Bachelor Thesis

Researching the stability of CaO from different precursors under varying absorption times

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Abstract

Climate change is becoming a serious issue and carbon dioxide emissions need to be cut drastically in order to avert disaster. One way of making sure carbon dioxide does not enter the atmosphere is by making sure it is filtered from the waste flow. Many different technologies are currently being researched, among which the calcium looping cycle. CaO could absorb CO_2 before it reaches the atmosphere and can be recovered through a relatively easy thermal treatment. Considering it is a very cheap material it is of importance to thoroughly investigate this subject.

Calcium carbonate, calcium L-ascorbate and calcium D-gluconate were chosen as precursors for CaO in this research. Using various calcination temperatures (750 °C, 800 °C, 850 °C, 900 °C) a plethora of different samples were synthesised, of which the ones with the highest absorption capability (read internal surface area) were chosen for absorption/desorption cycle research. The highest internal surface areas were found at a calcination temperature of 850 °C, at which the calcium carbonate produced the sample with the highest internal surface area (34,54 m^2/g).

The chosen samples underwent absorption cycles lasting 6, 12 or 30 minutes in order to investigate the effect of non-complete conversion of CaO on the stability of the sample. It became clear that shorter absorption cycles vastly increase the stability of the sample.

Theoretically speaking a calcium carbonate sample prepared at 850 °C would provide the best results utilising 6 minute absorption cycles. Of the tested samples in practice the calcium oxide sample from calcium L-ascorbate prepared at 900 °C yielded the best results utilising 6 minute absorption cycles, retaining 97,1% of its initial performance after 5 cycles.

Introduction

It is a widely accepted fact that the Earth is warming up due to a drastic increase in anthropogenic CO_2 in the atmosphere. Many efforts have been made to reduce these emissions (like more efficient installations, engines and sustainable alternatives to non-renewable resources) and a lot of research is currently vested in reducing the emissions even further. Among the options being researched for Carbon Capture and Storage (CCS) is the $CaO/CaCO_3$ cycle, which is very promising due to its high theoretical value of CO_2 storage per unit CaO (0,786 g CO_2/ g CaO). Its affordability and abundance make CaO an excellent candidate for carbon capture systems. However, after multiple cycles of absorption and desorption of CO_2 the performance of regular CaO plummets. This is thought to happen due to structural changes as CaO converts to $CaCO_3$ [1] and due to sintering of the sorbent at the elevated temperatures (~900 °C) [1-3] required for the decomposition.

It is therefore of vital importance to find ways to increase the stability of the produced CaO structure. Many possible solutions have been researched, including utilising naturally occurring limestone and the production of CaO through synthetic means. CaO from natural sources degrades too fast over several calcination cycles [4], which is why this research is focused on CaO from synthetic precursors. This category can be further divided into four main points of interest which are currently being investigated [4]:

I. CaO supported by an inert substance
II. CaO from organometallic precursors
III. Nanostructured CaO
IV. Doped CaO

Of these options, option II is easiest to realise and will therefore be the focus of this research, requiring the least amount of machinery and other equipment in order to obtain the desired effect. Options I and IV require premixing methods [5, 6] and option III requires advanced equipment by definition, whereas an organometallic precursor only requires thermal treatment to obtain the desired synthetic CaO structure.

The research itself will focus on synthesising and characterising porous CaO structures and comparing these with each other in unreported ways as of yet. The context of this research is fundamental; scaling the process up if it is successful is not part of this research.

Theory

Deformation of the CaO structure (at elevated temperatures) is the biggest challenge to face at this point in time. The first problem is the structural change as CaO converts into $CaCO_3$. Their molar volumes are 17 and 37 cm^3/mol [7] respectively. As a result, pores may be blocked as the absorption takes place, reducing the performance of the synthesised CaO structure.

The second and biggest problem in the absorption/desorption cycle is the stability of $CaCO_3$. Its Tamman temperature is only 561 °C [8], which means that sintering is a major problem when temperatures vary between 630 °C for absorption and 800 °C for desorption.

The four earlier named research categories all focus on modifying the structure of CaO by mixing it with sintering-resistant substances like Liu et al [3] have done by wet mixing a CaO precursor with either a similar magnesium or aluminium support. This has been done with a variety of different supports, including zirconium (Radfarnia et al, [9]), but also different synthesis methods like Florin et al have done (natural limestone with an aluminium hydroxide precursor through precipitation in a slurry bubble column) [10] in addition to what Broda et al have achieved with zirconia supports through the sol-gel method [11]. Another recent development is the use of more commonly available materials as support in order to find commercially attractive options like Qin et al have found out: they have produced CaO structures with a cement support [12]. There are even green alternatives, where fly ash has been utilised as an effective CaO support to prevent sintering by Yan et al [13].

Another point of research is the carefully adjustment of the structure itself to make sintering less likely by synthesising CaO from synthetic precursors like calcium propionate, calcium acetate, calcium acetylacetonate, calcium oxalate and calcium 2-ethylhexanoate [7] instead of natural limestone. Qin et al have produced CaO structures from calcium carbonate, calcium hydroxide, calcium d-gluconate monohydrate, calcium acetate hydrate, calcium formate and calcium l-lactate hydrate. In addition to that, Lu et al [14] have also produced these kind of structures from calcium nitrate.

Novel synthesis methods are currently being reported by Luo et al [15] and new materials to be used as support for CaO-based carbon capture are being discovered on frequent basis. However, none of the examined researches seem to have tried to vary conditions during synthesis to see what the effect would be on the subsequent structure and porosity of the resulting calcium oxide. Therefore I would like to pick a synthesis method and see which conditions would yield the best structures. In this case I would like to make use of just the thermal treatment to prepare the CaO samples, due to the fact that the comparison of different synthesis methods is not the focus of this research.

Furthermore the examined researches examine absorption/desorption cycles which take at least 15 minutes. Investigating the effect of a shorter absorption/desorption (A/D) cycle (~1-2 minutes) could very well prove to be worthwhile. The absorption phase (and also the desorption phase) can be divided in two stages: one controlled by the rapid filling/emptying of the easily accessible surface area and one controlled by CO_2 diffusion to/from the core. The first stage is very fast and covers the available internal surface area in a matter of a few minutes after which the second stage takes over. In this stage CO_2 has to diffuse into the CaO particles in order to adsorb, which obviously takes longer. During desorption all CO_2 on the inside of the particles will have to diffuse outward again, which will take more time than the liberation of CO_2 from just the surface of the CaO particles. It results in a longer time in the desorption phase and thus more sintering would occur due to the elevated temperatures during that phase. My hypothesis is that if only stage one absorption were allowed to happen, the sorbent would not have to spend as much time in the desorption phase and therefore the harmful sintering effect would be reduced. It would also help to deal with the first problem. The internal structure will remain mostly the same, because CO_2 will not get the chance to diffuse into the centre of the CaO particles due to the shorter cycles and react to form $CaCO_3$ which distorts and damages the existing CaO structure due to it taking more space [7].

By combining these two aspects in one research I would like to find out more about these under-examined aspects of CaO synthesis and usage.

Expected outcomes

- Higher temperatures will be beneficial to sample preparation, due to partial sample sintering promoting enhanced stability during desorption.
- Calcium D-gluconate will provide the best samples due to the liberation of its organic component (more so than ascorbate), leaving an open and porous CaO structure.
- Shorter A/D cycles will preserve the desired porous CaO structure better than longer A/D cycles.

Experimental procedure

Three CaO precursors were selected for use during this research. The first precursor is $CaCO_3$ (Sigma-Aldrich, 100%), the second is calcium L-ascorbate dihydrate (Aldrich Chemistry, 99%) and the final is calcium D-gluconate monohydrate (Alfa Aesar, 98+%), each of which underwent thermogravimetric analysis (TGA) in order to determine the decomposition temperature.

Utilising the TGA results four calcination temperatures were defined (750 °C, 800 °C, 850 °C, 900 °C) at which the samples would be prepared. The samples were spread out in a glass tray and inserted in a calcination tube. Gas flow (air) was regulated through an oven installation (Eurotherm International) and was kept constant at 25 ml/min. Temperatures were raised with a ramp of 15 °C/min and were eventually kept constant for 30 minutes once the desired temperature was reached. Cool down from the calcination temperature initially happened at 15 °C/min until the point where the temperature difference between the inside and outside of the oven did not facilitate such a cool down. The produced samples have been categorised as seen in table 1.

Table 1: Classification of the produced samples.

	Precursor		
Calcination temperature (°C)	**Calcium Carbonate**	**Calcium L-Ascorbate**	**Calcium D-Gluconate**
750	C750	A750	-
800	C800	A800	G800
850	C850	A850	G850
900	C900	A900	G900

Once calcined the samples were ground utilizing a pestle and mortar and were subsequently sieved. Two sieves (mesh size of max. 0,300 mm and max. 0,090 mm) were used to obtain particle sizes in the range of 90 – 300 µm. Any larger and smaller particles were collected and ground again using a pestle and mortar. The second batch was sieved again using the aforementioned equipment in order to maximise sample yield.

Some of the samples are designated XL in addition to their regular code. In this case the obtained powder was pressed into pellet form, subsequently crushed and sieved with two sieves (mesh size of max. 0,6 mm and max 0,3 mm) in the same manner as above in order to obtain larger particle sizes in order to make sure the sample would not block the gas flow and cause dangerous air tight blockages.

Samples were wedged in between two agglomerations of quartz wool within a glass reactor tube (4 mm internal diameter) which was subsequently placed within an experimental setup capable of supplying variable amounts of argon and carbon dioxide in the order of several tens of millilitres per minute and heating the sample up to 800 °C.

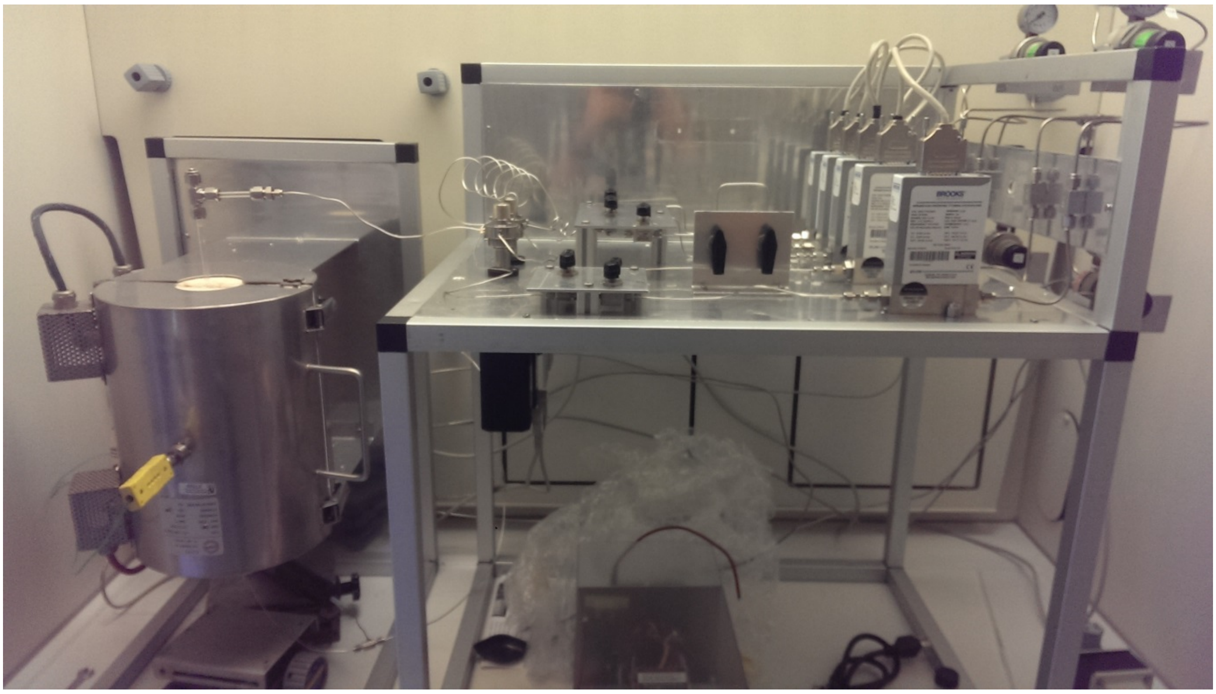


Figure 1: The utilised setup. The oven (manufactured by Elicra electrowarmte bv, max. temp = 1000 °C, 900 W power usage) containing the glass reactor can be seen on the left side, whereas gas controls (manufactured by Brooks Instrument) and tubing (manufactured by Swagelok) are found on top of the suspended surface. Below the oven part of the gas flow is redirected toward an Omnistar^{TM} Pfeiffer Vacuum spectrometer.

Once fixed within the setup the samples were first heated to 750 °C under a 30 ml/min argon flow in order to allow any water and carbon dioxide to escape which accumulated during storage, after which the sample was cooled down to 630 °C (absorption temperature). Depending on the type of absorption/desorption cycle researched, the sample would remain at 630 °C for 6, 12 or 30 minutes whilst exposed to a 5% CO_2 Ar flow* (1,5 ml/min CO_2, 28,5 ml/min argon). At the end of this period the CO_2 flow was terminated (30 ml/min argon gas flow) and subsequently the sample would be heated up to 800 °C at 20 °C/min, where it remained for 12 minutes independent of the type of cycle researched. Afterwards the sample would cool down again to 630 °C at 20 °C/min, completing one cycle and starting another from the starred step onward if necessary.

The outgoing gas flow is analysed by an Omnistar^{TM} Pfeiffer Vacuum spectrometer, which can accurately detect CO_2 concentrations of up to 10%. Higher concentrations can still be measured, though in that situation the linear correlation between the amount of absorbed CO_2 and the outgoing signal is lost. At sufficiently high temperatures the same effect occurs. However, it is unclear around which temperatures this happens.

Samples were analysed using BET surface analysis and were visualised using a SEM (manufactured by Carl Zeiss Microscopy GmbH).

Summarised, the samples which underwent A/D cycles are categorised as follows:

Table 2: Categorisation of the samples which underwent A/D cycles.

Precursor	Long absorption cycle (30 min)	Medium absorption cycle (12 min)	Short absorption cycle (6 min)
Calcium Carbonate	-	-	-
Calcium Ascorbate	A900-L-XL	A900-M	A900-S-XL
Calcium Gluconate	G900-L	G900-M	G900-S-XL

Calcium carbonate was not represented during the A/D cycle research due to the fact that it seemed to yield CaO powders with relatively low internal surface areas. Samples with lower calcination temperatures than 900 °C were excluded due to the fact that most samples below this temperature were not fully calcined by the end of the oven programme and had would not be of any use in accurate A/D cycle research. Unfortunately BET results were not in at this point of the research, so we were forced to rely on visual analysis of produced samples.

Results and discussion

A. *Precursor analysis*

At the start of the research thermogravimetric analysis was used in order to determine the temperature at which the Ca-based precursor would convert into CaO. See figures 2, 3 and 4 for the decomposition graphs.

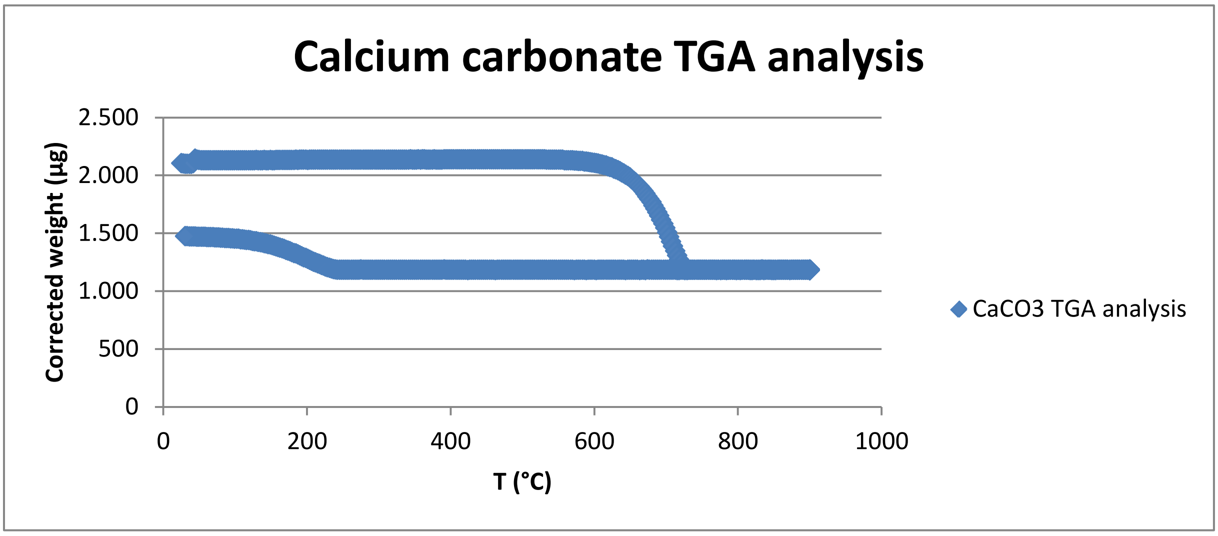


Figure 2: Calcium carbonate TGA analysis (T_{CaO} = 729 °C).

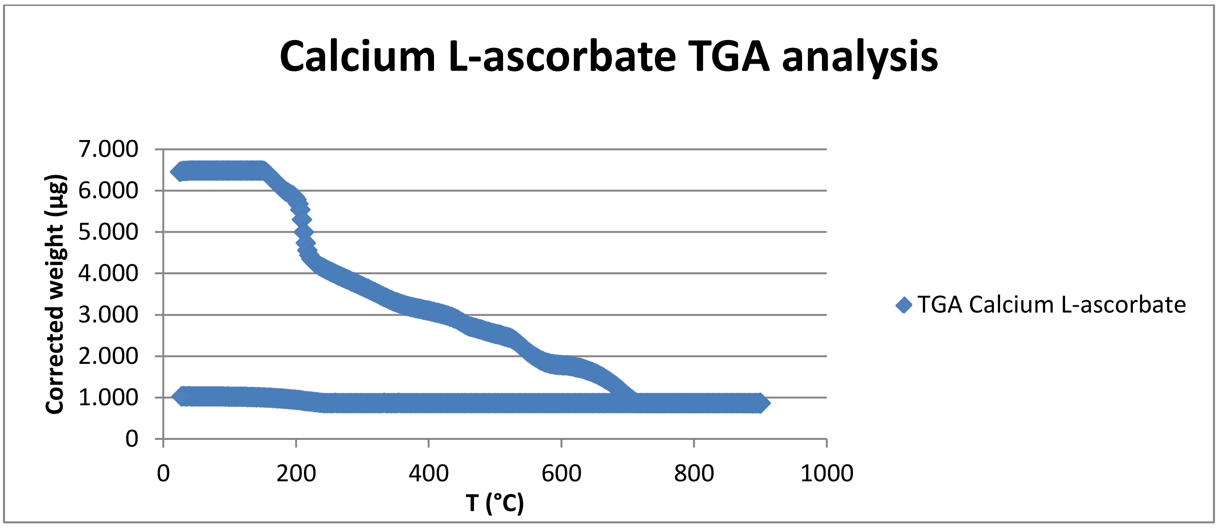


Figure 3: Calcium L-ascorbate TGA analysis (T_{CaO} = 718 °C).

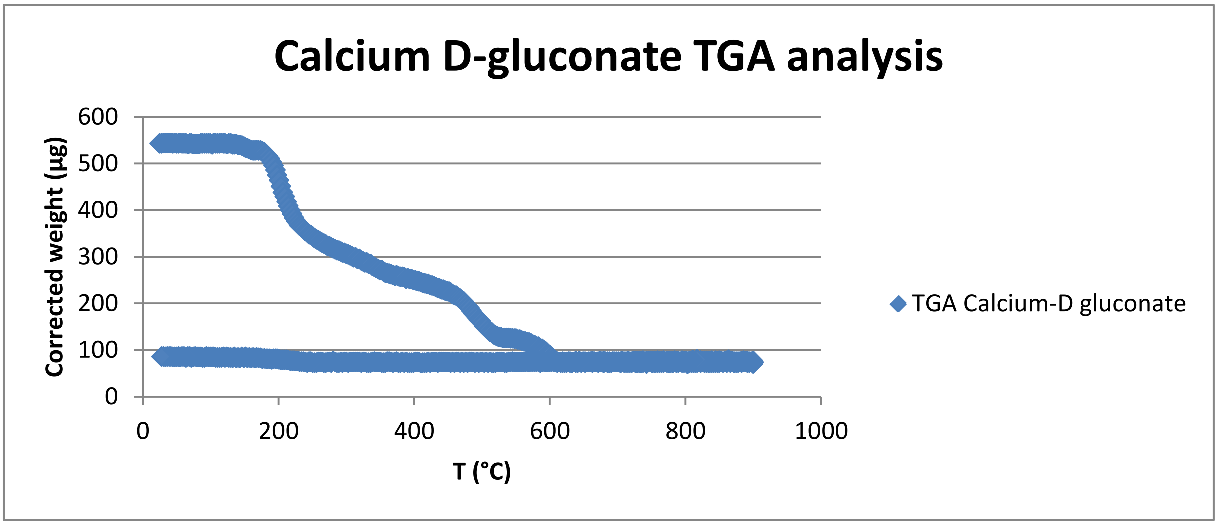


Figure 4: Calcium-D gluconate TGA analysis (T_{CaO} = 616 °C).

From this data it became abundantly clear that samples from all three precursors would all successfully convert to calcium oxide at calcination temperatures exceeding 729 °C. This is the reason why 750 °C was taken as the base calcination temperature, increasing by increments of 50 °C until 900 °C.

B. Sample synthesis

All samples from table 1 underwent BET analysis in order to determine their internal surface areas. See table 3 for the results.

Table 3: BET surface areas of the produced samples.

	Precursor		
Calcination temperature (°C)	**Calcium Carbonate (m^2/g)**	**Calcium L-Ascorbate (m^2/g)**	**Calcium D-Gluconate (m^2/g)**
750	N/A	40,40	-
800	12,84	27,56	16,28
850	34,54	34,15	20,49
900	10,05	16,80	11,22

Due to the BET results taking longer than expected it was hypothesised that the ascorbate and gluconate precursors would yield the best results and were therefore utilised in the final part of the research.

Additionally, higher calcination temperatures were thought to be more favourable over the lower ones due to the likely presence of residual organic matter originating from the raw precursor. Samples in the lower temperature ranges were often heavier than expected and sometimes were not even completely white. Whilst this was definitely the case for C750, A750, A800 and G800, it turns out that a peak value for the internal surface area is observed at T = 850 °C for all the observed samples, contrary to what was initially expected.

Elevated temperatures could cause sintering to occur within the calcium oxide structure, reducing its internal surface area and therefore giving rise to the observed performance drop based off these results.

The A750 sample has an abnormally high internal surface area. As seen in figure 5, this sample was grey instead of white, indicative of an incomplete calcination. This means that the calcium oxide structure was still fouled by 65,1 mg of extra material which should have vanished during calcination in order to obtain the planned 200 mg of CaO sample. This extra organic material must have contributed to the higher internal surface area of the sample. Unfortunately this sample is not useful within the context of this research, as the excess material would liberate from the sample at the desorption temperature of 800 °C, presumably resulting in a loss of internal surface area. A similar process is most likely at work in the A850 sample as well, albeit to a lesser degree.

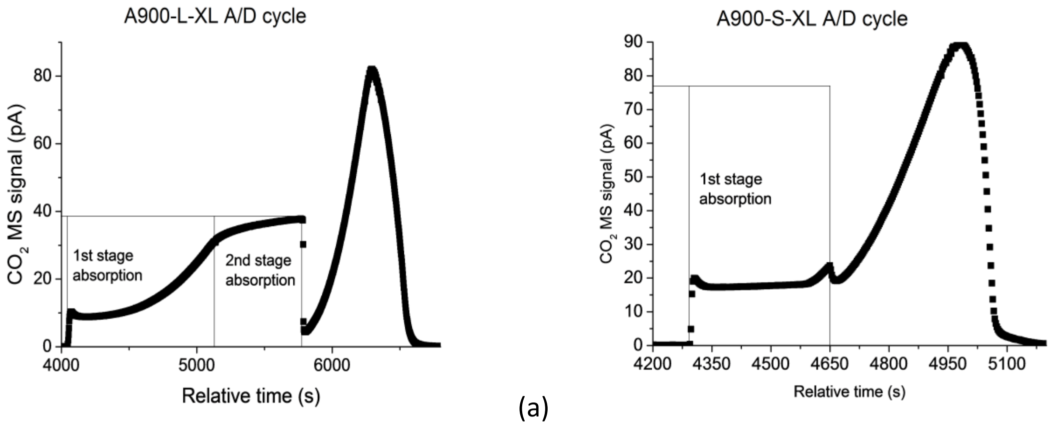
Figure 5: These are CaO samples A750, A850 and A900 from left to right.

Another unexpected outcome were the values for the internal area of the calcium carbonate samples. Due to the lack of an organic component it was thought that CaO from calcium carbonate could not produce the open, porous structures CaO from the other two precursors noticeably produced (freshly calcined samples from all three precursors were distinctly different, with calcium carbonate samples being the only ones to not expand noticeably after calcination). Some other mechanism must be responsible for the abnormally high surface area of especially C850, or the expansion of the sample during calcination must not have contributed as much to the internal surface area as was initially assumed.

The original plan was to continue the research with 2 – 4 of the best performing samples. However, the BET analysis took longer than expected, which is why the research continued along according to the predictions made beforehand.

C. *A/D cycle analysis*

Three types of A/D cycles were performed on the chosen samples (A900 and G900). Desorption time was kept constant at 12 minutes at a temperature of 800 °C, whereas absorption times differed between 6, 12 and 30 minutes. CO_2 absorption graphs were plotted with the obtained data and as a measure of the amount of absorbed CO_2 the area between the absorption curve and the 5% CO2 reference line was considered. The 5% CO_2 reference curve was determined at the start of a measurement series and was assumed to be constant throughout its entirety. See figure 6 for an example.



(a) (b)

Figure 6: (a) A single A900-L-XL A/D cycle, with the 5% CO_2 reference signal being positioned at an MS output of 39 pA. (b) A single A900-S-XL A/D cycle, with the 5% CO_2 reference signal being positioned at an MS output of 76 pA.

It was decided to work with the area corresponding with the amount of absorbed CO_2 instead of the easier to analyse desorption peak, because the CO_2 concentrations associated with the latter exceeded 5% by a large margin. It is suspected that CO_2 concentrations exceeded 10% during desorption and the temperature may have exceeded the linearity threshold as well, which means that the linear relationship between absorbed CO_2 and the outgoing signal of the spectroscope would no longer be valid, complicating things considerably.

Obtained absorption areas were normalised in respect to time in order to effectively compare areas from different cycles with each other. These areas are assumed to linearly proportional to the amount of absorbed CO_2.

Performance of a sample is defined on a per-cycle basis. See formula 1 for its definition.

Formula 1

$$P(n) = \frac{A_n}{A_i} \cdot 100\%$$

$P(n)$ = Performance of the nth cycle as a percentage of the initial area value.
A_n = Absorption area of the nth cycle enclosed by the relevant absorption line and the 5% CO_2 reference line.
A_i = Absorption area of the 1st cycle enclosed by the relevant absorption line and the 5% CO_2 reference line.

Cycle data for both precursors can be found below in figures 7 and 8.

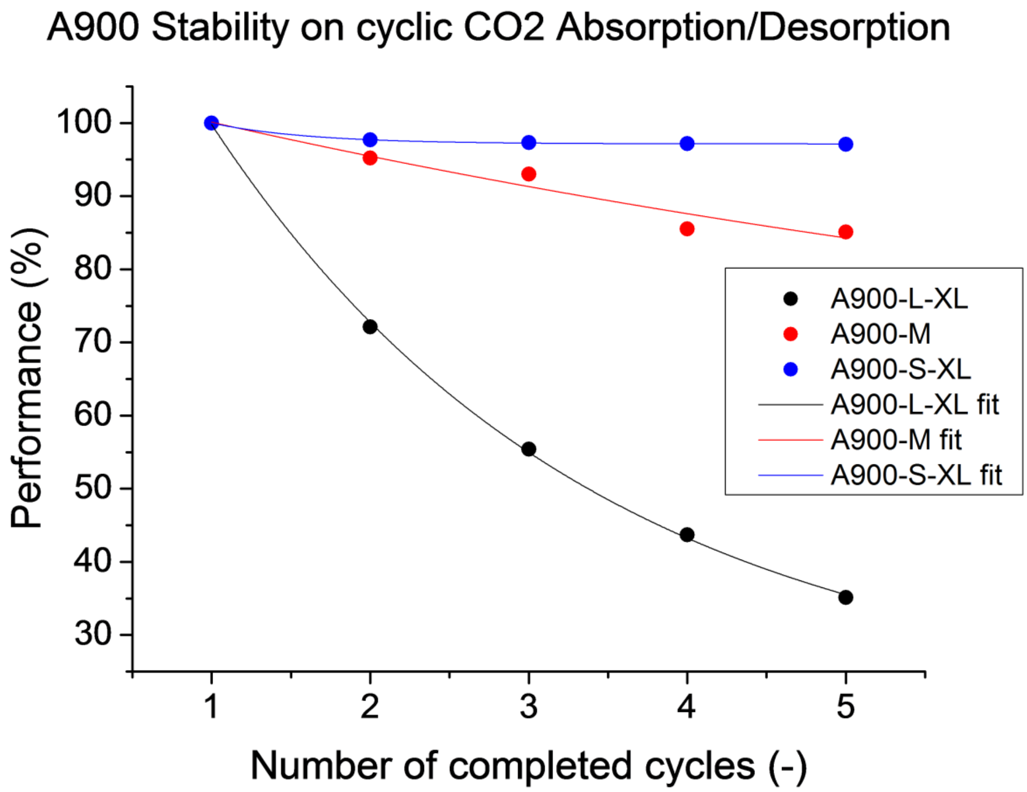


Figure 7: A900 sample stability whilst exposed to different A/D cycles. Data points were fitted with an exponentially decreasing function. Asymptotes of the fitted functions are at the following values: A900-L-XL (20,5% ± 2,5), A900-M (56,5% ± 85,0), A900-S-XL (97,1% ± 0,036).

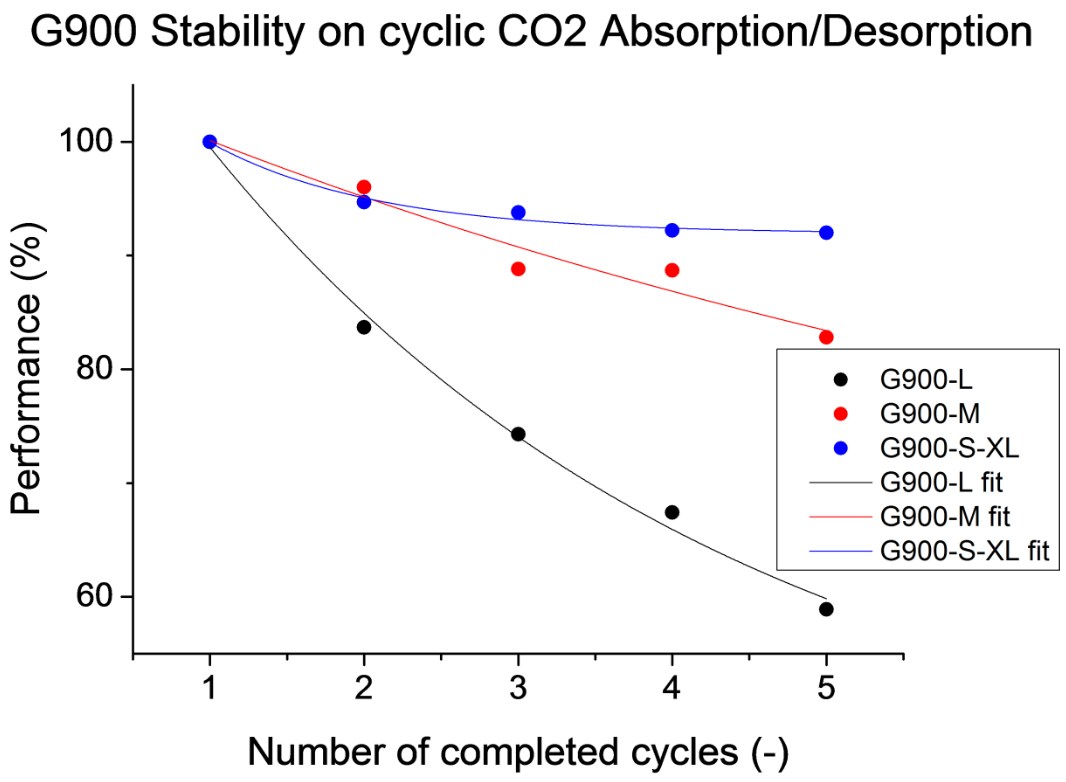


Figure 8: G900 sample stability whilst exposed to different A/D cycles. Data points were fitted with an exponentially decreasing function. Asymptotes of the fitted functions are at the following values: G900-L (41,8% ± 10,5), G900-M (56,5% ± 75,6), G900-S-XL (91,9% ± 0,58).

Even though the fits through mostly medium length cycles are inaccurate they are located within the expected region of the graph. Moreover the overarching trend is visible in both figure 7 and 8.

This data suggests that shorter absorption cycles vastly increase the stability of the used samples during multiple A/D cycles. However, these results are only indicative of the first five cycles. While it is expected that sample behaviour will not deviate much from the extrapolation it is entirely possible that sample performance could drop more significantly than currently predicted during exposure to more than 5 A/D cycles. This is definitely a suitable topic for continued research.

Especially the A900-S-XL sample could fall victim to possible continued degradation, considering the material has the potential to drop to a very low performance as seen in the A900-L-XL sample.

SEM pictures were taken of the relevant samples for side-by-side analysis.

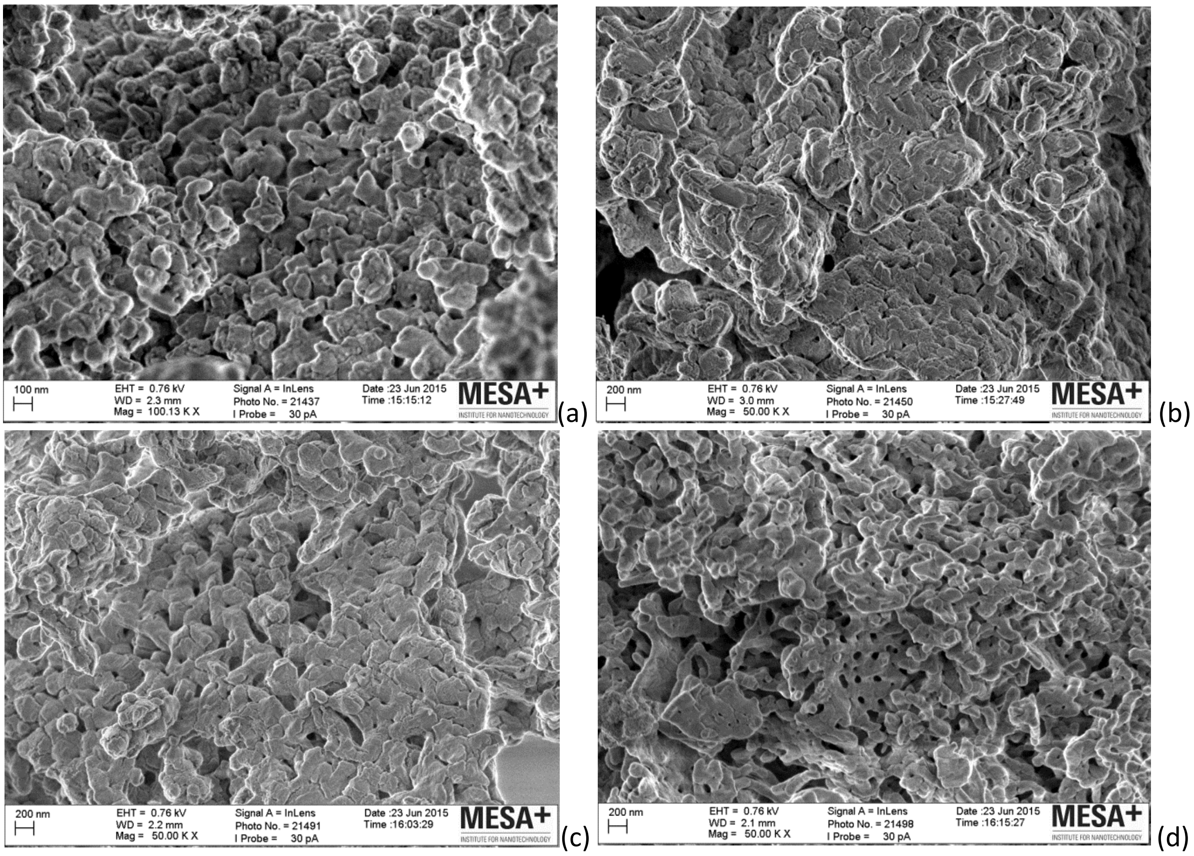


Figure 9: (a) SEM visualisation of unspent A900 sample, (b) SEM visualisation of the A900-L sample, (c) SEM visualisation of the A900-M sample, (d) SEM visualisation of the A900-S-XL sample.

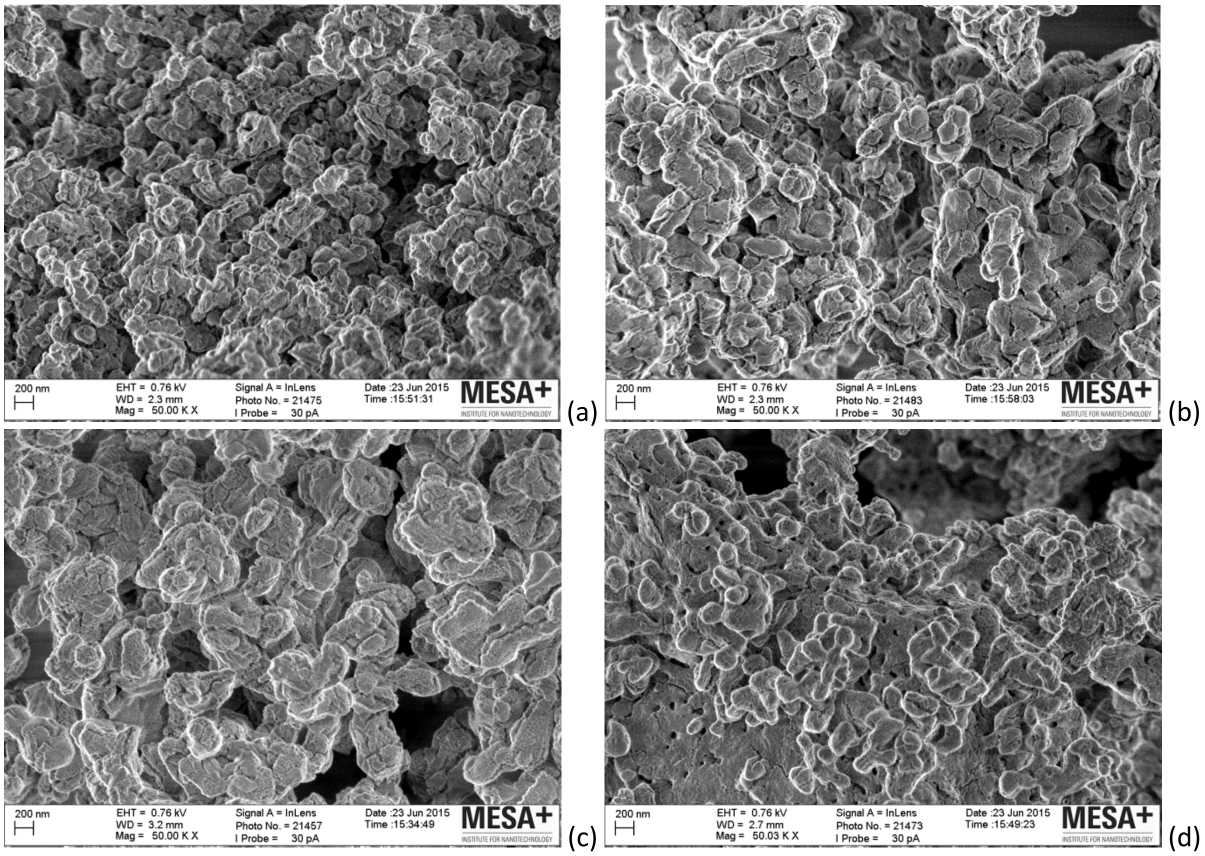


Figure 10: (a) SEM visualisation of unspent G900 sample, (b) SEM visualisation of the G900-L sample, (c) SEM visualisation of the G900-M sample, (d) SEM visualisation of the G900-S-XL sample.

It is clear that samples from both types of precursor are heavily affected by larger CO_2 loadings. Structures sinter and coalesce to form packed superstructures as seen in figure 9(b) and figure 10(b). The calcium L-ascorbate precursor seems to suffer worst from longer absorption cycles. Either pores close as calcium carbonate sinters during the absorption phase or grow considerably as structures make way to attach themselves to other growing particles. This is presumably causing the large performance drop.

On the other hand, it is the calcium L-ascorbate precursor as well which benefits most from shorter absorption cycles. As seen in figure 9(d) most of the original structure is maintained and occasionally mesh structures occur, of which an excellent example can be found slightly below the centre of figure 9(d). These mesh structures are very rigid, porous and provide a positive contribution to the internal surface area. Additionally they can withstand the negative influence of sintering over the course of many cycles, which is most likely the cause of the exceptional performance of the A900-S-XL sample.

By the look of these pictures one could conclude that the majority of the sintering happens when the sample is in the carbonate form at relatively low temperatures, considering the fact that all samples were heated to 800 °C and most CO_2 had already liberated by the time the temperature had finally reached the required value. At 800 °C pure CaO hardly sinters [16], so carbonate sintering must be the mechanism under which the long cycle samples have degraded so much. This also explains the effectiveness of the short cycles, as the sample spends a relatively short amount of time in the carbonate form and therefore does not have the opportunity to sinter as much as the other two samples.

Under careful examination a grain pattern can be distinguished on the surface of the sample in figure 8(d), most notably in the top-right corner of the picture. These could be nucleation sites where CaO can reversibly swell as it converts into $CaCO_3$. However, this is speculation and would require more thorough research if this were to be (dis)proven.

Conclusion

Of the researched samples A900-S-XL seems to perform best, seeming to stabilise at an impressive 97,1% of its initial performance. Furthermore the A900 sample has a superior internal surface area over G900 (16,80 m^2/g and 11,22 m^2/g respectively) and the short cycle absorption benefits the A900 sample more than G900, with A900-S-XL stabilising 5,2% higher than G900-S-XL.

Theoretically speaking C850-S-XL would most likely have the best results of all samples, closely followed by A850-S-XL. However, it is unknown how a calcium carbonate CaO sample would respond to exposure to shorter absorption cycles. Therefore it is likely that A850-S-XL would outperform C850-S-XL due to the excellent response of calcium L-ascorbate CaO samples to shorter absorption cycles.

Future research

Summarised, the following items are still in need of more extensive research:

- Confirmation of the long-term stability (20+ cycles) of short-cycle samples.
- Finding out how samples calcined at lower temperatures react to shorter A/D cycles.
- Finding out if shorter A/D cycles are still beneficial under more realistic operating conditions.
- Accurate definition of the amount of short A/D cycles equalling one long A/D cycle CO_2 loading-wise.

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Sources

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