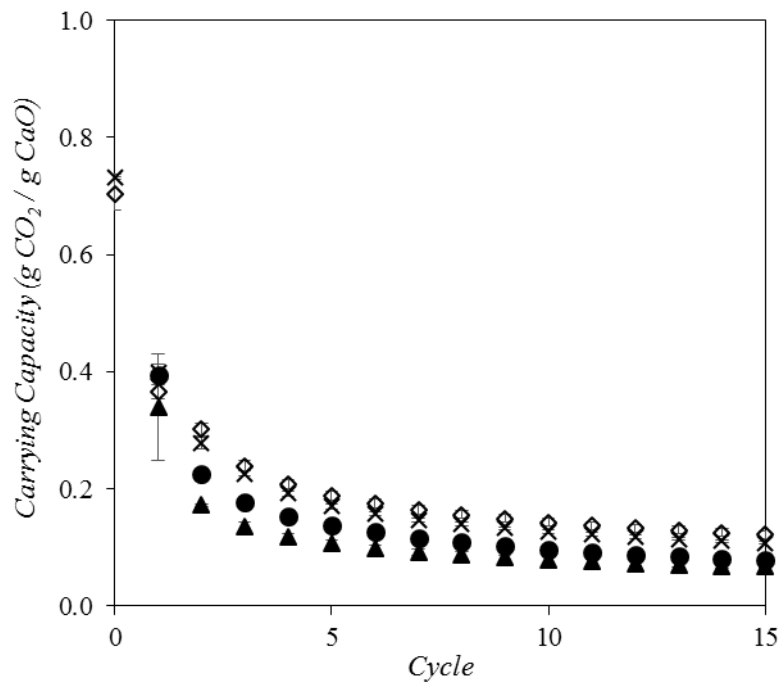


Figure 3: Carrying capacity comparison of the novel sorbent against two natural limestones. Both the limestones and the novel sorbent were calcined under 100% $CO_2$ at 950 °C for 1 minute using the temperature programmed ramping that was described earlier. Carbonation was performed at 650 °C for 5 minutes under 15% $CO_2$. FD = Freeze dried, HD = Heat dried. (x) Longcliffe limestone, (◇) Imeco limestone, (●) FD-$C_2S$-CaO 100% $CO_2$ calcination, (▲) HD-$C_2S$-CaO 100% $CO_2$ calcination.

The effect of realistic cycling conditions can be observed when comparing both the HD and FD novel sorbents against the two commercially available limestones in figure 3. It can be seen that when using harsh conditions, the final carrying capacity was not enhanced by the novel polymorphic spacers, despite the sorbent being very promising when calcined with no $CO_2$ present. All of the samples, including the two natural limestones (Longcliffe and Imeco) were examined on the same TGA under the same conditions to ensure that the results were directly comparable; the standard deviation of the three repeats is displayed as the error bars in figure 3. The novel sorbent demonstrates a similarly high $CO_2$ uptake, due to the high CaO to $C_2S$ ratio, before rapidly sintering and eventually leaving only around 20% of the initial CaO accessible for conversion to $CaCO_3$. For the novel sorbent, the 15th (g $CO_2$ /g CaO) cycle carrying capacities were slightly lower than that of the natural limestone, this was thought to be caused impurities or structural differences in the limestone preventing full sintering of the CaO.

## 4. Conclusions:

This TGA study has investigated a novel type of $CO_2$ sorbent based on the polymorphic ability of dicalcium silicate ($C_2S$) to change its volume and consequently generate pores during the temperature swings of the calcium looping process. The sorbent has previously displayed an excellent ability to retain a very high carrying capacity over multiple cycles, this study has investigated the sorbent's reactivity decay under more realistic conditions.

The operating conditions for calcination were set to be similar to those of an industrial calciner within a calcium looping process, namely a high $CO_2$ partial pressure and a correspondingly high temperature. The phenomenon of high temperature $CO_2$ sintering during the calcination dramatically affected the sorbent's ability to absorb and release $CO_2$. The same effect was observed with natural limestone too.

This paper further underlines the importance of conducting measurements of carrying capacity decay under realistic conditions when working with novel $CO_2$ sorbents so as to make a fair judgement as to the sorbent's actual potential. The authors have presented an advanced TGA method for assessing

a sorbents' $CO_2$ carrying capacity under realistic conditions by minimising the amount of over carbonation between cycles.

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