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

Myron Plugge
University of Twente
m.plugge@student.utwente.nl

Guido Giammaria
University of Twente
g.giammaria@utwente.nl

Leon Lefferts
University of Twente
l.lefferts@utwente.nl

ABSTRACT

CaO was prepared from three different precursors (calcium carbonate, calcium L-ascorbate, calcium D-gluconate). The samples were calcined at four different temperatures (750 °C, 800 °C, 850 °C, 900 °C) and those with the highest internal surface area were chosen for research on the absorption/desorption cycles.

The sample prepared from calcium carbonate and calcined at 850 °C had the highest internal surface area (34,54 m^2/g). The samples prepared from calcium ascorbate sample seemed to benefit most from shorter absorption cycles, increasing its projected long-term performance from 20,5% to an impressive 97,1%.

Keywords

CaO, absorption, short cycle, calcination

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. Furthermore, all of the current literature describes the use of complete absorption/desorption (A/D) cycles. CaO is allowed to fully convert to $CaCO_3$, only after which desorption is started. The absorption phase is divided into two phases: one rapid surface covering phase and a second diffusion controlled one [7], the latter of which requires most time to complete. It is hypothesised that if only the first stage absorption were to take place, the sample would not have to spend as much time at the desorption temperature and would therefore would not sinter as much, effectively increasing the stability of the sample should multiple short cycles degrade the sample to a lesser degree than a single long cycle.

These two problems form the foundation of this research. Which precursor/calcination temperature combination yields the sample with the largest internal surface area? In addition to that, what type of A/D cycle would be most beneficial to the stability of the examined sample?

It is suspected that higher calcination temperatures will benefit the internal surface area, as the organic component will surely be liberated from the sample in those conditions. Furthermore it is expected to sinter slightly, possibly enhancing its stability on the long term. Finally, shorter A/D cycles are expected to be beneficial to the stability of the sample, preserving its porous structure and enabling it to capture more CO_2 during long-term operation compared with 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.

Once calcined the samples were ground utilising 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.

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 (S, M and L, respectively) 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.

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

Summarised, the samples are categorised as seen in table 1. A900 and G900 samples were used in the A/D cycle research and therefore have multiple samples.

Table 1: Classification of the produced samples.

	Precursor		
Calcination temperature (°C)	**$CaCO_3$**	**Calcium L-Asc.**	**Calcium D-Gluc.**
750	C750	A750	-
800	C800	A800	G800
850	C850	A850	G850
900	C900	A900-L-XL A900-M A900-S-XL	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

The following results were obtained over all of the measurements. The first results (in order) were used to obtain the graphs further along this section, eventually enabling a conclusion to be drawn.

BET surface analysis

BET surface analysis yielded the results found in table 2.

Table 2: BET surface areas of the produced samples.

	Precursor		
Calcination temperature (°C)	**Calcium Carbonate (m^2/g)**	**Calcium L-Asc. (m^2/g)**	**Calcium D-Gluc. (m^2/g)**
750	N/A	40,4	-
800	12,8	27,6	16,3
850	34,5	34,1	20,5
900	10,0	16,8	11,22

It turns out that the highest internal surface areas are found at a calcination temperature of 850 °C instead of 900 °C. SEM imaging revealed the unspent 900 °C sample to have slightly sintered, explaining the higher internal surface area at 850 °C.

It is also worth noticing that calcium carbonate produced the best sample surface area-wise. It was expected that as the complex organometallic precursors decomposed a porous and open structure would be left with a higher internal surface area than the carbonate precursor.

A/D cycle research

Performance of a tested sample was defined as a percentage of its first performance in a measurement series. The amount of absorbed CO_2 is considered from spectrometer data. For a single cycle analysis, see figure 1.

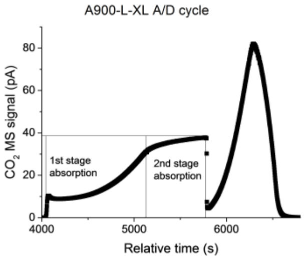

Figure 1: Analysis of a single A/D cycle, showing the two staged absorption and a final desorption peak.

During the measurement performed in figure 1 the 5% CO_2 atmosphere value was found at approximately 39 pA. It is possible to determine the total amount of absorbed CO_2 by calculating the area between the reference line and the absorption line. This area reduced under the influence of multiple cycles, which can be seen in figures 2 and 3.

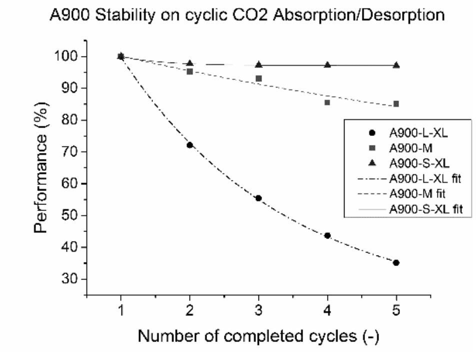

Figure 2: A900 sample capacity whilst exposed to multiple A/D cycles.

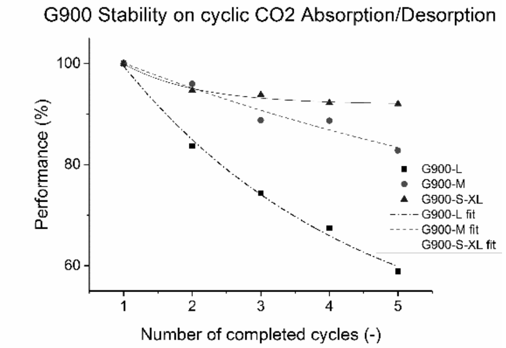

Figure 3: G900 sample capacity whilst exposed to multiple A/D cycles.

The data points in figures 2 and 3 were fitted with an exponentially decreasing function. The asymptote of said function is indicative of the projected long term stability in comparison with the first cycle. See table 3 for these values.

Table 3: Estimated asymptote values (percentage of initial performance).

	G900 samples	A900 samples
Long cycle	41,8% ± 10,5	20,5% ± 2,5
Medium cycle	56,5% ± 75,6	56,5% ± 85,0
Short cycle	91,9% ± 0,58	97,1% ± 0,036

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. Sample behaviour beyond the fifth cycle is unknown. Therefore, seeing that sample performance can potentially drop to a large degree during long term operation it remains to be seen by how much long term stability is enhanced by using short A/D cycles.

These samples were visualized using SEM imaging in order to compare the samples on a structural level.

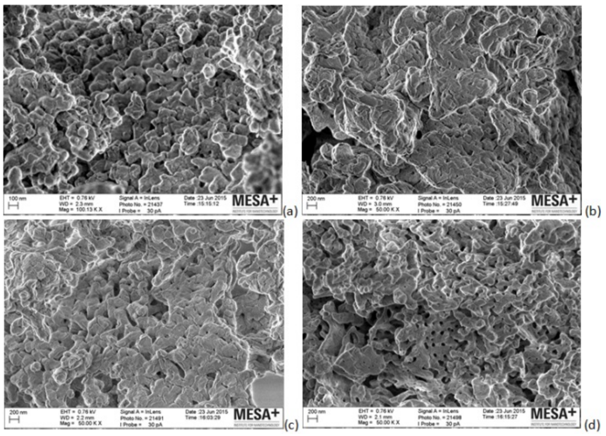

Figure 2:(a) unspent A900 sample, (b) A900-L sample (c) A900-M sample, (d) A900-S-XL sample.

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 3(b). The calcium L-ascorbate precursor suffered 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.

The calcium L-ascorbate precursor based samples are also the ones which benefit most from shorter absorption cycles. As seen in figure 3(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 3(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, as 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 [8], 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.

This opens up many new possibilities for future research, as each of the four types of CaO mentioned in the introduction might react differently to short cycles. This small step will hopefully lead to a better understanding of the underlying mechanisms.

CONCLUSION

BET analysis has shown that the C850 sample (see table 1 for sample classification) has the largest internal surface area (34,5 m^2/g), which contradicts initial expectations.

Of the samples which underwent A/D cycles 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. The hypothesis concerning shorter A/D cycles has not been disproven, but requires more research in order to fully (dis)prove it.

Theoretically speaking C850-S-XL would probably have the best results of all samples, followed by A850-S-XL.

There is still a long way to go if this method were to be applied in practice. It shows promise, but requires more research to see whether or not the discussed method is applicable under realistic operating conditions.

ROLE OF THE STUDENT

Myron Plugge was a bachelor student working under the supervision of Guido Giammaria when the research in this report was performed. The topic fell under the PhD research of the supervisor, who suggested to check different calcination temperatures with varying precursors. The student suggested the short cycle research, performed the research and made the majority of the samples himself. The student is responsible for this literature and conclusions drawn within.

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 if shorter A/D cycles are still beneficial under more realistic operating conditions (non-argon atmospheres).
- Accurate definition of the amount of short A/D cycles equalling one long A/D cycle.

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