Carbonate looping process
for CO$_2$ capture

Master Thesis

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Preface

This Master Thesis was carried out at the Combustion and Harmful Emission Control (CHEC) Research Centre at the Chemical Engineering Department in the Danmarks Tekniske Universitet (DTU). Supervisors for the project were Kim Dam-Johansen, Jytte Boll Illerup and Weigang Lin.

I would like to thank my supervisors for offering me such interesting and challenging project as well as to help me to improve my reports with imaginative suggestions and comments. I would like to thank all the technicians and PhD researchers that have also helped me in many questions I have had during these six months working in what for me was a new university when I began.
Abstract

Climate change is one of the greatest challenges issues facing the world this century. Cement industry represents around 5% of the total anthropogenic carbon dioxide emissions worldwide. The carbonate looping process seems a promising CO$_2$ capture technology for cement industry as the sub-product can be used in the cement manufacturing process. It is based in the reversible reaction between CaO and CaCO$_3$ to produce a stream with high CO$_2$ concentration. One of the main drawbacks of this technology is the loss of adsorption capacity of the sorbent.

Limestone samples have been calcined under different conditions in a tubular reactor and analyzed in the BET apparatus. Also, limestone was tested in a thermogravimetric analyzer (TGA). All experiments were performed at realistic carbonation-calcination conditions unlike most of the experimental work presented in the literature. The application of realistic conditions accelerates and increases sintering as well as the CO$_2$ carrying capacity of the sorbent.
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1. Background

1.1. Climate change and carbon dioxide emissions

Climate change is one of the greatest challenging issues facing the world this century. Carbon dioxide, methane, ozone, nitrous oxide, Sulphur Hexafluoride, Perfluorocarbons and Hydroflourocarbons are known as the Greenhouse Gases (GHG). Global GHG emissions have grown in the recent years. Figure 1.1 extracted from the European Environment Agency (EEA) shows the sources of GHG and the GHG gases distribution in climate change contribution:

![Figure 1.1. (a) Greenhouse gases emissions in the EU-27 by sector in 2009; (b) Greenhouse gases emissions in the EU-27 by gas in 2009 (1)](image)

1.2. Cement industry and carbon dioxide

A cement plant comprises the following steps: raw material preparation (crushing and milling), pre-heating, pre-calcining, kiln firing, clinker and additive mixing and cooling, cement milling and finally storage and packing.

![Figure 1.2. Cement plant scheme (2)](image)
The raw materials are crushed and milled into a fine powder before entering a pre-heater and being fed into a rotating kiln. Fuels are burnt at the lower end of the kiln so that it reaches 2000°C, allowing the materials to be heated to around 1500°C, where they become partially molten. When the limestone (mainly CaCO$_3$) reaches about 900°C, it undergoes the chemical reaction known as calcination (equation 1.1) and carbon dioxide is released and calcium oxide is produced. (2)

$$\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g) \quad (\text{Eq. 1.1})$$

Carbon dioxide emissions in the cement industry are accounted to be a 5% of the total anthropogenic emissions worldwide. Cement industry emits nearly 900kg of CO$_2$ per metric ton of cement produced (3). Around 50% of the total CO$_2$ is produced in the calcination process of limestone (equation 1.1), 40% from combustion of fuels (coal, coke, tyres, waste oil, solvents, sewage sludge...) in the kiln, 5% from transportation and the remaining 5% from the electricity used in manufacturing operations. The used fuel effects the cement plant emission distribution, with the ones that use coal releasing around 60-70% of CO$_2$ the total plant emissions from the fuel. (2)

Cement plants are large industrial sources of CO$_2$ emissions, with high concentrations of CO$_2$ in the flue gases (accounted to be 14-33%) in comparison with coal-fired plants (12,5-12,8 %) or gas-fired plants (7,4-7,7 %) (4). Thus, it represents a very interesting opportunity to implement Carbon Capture and Storage (CCS) technologies (2). Available technologies are: amine scrubbing, oxy-firing combustion and carbonate looping.

Amine scrubbing is a mature technology which consists to absorb the CO$_2$ from the flue gas in an amine (monoethanolamine) solution and its posterior separation from the sorbent in a stripping tower where pure CO$_2$ is obtained and the sorbent (amine) is regenerated to its posterior use in the absorption tower. The main challenge, however, lies in scale-up of this process and to adapt it for gases with several contaminants for the scrubbing performance.

Oxy-firing consists to replace the air used for the fuel combustion by pure oxygen with an air separation unit (ASU). The CO$_2$-rich flue gas is recycled to moderate the flame temperature, apart from obtaining a flue gas with a very high CO$_2$ content.

### 1.3. Carbonate looping for CO$_2$ capture

Carbonate looping is based on the separation of carbon dioxide from flue gases by the use of lime (CaO$_2$, generated from limestone calcination) in a cycled system. CaO particles react with CO$_2$ from the flue gas in a fluidized bed called carbonator at a temperature around 650°C, removing it from the flue gas until very low levels. The generated calcium carbonate (CaCO$_3$) is separated with cyclones from the flue gas and is fed to the second fluidized bed working around 900°C called calciner, where CO$_2$ is stripped and CaO is produced and recycled to the carbonator. The required energy in the calciner is supplied by oxy-firing, in order to create an almost pure CO$_2$ stream without N$_2$ at the exit of the calciner. A scheme of this process is shown in the Figure 1.3:
Some of the advantages of this process are listed below:

- Small efficiency penalty (accounted to be 6-8% considering \( \text{CO}_2 \) compression).
- Potential in large-scale plants.
- Excellent integration with cement manufacturing (spent CaO can be used in cement production).
- Cheap sorbent: CaO is produced from CaCO\(_3\), which has a high availability in the nature as well as its geographical distribution.
- Both carbonation and calcination take place at high temperature (higher than 600ºC), enabling an effective recovery of calcination energy in the carbonator.
- The system does not require high pressure conditions unlike the other carbon capture systems.

However, the main drawback of this technology is that the sorbent cannot be recycled for many cycles. The \( \text{CO}_2 \) adsorption capacity decreases with the number of cycles and a make-up flow of sorbent is necessary in order to replace the spent CaO. In fact, the present project will be focused to investigate the causes and parameters that affect the sorbent decay.

### 1.4. Scope of project

This project is focused in the decay of sorbent. Literature study, laboratory experiments and modelling work have been performed. The laboratory work has been carried out in the Combustion and Harmful Emission Control (CHEC) at the DTU Chemical Engineering Department. Experiments have been performed in a high speed thermal gravimetric analysis (TGA), horizontal tubular reactor, surface area and pore structure analysis (BET) and scanning electron microscopy (SEM).
Limestone has been tested under different carbonation/calcination conditions in a tubular reactor and the obtained samples were analyzed in a BET and SEM apparatus. The project has carried out experimentation about sintering under different conditions (various temperatures, residence times, atmosphere composition…) and investigation on SO₂ effect in different concentrations and stages of the process (carbonation and calcination) with the aim to investigate the sorbent decay.

A detailed explanation of the apparatus used in the experimental work can be found in Section 3.
2. Literature study

This section shows the most interesting works that have been read during the compilation of information. Works explaining the properties of the calcination and carbonation reaction, the parameters that influence the sorbent deactivation, investigation about sintering as well as modelling of the process are described in this section.

2.1. The reversible reaction of lime and limestone: Carbonation and calcination

2.1.1. Introduction

Carbonation is known as the formation of CaCO₃ from calcium oxide and carbon dioxide and calcination as the decomposition of limestone to CaO and CO₂. This reversible reaction is shown below:

\[
\text{CaO (s) + CO}_2\text{(g) } \leftrightarrow \text{CaCO}_3\text{(s)} \quad \Delta H_{r,298K} = -178 \text{ kJ/mol} \quad \text{(Eq 2.1.)}
\]

The carbonation reaction is exothermic and its reversible reaction (calcination) is endothermic. The reaction depends on the CO₂ partial pressure and follows the equilibrium described by Baker (6):

\[
\log P_e = 7.079 - 38.000 / 4.574T
\]

(Eq 2.2)

where \( P_e \) is the CO₂ partial pressure in atm and \( T \) the temperature in K. It was calculated using experimental data with temperatures above 1170K and CO₂ pressures above 101kPa, as is to be expected to correlate well with data in these conditions but there are some deviations at lower temperatures and lower CO₂ partial pressures. In fact, the carbonation reaction is produced at a temperature about 650-700°C and with CO₂ partial pressure about 10kPa. For that reason, another equation is utilized quoted by Silcox et al. (7). Temperature in K and pressure in atm:

\[
P_e = 4.137 \times 10^{-7} \exp \left( -\frac{20474}{T} \right)
\]

(Eq 2.3)

As it is observed in the following chart the equations 2.2 and 2.3 are represent quite similar numbers for temperatures between 750°C and 900°C while for temperatures above 700°C a difference can be seen.
Then, an upper limit to the CO$_2$ capture efficiency is given by the equilibrium of the carbonation reaction at the temperature and the pressure of carbonator. Figure 2.2 plots the mentioned equilibrium of the Equation 2.1:

\[ \text{Figure 2.1. Equations 2.2 and 2.3 comparison for a temperature range between 600 and 1000°C} \]

\[ \text{Figure 2.2. The equilibrium pressure of CO}_2\text{ over CaO (P}_{eq}\text{ in atm, T in °C) (3)} \]

### 2.1.2. Calcination reaction

Calcination of limestone is the main reaction in cement production. It is also used in the carbonate looping for CO$_2$ capture. Obtaining a reliable kinetic and mechanistic data for reversible solid-state decomposition processes such as calcination is difficult, mainly for (a) the CO$_2$ concentration, which inhibits the reaction, (b) particle size, which may
introduce thermal and mass transfer limitations and (c) catalysis or inhibition by impurities (8). By now, no unified expression has been established. Nevertheless, it does not have very importance as the calcination reaction completes quite fast at temperatures to overcome the limestone decomposition (920ºC). A wide compilation of kinetic equations is found in the work performed by B.R. Stanmore and P. Gilot (8).

As calcination is an endothermic reaction needs heat and high temperatures so sintering can happen. Sintering refers to changes in pore shape, pore shrinkage and grain growth that particles of CaO undergo during heating. Sintering is widely documented in the Section 2.3 due its important effects in loss of capacity of the sorbent and its importance in this project.

### 2.1.3. Carbonation reaction

Carbonation is characterised by a fast initial reaction rate followed by a transition to a very slow reaction rate. The rate of reaction of the fast stage depends on the surface area of the reacting particle whereas in the slow stage is controlled by the diffusion. The reason of this fact is that while CaCO$_3$ (molar volume of 36.9 cm$^3$/g) is being forming in the CaO (molar volume 16.9 cm$^3$/g) particle, a layer of the former product is created and the diffusion through it becomes the controller of the product formation impeding CO$_2$ transport. Thus, contrary to calcination, the carbonation reaction could not complete because of pore blockage.

The main problem of cycled calcinations/carbonations is the decrease of the sorbent adsorption capacity that undergo with the number of cycles. The Figure 2.3 shows the typical conversion curves versus time for different cycles in 5 minutes carbonation processes:

![Figure 2.3](image-url)

**Figure 2.3. Conversion curves vs. Time for different cycle numbers. Limestone Piaseck; dp 0,4-0,6mm; $p_{CO_2}$ 0,01MPa; $T_{carbonation}$ 650°C, for 5min; $T_{calcination}$ 900°C, for 5min (9)**

As it can be observed in the Figure 2.3 the adsorption capacity decreases with the number of cycles (from 0,6 for the first cycle to 0,13 for the 50$^{th}$ cycle). Nevertheless, the path followed to reach the maximum conversion is very similar. Sorbent decay for different conditions has been widely studied in the literature works which have performed experiences with different particle sizes, types of limestone, atmosphere, temperature, heating rate, etc. All they are summarized in Section 2.2.

Another important parameter in the sorbent decay is the presence of SO$_2$ in the gas. The molar volume of CaSO$_4$ is even higher than that of CaCO$_3$ (46,0 versus 36,9 cm3/mol), so the problem of pore plugging is accentuated (8).
Alvarez and Abanades (10) showed the variation of the conversion and the closed pore volume of a CaO particle with the time, as well as the CaO conversion with the closed pore volume for the 30th cycle. These results are presented in the Figure 2.4:

![Figure 2.4](image_url)

**Figure 2.4. Structural transformations of a calcine (30 cycles; recarbonation time, 30min) with carbonation conversion/time. Top(a): variation of carbonation conversion and product layer thickness with time. Middle (b): variation of the percentage of occluded pore volume with carbonation time. Bottom (c): variation of conversion and product layer thickness with the percentage of pore closure (10)**

Figure 2.4 (a) shows the two stages of carbonation: the fast one, produced in around 5 minutes where about 75% of the CO\(_2\) is captured; and the slow stage, controlled by diffusion of the CO\(_2\) in the layer product. Figure 2.4 (b) shows the same trend: half of the total pore occlusion occurs in the fast stage of carbonation. Finally, it can be shown in Figure 2.4 (c) the linear trend of conversion with the closed pore volume except in the beginning of the carbonation, where the reaction takes part without substantial pore blockage. Thus, it is clear that in the first stage of carbonation the conversion is quite fast as well as the process of pore closure. It is observed that in 5min of carbonation around 40% of the available pore volume has been closed and 10% of the particle has been converted (the maximum conversion was 14%).
2.2. Parameters influencing on CO₂ Carrying Capacity

In this section, the influence of various parameters in the CO₂ carrying capacity is shown. The most interesting results and experiments were determined and performed by Abanades et al (11) and Grasa et al (9).

2.2.1. Particle size

To investigate the possible effect of the particle size on the carbonation reaction rate, four narrow particle size fractions (0.25-0.4, 0.4-0.6, 0.6-0.8 and 0.8-1 mm) of a limestone named “La Blanca” were tested by Grasa et al (9) in a TGA apparatus. Particles with a pore structure similar to Figure 2.5 (left) correspondent to the CaO structure after one calcination were expected to show increasing resistance to CO₂ diffusion towards the free CaO surfaces in the interior of the particle as the particle sizes increased. As it can be seen in the Figure 2.6 (left): the more particle size, the less reaction rate. Thus, it can be concluded that for the first calcination, diffusion effects must be responsible for the slower carbonation rates of the larger particles. However, the quantitative differences in the slopes of the carbonation curves are modest as well as the maximum conversion achieved was very similar for all the particle sizes (9):

![Figure 2.5. View of the interior of a particle of CaO after one calcination (left) and after 30 carbonation/calcination cycles (right) (9)](image)

![Figure 2.6. Conversion curves vs. Time for different particle size. Limestone: La Blanca, \(p_{\text{CO}_2}\) 0.01MPa, \(T_{\text{carbonation}}\) 650°C, for 20min; \(T_{\text{calcination}}\) 850°C, for 15min. (Left) cycle 1; (right) cycle 20. Note that the Y-axis is different for both figures. (9)](image)
The Figure 2.6 (right) shows the conversion of CaO in the 20th cycle. As it is expected, the sorbent capacity (conversion at the end of the period) is lower for higher cycles. Also, the different slopes of the first calcinations cycle have disappeared, meaning that there are no diffusion effects in the interior of the particles and the reaction rate must be controlled by the reaction mechanism taking place uniformly on a free surface of CaO.

It can be also concluded from the Figure 2.5 that the particles with smaller pore size (left of Figure 2.5) show higher CO$_2$ resistance but have higher superficial area meaning in higher conversions. On the other hand, higher diameters (Figure 2.5, right) mean an easier transport of CO$_2$ in the interior of the particle but at the same time a decrease of the superficial area which leads to lower conversions.

In another publication of G. Grasa and Abanades (11), it was concluded that the particle size does not have an effect in the CO$_2$ adsorption capacity of the sorbent that remains determined only by the number of carbonation/calcination cycles as it can be seen in the Figure 2.7.

![Figure 2.7. Conversion vs cycle number for experiments carried out with different particle size intervals. Limestone: La Blanca. Calcination temperature 850°C, 20min; carbonation temperature 650°C, 20min; p$_{CO2}$ 0.01MPa (11)](image)

### 2.2.2. Limestone type

The issue of how much the type of limestone (or dolomite) affects the carbonation capacity has been a subject of debate. It is known that limestone type can strongly affect the performance of CaO as a SO$_2$ from combustion gases to form CaSO$_4$. Different limestone can generate very different textures on calcinations and this can lead to different sulfation patterns and maximum levels of sulfation (9). However, the sulfation reaction mechanism is different of the carbonation mechanism. In the first case, there is a pore blockage because of the calcium sulphate molar volume, higher than CaO and CaCO$_3$.

Figure 2.8 shows the conversion curves for five different types of limestone (La Blanca, Piaseck, Cadomin, Havelock, Gotland) for the cycle number 40. As it can be observed, there are no appreciable differences in the slopes of the fast stage of carbonation. A little difference can be appreciated during the slow carbonation stage, which is governed by the diffusion of the reactant through the product layer of CaCO$_3$. Nevertheless, the residual conversion for all the tested limestones is between 0.05 and 0.15.
Figure 2.8. Conversion curves vs. Time for different limestone types. Particle size 0.4-0.6mm, $p_{CO_2}$ 0.01MPa, Tcarbonation 650°C, for 20min; Tcalcination 850°C, for 15min (9)

Figure 2.9 shows the experiences performed by Grasa and Abanades (11). Six types of limestone and a dolomite (Sierra de Arcos, approx. 50% MgCO$_3$) were tested. As before, it shows small differences except for the case of the dolomite and the Gotland limestone. Gotland limestone shows a remarkably poor performance from the first few cycles whereas the dolomite shows a high calcium conversion, but around 50% of the sorbent is unconverted MgO.

Figure 2.10 plots the weight fractions (grams of CO$_2$ captured per gram of parent sorbent) and it can be seen that dolomite shows a very similar tendency to the majority of limestones.

Figure 2.9. Conversion vs number of cycles for experiments carried out with different types of limestones. Particle size 0.4-0.6mm. Calcination temperature 850°C, 10min; carbonation temperature 650°C, 10min; $p_{CO_2}$ 0.01MPa (11)
Figure 2.10. Comparison of sorbent capture capacity (for Piaseck limestone and dolomite) along the cycles in terms of grams of CO$_2$ captured per gram of parent sorbent. Calcination temperature 900°C, 10min; carbonation temperature 650°C, 10min; $p_{CO_2}$ of 0.01MPa (11)

The small differences between limestones can be associated to impurities on the free surfaces of CaO that can lead to a different reaction patterns as in the case of the SO$_2$ presence.

2.2.3. Calcination temperature

S. Senthoorselvan (12) carried out some experiences in order to determine the calcinations temperature effects in the CaO conversion rate. Figure 2.11 shows these conversion for the first four cycles at which samples were calcined at 930°C, 875°C, 800°C and 750°C. It was observed that the higher calcinations temperature, the lower conversion. Also, it is seen that the absorption capacity decreases with the number of cycles.

Figure 2.11. Gotland limestone conversion of CaO (%mol) to CaCO$_3$ is plotted as a function of the number of cycles for a range of calcinations temperatures from 750°C to 930°C (12)

However, the higher calcination temperature means a higher calcination rate as it is shown in the Figure 2.12 representing the calcinations rates for the first cycle:
Grasa and Abanades (11) performed experiments with different calcinations temperatures as well. As it can be seen in the Figure 2.13, there is a range of temperatures (up to 950°C) where the calcinations temperature does not affect the sorbent performance much. At the lower temperatures, there is only a little improvement in the results.

The curve correspondent to a calcinations temperature of 1060°C showing a high conversion is added from the experimental work done by Curran et Al. (13). The curve for temperatures higher than 1200°C is extracted from the works performed by Deutch and Heller-Kallai (14) and were included in the graph as an example of high sintering conditions (calcinations temperature over 1200°C for several minutes, under $p_{\text{CO}_2}$ of 0.1MPa).

Increasing the temperature up to 1000°C can clearly cause the behaviour of the sorbent to deteriorate. The sintering mechanism is the responsible for this decay of the CO$_2$ carrying capacity and is drastically enhanced with temperature over 950-1000°C. However, further investigation is needed as other investigations that have been performed show some discrepancies with these results.
2.2.4. Calcination times

At a determined temperature, calcinations time is known to affect the texture of the calcines derived from limestone. Figure 2.14 shows that the maximum conversion can vary considerably for the first cycle. However, this difference disappears when the number of cycles is increased. The sintering mechanism imposes a decay process much stronger than the one given by extended calcinations times (11).

![Figure 2.14. Sorbent conversion along the number of cycles for different calcination times. Limestone: La Blanca 0.4-0.6mm. Calcination temperature 950°C, 5min; carbonation temperature 650°C, 5min; \( p_{\text{CO}_2} 0.01\text{MPa} \) (11)](image)

2.2.5. Carbonation temperature

A range of temperatures between 550 to 700°C, close to the operation conditions for the typical capture systems, were analysed by Grasa et Al (9). Figure 2.15 plots the conversion curves for the cycle 40 and 150. The slopes corresponents to the fast carbonation stage are very similar for the range of temperatures studies. This indicates the poor dependency of the kinetic parameter on temperature.

![Figure 2.15. Conversion curves vs time for different Tcarbonation. Limestone: Piasek, dp 0.4-0.6, \( p_{\text{CO}_2} 0.01\text{MPa}, T\text{calcination} 900^\circ\text{C}, 15\text{min}. (\text{Left}) \text{cycle} 40; (\text{right}) \text{cycle} 150 \) (9)](image)
2.2.6. Reaction atmosphere

The fast period of the carbonation stage has been reported to correlate with a first-order kinetic whereas the slow stage has been reported to be independent of CO\textsubscript{2} partial pressures except when close to equilibrium. Bhatia and Perlmutter (15) showed that when the partial pressure of CO\textsubscript{2} is well above the decomposition pressure, it has a little effect on the carbonation rate.

Grasa et Al (9) experimented with carbonation/calcination cycles varying the CO\textsubscript{2} concentration in the reaction atmosphere, ranging from 0.002 to 0.1MPa. Figure 2.16 (left) shows the conversion curves for different CO\textsubscript{2} atmospheres and Figure 2.16 (right) shows the linearity (first-order reaction) for the fast stage of the carbonation. It can be appreciated that the slopes for the fast stage are strongly affected by the concentration of the reactant.

![Figure 2.16](image1)

*Figure 2.16. (Left) Conversion curves vs time for different p_{CO2}, cycle 1. Limestone: Piaseck, dp 0.4-0.6mm, Tcarbonation 650°C, 20min; Tcalcination 900°C, 15min (right) relative reaction rate vs CO\textsubscript{2} concentration (9)*

The carbonation curves for the cycles 10 and 40 are also plotted in the Figure 2.17:

![Figure 2.17](image2)

*Figure 2.17. Conversion curves vs time for different p_{CO2}. Limestone: Piaseck, dp 0.4-0.6mm, Tcarbonation 650°C, 20min; Tcalcination 900°C, 15min. (Left) cycle 10; (right) cycle 40 (9)*
Further research by the group of Grasa et al (11) for the same range of CO₂ concentrations but for different conditions was performed. Data from an experience from Curran et al with a CO₂ partial pressure of 0.4MPa was also included in the results. It can be observed that the maximum carbonate rate is dependent on the CO₂ partial pressure. However, this difference disappears when the cycle number is increased. Figure 2.18 shows these tendencies:

![Conversion vs cycle number for different carbonation/calcination atmospheres. Limestone: La Blanca 0.4-0.6mm. Calcination temperature 950°C; carbonation temperature 650°C, 5min (11)](image)

**Figure 2.18.** Conversion vs cycle number for different carbonation/calcination atmospheres. Limestone: La Blanca 0.4-0.6mm. Calcination temperature 950°C; carbonation temperature 650°C, 5min (11)

### 2.2.7. Comments

The parameters influencing the CO₂ carrying capacity have been well investigated by the Spanish research group for many years. Further experimentation could be carried out with more realistic conditions for carbonate looping integrated in the cement industry using also oxi-firing. It means a change in the atmosphere conditions in both calcination (around 90% of CO₂) and carbonation (around 20% CO₂). However, the work summarized in this section gives a general idea about the influence of the analyzed parameters in the sorbent decay.

### 2.3. Sintering

Sintering of CaO is believed to be the main cause of sorbent deactivation, as evidenced by the change of sorbent surface texture after multiple cycles. The surface textures of cycled limestones usually show growing macropores, as well as shrinkage of smaller pores.

#### 2.3.1. Surface area

R. Borgwardt (16) investigated the sintering process for CaO obtained from pure calcium oxide and from limestone. The results show that the higher temperature produces a higher reduction on surface area. Figure 2.19 and Figure 2.20 plot these results:
R. Borgwardt correlated the loss of surface area and porosity after 15min sintering for different temperatures in a nitrogen atmosphere. It can be observed how increasing the temperature accelerates sintering. Figure 2.21 shows this fact:
Figure 2.21. Porosity and surface area of 2-µm limestone CaO particles after 15min of sintering in a N\textsubscript{2} atmosphere (16)

2.3.2. Pore size distribution

Sun et al (17) performed several experiences in samples for various calcination/carbonation conditions. A sintering model was formulated in order to explain the behaviour of sorbents during cyclic calcination and carbonation.

The PSDs (Pore Size Distributions) after different carbonation/calcination times show that changing the carbonation time does not affects the subsequent calcine structure at 850°C, as it can be observed in the Figure 2.22.

![Figure 2.22. PSD: Effect of carbonation time. Experiments at 850°C for calcination and carbonation in thermogravimetric reactor (TGR). 215-250µm Strasburg particles. Calcination with 100% N\textsubscript{2}; carbonation with 100% CO\textsubscript{2}, fast stage completed (17)](image)

In these experiments each carbonation step was allowed to proceed long enough to complete the fast stage. Thus, it implies that lime sintering has no memory in carbonation history for the first cycle, or that the carbonation makes no contribution to CaO sintering. It is believed that during calcination the recrystallization from CaCO\textsubscript{3} to CaO eliminates all structural differences caused by carbonation if without sintering. (17)

The P.Sun et al. report concluded that calcination is the sole stage considered for sintering. With the purpose to investigate if the carbonate process blocks the pores as it is usually found for CaO sulfation the following procedure was done. A calcined sample was carbonated long time in order to allow completing at least the fast stage of the process and the obtained product was split in two parts. One of these parts was grounded into a fine powder to expose the blocked pores and both were analyzed using mercury intrusion. Figure 2.23 shows the PSDs of the two carbonated samples (grounded and non-grounded) and the calcine prior to being carbonated. As it can be seen, no appreciable differences are observed in the PSD diagram.
In the same investigation carried out by Sun et al pore size distributions (PSDs) for different calcinations holding times at a temperature of 850ºC were obtained. The results showed that without cycling, longer calcination times reduced the pore volume for pores <200nm, but the pore distributions were all similar, with one major peak below <220nm. It can be observed in the Figure 2.24:

If the sorbent is cycled between carbonation and calcination during 80min resulted in a different PSD if it is compared with the one without cycling prolonged to 82min (Figure 2.24, legend: Calcine after 6th cycle, 80min). For the cyclic run, except for reduced pore volume of pores <220nm (denoted $V_1$ pores), pore volume growth can be observed for pores larger than 220nm (denoted $V_2$ pores).

Further evidence of the bimodal distribution ($V_1$ and $V_2$ pores) is shown in the following PSDs distributions (Figure 2.25) represented for different number of cycles. Generally, with an increase in the number of cycles, the $V_1$ pore volume decreased, whereas the $V_2$ volume increased.
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Figure 2.25. PSD: calcines after various number of calcinations/carbonation cycles. Test conditions as in the other Figures (17)

To identify the upper limit of the pore sizes in Figure 2.25, a SEM picture of a highly cycled calcine in Figure 2.26 shows that no pores larger than 1µm can be observed on the surface of the cycled sample. Thus, the inflection point (at ~610nm) in Figure 2.25 should mark the limiting size for the largest interparticle pores. Pores larger than 610nm are believed to be interparticle voids (17).

Figure 2.26. SEM picture of cycle Strassburg calcine sample after 15 calcinations/carbonation cycles at 850°C. Test conditions as in the other Figures (17)

D. Alvarez et al (10) investigation sintering by comparing fresh CaO and presintered samples (initiated with a 90 minutes residence time of the sample in calcinations position). Figure 2.27 plots the mercury intrusions curves of the selected calcines (left) and recarbonated (right) samples from two series of experiments carried out using 5 minutes of carbonation time, without (top) and with (bottom) initial presintering. It can be noticed that the presintered for the first sample caused important changes in the pore network, peaking at 189nm (left bottom), more than twice of the size (85nm, left top) of the pores in the fresh CaO, calcined for 10min. However, the behaviour of both samples rapidly converges to become almost the same from each other before the 30$^{th}$ cycle. This is due to the fact that calcium carbonate formed during carbonation does not keep memory of its previous calcinations and recarbonations (10). Thus, when the sintered sample is carbonated and calcined again (without sintering), the obtained texture is almost the same as that in the fresh calcine of the non-sintered series.
As the carbonation progresses from the exterior free surfaces to inwards, unreacted CaO will be present in the interior of the sample. When it is calcined again, a network of small pores (85nm) is formed on the surface of the larger pores formed during the first calcinations (+ sintering). Also the large pores will continuously increase in size with the number of cycles as a consequence of the internal sintering produced during calcinations. It explains why the initial pore size distribution splits into two populations of pores: a decreasing one, normally peaking around 90nm and other shifting to bigger sizes. (10)

This can be observed in the Figure 2.28 where SEM pictures are shown. The outer surface of a recarbonated particle (3a) can be seen as a mosaic pattern with some large pores connecting to the inner parts. The inner surfaces (3b) show a network of very large pores of ~1µm diameter. The outer surface of the calcined sample (3c) is seen as an arrangement of CaO spheres leaving between networks of very small pores. The inner surface of the calcined sample (3d) shows a very similar pore network of the carbonated sample but with a grainy appearance in the surface of these pores, corresponding to the calcinations of the carbonate thin product layer formed in the previous cycle (10).

Figure 2.27. Intrusion curves of selected samples from the fresh CaO series (top) and the presintered series (bottom). Curves on the left correspond to calcined samples, and those on the right are obtained from their recarbonated counterparts (10)
The workgroup of V. Manovic et al. (18) tested the loss of sorbent activity on two different limestones during calcining in two different conditions: in N\textsubscript{2} at low temperature (typically investigated laboratory-scale conditions) and in CO\textsubscript{2} at high temperature (realistic conditions in a calciner). Havelock limestone (HV), particle size 0.45-1.0mm, from Canada and Katowice limestone (KT), particle size 0.4-0.8mm, from Poland, were investigated. Scanning electronic microscope was used for analyzing calcined samples obtained in a TGA while bigger amounts of calcined samples were obtained for BET analyzing in a tubular furnace.

As observed in the SEM images (Figure 2.29) for the HV limestone, the grains of ~10µm size are well defined despite the calcination conditions. At magnifications, sub-grains can be seen only in the sample calcined in CO\textsubscript{2}. It is expected that the surface morphology of the sample calcined in CO\textsubscript{2} is less developed because the sintering experienced in this atmosphere and high temperatures. Higher image definitions (Figure 2.29 c) show that where very small sub-grains can be observed in the sample calcined at milder conditions (N\textsubscript{2} and low temperatures). Thus, the grainy surface of the N\textsubscript{2} calcined sample has suffered less sintering and has a higher superficial area as well as a pore size distribution (PSD) with a higher number of small pores.
The same differences can be observed in the KT limestone (Figure 2.30): micro-grains in samples obtained in different conditions are noticeable. Smaller grains can be seen in the sample calcined in milder conditions.

The following Table 2.1 shows the results in BET analysis for cycled samples (in a tubular furnace) and once-calcined samples. It is observed that the largest BET surface is obtained for the samples that have been calcined in N₂ whereas the greatest loss of surface area is found for the samples calcined in CO₂ and at high temperature.
The pore size distributions represented in Figure 2.31 show two peaks (around 3 and 30nm). The influence of calcinations/cycling conditions on small pores (~3nm) is more pronounced for KT limestone. This peak is smaller for when calcining in CO2 and high temperatures. Similar conclusions can be extracted for the peak ~30nm, but it should be pointed out that smaller pores influence carbonation conversions with increasing reaction cycles more than do larger pores.

![Figure 2.31. Pore size distributions of samples calcined/cycled under different conditions: (a) HV limestone, and (b) KT limestone (same designations as in Table 2.1).](image-url)
2.3.3. Particle diameter and porosity

In a very recent publication, Y. Wu et al (19) examined the particle length changes and its effects in the porosity. Four limestones were examined: Purbeck (PB), Katowice (KW), Havelock (HL) and Kelly Rock (KR). The following Figure 2.32 shows the normalized particle linear length (diameter of the major axis) change during carbonation and calcinations cycles. Figure 2.32 (a) and (b) plots these results for HL and KW limestones respectively. It can be noticed that the two limestones behave similarly in terms of size change, with a reduction of 7% of the particle diameters after 4 cycles and a little reduction for further cycling. According the authors, these results are quite consistent as several tests were performed.

KR and PB limestones showed less shrinkage as it can be observed. KR particles experimented less than 2% in diameter shrank whereas PB limestone showed irregular results. Particles called PB1 has more shrinkage that PB2 and PB3, which showed only around 0.5%. The maximum shrinkage observed was found in PB4 and it was accounted to be about 5%.

This work also investigated the decrease in porosity. Figure 2.33 shows that both HL and KW particles have a significant decrease, accounted to be around 15-20% in the first 4 cycles, whereas a smaller decrease in porosity (5%) was observed for KR and PB limestones.
2.3.4. Effect of chloride on sintering

Bardakci (20) carried out experiences in order to determine the effect of the sodium chloride on the surface area of the calcined limestone. Calcinations were performed at 850°C under N₂ atmosphere. Salt (NaCl) was added to the samples being dissolved in deionised water and added to the limestone. The limestones samples were dried in an oven at 150°C.

Experiences showed that the surface areas are inversely proportional to the amount of sodium chloride added, thus indicating that sodium chloride addition increases the sintering phenomenon. Bardakci also determined that the average pore radius decreases during the calcinations due to the increased surface areas, but then decreases due to the sintering and reduction of surface area as it has been explained in the present section.

The following Figures show the surface area and percentage weight loss in experiences with different percentage of salt compositions:

Figure 2.33. Particle porosity changes versus carbonation/calcination cycles for four limestones particles. Calcination temperature, 900°C, for 5min; carbonation temperature, 650°C, for 5min; $p_{\text{CO}_2}$ 0.015MPa (19)

Figure 2.34. Surface area and percentage weight loss for Greer Limestone as a function of calcinations time (no salt added) (20)
As it can be observed in the Figures above, with no salt added the surface area achieves a value higher than 8m$^2$/g after two hours of calcinations and decreases this value because of sintering. With a 0.1% NaCl content the same value is achieved but for two hours of calcinations but the decrease because of sintering is higher. Finally, for the sample with 5% of NaCl, after two hours of calcination only 2m$^2$/g is achieved, a value that barely decreases with prolonged calcinations time (sintering).

A work performed by Shearer et al (21) determined that the reactivity of CaO to CaSO$_4$ reached a maximum with a salt content near 0.5%wt for most of the tested limestones.

2.3.5. Comments

From the summarized works it is clear the effects on sintering at microscopic levels (porosity, pore distributions, pore diameters...) but further experimentation could be performed in order to determine the and compare the sintering in
other conditions. For example, different particle sizes can be tested as well as other limestones. Also, investigation of sulphur dioxide presence can be studied. The present project has the aim of investigating the parameters that can influence sintering.

2.4. Sulfation

Most of the fuels used in combustion processes contain a certain quantity of sulphur that once combusted is converted to SO₂. If sulphur dioxide is released to the atmosphere reacts with water vapour and is converted to sulphuric acid producing the well-known acid rain. The literature study has been focused in the sulphation process taken part in the carbonate looping process in order to be compared with the carbonate reaction.

2.4.1. Sulfation problem

If SO₂ is present in the flue gas can react with the sorbent (CaO) in presence of oxygen according the following reaction:

\[
\text{CaO (s) + SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) \rightarrow \text{CaSO}_4 (s)
\]  

(5.1)

Direct desulfuration also occurs in systems with high CO₂ partial pressure, such as oxy-fuel combustions systems:

\[
\text{CaCO}_3 (s) + \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 (s) + \text{CO}_2 (g)
\]  

(5.2)

Within the range of typical temperatures for CO₂ adsorption in the carbonate looping process, sulfation is thermodynamically allowed and both reactions (carbonation and sulfation) occur at the same time. Both of these are typical heterogeneous gas-solid reactions, and deactivation due to sulphation is produced because of solid product formation at the reacting surface. Moreover, CaSO₄ is thermodynamically stable at temperatures of interest for sorbent regeneration (~900°C) and obstructs carbonation during the carbonation(calcination) cycles. Thus, CaO reacts with SO₂ and cannot react with CO₂ because of the CaSO₄ product layer formed in the particle surface.

2.4.2. Sulfation process description

The sulfation process is normally viewed as continuing until blocking of external pores occurs, leading to the formation of impenetrable (due to the molar volumes of the involved molecules) CaSO₄ shell which leaves a significant amount of unreacted CaO core. Based on the data in Table X00, the maximum possible conversion for non-porous limestone ought to be 69%, although in practice much lower conversion figures are typical in fluidized bed combustors (FBC).
Laursen et al (23) demonstrated that sorbent particles might sulphate in three different ways: unreacted core, network and uniform, depending how the sulphur is distributed through the sorbent particles. These sulfation trends depend on the morphology (for example, porosity, grain size, fracture size and configuration) of calcined limestone. The following Figure 2.37 shows the sulfation reaction patterns:

![Figure 2.37. Schematic sequence of sulfation of three different types of sulphated limestone particles. Adapted from Laursen et Al (23)](image)

Investigations performed by Ho-Jung Ryu et Al (24) demonstrated that Strassburg and Luscar limestones follow the unreacted core and uniform sulfation patterns, respectively. It is observed in Figure 2.38:

![Figure 2.38. Illustration of two different sulfation patterns. Adapted from Laursen et Al. (24)](image)
For the unreacted core-type sulfation, the reaction between the CaO and SO$_2$ takes place in the outer layer of the limestone particle, and a dense, nearly nonporous CaSO$_4$ layer or shell forms on the outside. On the other hand, the uniform-type sulfation forms CaSO$_4$ in the outer layers of individual CaO grains through the sorbent particles.

Figure 2.39 shows several cycles of calcination, sulfation and carbonation, occurred in this order. Some CO$_2$ can penetrate through the CaSO$_4$ layer because its molar volume is lower than SO$_2$. The CaCO$_3$ formed has a larger molar volume than CaO, causing fissures in the sulfated shell according Yan Li et al (25). The experiment was performed with a cyclic sequence of calcination-sulfation-carbonation and concluded that the partially sulfated limestone particles can capture CO$_2$ and the ability of a limestone to capture SO$_2$ increases after carbonation and recalcination.

![Figure 2.39. Schematic sequence of limestone calcination, sulfation and carbonation reactions (modified from Laursen et al) (25)](image)

2.4.3. Simultaneously calcination and sulfation

Ho-Yung Ryu et al (24) investigated the SO$_2$, CO$_2$ and total capture capacity of three different limestones with the number of cycles for different SO$_2$ concentrations. These parameters are defined below:

\[
\text{CO}_2 \text{ Capture Capacity} = \frac{\text{moles of CO}_2 \text{ absorbed}}{\text{moles of Ca in the sorbent}} \quad (\text{Eq 2.4})
\]

\[
\text{Cumulative SO}_2 \text{ Capture Capacity} = \frac{\text{cumulative moles of absorbed SO}_2}{\text{moles of Ca in the sorbent}} \quad (\text{Eq 2.5})
\]

\[
\text{Total Calcium Utilization} = \frac{\text{cumulative moles of absorbed CO}_2 \text{ and SO}_2}{\text{moles of Ca in the sorbent}} \quad (\text{Eq 2.6})
\]
It can be observed that for all the analyzed limestones, the CO₂ capture capacity decreases with the increasing number of cycles and SO₂ concentration. Increased exposure to SO₂ clearly reduces the CO₂ capture. At the same time, the SO₂ capture increased with the number of cycles because absorbed SO₂ during simultaneous CO₂/SO₂ capture was not desorbed during the regeneration. The cumulative SO₂ capture capacity also increases with the SO₂ concentration (24). The investigation concluded that even with little amounts of SO₂ can mean a decrease of the CO₂ capture reaction for simultaneous CO₂/SO₂ capture conditions.

Investigation carried out by Mahesh et al (26) shows the data obtained on the carbonation and sulfation as a result of simultaneous exposure of a synthetic calcined sorbent (called PCC-CaO) to a gas mixture containing 10% CO₂, 3000ppm of SO₂ and 4% O₂. However, the results are very similar that the ones obtained for a normal sorbent. Figure 2.41 depicts these data:
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Figure 2.41. Effect of residence time on the conversion of PCC-CaO for pure carbonation, pure sulfation and combined reactions at 700ºC (3000ppm of SO$_2$, 10% CO$_2$ and 4% O$_2$) (26)

The same investigation showed similar results that other conclusions found in the literature study. For example, the effect of the residence time on the extent carbonation and on the effect of the same parameter on the sulfation for multiple cycles are depicted in Figure 2.42 and Figure 2.43 respectively.

Figure 2.42. Effect of the residence time on the extent of carbonation of PCC-CaO for multiple cycles at 700ºC (3000ppm of SO$_2$, 10% CO$_2$ and 4% O$_2$) (26)

Figure 2.43. Effect of the residence time on the extent of sulfation of PCC-CaO for multiple cycles at 700ºC (3000ppm of SO$_2$, 10% CO$_2$ and 4% O$_2$) (26)

Figure 2.44 plots the ratio (R) obtained from data collected from pure carbonation and sulfations of the synthetic sorbent described in the Figure 2.44:
Figure 2.44. Effect of the residence time on the ratio of carbonation to sulfation of PCC-CaO for multiple cycles at 700ºC (3000 ppm of SO$_2$, 10% CO$_2$ and 4% O$_2$) (26)

V. Manovic and E. Anthony (27) compared the behavior of a limestone and a synthetic sorbent (calcium aluminate pellets) for different SO$_2$ concentrations (0.05, 0.5 and 0.1%). As it is observed in the other works, the carbonation activity was higher when gas with lower SO$_2$ concentration was used. At the same time, it is seen that the sulfation conversions decrease with lower SO$_2$ concentration. Figure 2.45 shows these experiments:

Figure 2.45. Conversions during sulfation/carbonation/calcination cycles with different concentrations of SO$_2$: (a) 0.5, (b) 0.05 and (c) 0.1% (27)
It can be also noticed that the total conversion has a minimum value for both sorbents in the experiences with 0.5 or 0.05% of SO₂. After the minimum the concentration increases with the number of cycles. It is explained by enhanced sulfation that is a result of the favorable influence of CO₂ cycles on sulfation activity of the sorbents (27). It cannot be observed in the experience with 0.01% SO₂ because there was insufficient SO₂ in the reacting gas.

2.4.4. Comments

Several works performed in the field of sulfation have the aim to capture this substance meaning in a loss of sorbent. In fact, the removal of SO₂ must be considered in order to accomplish with the environmental protection laws. In the opinion of the author, the simultaneous removal of carbon dioxide and sulfur dioxide should be studied with the purpose of being carried out at the same time. Thus, studies of make-up sorbent must be done in order to check the reliability of the both substances capture.

2.5. Modeling

2.5.1. Loss of capacity

Abanades et al (28) determined that the main mechanism of sorbent decay was sintering and propose the following equation to explain the behavior of the loss of capacity:

\[ X_N = f_m^N (1 - f_w) + f_w \]  \hspace{1cm} (Eq 2.7)

Where \( f_m \) and \( f_w \) are fitting parameters and \( X_N \) the adsorption capacity at the cycle N. It was checked that the equation fits really well for values of \( f_m = 0.77 \) and \( f_w = 0.17 \). Nevertheless, the data fitted in this equation contained less than 50 cycles.

Wang and Anthony (29) propose a simple equation containing only one parameter. It was considered that the decay in activity was dependent on the activity itself (the lower activity, the lower decay). The equation (2.8) shows how the sorbent decay also depends on the activity:
Expressing the equation as it can be seen in equation 2.9 and substituting in the equation 2.10, the expression can be approximated in differential form (Eq 2.11):

\[ X_N - X_{N-1} = -kX_{N-1}^2 \]  

(Eq 2.9)

\[ \frac{X_N - X_{N-1}}{N - (N - 1)} = \frac{\Delta X}{\Delta N} \]  

(Eq 2.10)

\[ \frac{dX}{dN} = -kX^2 \]  

(Eq 2.11)

Finally, integrating the equation 2.12 as a function of \( N \), Wang and Anthony obtained the following equation (6.6) in order to explain the sorbent decay in only one parameter:

\[ X_N = \frac{1}{1 + kN} \]  

(Eq 2.12)

Further experimentation performed by Grasa et al (11) improved the equation (6.1) proposed by the same investigation group. Due to an extensive investigation the team observed that the sorbent decay has a residual value that maintains almost constant from \( N>50 \) to up to 500 cycles. From the investigations carried out by Calvin H. Bartholomew (30) we have the equation 2.13:

\[ -\frac{d(S / S_0)}{dN} = k \left( \frac{S}{S_0} - \frac{S_f}{S_0} \right)^2 \]  

(Eq 2.13)

If we consider the proportionality between conversion (\( X \)) and surface area (\( S \)) as \( X=S/S_0 \) and if the equation is solved integrating the following equation 2.14 is obtained:
From here, the described equations are known to be for calcination temperatures lower than 950ºC. B. Gonzalez et al (31) propose an equation in order to describe the sorbent conversion as a function of the number of cycles, the calcination temperature and the calcination time. A term of sorbent decay due to thermal sintering produced by high calcination temperatures was considered as it can be observed in the Figure 2.46:

\[ X_N = \frac{1}{1 + Kn} + X_r \]  
\[(Eq 2.14)\]

The chart shows that the resulting maximum carbonation conversion \(X_{ni}\) is equal that the one obtained in “normal” conditions minus the loss conversion provoked by thermal sintering. After some calculations the obtained equation must be spited in two parts:

For \(X_{n-1} > X_r\),

\[ X_N = \left( \frac{1}{[1/(X_{n-1}) - X_r + k] + X_r} \right) \times \left[ 1 - \left( k \exp\left( -\frac{E_a}{RT} \right) \right)^{\frac{1}{\alpha}} \right] \]  
\[(Eq 2.15)\]
For $X_{n-1} < X_r$,

$$X_N = X_{N-1} \left[ 1 - \left( k_0 \exp \left( - \frac{E_a}{RT} \right) \right)^{\frac{1}{n}} \right]$$

(Eq. 2.16)

This split is because when the particle conversion is below $X_r$, the deactivation mechanism associated with the number of cycles is no longer present, and the only mechanism present is thermal sintering.

### 2.5.2. Carbonation-calcination looping: mass and energy balances

Abanades et al (32) illustrated the process in the Figure 2.47 below and proposed the following equation to calculate the CO$_2$ capture efficiency, carbonation efficiency and the average capacity of the sorbent in the system (Section 3).

![Figure 2.47. Illustration of the standard design of the Carbonate Process Looping (33)](image)

Abanades et al used the same nomenclature used in other studies. $F_R$ and $F_0$ are the recirculation and make-up flows respectively; $F_{CO2}$, the molar CO$_2$ flow released in the combustor; $F_{flue}$, flue gas molar flow; $F_{inert}$, the circulating flow of ashes due to fuel combustion; $y_{comb}$, the fraction of fuel used in the combustor; and $E_{carb}$, the carbonator efficiency. The workgroup presented the equation 2.17 below to calculate the CO$_2$ capture efficiency:

$$E_{cap} = \frac{y_{comb} \cdot E_{carb} + \frac{F_0}{F_{CO2}} y_{comb} + (1 - y_{comb})}{1 + (1 - y_{comb})}$$

(Eq. 2.17)
Where the carbonator efficiency ($E_{\text{carb}}$) is calculated as the maximum between the captured CO$_2$ in the recirculated flow divided by the total CO$_2$ produced and the efficiency imposed by the equilibrium of CO$_2$ over CaO:

$$E_{\text{carb}} = \min \left( \frac{F_R \cdot X_{\text{ave}}}{F_{\text{CO}_2}}, E_{\text{eq}} \right)$$  \hspace{1cm} (Eq 2.18)

Where $X_{\text{ave}}$ is the average adsorption capacity of the particles in the carbonate looping system.

The calcination will require heat to warm up the solid stream ($F_{\text{CaO}} + F_{\text{inert}} + F_{0}$), defined as $H_{\text{in}}$. It can be calculated with the formula (2.19) below proposed by N. Rodriguez et al (34):

$$\frac{H_{\text{in}}}{F_{\text{CO}_2}} = \Delta H_{\text{carb}} \left( \frac{F_{\text{CaO}}}{F_{\text{CO}_2}} X_{\text{carb}} + \frac{F_{0}}{F_{\text{CO}_2}} \right) + \Delta T_{\text{cal}} \left[ C_{P_{\text{CaO}}} F_{\text{CaO}} \frac{F_{\text{CaO}}}{F_{\text{CO}_2}} (1 - X_{\text{carb}}) + C_{P_{\text{CaCO}_3}} \frac{F_{\text{CaO}}}{F_{\text{CO}_2}} X_{\text{carb}} + C_{P_{\text{CaSO}_4}} \frac{F_{\text{CaSO}_4}}{F_{\text{CO}_2}} + C_{P_{\text{Ash}}} \frac{F_{\text{Ash}}}{F_{\text{CO}_2}} \right] + \frac{F_{0}}{F_{\text{CO}_2}} C_{P_{\text{CaCO}_3}} \Delta T_{F0}$$  \hspace{1cm} (Eq 2.19)

Finally, a correlation (Eq. 2.20) to approximate the fraction of coal combusted at the power plant ($Y_{\text{comb}}$) with the total electricity generation, considering the discount due to the compression and purification stages which are accounted to be around 5 points of net efficiency (34):

$$\eta_{\text{capture}} = \eta_{\text{reference}} f_p + \eta_{\text{oxyfuel}} (1 - f_p) - 0.05 f_p$$  \hspace{1cm} (Eq 2.20)

### 2.5.3. Average capacity

Make-up flows of fresh sorbent are required in a carbonate looping process in order to deal with the sorbent decay. Thus, sorbent particles with different adsorption capacities are recirculated between the calcination and carbonator which means the need to define an average activity for these particles. Abanades et al (32) proposed an equation with the purpose to describe the average activity of the sorbent in the system.
The average capacity can be described as:

\[
X_{\text{ave}} = \sum_{N=1}^{N=\infty} r_N X_N
\]

(Eq 2.21)

Where \(X_N\) is the \(\text{CO}_2\) carrying capacity and \(r_N\) the fraction of particles that have been recirculated \(N\) times. The fraction of recirculated particles can be calculated with the following expressions (2.22) and (2.23):

\[
r_N = p(1 - p)^{N-1}
\]

(Eq 2.22)

\[
p = \frac{F_0}{F_0 + F_R}
\]

(Eq 2.23)

If the equations 2.22 and 2.23 are combined and applied in the equation 2.21 when the sorbent deactivation is represented by equation 2.7, the expression below (Eq 2.24) is obtained in order to calculate the average activity:

\[
X_{\text{ave}} = \frac{k \cdot (1 - X_r) \cdot F_0}{F_0 + F_R \cdot (1 - k)} + X_r
\]

(Eq 2.24)

In case of deactivation by \(\text{SO}_2\) presence and \(\text{CaSO}_4\) formation, Abanades et al (32) also proposed a specific formula supposing that all the sulfur present in the fuel reacts quantitatively with the active fraction of \(\text{CaO}\):

\[
X_{\text{ave}} = \frac{k \cdot (1 - X_r) \cdot F_0}{F_0 + F_R \cdot (1 - k)} + X_r - \frac{F_{\text{CO}_2}}{F_0 \cdot r_{\text{C}_1.5} \cdot \text{comb}}
\]

(Eq 2.25)

Figure 2.48 (32) shows the dependency of the capture capacity with flows ratios. For \(F_0/F_{\text{CO}_2}\) ratios lower than 0.05 the Figure 2.48 has been left undefined because most sorbent particles in the system have been experienced a number of cycles much higher than 50 and some of the equations proposed for sorbent activity calculation (equation 1 and 8) can only describe the sorbent performance for \(N<50\) cycles:
As it can be observed, the capture efficiency can be kept high if the $F_R/F_{CO_2}$ and/or $F_0/F_{CO_2}$ ratios are increased. Nevertheless, $F_R/F_{CO_2}$ ratio must be maintained close to the unity to minimize solid flows between carbonator and calcinator and maximize the residence times in both units. Furthermore, the $F_0/F_{CO_2}$ ratio is the make-up of limestone and it must be kept as low as possible in order to minimize the operational costs.

### 2.5.4. Sintering equations

A model for pore evolution during cyclic calcination/carbonation was presented by P.Sun et al (17). They considered that the pore volume of smaller diameters (<200nm) determines the achievable extent of carbonation during the fast stage of carbonation. When the <200nm pores are filled, a much slower carbonation occurs. An equation in order to calculate the conversion of CaO to carbonate based on the porosity is given:

$$X = \frac{\varepsilon_0}{(1/Z-1)(1-\varepsilon_0)} \quad (\text{Eq 2.26})$$

Where the porosity is related to the specific pore volume, according the expression (Eq 2.27):
\[ \varepsilon_0 = \frac{V}{V + \frac{1}{\rho_{\text{CaO}}}} \]  

(Eq 2.27)

P. Sun et al also presented a relationship between the pore volume for <200nm and the specific surface area:

\[ dS = A \cdot dV_i \]  

(Eq 2.28)

where \( V_i \) are the pore volume for <200nm. It can be considered that \( S = S_g \) (surface for freshly calcined limestones with zero degree of sintering and grains ideally spherical) when \( V_i = V_g \); and \( S = S_a \) (asymptotic specific surface area when the sample is sintered for an extremely long time) when \( V_i = V_a \). Subscript “\( g \)” refers to a “green state” (no sintering and spherical grains) whereas “\( a \)” subscript means a long time sintering. A value of \( S_g = 70 \text{m}^2/\text{g} \) is usually taken. \( V_g \) is estimated from the following equation 2.29:

\[ V_g = \frac{\varepsilon_g}{\rho_{\text{CaO}} (1 - \varepsilon_g)} \]  

(Eq 2.29)

Where \( \varepsilon_g \) is calculated from the equation 2.26 using \( X = 1 \). Integration of the equation 2.28 gives:

\[ V_i = \frac{S - S_a}{A} + V_a \]  

(Eq 2.30)

\[ A = \frac{(S_g - S_a) \cdot (1 - \varepsilon_g) \cdot \rho_{\text{CaO}}}{\varepsilon_g} + V_a \]  

(Eq 2.31)

In the same work, a model for macroscopic sintering during cyclic calcination/carbonation was described. It was considered that sintering occurs at the same time with calcinations. Thus, the CaO surface depends of both calcinations and sintering as the next equation 2.32 shows:

\[ \frac{dS}{dt} = \left( \frac{dS}{dt} \right)_{\text{calcination}} - \left( \frac{dS}{dt} \right)_{\text{sintering}} \]  

(Eq 2.32)
An empirical equation is given to describe the surface evolution in absence of sintering and it is transformed to a differential expression (equations 2.33 and 2.34 respectively):

\[ S = S_g \cdot X_{carb} (n) \cdot X \]  \hspace{1cm} (Eq 2.33)

\[ \left( \frac{dS}{dt} \right)_{calcination} = S_g \cdot X_{carb} (n) \frac{dX}{dt} \]  \hspace{1cm} (Eq 2.34)

The surface reduction due to sintering involves kinetics and is defined by the following equation 2.35:

\[ \left( \frac{dS}{dt} \right)_{sintering} = k_s \cdot (S - S_a)^2 \]  \hspace{1cm} (Eq 2.35)

Where \( k_s \) is calculated as:

\[ k_s = 2.45 \cdot \exp\left( -0.0029 \cdot \exp(3.106 \cdot 45.276 \cdot T) \right) \]  \hspace{1cm} (Eq 2.36)

Wu et al (19) observed that after about 10 cycles the particle diameter reaches an asymptote which was analogous to the decay in the carrying capacity of the limestone, expressed in the equation 2.14. Thus, the equation that the group proposed was:

\[ d_N = \frac{1}{1 - d_{\infty}} + d_{\infty} + k_s \]  \hspace{1cm} (Eq 2.37)

where \( d_{\infty} \) is the final particle size and \( k_s \) is the decay for the particle size. The greater \( k_s \) value, the smaller tendency for shrinkage.
Wu et al. also proposed a method to calculate the particle porosity. First, it is necessary to assume that the number of moles of CaCO$_3$ and CaO before calcination is equal. For a spherical particle we have:

$$\frac{4 \pi r_0^3 \rho_{CaCO_3} (1 - \varepsilon_0)}{M_{CaCO_3}} = \frac{4 \pi r_c^3 \rho_{CaO} (1 - \varepsilon_c)}{M_{CaO}}$$

(Eq 2.38)

Where $\rho$ and $M$ are density and molar weight respectively, $r_0$ and $\varepsilon_0$ the initial particle radius and porosity respectively and $r_c$ and $\varepsilon_c$ the radius and porosity after first calcination. As the normal porosity of limestone is quite low, the work recommends to consider that the limestone porosity is $\varepsilon_0 = 0$. Following the first calcinations, the equation below can be obtained from molar conservation of CaO between the carbonation/calcinations cycles:

$$\varepsilon_t = 1 - \left(\frac{r_c}{r_0}\right)^3 (1 - \varepsilon_c)$$

(Eq 2.39)

### 2.6. Others

#### 2.6.1. Steam reactivation

Hydration has been investigated as a way to improve the CO$_2$ carrying capacity, mostly for the sorbent that react with SO$_2$ present in the flue gas. It is based in the difference molar volumes between CaSO$_4$, CaO and Ca(OH)$_2$ (46.0-48.1, 16.9 and 33.1 cm$^3$/mol, respectively). CO$_2$ cannot penetrate the CaSO$_4$ layer formed during sulfation whereas H$_2$O can do it and react with the CaO still present in the core of the particle according the following equation:

$$CaO(s) + H_2O(g) \rightarrow Ca(OH)_2(s) \quad \Delta H_{r,298K} = -109 \text{ kJ/mol}$$

(Eq 2.40)

Because the molar volume of Ca(OH)$_2$ is larger than the molar volume of CaO, the core expands and particle fracture meaning an increase of surface area and porosity of CaO available for a further reaction.
Wu et al. (19) investigated the sorbent hydration in a thermogravimetric analyzer (TGA). The steam reactivation was performed at atmospheric pressure during 5min at 130°C of particles that had experimented 10 cycles. The results were quite promising: after the steam treatment the CO₂ carrying capacity increased by 45-60% points.

![Graph showing the decay curves for four different limestones.](image)

**Figure 2.49.** Effect of steam reactivation on four limestones (bulk samples). Calcination temperature, 900°C, for 5min; carbonation temperature, 650°C, for 5min; p\(_{\text{CO}_2}\), 0.015MPa; steam temperature, 130°C (p\(_{\text{CO}_2}\), 0.1MPa), for 5min (19)

Figure 2.49 shows the decay curves for four different limestones. It can be observed that steam regeneration improves the CO₂ carrying capacity for each limestone. However, very different results were observed in the work carried out by Blamey et al. (35) in a laboratory-scale reactor capable to operate in more realistic conditions instead of a TGA. The sorbent was reactivated by hydration after a number of cycles and exposed to further carbonation/calcinations cycles as well. Havelock, La Blanca and Purbeck limestone were tested. Results of the investigation are shown in the Figure 2.50 and Table 2.3 below:

![Graphs showing cycling experiments varying Tcalc (1113K, 1173K, 1223K and 1273K) before hydration for Havelock, La Blanca, and Purbeck limestone.](image)

**Figure 2.50** Cycling experiments varying T\(_{\text{calc}}\) (1113K, 1173K, 1223K and 1273K) before hydration for (a) Havelock limestone, (b) La Blanca limestone and (c) Purbeck limestone (35)
Table 2.3. Reactivation extents from varying Tcalc before hydration (35)

<table>
<thead>
<tr>
<th>Limestone</th>
<th>Calcination temperature (K)</th>
<th>Increase in carrying capacity after hydration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Havelock</td>
<td>1113</td>
<td>99</td>
</tr>
<tr>
<td>Havelock (slow heat)</td>
<td>1113</td>
<td>57.8</td>
</tr>
<tr>
<td>Havelock (slow heat, low flow)</td>
<td>1113</td>
<td>163</td>
</tr>
<tr>
<td>Havelock</td>
<td>1173</td>
<td>82.4</td>
</tr>
<tr>
<td>Havelock</td>
<td>1223</td>
<td>-1.0</td>
</tr>
<tr>
<td>Havelock</td>
<td>1273</td>
<td>-82.6</td>
</tr>
<tr>
<td>La Blanca</td>
<td>1113</td>
<td>368</td>
</tr>
<tr>
<td>La Blanca</td>
<td>1173</td>
<td>231</td>
</tr>
<tr>
<td>La Blanca</td>
<td>1223</td>
<td>298</td>
</tr>
<tr>
<td>Purbeck</td>
<td>1113</td>
<td>9.7</td>
</tr>
<tr>
<td>Purbeck</td>
<td>1173</td>
<td>-13.8</td>
</tr>
<tr>
<td>Purbeck</td>
<td>1223</td>
<td>0.0</td>
</tr>
</tbody>
</table>

As it is observed, only for mild calcinations conditions (1113 and 1173K) and for Havelock and La Blanca limestones a considerable increase in carrying capacity is produced. Nevertheless, the increase is substantial and reaching values of 368% for La Blanca limestone at calcinations conditions of 1113K.

2.6.2. Pretreatment at high temperature

V. Manovic et al (36) performed experiences with different limestones in order to check if thermal pretreatment of the sorbent before the cycling process is effective. The pretreatment was carried out during 24h at 1000°C in 100% of CO₂. Figure 2.51 shows the conversion in a series of carbonation/calcinations cycles after sorbent pretreatment.

![Carbonation-calcination cycles of pretreated Kelly Rock limestone sample (0.300-0.425 mm). Pretreatment conditions: TGA, 24h at 1000°C in 100% CO₂; cycle conditions: TGA isothermally at 800°C, carbonation in 100% for 10min, calcinations in 100% for 10min (36)](image)

The investigation also compares different times pretreated sorbent with the original sorbent without pretreatment (Figure 2.52):
For Katowice limestone it can be observed that the CO$_2$ carrying capacity decreases in the initial cycles for all the pretreatment times. However, it increases after a number of cycles but it decreases again. Nevertheless, the residual adsorption capacity is higher for the thermal pretreated samples.

On the other hand, La Blanca limestone showed very different results. Thermal pretreatment decreased the CO$_2$ adsorption capacity. In fact, it was never higher than the non-treated sorbent as well as the residual CO$_2$ carrying capacity.

### 2.6.3. New sorbents

Feng et al. (37) proposed a method of fabricating a CaO-based sorbent in order to deal with the loss in capacity problem. The paper proposed the use of fine CaO particle by fabricating a sorbent from γ-alumina and CaCl$_2$ as raw materials. Great results were demonstrated as the synthetic sorbent showed full reversibility of the CaO-CO$_2$ reaction and very high degree of reaction, higher than 90% (even higher than raw CaO).

One method presented by Albrecht et al. (38) consisted to incorporate an "inert" material in the sorbent. It was observed that by incorporating finely dispersed MgO in the sorbent, the adsorption capacity is logically reduced since MgO does not adsorb CO$_2$ but for a large number of cycles, the adsorption capacity for a limestone with 20%$_{wt}$ of MgO was 45% greater than that for a similar material without MgO.

Yingjie Li et al. (39) proposed using shells as a sorbent for the carbonation/calcinations cycles. The investigations showed that shells have a larger number of >230nm pores than limestones and that these pores do not sinter for

---

**Figure 2.52.** Carbonation-calcination cycles (isothermally 800°C, carbonation 50% CO$_2$ and calcinations in 100% N$_2$, each for 10min) of Katowice limestone (top) and La Blanca limestone (bottom) (36)
shells. It was also observed that shells contain more sodium ions than limestone, reported to show a better cyclic CO$_2$ capture performance if they are present in an appropriate amount.

2.6.4. Partial carbonation

Grasa et al (40) studied the effect of partial carbonation on the CO$_2$ carrying capacity. Experiments were performed in a TGA prepared to interrupt the carbonation reaction in each cycle before the end of the fast carbonation stage. Results showed that particles experienced a “younger” behavior after partial carbonation. The fact that the particles did not reach the maximum carbonation conversion meant an improvement in the overall transport capacity. According the authors of these work, adjusting the carbonation residence times allow better conversion.
3. Experimental procedure

The following sections provide an overview of the used apparatus (TGA, BET, horizontal reactor, SEM) as well as of the experimental setups and the problems found when carrying out the experiments. Thermogravimetric analyses were performed to determine the mass variation of a limestone sample in different temperatures and atmospheres. Because of the small sample that this apparatus required it was not possible to analyze it in a BET (see Appendix 04 for description) apparatus. Then, limestone samples were calcined once in a tubular (horizontal) reactor where bigger calcined sample were possible to be obtained and then were analyzed in a BET apparatus. In order to complement the experiments, some samples were analyzed in a scanning electronic microscope (SEM, see Appendix 05 for description), where no matter of how big the sample is.

3.1. Limestone

All the experiments are carried out with Faxe Bryozo limestone. The composition determined by Guilin et al for Faxe Bryozo limestone is shown in the following table:

<table>
<thead>
<tr>
<th>Compositiona</th>
<th>CaCO$_3$ (wt %)</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Zn</th>
<th>Sr</th>
<th>Particle size (mm)</th>
<th>Total surface area$^1$ (m$^2$/g)</th>
<th>Porosity$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental analysis (wt %)</td>
<td>97</td>
<td>&lt;detection limit of 0.001</td>
<td>0.26</td>
<td>0.026</td>
<td>0.23</td>
<td>0.014</td>
<td>0.03</td>
<td>0.0054</td>
<td>39</td>
<td>0.002</td>
<td>0.002</td>
<td>&lt;detection limit of 0.001</td>
<td>0.02</td>
<td>0.047</td>
<td>0.0014</td>
<td>0.042</td>
<td>0.063–0.18</td>
<td>0.79</td>
<td>0.3</td>
</tr>
</tbody>
</table>

An analysis in a BET showed that the surface area of the limestone (Faxe, 0-250μm) used in the experiments is 0.923m$^2$/g. This value is slightly different that the one shown in the Table 3.1. It can be attributed to small variation of limestone composition and possible variations during the different experimental analyses.

The characteristics for the calcined Faxe limestone are shown in Table 3.2:
### 3.2. Thermogravimetric analysis (TGA)

A TGA was used to measure the mass variation of a sample in different atmospheres and temperatures during calcinations and carbonations. The apparatus is situated in the Building 229 Room 137.

#### 3.2.1. TGA theory

Thermogravimetric analysis is used in order to determine the weight changes of a sample in relation of temperature variation in a surrounding gas atmosphere. TGA is commonly used in determination of degradation temperatures such as polymers, absorbed moisture content of materials, level of organic and inorganic components in materials, etc. It can be also used for simulation of gas-solid reactions involving mass change as for example, the carbonation and calcination of limestone.

Figure 3.1 below shows a sectional view of a TGA. It consists in a high-accuracy balance measuring the mass of a sample exposed at temperatures changes and different atmospheres. The furnace is electrically heated and the temperature of the sample is measured through a thermocouple.
The furnace allows a maximum heating and cooling rate in the STA 449 F3 Jupiter of 3000K/min and 300K/min respectively. The sample carrier is a ceramic holster at the tip which is in contact with the crucible, only separated around 0.8mm and ensuring that the recorded temperature is very close to the sample temperature. The system disposes of three mass flow controllers: two for purge gases (CO\textsubscript{2} and N\textsubscript{2} or SO\textsubscript{2} in N\textsubscript{2}, entering at the bottom of the furnace) and one protective gas (sent through the balance system to avoid the intrusion of purge gases from the furnace).

The buoyancy because of the gases flowing through the apparatus exposed at temperature changes of the crucible that holds the sample needs a correction file. Thus, it means that for each temperature and gas program the experiment must be executed twice: one for the correction file and another for the sample analysis.

### 3.2.2. Limitations of STA

High pressures cannot be used in STA. For that purpose a high pressure STA must be purchased. Thus, it is not possible to carry out experiments for simulating pressurized calcinators and carbonators.

Water concentration in gas: it must not be higher than the water saturated point at 25°C (3,17kPa). Thus, reactivation by steam in realistic conditions is not allowed.

Using SO\textsubscript{2} in experiences: in order to use SO\textsubscript{2} in the TGA apparatus the pure nitrogen supply have to be changed by one of the cylinders with certain SO\textsubscript{2} content. Thus, the protective gas must be used in order to achieve specific SO\textsubscript{2} and CO\textsubscript{2} concentrations meaning that different oxygen concentrations might be present in the different experiences and as it is known, sulfation reaction depends on oxygen concentration. It must be consider when analyzing the results. However, differences in O\textsubscript{2} concentration will probably only noticed in low oxygen concentration as it is known.
that for concentrations higher than 2% does not influence the sulfation rate (according talks with people working in this field). Gas compositions for experiments using SO$_2$ are shown in Appendix 06.

### 3.2.3. Experimental procedure

As said before it is necessary to run the experiments twice: for the calibration and for the sample analysis. The defined stages during the calibration will be the same as the ones in the analysis. In order to simulate calcination/carbonation cycles the following stages must be defined:

1. Heating from 650°C to 950°C at a high heating rate.
2. Isothermal at 950°C in a high CO$_2$ content (around 90%) for calcination simulation.
3. Cooling from 950°C to 650°C at high cooling rate.
4. Isothermal at 650°C in low CO$_2$ content (around 20%).

In fact, furnace temperatures must be programmed instead of sample temperatures. It supposed a problem because the correlation between both temperatures was not easy. Also, when carbonation and calcination temperatures set in the program are achieved, the sample temperature takes some time to stabilize. For this reason, a correct selection of the program must be done meaning long time consuming in order to achieve stable calcination and carbonation stages as well as the heating and cooling processes. For example, the following temperature and heating/cooling rate program (Table 3.3) gives the real temperatures shown in Figure 3.2 and Figure 3.3:

#### Table 3.3. Segment programming for obtaining a calcination-carbonation cycle

<table>
<thead>
<tr>
<th>Segment</th>
<th>Stage</th>
<th>Temperature</th>
<th>Heating/cooling rate</th>
<th>Purge 1 N$_2$</th>
<th>Purge 2 CO$_2$</th>
<th>Protective gas (air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Heating</td>
<td>1320</td>
<td>400</td>
<td>155</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Cooling</td>
<td>1235</td>
<td>50</td>
<td>5</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Isothermal</td>
<td>1235</td>
<td></td>
<td>5</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Cooling</td>
<td>805</td>
<td>300</td>
<td>155</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Heating</td>
<td>870</td>
<td>50</td>
<td>120</td>
<td>35</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Isothermal</td>
<td>870</td>
<td></td>
<td>120</td>
<td>35</td>
<td>20</td>
</tr>
</tbody>
</table>

![Figure 3.2. Real temperature profile for the first cycle](image-url)
Figure 3.2 shows the real temperature in the first cycle for the 6-segment programmed furnace temperatures. As it can be observed, for the second cycle (Figure 3.3) the sample temperatures have suffered a variation during the calcinations stage. It might be because in the first cycle the sample is heated from ambient temperature and in the following cycles the sample is heated from carbonation conditions (650°C). As it can be observed, even using 6 segments it very difficult to simulate the carbonation-calcination process in 4 segments representing the 4 processes (heating, calcination, cooling, carbonation).

Another thing that influence in the non-ideality when simulating the process is that the gases have a residence time inside the STA. The gas composition does not change just immediately when changing the inlet gas flows. Also, there is a minimum segment time: for the dynamic stages (heating or cooling) cannot be shorter than 12 seconds, and for the isothermal stages that cannot be shorter than 1 minute.

Running the experiments with a certain protective gas flow is important in order to avoid the purge gases from entering the balance system of the TGA. For that reason, the protective gas is introduced in the balance system while the other gases are introduced in the bottom of the furnace.

When using SO$_2$ a special attention must be paid. As said, a valve is used to switch between pure nitrogen or SO$_2$ in nitrogen. Before beginning an experiment the systems must be flushed using pure nitrogen to clean the possible impurities or water because by reaction with SO$_2$ can form sulfuric acid. Actually, if the gases come from cylinders no water vapor content will be found but the flushing process must be done in order to preserve the TGA apparatus and ensure its good working for long time. Once done it, the valve can be switched to SO$_2$ position and the experiment can be carried out. When the experiment is over the valve must be switched again to pure nitrogen position and flush the system again before lift the furnace and manipulate the crucible. In a very conservative calculation, 10 minutes flushing are enough to remove all the SO$_2$ that might be present in the furnace.

Performing experiments of carbonation-calcination cycles in a TGA need short preparation time but experiments take long time. When the desired temperature program is introduced in the software, the crucible is pulled out from the slot (using always gloves), is cleaned (if proceed) with compressed air and a sample of limestone (normally around 20-30µg) is weighted inside it using the high precision balance. A plastic support can be used for weighting the sample. The crucible with the sample can be fitted again in the slot. It must be placed carefully because the TGA balance is very sensible and it could break down with a little coup.
3.2.4. Data analysis and equations

Once the experiment is over a graph as the one as follows (Figure 3.4) is obtained:

![Graphical representation of experimental parameters given by the software](image)

Data from TGA can be exported to an Excel file for its posterior analysis. The generated file contains registers of time, temperature, mass variation and gas flows. For example, temperature and mass data can be plotted vs time experiment:

![Sample mass and temperature variation vs experiment time](image)

From these data the CO₂ Carrying Capacity can be calculated with the following formula determined by Jon Christensen (43):
Carbonate looping process for CO\textsubscript{2} capture

Master Thesis

\[ CO_2 \text{Carrying Capacity} = \frac{\text{Moles of CO}_2 \text{ captured in cycles N}}{\text{Moles of CaO in completely calcined sample}} \times 100 = \frac{n_{\text{CO}_2, \text{captured}(N)}}{n_{\text{CaO, sample}}} \times 100 = \frac{m_{\text{CO}_2, \text{captured}(N)}}{\frac{M_{\text{CO}_2}}{m_{\text{sample}} \cdot x_{\text{CaO, sample}}} \cdot \frac{M_{\text{CaO}}}{M_{\text{CaO}}}} \]

(Eq. 3.1)

Where the mass captured in the cycles N is calculated by:

\[ m_{\text{CO}_2, \text{captured}(N)} = \text{Mass at the end of carbonation N} - \text{Mass at the end of calcination N} \]

(Eq. 3.2)

When SO\textsubscript{2} is used in the experiments the following formula (3.3) can be used in order to calculate the degree of sulfation (43):

\[ \text{Degree of sulfation} = \frac{\text{Moles of CaSO}_4 \text{ captured after N cycles}}{\text{Moles of CaO in the calcined sample}} \times 100 = \frac{n_{\text{CaSO}_4(N)}}{n_{\text{CaO, sample}}} \times 100 \]

\[ = \frac{x_{\text{CaO, sample}} \cdot m_{\text{sample}}}{M_{\text{CaO}}} \]

(Eq. 3.3)

The mass of captured CaSO\textsubscript{4} can be calculated as:

\[ m_{\text{CaSO}_4} = \frac{m_{\text{SO}_3 \text{ as CaCO}_4(N)}}{M_{\text{SO}_3}} \cdot M_{\text{CaSO}_4} \]

(Eq. 3.4)

Where,

\[ m_{\text{SO}_3 \text{ as CaCO}_4(N)} = \text{Mass at the end of calcination N} - \text{Mass at the end of calcination 1} \]

(Eq. 3.5)

Jon Christensen (43) presented this formula for experiments that used SO\textsubscript{2} from the first cycle to assure that the calcinations has completed. However, the pipe that goes from the switching valve to the TGA furnace will still contain some nitrogen and the SO\textsubscript{2} will take some time to be in contact with the sample. In this work, SO\textsubscript{2} is introduced in the first cycle and it is considered that it has no effect in the calcination and that it is completed.

### 3.3. Horizontal tube furnace reactor

A tubular reactor was used in the experiment with the purpose to obtain realistic calcinations conditions (90% CO\textsubscript{2} and 950°C). Samples were introduced and pulled out from the reactor with a ceramic crucible. The apparatus is situated in
the up floor of the pilot plant (Building 228). The TGA was not used as samples of at least 0.5-1 gram are required for BET analysis whereas TGA needs samples around 20-30µg.

The tubular reactor has 3 separated heating zones where temperature can be set. Gases are introduced in one of the flanges of the system and exhausted gases can be vented to the atmosphere or analyzed. In order to be able to push and pull out the crucible with sample and to not get burnt the flanges are refrigerated with a water circuit. Some parameters of the process (temperature, exhaust gas composition...) can be recorded with a computer.

A sketch of the horizontal reactor is shown in the next Figure 3.1 and explained in detail in Appendix 02:

3.3.1. Performing experiments

Before heating up the furnace, the cooling water must be turned on and the tubular reactor must be cleaned. Also, the inlet gas pipe has to be connected. Once done it, the furnace controllers can be turned on by pressing the green button and the temperatures can be introduced in the three screens. Heating is switched on by pressing the red button. The heating process can last around 4-5 hours if temperatures of 950°C are required. The variation of temperature inside the furnace can be recorded by using a thermocouple and the Labview software.

When the desired temperature is achieved the reactor is ready to calcine a sample. The inlet gas flange is disabled and the crucible with the sample previously weighted is placed inside it and is pushed to the heated zone of the tube with a high-resistant temperature wire, which will be used to pull the crucible out at the end of the calcinations. Once the hot crucible is pulled out, it is recommended to let it cool down during 10min in the cooled flange zone in order to avoid to handle with the crucible. Even using high temperature resistant gloves, they can be burnt by touching the hot crucible meaning rests of them in the as well as the hazard to get burnt. If the crucible is pulled out from the reactor it is recommended to cool it down to a metallic surface because it can produce burns in other material surfaces (as for example, wood or plastic tables) meaning again rests of burnt material in the crucible. Once the crucible has lowered its temperature (without allowing to cool down it completely because can absorb some water from the ambient) it can be weighted in the high precision balance. Thus, by the difference of weights the rate of reaction can be
3.3.2. Experimental problems

Cycling a sample inside the furnace is not possible because of the temperature profile inside the furnace. Only the second stage has a temperature profile more or less uniform whereas the first and third stages this profile varies considerably. Thus, it is not possible to obtain two zones with stable temperature where to move the crucible. For example, by setting the temperature screens at 850, 1000 and 700°C the following temperatures measured in the represented points (Figure 3.7) are obtained:

![Figure 3.7. Positions for temperature measuring with thermocouple in the horizontal reactor](image)

<table>
<thead>
<tr>
<th>Position</th>
<th>Distance [cm]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X0+12cm</td>
<td>52</td>
<td>942,9</td>
</tr>
<tr>
<td>X0+9cm</td>
<td>49</td>
<td>951,0</td>
</tr>
<tr>
<td>X0+6cm</td>
<td>46</td>
<td>957,0</td>
</tr>
<tr>
<td>X0+3cm</td>
<td>43</td>
<td>956,8</td>
</tr>
<tr>
<td>X0</td>
<td>40</td>
<td>953,0</td>
</tr>
<tr>
<td>X0-3cm</td>
<td>37</td>
<td>945,8</td>
</tr>
<tr>
<td>X0-6cm</td>
<td>34</td>
<td>933,5</td>
</tr>
<tr>
<td>X1=X0-10cm</td>
<td>20</td>
<td>777,1</td>
</tr>
<tr>
<td>X1-5cm</td>
<td>15</td>
<td>653,5</td>
</tr>
<tr>
<td>X1-10cm</td>
<td>10</td>
<td>561,9</td>
</tr>
<tr>
<td>X1-15cm</td>
<td>5</td>
<td>490,1</td>
</tr>
<tr>
<td>X2=X1-20cm</td>
<td>0</td>
<td>300,0</td>
</tr>
</tbody>
</table>

Distances from the begging of the furnace (X2)

As it can be observed in the first stage (from X2 to 30cm) the temperature in not uniform and varies considerable. Between 30 and 50cm temperature is quite uniform as it can be seen in Table 3.4. This variation is represented in the following Figure 3.8:
Another issue to consider is that when the crucible with the sample is introduced and pulled out the reactor is disassembled with the consequence that it is opened and not sealed. Thus, when the sample is introduced in the required place of the furnace, it is being heating while the flange where the sample has been introduced is still opened. Sealing again the flange (connecting the gas pipe, put four screws and adjust them) can last around 30 seconds. Even more, it will also take some time to flush the air that has entered in the system with the inlet gas. This procedure might be performed introducing first the crucible in the water-cooling flange, sealing it and pushing the sample with the high-temperature resistant wire. To do it in this way is necessary a crucible with a hole where to fit the wire in order to push it when the reactor is closed. Unfortunately, no crucible with hole was available.

During the experiences was realized that if a big amount (1-1.5 grams) of sample was used for simulating calcinations at low residence times or low temperatures not all the limestone was calcined. These results are shown in Appendix 03. From the literature study is known that with a few minutes (1-3 min) calcination process is completed whereas calcinations of around 1 gram of Faxe limestone during 10 minutes barely gave a 30-40% of conversion. It is suspected that if a big sample is used only the highest part of the limestone layer placed in the crucible reacts. However, this fact is not observed for samples calcined at higher temperatures than 950°C or higher residence times than 30 minutes. It might be because the released carbon dioxide in the calcination process situated in the lower part of the layer has enough time to cross the sample situated over itself. It was experimented that by using small samples calcinated during 10 minutes the conversions were complete. We can conclude that the carbon dioxide released in the lower part of the layer takes long time to be released. In order to check this affirmation the author proposes analyzing the exhaust gas leaving from the tubular reactor with the purpose to know how much CO₂ is released during the experiment.

Due to these experimental constraints the horizontal reactor was only used to calcine limestone for its posterior analysis in a BET in order to know sintering effects in different calcination conditions.
4. Results and discussion

In this section, results obtained from the experimental data and are discussed. Sintering was determined in different limestone samples after calcination at different temperatures, residence times, particle size and atmospheres. Also, the influence of SO$_2$ was investigated under various concentrations and stages of the process (calcination and carbonation).

4.1. Sintering

As it is explained in the Literature Study of this project, sintering is caused by high temperatures meaning changes in pore shape and distribution as well as pore shrinkage. Smaller pores are reduced meaning a pore distribution shifted to bigger pores. Thus, a reduction of the superficial area of the sorbent (CaO) and a loss in CO$_2$ carrying capacity are produced.

This section presents the results from experimentation of sintering in different conditions as atmospheres, temperature, particle size and residence time. The experiment consisted in calcining a sample of limestone in different conditions in a high heated horizontal reactor and their posterior analysis in a BET surface area apparatus. Also, some of the calcined samples from these experiments were sent to be analyzed in a scanning electronic microscope (SEM) in order to obtain further information as surface structure of limestones after calcinations as well as the size of grains and subgrains.

4.1.1. Particle size

A wide range of particle size of Faxe limestone was analyzed. Experiments were carried out with the following ranges: 0-250μm, 355-425μm, 500-600μm and 1-2mm. Results are depicted in Figure 4.1 and can be read in Table 4.1:

Table 4.1. Superficial areas obtained after calcining limestones with different particle size.

<table>
<thead>
<tr>
<th>Size range [μm]</th>
<th>Superficial area [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-250</td>
<td>3.875</td>
</tr>
<tr>
<td>355-425</td>
<td>3.769</td>
</tr>
<tr>
<td>500-600</td>
<td>3.536</td>
</tr>
<tr>
<td>1000-2000</td>
<td>3.548</td>
</tr>
</tbody>
</table>
Figure 4.1 above shows that no appreciable differences on superficial area between the studied ranges can be seen. It means that sintering has the same effect for all the particles size. The higher value barely reaches 4 m$^2$/g whereas the lower value is found over 3.5 m$^2$/g. Thus, we could say that particle size has no influence in sintering process.

It must be considered that in calcination-carbonation cycles as the carbonation progresses from the exterior free surfaces to inwards, unreacted CaO can be present in the interior of the sample and the unreacted CaO could be higher in big particles. Results presented previously take into account the first calcination and nor a process of carbonation so it could have some influence in sintering. Figure 4.2 shows the results of an experiment cycling limestones in a thermogravimetric analyzer (TGA) with different particle sizes was carried out and demonstrated that there were no differences in the adsorption capacity of the sorbent for the different particles. Even though, we should consider that experiment calcinations were carried out during only 3 minutes instead of the 30 minutes used in the horizontal reactor calcinations. Thus, sintering process is longer in the experiments in the horizontal reactor of course. However, Figure 4.2 shows that the adsorption capacities for the different particle sizes are almost the same and only differ a little during the firsts five cycles.

Figure 4.2 shows the CO$_2$ carrying capacity for 15 cycles. It can be observed that the sorbent capacity is almost the same for the different sizes experimented:
Figure 4.2. CO₂ carrying capacity vs number of cycles for different particle sizes (0-250µm, 500-600µm and 1-2mm).
Limestone type: Faxe Bryozo. Calcinations: 960°C; 3min; 85.7% CO₂. Carbonation: 650°C; 15min; 20% CO₂

The results in sorbent capacity decay obtained in the TGA are in agreement with the work performed by Jon Christensen (43) as well as the works cited in the literature (Abanades et al and Grasa et al, see Literature Study Section 2.2.1). All of them showed the same tendency even that they were carried out in different calcination-carbonation conditions.

Calcined particles of 0-250µm and 1-2mm were sent to be analyzed in a SEM. Particles of 1-2mm were grinded with the purpose to observe the surface texture and grain distribution in the free surface and the inner of the particle. The following SEM pictures were obtained:

Figure 4.3. SEM picture of calcined limestone. Characteristics: 0-250µm; 950°C; 30min; 90% CO₂
Comparing the left side (scale 10µm) of Figure 4.3, Figure 4.4 and Figure 4.5, it can be observed that the surface of the 0-250µm calcined particles and the inner of 1-2mm particles (Figure 4.3 and Figure 4.4, respectively) have a similar texture which is grainier whereas the free surface of the particle of 1-2mm (Figure 4.5) has a less grainy surface.

Observing the particles in a higher magnification (1µm, right side of figures above) it can be concluded that the grain size is very similar but the free surface of the 1-2mm calcined particle seems to have less big voids than the inner surface of the same particle. It can be attributed to the more homogeneous surface that the outer surface have.

### 4.1.2. Reaction atmosphere

Calcinations in different atmospheres were tested in order to know the effects in sintering. Several literature works are performed in non-realistic conditions (Literature Study, Section 2.3.1) and were carried out in a nitrogen atmosphere. A content of CO$_2$ around 90% would be a typical concentration in the calcinator. Also, concentrations of 0% and 50% of CO$_2$ have been tested. Results are shown in Table 4.2 and Figure 4.6.
Table 4.2. Superficial areas obtained after calcining limestones with different atmospheres. Conditions are the same than Figure 4.6.

<table>
<thead>
<tr>
<th>CO₂ concentration</th>
<th>Superficial area [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>11,448</td>
</tr>
<tr>
<td>50%</td>
<td>4,591</td>
</tr>
<tr>
<td>90%</td>
<td>3,875</td>
</tr>
</tbody>
</table>

Figure 4.6. Superficial area of calcined limestones for different atmospheres after calcining for 30min. Limestone type: Faxe Bryozo. Temperature: 960°C. Gas flows: 5,4L/min for 0% and 90% CO₂; 11,9L/min for 50% CO₂; rest of flow was air.

Lower CO₂ concentrations mean a higher superficial area in the sorbent. Thus, sintering is reduced in low CO₂ atmospheres. However, in calcination combustors using oxy-firing generate an atmosphere of 90% CO₂. Thus, reducing sintering in a real process plant by not using oxy-firing and getting lower carbon dioxide concentration would not be a recommendable choice as the captured CO₂ in the process would be less concentrated and it might not fulfil the specifications for storage or other applications.

For the limestone sample calcined in 0% of CO₂ almost no sintering has been produced. A typical calcined Faxe limestone without allowing sintering has a superficial area around 12m²/g (according conversations with people experimenting in the same field) whereas the calcined sample in 0% CO₂ has a value of 11,448m²/g. It means that high carbon dioxide concentrations during sintering have a significant effect on this process. Nevertheless, as explained before, in a carbonate process high CO₂ concentrations will be present during calcinations because of the use of oxy-firing combustion. In fact, the higher CO₂ concentration in the calciner, the higher CO₂ stream for storage although it means higher sintering in the sorbent.

From the Literature Study (Section 2.2.6.) it can be seen that higher CO₂ pressures when cycling a sample mean a higher deactivation of the sorbent. Now, this can be contrasted with the experiments carried out in the BET apparatus that show that for higher concentration of CO₂, higher sintering is produced. Thus, experiments performed in the TGA (from literature) and the BET are in agreement.

In order to know how is the decay of surface area versus the CO₂ concentration further experimentation should be done. For example, it would be recommendable to carry out experiments with 1, 5 and 10% of CO₂ in the tubular
reactor. Thus, a chart with much information will be obtained and will be possible to know how the decrease of surface area in lower CO$_2$ concentrations is. Also, the gas analyzer for the exhaust gas could be used with the purpose to know if higher concentrations of CO$_2$ in the tubular reactor lead to longer time to calcine completely a sample.

The samples were sent to be analyzed in a scanning electronic microscope in order to observe the surface texture and the size of the pores formed after the calcinations:

From the figures above it is observed that the texture of the surface in the 10µm scale (x1.000 magnification) are very similar as well as for the sample calcined in 90% of CO$_2$ (Figure 4.3). From the right part of the figures above and Figure 4.3, smaller subgrains can be observed for the sample calcined with no CO$_2$ as well as a bigger volume surrounding the surface. A very similar surface for the samples calcined in 50% and 90% of CO$_2$ is observed. Thus, from this images and from the BET analysis we can say that the sample calcined in 0% CO$_2$ seems that have not suffered sintering while the others two samples (even for 50% CO$_2$) seem to have experienced higher sintering process. Although the SEM pictures seem to show lower sintering when lower carbon dioxide concentrations it is quite difficult to see and can be difficult to extract conclusions.
4.1.3. Temperature

From the literature study it is known that high temperatures provoke higher loss of capacity in the sorbent as well as an increase on sintering process. R. Borgwardt (Literature Study, Section 2.3.1) studied the temperature effect on sintering using \( \text{N}_2 \) atmospheres and showed this reduction tendency with the temperature. Only the samples that showed complete calcinations were analyzed and the ones that shown low conversions (when the temperature was 850 or 900°C) were discarded.

Table 4.3. Superficial areas after calcining limestones with different temperatures. Same conditions than Figure 4.9.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Superficial area ([\text{m}^2/\text{g}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>2,467</td>
</tr>
<tr>
<td>950</td>
<td>3,875</td>
</tr>
<tr>
<td>925</td>
<td>4,151</td>
</tr>
</tbody>
</table>

Lower temperatures than 925°C were tested (850 and 900°C) but they showed low conversion and were not analyzed in BET. These conversions can be seen in Appendix 03. As expected, higher temperatures cause a decrease of the superficial area of the sorbent.

![Figure 4.9. Superficial area of calcined limestones for different temperatures after calcining for 30min. Limestone type: Faxe Bryozo. Calcination conditions: 90% \( \text{CO}_2 \), 5,4L/min](image)

The calcined sample at 1000°C was analyzed with scanning electronic microscopy:

![Figure 4.10. SEM picture of calcined limestone. Characteristics: 0-250µm; 1000°C; 30min; 90% \( \text{CO}_2 \)](image)
As it can be seen in the figure above and the Figure 4.3, with magnifications of x1.000 (10µm scale) it is not possible to extract conclusions but with higher magnifications (x10.000; 1µm scale) higher sub-grain size seems to be observed, meaning that sintering has had a bigger effect in the 1000°C calcined sample as expected. Again, it is quite difficult to observe the differences and it is quite difficult to extract conclusions with SEM images.

### 4.1.4. Residence time

From the literature study it is also known that higher residence times mean higher sintering, with the consequent change of sorbent surface and pore distribution. R. Borgwardt also showed this fact working in N$_2$ atmospheres. The results are the expected and shown in Table 4.4 and Figure 4.11. Only the samples that showed complete calcinations were analyzed and the ones that shown low conversion (when the residence time was 5min, for example) were discarded. Anyway, for the sample of 10min calcination a smaller amount of limestone was used for calcination in order to achieve the total conversion as it is explained in the Section 3.3.2.

<table>
<thead>
<tr>
<th>Residence time [min]</th>
<th>Superficial area [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8,405</td>
</tr>
<tr>
<td>30</td>
<td>3,875</td>
</tr>
<tr>
<td>60</td>
<td>2,773</td>
</tr>
</tbody>
</table>

No shorter residence times were tested as the calcinations was not completed as explained in Section 3.3.2 and showed in Appendix 03. It can be observed that for a residence time of 10 minutes a superficial area of 8,405 m$^2$/g is obtained, not far from the calcined limestone without sintering (around 12m$^2$/g). In fact, according to the literature study (see Section 2.2.3) calcination is completed in 200s at 930°C in 100% of N$_2$ (12).
The samples with residence times of 10 and 60 minutes were also analyzed in a SEM:

![Figure 4.12. SEM picture of calcined limestone. Characteristics: 0-250µm; 950°C; 10min; 90% CO₂](image1)

![Figure 4.13. SEM picture of calcined limestone. Characteristics: 0-250µm; 950°C; 60min; 90% CO₂](image2)

From the Figure 4.12 and Figure 4.13 above is observed that the subgrain of the surfaces is smaller for the 10 minutes calcined sample which means that sintering has had less effect in this sample. Although some soft surfaces are seen in the 10µm scale images when used a higher magnification it was observed that they had a grainy size.

### 4.2. Sulfur dioxide presence

Several experiments of cycling a limestone sample in a TGA in sulphur dioxide presence were carried out. The results are showed and commented in the present section. Calcination-carbonation cycles were performed in SO₂ presence during calcination (100 and 700ppm) and carbonation (100ppm) in realistic conditions: 80% of CO₂ during calcinations (lower than 90% in order to adjust the SO₂ concentrations) at around 950°C and 20% CO₂ during carbonations at
650°C. A sample cycling in non-realistic conditions (no CO$_2$ during calcinations) was carried out with the purpose to observe the sulfation behaviour. On the contrary what it was expected and what was found during the literature research, simultaneous capture of CO$_2$ and SO$_2$ seems not prohibitive as no high decreases of CO$_2$ carrying capacity were found (24) (27).

### 4.2.1. Sulfation in realistic and non-realistic conditions

An experiment with calcination in milder conditions (Experiment 2, 0% of CO$_2$) was done with the purpose to check if the sulfation process was faster without CO$_2$ atmospheres. Only the SO$_2$ was introduced during calcinations as it is the stage where it is supposed to be because the presence of sulphur in fuels used in oxy-firing. SO$_2$ concentrations of 100ppm were assumed. The filled marks correspond to the CO$_2$ carrying capacity data (left scale) and the non-filled marks correspond to the degree of sulfation data (right scale). Also, an experiment without sulfation (0-250µm Faxe limestone, same conditions as Figure 4.2) was included in the chart with the purpose to compare the data. Results are presented in the following Figures and more detailed composition of the gas is shown in Appendix 06:

![Graph showing CO$_2$ Carrying capacity and degree of sulfation in realistic and non-realistic conditions. Calcination: 80% CO$_2$, 960°C; 3min. Carbonation: 20% CO$_2$; 650°C; 10min.](image)

As it can be observed in Figure 4.14, it does not have any effect on CO$_2$ carrying capacity as the three curves of data follow the same tendency and only differ in the beginning. In the first cycle the high adsorption capacity is seen for the experiment with 100ppm SO$_2$ and 0% CO$_2$ in calcination because as it said in others sections CO$_2$ has a great effect on the CO$_2$ carrying capacity. However, it is only seen for the firsts 5 cycles. Thus, no significant difference is observed in CO$_2$ carrying capacity compared to the experiment carried out with calcinations in 90% CO$_2$. The degree of sulfation is represented as well. It is possible to observe that despite of giving a very disperse values, the two experiments follow the same tendency.
4.2.2. SO₂ concentration

A concentration of 100ppm (Experiment 1) and 700ppm (Experiment 3) were tested during calcinations in 80% of CO₂. As expected, higher SO₂ contents gave higher degrees of sulfation but did not show a higher decay of adsorption capacity of CO₂. A detailed composition of gases can be seen in Appendix 06.

![Figure 4.15. CO₂ Carrying capacity and degree of sulfation in different SO₂ concentrations during calcination. Calcination: 80% CO₂, 960°C; 3min. Carbonation: 20% CO₂; 650°C; 10min.](image)

The Figure 4.15 shows that the CO₂ carrying capacity of the sorbent is quite similar but the decay curve for the experiment that used 100ppm it is found a bit over the other. It is attributed of course to the formation of CaSO₄ that causes a pore blockage in the sorbent meaning in fewer pores for CO₂ reaction. Again, higher influence of SO₂ in CO₂ carrying capacity was expected but contrary to results it was not shown. CaSO₄ formation is supposed to block the pores and not allow the CO₂ to go through the particle causing the expected reduction of adsorption capacity. However, it was not observed or observed with a very small effect. This can be attributed to the formation of higher voids during calcination-carbonation cycles where the CaSO₄ particles can be formed without obstructing the movement of CO₂.

The chart also shows that the degree of sulfation is much higher for 700ppm, around 10 times higher in the 15th cycle. Thus, for seven times the SO₂ concentration a 10 times higher degree of sulfation is found meaning that it does not follow a proportional tendency. Nevertheless, further experiments with different SO₂ concentrations should be done to confirm this fact.
A concentration of 100ppm was added during carbonations (Experiment 4) while no sulfur was used in calcinations. Results are presented in Figure 4.16:

![Figure 4.16. CO₂ Carrying capacity and degree of sulfation during calcination and carbonation. Calcination: 80% CO₂, 960°C; 3min. Carbonation: 20% CO₂; 650°C; 10min.](image)

It can be seen that during carbonation process sulfation of the sorbent is higher than in calcination but the CO₂ carrying capacity does not present different sorbent decays.

Looking at the figure above one can think that during carbonation process sulfation of the sorbent is higher than in calcination. Carbonation last 10 minutes while calcination last 3 minutes so SO₂ has more time to react with CaO. Even more, CaO is fed in carbonator whereas CaCO₃ is fed in calcinator where is calcined and converted to CaO. From the literature it is known that direct sulfation (directly from CaCO₃) occurs in systems with high CO₂ partial pressure. If CaCO₃ does not react with SO₂ and we consider that it takes around 1 minute to be calcined only 2 minutes for sulfation are available.

From the previous works it is known that CaSO₄ is a stable product between the working temperatures. However, its stability decreases with increasing temperatures. It might affect the rate of sulfation.

Also, different oxygen concentrations were used during the experiments by using air in order to obtain the desired SO₂ concentrations (see Appendix 06). Oxygen is not supposed to have some effect in the sulfation rate above 2% as said previously. According to Jon Christensen (43) the heating element made of platinum could have some effect in the sulfation reaction as it is known to be a good catalyst for SO₂ oxidation to the highly reactive SO₃.

After extract conclusions if carbonation has higher sulfation than calcination, further experimentation should be done with the purpose to know the effect of the parameters than can influence sulfation (temperature, oxygen concentration, etc). However, considering that a degree of sulfation of 1.7% during 10min in carbonation and 0.5%
during 3min in calcinations, almost the same sulfation rate is obtained: 0.17%/min and 0.166%/min for carbonation and calcinations respectively.

4.3. Conclusions and suggestions for further experimentation

With the performing of the experiments and the results obtained some clear conclusions can be extracted:

It has been possible to know that particle size has no effect in sintering. Also, the significant influence of temperature and residence time on sintering has been checked in the typical conditions of a carbonate looping system. The influence of the atmosphere (CO$_2$ concentration) has found to have a big importance on sintering. Very little documentation was found regarding the effect of this parameter on sintering during the literature research.

Sulfation has found to have a little effect on the CO$_2$ carrying capacity when all works in the literature research showed a great decrease of it with higher SO$_2$ concentration. The work carried out by Jon Christensen (43) agrees with the results of the experiments of the present project.

In order to improve the experiences and to complement the experiments that have been carried out the author proposed the following work:

Although experiences in the tubular reactor and the TGA were performed in realistic conditions, in a real plant fluidized beds are used. The most exact and realistic experiments should be carried out in fluidized beds in order to calcine limestone samples. Thus, instead calcining a sample inside a crucible it should be calcined in a fluidized reactor in order to achieve even more realistic conditions.

When experimenting in the TGA with SO$_2$ is not possible to control the oxygen flow because the protective gas is used for achieving the desired CO$_2$ and SO$_2$ concentrations instead of N$_2$, which supply has been changed by sulphur dioxide in nitrogen as the apparatus has three gas pipe inputs. Thus, for each experiment we have different O$_2$ content that influence in the sulfation reaction. The TGA has been designed only for three inputs and the addition of an extra input will not be possible. The solution proposed by the author is to install a mixer where to mix the SO$_2$ in nitrogen and pure nitrogen flow before the low delta-P mass flow controllers. Thus, the system will have another flow in order to have the desired CO$_2$ and SO$_2$ concentrations and will allow keeping the protective gas flow constant in all the experiences, meaning a constant oxygen flow as well.

Further experimentation can be performed on sulfation and sintering. For example, cycles samples in a thermogravimetric analyser (TGA) using certain SO$_2$ content can be analyzed in a scanning electronic microscope (SEM) with the purpose to determine exactly where the sulfation takes part. It can be also useful to observe the pore texture of the sorbent for the different sulfation conditions (concentration, stage when sulfation is produced...). As said before, an atmosphere of CO$_2$ seems to have a higher effect on sintering than expected. Thus, further experiment could be carried out using atmospheres with low CO$_2$ content (20, 10, 5 and 1%) in order to know how much sintering is produced in these conditions.
5. Modelling

In this section, different equations for sorbent deactivation have been used with the coefficients given by the authors and new coefficients have been also proposed in order to fit better the experimental data. The average particle activity that is circulated in a real carbonate looping system has been represented using the best sorbent deactivation equation and for different operational values of the plant ($F_0/F_{CO_2}$ and $F_{CaO}/F_{CO_2}$ ratios, molar flows of fresh limestone and recirculation per CO$_2$ entering in the carbonator respectively). Also, the input heat necessary in the calciner is calculated for the same flow ratios without considering the maximum conversion in the carbonator (correspondent to the average capacity calculated previously). Finally, considering a real cement plant some operational values that lead to low heat and limestone consumption are proposed.

5.1. Sorbent decay behaviour

Available equations

Several equations have been presented in order to determine and adapt the sorbent decay. For example, Grasa and Abanades et al (11) presented the following equation that has been proven to be valid for many limestones up to 500 cycles:

$$X_N = \left( \frac{1}{1 - X_r} + kN \right)^{-1} + X_r$$  \hspace{1cm} (Eq. 5.1)

Where $X_r$ is the residual conversion of CaO after an infinite number of cycles and $k$ is the deactivation constant. According these authors, this equation fits very well for $X_r=0.075$ and $k=0.52$.

Another equation was also presented by Abanades and Alvarez (28):

$$X_N = f_m^N (1 - f_w) + f_w$$  \hspace{1cm} (Eq. 5.2)

Where $f_m$ and $f_w$ are fitting parameters. It was checked that for values of $f_m=0.77$ and $f_w=0.17$. However, most of these data was fitted from experimental series of less than 50 cycles.

Wang and Anthony (29) obtained the following equation in order to explain the sorbent decay in only one parameter:

$$X_N = \frac{1}{1 + kN}$$  \hspace{1cm} (Eq. 5.3)

Recently, Lysikov et al (44) used the following equation to fit experimental data:
\[
    a_N = \frac{1 - a_\infty}{(1 - kN)^n} + a_\infty
\]

(Eq. 5.4)

Where \( a_N \) is the degree of recarbonation on the \( N \)th cycle, \( a_\infty \) is the residual conversion after an infinite number of cycles, and \( k \) is the parameter which is directly proportional to the sintering rate.

**Adjusting parameters**

Here, the parameters for adjusting the equations presented above are fitted to the experimental results from cycling a sample in the TGA. Experiment conditions were: carbonation at 650ºC during 15min at 20% CO\(_2\), calcination at 960ºC during 3min at 90% CO\(_2\). Sulfur dioxide was not used in calcination and neither in carbonation.

Equations (1), (2), and (3) are used to fit the behaviour of sorbent decay. The equation proposed by Grasa and Abanades (Eq. 1) and Abanades and Alvarez (Eq. 2) were fitted for the parameters proposed by the authors of these works and for new parameters. The new parameters are calculated using the Solver Excel tool. When the relative error between the experimental correlation and the correlation given by the deactivation equation is minimal, it means the tool have found the best fitting parameters. Values of \( k=2.47 \) and \( X_r=0.044 \) were obtained for equation 1 while values of \( f_m=0.358 \) and \( f_w=0.081 \).

Figure 17 depicts the experimental data and the sorbent deactivation represented by the equations proposed for the original and new parameters. It can be also seen that Equation 2 has a higher decrease in the first cycles and gets stable much before than Equation 1. Equation 3 does not fit very well with the experimental data for a value \( k=1.25 \) but it must be considered that only has one parameter to adjust.

![Figure 17. Different correlations for describing the CO\(_2\) carrying capacity of a sample during calcination-carbonation cycles](image-url)
It is seen the correlation that suits better is when using the Grasa and Abanades equation (Eq. 1) for the parameters proposed in this work ($X_r=0.044$ and $k=2.46$). The sorbent decay described with these parameters follows almost the same tendency that the experimental data. From this conclusion, the following calculations are carried out with the parameters proposed in this work as it is the correlation that better represents the sorbent decay.

5.2. Average capture capacity of CaO

The following Figure 18 shows a scheme for CO$_2$ capture with CaO. Carbon dioxide from the cement manufacturing process (or from the flue gas if it is set up in a power generator plant) enters in the system in the carbonator (\(F_{CO_2}\), kmol/s) where encounters and reacts with a calcium oxide flow (\(F_{CaO}\), kmol/s) that comes from the calcinator. The produced CaCO$_3$ from the reaction and the unreacted CaO is separated from the remaining flue gas in a cyclone. The solid stream is sent to the calcinator where are calcined with the purpose to obtain CaO again. The solid stream obtained from calcinations (CaO) is separated from the CO$_2$ also obtained in the calcination process in a cyclone before to be sent to the carbonator again. The calciner contains a purge in order to remove the ashes, CaSO$_4$ (when SO$_2$ presence) and spent CaO that is replaced for a flow of fresh limestone (\(F_0\), kmol/s).

Figure 18. Scheme of a CO$_2$ capture system by adsorption on calcium oxide (45)
Considering that calcination process is fully completed, that there is enough time for the completion of the fast carbonation stage and the solids are well mixed in both carbonator and calcinator, the average capture capacity of the CaO circulating in the system can be calculated by the expression:

\[
X_{ave} = \sum_{N=1}^{N=\infty} r_N X_N
\]  
(Eq. 5.5)

It is the maximum conversion that can be achieved in the carbonator. Where \(X_N\) is the CO\(_2\) carrying capacity in cycle N (see equations in previous section) and \(r_N\) is the fraction of solids entering the carbonator that have circulated exactly N times through the loop and is given by:

\[
r_N = p(1 - p)^{N-1}
\]  
(Eq. 5.6)

Where,

\[
p = \frac{F_0}{F_0 + F_{CaO}}
\]  
(Eq. 5.7)

This equation is derived in Appendix.

When there is SO\(_2\) presence in the flue gas N. Rodriguez et al (34) proposed the equation 7 that supposes that all sulphur present in the fuel reacts quantitatively with the active part of CaO. This equation is adopted assuming that the fate of all S entering the system will be to irreversibly deactivate only the CO\(_2\) active part of CaO forming CaSO\(_4\).

\[
X_{ave} = \sum_{N=1}^{N=\infty} r_N X_N - \frac{F_{CO2}}{F_0 r_{C/S}}
\]  
(Eq. 5.8)

Where \(r_{C/S}\) is the C/S ratio in the fuel. According these authors this equation may be an excessively assumption because part of the CaO that is not active for carbonation can actually be active for sulfation reaction.

**Average capacity for Grasa and Abanades parameters**

With the purpose of calculation the average conversion different values of \(F_0/F_{CO2}\) and \(F_{CaO}/F_{CO2}\) are used. The mathematical operations were carried out with MATLAB 7.0 and the scripts are shown in Appendix. Figure 03 represents \(X_{ave}\) for a range of conditions of interest.

Equation 8 given by N. Rodriguez et al (34) is used for systems where the sulfation is produced in the carbonator and for CO\(_2\) capture from power generation systems. In fact, \(r_{C/S}\) refers to the relation of carbon and sulphur in the fuel used for generation of power. In this work, it has been considered that the sulfation in a CO\(_2\) capture system with CaO is produced in the calcinatory because of the sulphur content of the fuel as the CO\(_2\) captured in the carbonator comes from the limestone calcination process and does not have sulphur dioxide.
Thus, if a fuel with a relation of $r_{C/S}=100$ means that for each mol of sulphur dioxide produced in the combustion, 100 mol of carbon dioxide are also formed and both components will get in the carbonator where sulfation will be produced. If we consider sulfation in the calciner because of the sulphur content of the oxy-fired fuel the expression would not be valid as the flue gas of the oxy-firing will be mixed with the carbon dioxide released from the CaCO$_3$ calcination. N. Rodriguez et al did not consider sulfation in the calciner.

However, in this section it has been considered that the expression is valid although the sulfation as said before is produced in the calciner. The first Figure 19 shows the $X_{ave}$ for the original values of the Grasa and Abanades while the other (Figure 04) shows for the values proposed in this work. $X_{ave}$ is given per different relations of $F_{CaO}/F_{CO2}$ and $F_0/F_{CO2}$. The discontinuous and numbered lines represent $X_{ave}$ when using different fuels (coal: lignite and anthracite of 3 and 1% of sulphur respectively and fuel oil of 0.15%S; it is considered that natural gas has no sulphur) with some sulphur content for a relation $F_{CaO}/F_{CO2}=2$.

![Figure 19. $X_{ave}$ as a function of ratio $F_0/F_{CO2}$ and $F_{CaO}/F_{CO2}$ including the effect of using fuels with sulfur: (1) fuel-oil, $r_{C/S}=1300$; (2) Coal: anthracite, $r_{C/S}=244.8$; and (3) Coal: lignite, $r_{C/S}=62.4$. See Appendix 11 for compositions considered for calculating $r_{C/S}$. For original parameters: $X_{r}=0.075$ and $k=0.52$](image)

Clearly, the average capture capacity can be kept high by increasing the fresh limestone ratio (meaning also higher limestone consumption) because fresh sorbent with high adsorption capacity will be circulating in the system. The conversion of a real carbonation reactor is equal at $X_{ave}$ at much but it is known that for carbonators with enough residence time (1-3min) it should be possible to yield conversions close to the maximum (34). On the other hand,
when the \( \frac{F_{CaO}}{F_{CO2}} \) is increased lower average capacity is obtained because the lower residence times in the fluidized reactors.

As expected, the more sulphur content in the fuel, the lower average capacity in the particles circulating in the system when it is modelled with the N. Rodriguez et al equation (Eq.8). Values of \( X_{ave} \) below zero in the two figures above correspond to a lack of fresh limestone to maintain the capture of the sulphur contained in the fuel as \( CaSO_4 \).

When the same chart is done for the new parameters for the \( CO_2 \) capture capacity it is obtained that much lower average conversions are achieved. It was clearly expected because as it can be seen in the Figure 20 the \( CO_2 \) capture capacity obtained in the experimental experiences is much lower than the equation described by Grasa and Abanades with the original values (\( k=0.52; \; Xr=2.83 \)).

![Figure 20](image-url)

**Figure 20.** \( X_{ave} \) as a function of ratio \( F_0/F_{CO2} \) and \( F_{CaO}/F_{CO2} \) including the effect of using fuels with sulfur when \( F_{CaO}/F_{CO2}=2 \): (1) fuel-oil, \( r_{C/S}=1300 \); (2) Coal: anthracite, \( r_{C/S}=244.8 \); and (3) Coal: lignite, \( r_{C/S}=62.4 \). See Appendix 11 for compositions considered for calculating \( r_{C/S} \). For original parameters: \( Xr=0.044 \) and \( k=2.46 \).

For example, when the flow ratios are \( F_0/F_{CO2}=0.30 \) and \( F_{CaO}/F_{CO2}=1 \) for the original fitting values a \( X_{ave} \) between 35 and 40% is obtained while for the more realistic values that fit better to the experimental data \( X_{ave} \) takes a value around 12%.
The presence of sulfation during the experimental calcination-carbonation cycles in TGA produced in the calcination stage has been also represented (Figure 21) in the $X_{ave}$ chart using the parameters that fitted in the Grasa and Abanades equation for the CO$_2$ carrying capacity for these experiments. For the experience of 100ppm of SO$_2$ during calcination stage they were found to be $k=2.20$ and $X_r=0.037$. For the experience of 700ppm of SO$_2$ during calcination stage they were found to be $k=1.91$ and $X_r=0.02$. These parameters can be also seen in Appendix 09.

![Figure 21. $X_{ave}$ as a function of ratio $F_0/F_{CO2}$ and $F_{CaO}/F_{CO2}$ including the effect of using fuels with sulfur when $F_{CaO}/F_{CO2}=2$ using parameters fitted for the experimental cycling of a sample in SO$_2$ presence (100 and 700ppm) in the calcination stage. For 100ppm: be $k=2.20$ and $X_r=0.037$. For 700ppm: $k=1.91$ and $X_r=0.020$.](image)

The Figure 21 represents $X_{ave}$ with two different SO$_2$ contents (100 and 700ppm) when the ratio $F_{CaO}/F_{CO2}=2$. As it can be observed, the curves correspondent to the sulfation are higher than the curve for $F_{CaO}/F_{CO2}=2$ for most of the $F_0/F_{CO2}$ ratios. It cannot be possible as the sulfation curves must be below the curve for no sulfation. This is due because of the slightly different conditions that the experiments with and without sulfation (with SO$_2$ presence the conditions in TGA were: calcination at 960°C during 3min with 80%CO$_2$; carbonation: 650°C during 10min with 20%CO$_2$) were performed and also because of the fitting parameters of the equations as at $F_0/F_{CO2}=0.4$ they cross. Nevertheless, it can be observed for the zone where these curves are below the no-sulfation curve that they decrease.
more for the sulfation experiments. But in no case this decrement is as high as the one described used the N.Rodriguez et al expression (Eq. 8).

For example, if we consider an oxy-firing process where no excess of oxygen is used for the fuel-oil with 0.15% of sulphur, a concentration of 770ppm will be obtained in the flue gas of this combustion process. As it can be seen in the figures above, when using the equation for sulfation the decay of $X_{ave}$ is higher (Figure 20, curve number 1: fuel-oil 0.15%S) than the decrease showed by using experimental data (Figure 21, 700ppm).

5.3. Heat requirements in the calciner

The calcination will require heat to warm up the solid stream ($F_{CaO} + F_{ inert} + F_{0}$), defined as $H_{in}$. It can be calculated with the formula (Eq. 9) below proposed by N.Rodriguez et al (34). This formula considers that the calorific values for the different substances involved are constant for the range of temperatures that they are found. Nevertheless, in the present work average calorific values were calculated for each substance and for each temperature range. For example, the calorific value for CaCO3 will not be the same value in the recirculated stream (carbonation-calcination) and in the fresh limestone input because they are heated from carbonation and ambient temperature respectively to the calcination temperature. It must be also considered that the equation is only for a stationary state:

\[
\frac{H_{in}}{F_{CO2}} = \Delta H_{carb} \left( \frac{F_{CaO}}{F_{CO2}} X_{carb} + \frac{F_{0}}{F_{CO2}} \right) +
\]

\[
\Delta T_{calc} \left[ C_{p_{CaO}} \frac{F_{CaO}}{F_{CO2}} (1 - X_{carb}) + C_{p_{CaCO3}} \frac{F_{CaO}}{F_{CO2}} X_{carb} + C_{p_{CaSO4}} \frac{F_{CaSO4}}{F_{CO2}} + C_{p_{Ash}} \frac{F_{Ash}}{F_{CO2}} \right] + \]

\[
\frac{F_{0}}{F_{CO2}} C_{p_{CaCO3}} \Delta T_{F0}
\]

(Eq. 5.9)

The equation above takes into consideration the heat required for calcination reaction (first row of the equation above) of the limestone produced in the carbonator by CaO conversion and the fresh limestone needed to replace the spent sorbent. The energy necessary to heat up the recirculation flow coming from the carbonator containing unreacted calcium oxide, calcium carbonate and inert (CaSO4 and ashes) to the calcination temperature to produce the calcinations of these products is seen in the second row. The equation also considers the energy necessary to heat up the make-up flow (fresh limestone) until the calcination temperature, shown in the third row of the formula. Values for the parameters for the equation 9 and how the Cp are calculated are shown in
Appendix.

During the calculations the calcium sulfate and ash flows were not considered. It was considered that the fuel used in oxy-firing is a fuel free of sulphur. The following figures were built considering a carbonation efficiency of \( E = 70\% \) in order to compare the results for different values for the CO2 adsorption capacity equations. Each point is a choice of \( F_0/F_{\text{CO2}} \) and \( X_{\text{carb}} \). From \( X_{\text{carb}} \) and \( E \) the \( F_{\text{CaO}}/F_{\text{CO2}} \) ratio can be deduced from the equation below:

\[
E_{\text{carb}} \cdot F_{\text{CO2}} = F_{\text{CaO}} \cdot X_{\text{carb}} \tag{Eq. 5.10}
\]

As said before, the carbonator conversion ranges from 0 to the average conversion attainable for the particles \( (X_{\text{ave}}) \). The discontinuous black line in the Figure 22 and Figure 23 shows the limit imposed by this limitation. Thus, it is not possible to achieve conversion behind the discontinuous line.

Figure 22 represents the input heat in the calciner for different values of \( F_0/F_{\text{CO2}} \) and \( X_{\text{carb}} \) when the original Grasa and Abanades coefficients for the CO2 carrying capacity equation are used while Figure 23 shows the same for the new coefficients:

![Figure 22. Input heat in the calciner for different values of \( F_0/F_{\text{CO2}} \) and \( X_{\text{carb}} \). Discontinuous line is the limit imposed by \( X_{\text{ave}} \). Equation coefficients: \( k=0.52, X_r=0.075 \). \( H_{\text{in}} \) in kJ/kmol CO2.](image-url)
As it can be observed the minimum heat required corresponds to a value of $X_{\text{carb}}$ of 0.21 meaning a heat input of $H_{\text{in}}=250 \text{kJ/kmol CO}_2$ for the ratios $F_0/F_{\text{CO}_2}=0.25$ and $F_{\text{CaO}}/F_{\text{CO}_2}=3.33$ (from equation 10). The minimum in the discontinuous line appears because of the opposite effect of increasing $F_0/F_{\text{CO}_2}$. Low values of this ratio lead to low values of $X_{\text{carb}}$ because more heat is required to warm up a bigger amount of unreacted CaO (1-$X_{\text{ave}}$). When increasing $F_0/F_{\text{CO}_2}$ the adsorption capacity (higher $X_{\text{ave}}$) will improve. Thus, less flow between reactors will be circulating and the heat requirements for this flow will be lower. However, the necessary heat to calcine fresh limestone will be higher. Then, there is an optimum value that minimizes the overall heat requirement in the calciner.

As the solid lines indicate, the heat requirements in the calciner increases when $X_{\text{carb}}$ diminishes because of higher heat necessary for warming up the unconverted solids from the carbonator that are bigger in this case (see equation 10).

![Figure 23. Input heat in the calciner for different values of $F_0/F_{\text{CO}_2}$ and $X_{\text{carb}}$. Discontinuous line is the limit imposed by $X_{\text{ave}}$. Equation coefficients: $k=2.46, X_r=0.044$. $H_{\text{in}}$ in kJ/kmol CO$_2$.

When modelling with the new coefficients it is observed that lower $X_{\text{carb}}$ and higher heat requirements are obtained. The minimum heat requirement (335 kJ/kmol CO$_2$) corresponds to a carbonator efficiency of $X_{\text{carb}}=0.08$ for a bit less than a ratio $F_0/F_{\text{CO}_2}=2.2$ and $F_{\text{CaO}}/F_{\text{CO}_2}$ ratio of 8.75. It means that, apart from the need of higher heating capacity the recirculating flow ratio is much higher which means that bigger installations will be needed with the consequent increase of the investment costs.
Thus, it is possible to say that if the same fuel is burned in the oxy-firing process the fuel consumption will be 30\% higher for the more realistic case (new parameters for CO\textsubscript{2} carrying capacity equation) meaning an increase of the operation costs. According the author of this report the operation costs will be owned to the fuel consumption as the price of limestone cannot be compared to the fuel. However, costs for the air separation unit (ASU) and concentrated CO\textsubscript{2} stream compressor must be also considered.

Furthermore, the spent sorbent can be used in the cement manufacturing process if the CO\textsubscript{2} capture system is integrated in this kind of industry. For this reason, a bigger model integrating the carbonate looping process in the cement manufacturing industry should be considered. When a CO\textsubscript{2} capture system is implemented it means that the spent sorbent can be used in the cement manufacturing process and lower limestone will be needed in the kiln to be calcined to CaO, which means lower heat requirements in the cement production process. Thus, the author of this work proposes a model of the CO\textsubscript{2} looping system integrated in the cement manufacturing process.
6. General conclusions

The main conclusions that have been reached are:

1. Experiments have to be performed at realistic conditions (the ones that represent the carbonate looping process)
2. Particle size does not have any effect on sintering.
3. Carbon dioxide atmospheres have higher effect on sintering than expected.
4. Sulfation has found to have less effect on CO$_2$ carrying capacity than expected.
5. Modelling using better parameters for CO$_2$ equations and integrating the CO$_2$ looping process in the cement manufacturing process must be carried out.

During the literature research it was found that a wide investigation has been carried out in many research groups. Nevertheless, many of the experimental works showed in them have been performed under unrealistic conditions. When performing calcination-carbonation cycles under more realistic conditions is observed that the CO$_2$ carrying capacity has a higher decrease in comparison to the experiments in non-realistic conditions. For example, results from cycling different particle size of limestone show that the decay of sorbent capacity is significantly increased if they are compared with the works cited in the literature research.

The sintering effect on particle size was investigated in the experimental work carried out in the present project. It was observed that it has no influence in sintering even testing very different particle ranges (0-250µm, 355-425µm, 500-600µm and 1-2mm). All superficial areas determined by BET analysis were found to give very similar results. Other results from calcining samples at different temperatures, residence times and atmospheres were in agreement with the investigation work found in the literature research. Higher calcination times, residence times and atmospheres with higher CO$_2$ concentration were proved to increase the sintering process as expected.

High CO$_2$ concentrations during calcination were found to be more significant than expected. When calcining a limestone sample at the same conditions but only varying the atmosphere concentration very different superficial areas were obtained in BET analysis. Thus, it means that CO$_2$ concentration has high influence in sintering process. For example, a limestone sample calcined in a free CO2 atmosphere (only air was used) gave a superficial area of 11.448m$^2$/g while a sample calcined in 90% of CO$_2$ gives 3.875 m$^2$/g.

Sulfation was found to be much less problem than it was showed in the literature study. Almost the same CO$_2$ carrying capacities were obtained when a sample was calcined in the TGA at concentrations of 100 and 700ppm of SO$_2$. Unlike the literature works found, SO$_2$ was used during calcinations as in a cement manufacturing industry the stream treated in the carbonator comes from the calcination process of the limestone in the kiln. Sulphur dioxide presence in calcination process is due to the fuel combusted to keep the calciner at 950ºC. Nevertheless, it was also experimented with sulfation in the calciner and the same sulfation rates were obtained.

Finally, new parameters were suggested for the equations proposed in the literature study. These parameters fitted better with the experimental data obtained by cycling a sample in a TGA. When using these new parameters in the proposed models in the literature and comparing the results to the results from model with original parameters it is observed that higher energy is necessary for heating up the calciner. Nevertheless, a model integrating the CO$_2$ capture system in cement industry should be implemented.
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Appendix 01
Parts of Netzsch TGA

Experiments were performed in a Netzsch STA 449 F1 Jupiter. A view of the apparatus is presented in the Figure 3.1.

In comparison with others thermogravimetric apparatus, the purchased STA has high heating and cooling rates (3000K/min and 300K/min, respectively) and has the mass flow controllers (MFCs) outside in a separate plate. It allows working with corrosive gases (SO₂, for example) as a purge gas. Thus, experimentation on sulfation during calcination-carbonation cycles can be carried out.

Figure 0.1. Picture of Netzsch STA 449 F1 Jupiter used for experiments.

The parts of the Netzsch TGA are explained below:

Furnace

The maximum heating and cooling rates achievable in the STA 449 F3 Jupiter are 3000K/min and 300K/min respectively. In a typical TGA configuration, the heating element would be surrounding the protective tube which again would be surrounding the sample. However, in this STA a platinum mesh is located inside the protective tube, working as the heating element. It is equipped with a thermocouple although during the experiments the sample temperature is recorded. Nevertheless, the furnace temperature can be shown by typing in the main window the following character sequence: f-u-r-n-a-c-e.

Sample carrier

The sample carrier that was used during experimentation is a ceramic holster with a type S thermocouple (maximum temperature: 1650°C) at the tip which is in contact with the crucible, only separated around 0.8mm and ensuring that the recorded temperature is very close to the sample temperature. At the bottom it has a gold plated plug, which is inserted into a socket above the balance. The crucible is placed on top of the sample carrier to contain and weigh the sample. All crucibles have a slot at the bottom that fit in the carrier. Figure 0.2 shows the crucible chosen (TG) for the experiments:
Other crucibles are available and distributed by Netzsch. Figure 0.3 shows other crucibles available:

![Figure 0.3. Other crucibles available for STA Netzsch](image)

**Mass flow controllers**

The apparatus is equipped with three “Bronkhorst Low Delta-P’’ mass flow controllers (MFCs). They are placed outside the equipment because it is necessary for the corrosion resistant version of the STA 449 F1. Since they are low delta-P, the pressurized side of the controllers must not exceed 0.5 barg. It is achieved by reducing the pressure in the cylinders with several valves.

Two of these MFCs are for purge gases (referred as reaction gases) and sent directly to the sample, entering from the bottom of the furnace. Purge 1 is 99.999% \( \text{N}_2 \) or mixtures of \( \text{SO}_2 \) in balance of \( \text{N}_2 \). Purge 2 is 99.999% \( \text{CO}_2 \). The maximum flow is 250ml/min for \( \text{N}_2 \) and 186ml/min for \( \text{CO}_2 \) and the minimum is 5ml/min for both gases.

The third gas is called protective gas (99.999% of synthetic air, 20.8% oxygen) and sent through the balance system. For this reason, it must be always a protective gas flow. The maximum gas flow for protective gas is 249ml/min.

A three-way valve (Figure 0.4 below, left down corner) is used to switch between the nitrogen gas and \( \text{SO}_2 \) in nitrogen. Available cylinders with \( \text{SO}_2 \) content are: 970±2ppm in nitrogen; 5000ppm in nitrogen and 1% in carbon dioxide.

![Figure 0.4. Picture of the mass flow controllers](image)
Others

Evacuating system: The system it is equipped with a vacuum pump to obtain pressures below to $10^{-4}$ mbar.

Additional equipment: In order to weight the sample to analyze in the STA a balance VWR Sartorius ED224S is available. It has a measuring rate up to 250g and a 0,1mg resolution.
Appendix 02
Horizonal reactor: system description

1. Gas manifold: air and \( \text{CO}_2 \) can be used. Mass flow controller 4 allows the running of air and/or \( \text{CO}_2 \) by opening the valves and controlling the flow through a controlling box (BOX 27) while MFC1 can allow the running of air and controlling the flow with the BOX 27 as well. The percentage of required flow is set in BOX 27, supplying a maximum of 10l/min for each source.

2. Sample probe, thermocouple and primary gas inlets: In order to avoid leaking of gases, the probe inlet must be sealed using a Teflon tape and using all the screws. When the thermocouple or the wire for moving the sample are used a correct seal must be selected to avoid leaking.

3. Water-cooled flanges: With the purpose of introducing and pull out the crucible with the sample, using the thermocouple and connecting the gas pipe the flanges are refrigerated with a water circuit. It is important to check that the water temperature does not exceed 100°C. Normally it is found at 20°C.

4. Alumina exit tube: This straight pipe couples the furnace exit to the exhaust tubing. The exhaust gas is led to the general ventilation system and released to the atmosphere.

5. Gas analyzers: The gas analysis instruments are located on the first floor of Building 228. Oxygen, carbon dioxide, sulfur dioxide and carbon monoxide can be measured. However, gas controller was not used in the present work.

6. Tube furnace: Power is required for temperature control working and heating elements. However, the set temperature in the screens is not the real temperature inside the furnace tube and it must be measured with a thermocouple. The Labview software does not control these elements. The tube has 3 different heated zones of 20, 40 and 20cm respectively. Creating temperature profiles or measure the real temperature is highly recommended.

7. Computer: A PC running near the furnace is used to record the data obtained in the analyzers, thermocouples, etc.
8. Others: A Sartorius LP 1200S balance (maximum weight: 1200g; precision: 0.001g) is placed in the laboratory with the purpose of weight the crucible and the limestones samples.

Figure 0.2. Picture of the horizontal reactor used in the calcinations
Appendix 03
Calcined samples in the horizontal reactor

<table>
<thead>
<tr>
<th>N</th>
<th>Day</th>
<th>Tcalc [°C]</th>
<th>Particle Size [µm]</th>
<th>Time [min]</th>
<th>Gas [% CO₂]</th>
<th>m₀ [g]</th>
<th>m₁ [g]</th>
<th>Conv. [%]</th>
<th>Surface area [m²/g]</th>
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NOTES:

The samples that were not analyzed in BET was due to for one of the following reasons: low conversion, burns in gloves (when pulling out the hot crucible), small samples (with not enough for analyzing in BET).

Samples 6 and 7 (analyzed together) are marked in red because they gave unexpected results in BET. They were analyzed again giving the expected results and it was considered that something went wrong in the first analysis.
Appendix 04

BET description

Method theory

The determination of specific surface by BET theory is based on the phenomenon of physical adsorption of gases on the external and internal surfaces of a porous material. The material is surrounded by and in equilibrium with a certain gas which has certain temperature (T) and relative vapor pressure (p/p₀), adsorbs physically a certain amount of gas. The quantity of adsorbed gas is proportional to the total external and internal surface of the material. The connection between relative vapor pressure and amount of adsorbed gas at a constant temperature is called an adsorption isotherm. Before carry out an experiment the sample must be degassed in order to remove any gas already adsorbed on the surface (46).

Apparatus

Surface areas were determined with a Quantachrome Autosorb iQ apparatus.

Figure 0.1 shows the main parts of the apparatus, explained below:

- Vacuum degasser: Cells containing the samples are connected in the vacuum degassers for drying by applying low pressures and high temperatures. The degassing program is set in the software and must be selected depending on the samples. The apparatus has two vacuum stations that can be used at the same time.
- Heating mantles: For supplying the heat during degassing process. Two heating mantles are available.
- Cold trap dewar: Filled with liquid N₂, it is used for degassing process.
- Measuring dewar: Cells containing the dried samples are submerged in the liquid N₂ for surface area analysis.
- Measuring stations: Once the sample is dried is placed in the degassing station for analyzing. The two available measuring stations can be used at the same time and also at the same time that the vacuum stations are being used.
- External degassing station: Used for drying the sample. Consists in a heating mantle where the bulb is placed and six small tubes blowing dry air. Thus, drying six samples at the same time is possible.
- Other equipment: A Mettler AJ150 balance (maximum weight: 150g; precision: 0.1mg) is available for measuring the weight of cells and samples.
Experimental procedure

Starting up

Samples are contained in a cell with a large bulb at the bottom during degassing and analysis. Before starting up an experiment a cell must be selected. Cells of 6, 9 and 12mm are available and the most common type is 9mm. Cells with smaller bulbs are also available for samples with high superficial area. During analysis only the bulb is submerged into liquid nitrogen. Ideally, the surface area should be between 10 and 20m$^2$ but down to 1m$^2$ also gives good results. The cell must be weighted before and after introducing the sample.
Because of the problems of using big samples of limestone in the horizontal reactor, only samples around 1-1.5g were calcined, which means a final mass after calcinations around 0.56-0.84g of calcined limestone because the loss weight due to CO₂ formation. BET analysis were performed with weights obtained in the tubular reactor and gave good results. It is known that a calcined sample of limestone without sintering has a surface area around 12m²/g while a limestone sample without calcining has around 0.9m²/g.

**Degassing**

As explained before, degassing is carried out in order to remove water or other volatile species adsorbed on the surface and inside the pores. The Quantachrome apparatus has two options for degassing: external flow degasser and internal degassing station. The first one consists in external heating with small flow of dry air whereas the other consists in vacuum degassing while heating. The flow degasser is recommended for fine powders, especially if they are non-porous and surface area is only needed to measure. Six samples can be degassed externally but only analyze two in the apparatus. Vacuum degasser is recommended for porous materials or samples with large particle pellets. Two samples can be degassed with vacuum.

During the experiments, all calcined limestones were degassed by vacuum. Once the sample is inside the bulb cell, weighted and the heating mantles are surrounding the bulb, it can be placed in the vacuum station and adjusting the screw by hand (never using tools). The vacuum program is set through the software ASiQwin. The program chosen for sample degassing in the experiments was a target temperature of 250°C during 60min with a heating rate of 10°C/min. A thorough degassing program is to heat at 350°C at 10°C/min and holding for 10h.

**Measuring**

Once the sample is dried it is weighted in the precision balance. After inserting the filler rods in the cell, it is place in the measuring station. The adsorbate gas is nitrogen. Analysis program can be set by different measuring points using the software. Three measuring programs are preset: 7 point BET, micro-porous and meso-porous. Also, the software permits to type a name for the file as well as many other options that have not been used in the experiments. Once the analysis is done, cell must be unscrewed and clean for its posterior use.
Appendix 05
SEM description

The scanning electronic microscope (SEM) uses a focused beam of high-energy electrons instead of light to form an image. Images with higher resolution can be obtained. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition (using ESD), and crystalline structure and orientations (using EBSD) of materials making up the sample.

Fundamental principles of SEM

The high-energy beam of electrons is dissipated as a variety of signals produced by the interaction of electron-sample. These signals are: secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD, used to determine crystal structures and orientations of minerals), photons (characteristics X-rays, used for elemental analysis and continuum X-ray), visible light and heat. Secondary electrons are the most valuable for showing morphology and topography of samples.

The electron beam is produced at the top of the microscope by an electron gun. The electron gun follows a vertical path through the microscope, which is held within a vacuum. Electromagnetic fields and lenses focus the beam down toward the sample. Once the beam heats the sample the signals are produced. Detectors collect the secondary electrons, backscattered electrons and X-rays.

![Figure 0.1. Schematic representation of SEM principle](image-url)
Sample preparation

A special preparation must be done for the samples in order to remove water and non-conductive materials. All water must be removed from the sample because water will vaporize in the vacuum. Metallic materials are conductive and do not need preparation before but the non-metallic materials need to be made conductive by covering the sample with a thin layer of conductive material. This is done using a device called “sputter coater”.

It uses an electric field and argon gas. The sample is placed in a small chamber that is at vacuum. Argon gas and the electric field cause an electron to be removed from the argon, making the atoms positively charged. The argon ions then become attracted to a negatively charged gold foil. The argon ions knock gold atoms from the surface of the gold foil. These gold atoms fall and settle the surface of the sample producing a thin gold coating. As calcined limestones (and limestones) are non-conductive, coating will be necessary before SEM analysis.

Experimental procedure

Calcined limestone samples and a fresh limestone sample were brought to the Mechanical Engineering Department in DTU (Building 204) where were analyzed with a JEOL JSM-5900 scanning electronic microscope. Samples were coated around 7-8 times with gold because their non-conductive properties, meaning a gold layer around 120nm. SEM pictured were taken at magnifications of x1.000, x5.000 and x10.000 which suppose a scale in the pictures of 10µm, 5µm and 1µm respectively at 10kV.

During picture capture it was found that samples were charged and captured images were moved or shifted. By coating more times the samples the image quality improved and after 7-8 coating images with x10.000 magnification were obtained with good resolution.
## Appendix 06
Flows and gas composition in cycles with SO\textsubscript{2} presence

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<tr>
<th></th>
<th>Flows</th>
<th>Composition</th>
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<td></td>
<td>N\textsubscript{2}-SO\textsubscript{2}</td>
<td>CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>ml/min</td>
<td>ml/min</td>
</tr>
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<td></td>
<td>Carbonation</td>
<td>14</td>
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Appendix 07
Fraction of recirculated particles

Abanades (47) showed that the fraction of solids that have recirculated N times can be derived from the following.

The fraction of fresh particles that have been recirculated one time is the fresh limestone \( F_0 \) divided the total sorbent sent to the carbonator \( (F_0 + F_{CaO}) \):

\[
r_1 = \frac{F_0}{F_0 + F_{CaO}}
\]

(Eq A1)

The particles that have been recirculated two times can be calculated as the fraction of total recirculated particles multiplied for the fraction of particles that have been recirculated once.

\[
r_2 = r_1 \frac{F_{CaO}}{F_0 + F_{CaO}}
\]

(Eq A2)

For the cycle N:

\[
r_N = \frac{F_0 F_{CaO}^{N-1}}{(F_0 + F_{CaO})^N}
\]

(Eq A3)

If we define the ratio \( p \):

\[
p = \frac{F_0}{F_0 + F_{CaO}}
\]

We can express the equation as:

\[
r_N = \frac{F_0}{F_0 + F_0} \left( \frac{F_{CaO}}{F_0 + F_0} \right)^{N-1} = p(1-p)^{N-1}
\]

(Eq A4)
Appendix 08
MATLAB scripts

MATLAB scripts can be found jointly with this present report.
In each folder there is a file called script and heat (for $X_{ave}$ and $H_{in}$ calculations respectively). The content of these files must be copied to the main screen of MATLAB software. Pressing intro button the calculations will run. Other MATLAB files (*.m) are functions that are called during the calculations. Files with other extensions are the charts obtained with the scripts.
Appendix 09

Fitting parameters for experiments with sulfation

Fitting parameters were obtained for the experimental work when using some SO$_2$ in the calcination-carbonation cycles carried out in the TGA. They are calculated in the same way that the coefficients calculated for the data with no sulfation: fixing Xr and calculating k with the Solver tool of Excel.

![Experiment with 100ppm SO$_2$](image1)

![Experiment with 700ppm of SO$_2$](image2)
Appendix 10
Calculation of heating values and parameters

$\Delta H_{\text{carb}}$, 168.5kJ/mol CaCO$_3$, calcination heat reaction at 900°C

$X_{\text{carb}}$, average conversion attainable by the sorbent in the carbonator reactor

$\Delta T_{\text{calc}}$, 310K, variation of temperatures between carbonator and calcinator

$\Delta T_{\text{fro}}$, 935K, variation of temperature between fresh sorbent and calcination temperature. Fresh sorbent is considered to be at 25°C

The heat capacity calculations for the different substances are calculated from correlations of this property with the temperature.

For calcium oxide the correlation is valid from 298-3200K and was:

$$Cp = A + B \cdot t + C \cdot t^2 + D \cdot t^3 + E \cdot t^4 \quad [J/mol \cdot K]$$

$$t = T / 1000 \quad [T, \text{temperature in K}]$$

$A = 49.95403$

$B = 4.887916$

$C = -0.352056$

$D = 0.046187$

$E = -0.825097$

The values for the range of temperatures and the average Cp considered are:
For calcium carbonate the correlation is valid from 273-1033K and was:

\[ Cp = a + bT + c/T^2 \quad [J/mol\cdot K], \quad T[K] \]

\[ a = 82.34 \]

\[ b = 4.975 \times 10^{-2} \]

\[ c = -12.87 \times 10^3 \]

For the calcium carbonate two values must be taken into account: for the fresh limestone (and for the CaCO\(_3\) coming from the carbonator. The former is:

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Average 134.58 J/molK
For the latter:

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Average 117,24 J/molK
Appendix 11
Calculation of $r_{C/S}$

The typical compositions for coal (lignite and anthracite) and fuel-oil are:

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<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>C[%]</td>
<td>83-87</td>
</tr>
<tr>
<td>H[%]</td>
<td>11-15</td>
</tr>
<tr>
<td>O[%]</td>
<td>0,3-1,2</td>
</tr>
<tr>
<td>S[%]</td>
<td>0,1-6</td>
</tr>
<tr>
<td>N [%]</td>
<td>0,1-1,5</td>
</tr>
</tbody>
</table>

When calculating the $r_{C/S}$ ratio for lignite 70% of carbon and 1% of sulphur was considered. Then, we have:

$$\frac{70\, kg\, C \times 32,1\, kg\, S \times 1\, kmol\, C}{3\, kg\, S \times 1\, kmol\, S \times 12\, kg\, C} = 62,42$$

For anthracite: 91.5% C and 1% S.

$$\frac{91,5\, kg\, C \times 32,1\, kg\, S \times 1\, kmol\, C}{1\, kg\, S \times 1\, kmol\, S \times 12\, kg\, C} = 244,8$$

For fuel: 85% C and 0.15% S.

$$\frac{85\, kg\, C \times 32,1\, kg\, S \times 1\, kmol\, C}{0.15\, kg\, S \times 1\, kmol\, S \times 12\, kg\, C} = 1300$$

If the fuel-oil is combusted in an oxy-firing system the flue gas will contain around 770ppm of $SO_2$, according the following simple calculation considering that all carbon will be converted to $CO_2$ and all sulphur will be converted to $SO_2$. As one mole of C or S give one mol of $CO_2$ or $SO_2$ respectively we have:
\%S = \frac{1}{1300 + 1} \times 100 = 0,077\% \\
\frac{0,077 \text{ m}^3 \text{ SO}_2}{100 \text{ m}^3 \text{ flue gas}} \times 10^6 \text{ mL} = 769,06 \text{ ppm SO}_2