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Superheating of Ca(OH)$_2$ and its application as a Reactivation Method for Ca Looping Sorbents

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Supervised by

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Abstract

The CaO-CaCO₃ thermochemical cycle (Ca looping) is an emerging technology in a range of energy applications. One of the major limitations of this process is the progressive deactivation of the CaO sorbent with increasing cycle number which leads to sub-optimal performance of Ca looping systems. This work focuses on a new, promising, technique for restoring CaO sorbent activity without compromising its mechanical strength. This technique makes use of the inhibition of the dehydration of Ca(OH)₂ in the presence of CO₂ at high temperatures, called Ca(OH)₂ superheating, which is observed in some cases. However, the further development of such a method is greatly limited by the near-complete absence of knowledge in the literature about the behaviour of Ca(OH)₂ in the presence of CO₂ at high temperature. This work aims to explore the nature and causes of the superheating phenomenon. Thermogravimetric analyses have been undertaken to determine critical parameters for the occurrence of Ca(OH)₂ superheating and to investigate the kinetics of the reaction system. It was found that the porosity of Ca(OH)₂ was the key parameter controlling its high temperature behaviour. Kinetic analyses suggested the existence of a new mechanism for the carbonation for Ca(OH)₂ taking place at high temperatures and in the absence of water. This mechanism presented a range of unusual properties that could not be described by typical solid-gas reaction models e.g. the time-independence of the reaction extent. It was also postulated that Ca(OH)₂ superheating itself was a side-effect of this direct carbonation mechanism. A range of testable hypotheses, explaining all the experimental observations were formulated and are expected to provide a framework for further research work. Furthermore, a new attrition testing method was developed to investigate the evolution of the mechanical strength of the CaO sorbent during and after reactivation by superheating. Dehydration of Ca(OH)₂ was found to introduce a structural weakness in the dehydrated CaO sorbent. Thus, the direct carbonation of Ca(OH)₂ occurring during superheating, was postulated to be essential to maintaining the mechanical strength of the reactivated sorbent. Further avenues for the development of the reactivation process were proposed.

Dedication

This work is dedicated to my grandfather, Branko Bajčetić, who would have been so proud to see me complete it.

Acknowledgements

I would like to acknowledge all the people that have supported me on this journey, without whom I would not have started or made it to the end: Stuart Smedley, Robert Holt, Susan Edwards, Ian Brown and Carolyn Sheppard.
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Publications preceding the beginning of the PhD program


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Results from Section 2.2.2 were published as:

Results from Section 2.2.4 were published as:

Results from Section 3.2.1 were published as:

Results from Section 3.2.2 were published as:

The actual co-authorship forms for these articles are presented in Appendix 4.
Chapter 1
Introduction

1.1 Introduction

The topic of this work is an unusual behaviour of calcium hydroxide (Ca(OH)$_2$), named “Ca(OH)$_2$ superheating”, and its application for activating sintered and unreactive calcium oxide (CaO). The aim of this work is to understand the causes and the mechanism underlying this behaviour, which was first reported by the author of this thesis.

Namely, it was reported that the presence of carbon dioxide (CO$_2$) in the gas phase could increase the temperature at which Ca(OH)$_2$ started decomposing to 620°C (1). As a result, some Ca(OH)$_2$ remained stable at temperatures much above its normal decomposition temperature (≈400°C) and therefore was said to be “superheated”.

Superheating Ca(OH)$_2$ particles was found to improve their mechanical strength and to increase their subsequent reactivity towards CO$_2$. As a result, it was proposed by the author and colleagues that Ca(OH)$_2$ superheating could be used as a method to improve the mechanical strength and reactivity of sintered CaO. This method is particularly relevant to a family of processes, named Ca looping (2), in which CaO is cyclically carbonated and calcined. Indeed, one of the major limitations of these processes is the progressive deactivation of the CaO sorbent through sintering (3), which could be overcome in an effective way by the proposed reactivation method (1).

However, the lack of understanding of the causes and mechanisms of Ca(OH)$_2$ superheating represents a major obstacle to the development of the proposed reactivation method. Indeed, it is difficult to design and control a chemical process if one does not understand the process chemistry.

Therefore, the work presented in this thesis has both a practical and a theoretical aspect. On one hand exploring an unknown chemical phenomenon is valuable from an academic and theoretical perspective; there is very little information in the literature on the chemistry of the interaction of Ca(OH)$_2$ with CO$_2$ at high temperatures. On the other hand, providing a better understanding of Ca(OH)$_2$ superheating also has a practical value insofar as it can facilitate the development of a new chemical process.

The first part of this chapter will present information gathered during a literature review to provide some context on the nature of Ca looping processes, the issue of the progressive deactivation of CaO and the methods proposed so far to alleviate this issue.

The second part of this chapter will focus on the topic of this work – Ca(OH)$_2$ superheating – and what was known about it at the outset of this work. This information will then be used to formulate a framework and an approach to exploring the chemical and physical aspects of Ca(OH)$_2$ superheating.
1.2 Literature review

Ca Looping
The CaCO₃-CaO thermochemical cycle, also known as Ca looping, is a process in which particles of a calcium containing solid material – the sorbent – are cyclically carbonated/calcined according to the reaction described in eq. 1.

\[
\text{CaO + CO}_2 \leftrightarrow \text{CaCO}_3 \quad \Delta H^\circ = -173 \text{ kJ.mol}^{-1}
\] (1)

Although in theory any solid that contains calcium can be used as a sorbent for Ca looping, ground limestone is considered to be the default sorbent due to its high availability and low cost (2,4). Nevertheless, as discussed below, there are several groups worldwide working on the development of synthetic sorbents with improved characteristics.

Ca looping is typically operated at high temperatures (>600°C) (2) and, as can be deduced from eq. 1, is accompanied by the absorption and release of relatively large amounts of heat and CO₂. During calcination, typically 850–950°C, the heat of reaction is “absorbed” by the sorbent and CO₂ is released from it. The reverse happens during carbonation (600–700°C) as the CO₂ is absorbed by the sorbent and heat is released from it.

Performing the calcination and carbonation reactions in separate reactors allows the transfer of latent heat from the calciner to the carbonator reactor and, simultaneously, the transfer of CO₂ from the carbonator to the calciner reactors. This ability of Ca looping forms the basis of a range of processes in the energy field discussed in detail below (2,5) and is illustrated in Figure 1.

The theoretical carrying capacity of limestone for both heat and CO₂ is very high because of the high enthalpy of reaction and low molar mass of CaO. Indeed, the maximum heat storage capacity of CaO is 3.1 MJ.kg⁻¹ or 6.3 MJ.l⁻¹, which is approximately 60% of the energy density of dry wood (6). Furthermore, the theoretical CO₂ carrying capacity of CaO is considerably higher than that of other known CO₂ sorbents (7) as shown in Table 1.

![Figure 1. Schematic illustrating the Ca looping thermochemical cycle operating between two reactors.](image-url)
Table 1. Carrying capacities and reaction heat of selected CO₂ sorbents.

<table>
<thead>
<tr>
<th>CO₂ Sorbent</th>
<th>Carrying capacity CO₂ (g.kg⁻¹)</th>
<th>Heat (Mj.kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>786</td>
<td>3.1</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>250</td>
<td>1.9</td>
</tr>
<tr>
<td>Monoethylamine</td>
<td>36</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Ca Looping Processes

The ability of Ca looping to transfer heat and CO₂ between reactors has been exploited in a number of process concepts in the energy field (2,5). Three major types of processes using Ca looping have been reported in the literature, with varying emphasis on the ability to transport heat and/or CO₂.

Thermal Energy Storage The use of Ca looping as a thermal energy storage system has been proposed in a number of studies (8,9,10). In this type of process, high temperature heat is absorbed in the calciner to form CaO and CO₂, which are then stored separately. This latent heat, stored in the form of potential chemical energy, can subsequently be released when the stored CaO and CO₂ are contacted. The use of a thermal energy storage system was proposed for both nuclear and solar power plants in order to enable shifting the production of power to meet demand.

The ability to operate at temperatures >500°C represents a major advantage of Ca looping systems in this application. Indeed, heat of carbonation is released at temperatures sufficiently high (600–700°C) to operate a power cycle at high efficiency e.g. a high temperature Rankine steam cycle.

A variant on this system was also proposed, using the reversible Ca(OH)₂/CaO reaction for thermal energy storage (11,12). This system would operate in a similar fashion to Ca looping with the difference being that the sorbent is repeatedly hydrated/dehydrated and the temperature of operation is lower (300–500°C).

Ca looping heat storage systems are currently running only at a laboratory scale and no pilot plants or economic assessment for these systems has been reported in the literature.

CO₂ Capture The use of Ca looping as a post-combustion CO₂ capture system, initially proposed by Shimizu et al. (13), has been the focus of a large body of work in the last decade, discussed in an excellent review by Dean et al (5). In these systems, the Ca looping cycle is used to separate CO₂ from power plant flue gas and release a concentrated CO₂ stream suitable for long-term geological sequestration.

To achieve this, flue gas from the power plant is passed through the carbonator where CO₂ is absorbed by the sorbent (as CaO), releasing the heat of carbonation. The carbonated sorbent is then transferred to the calciner and heated to the temperature of calcination, leading to the release of a concentrated stream of CO₂. A number of systems for supplying heat to the calciner without compromising the purity
of the released CO$_2$ have been proposed (14), but using an oxy-fired calciner is the current technology of choice due to its ready availability.

The high temperature operation of the cycle also represents a major advantage in this application as the heat supplied to the calciner to release CO$_2$ is recovered at temperatures high enough to produce power at a high efficiency. As a result, the energy penalty of CO$_2$ separation is low and a number of economic studies have shown that the Ca looping process, once developed, is likely to outperform current CO$_2$ separation technologies, based on oxy-fuel combustion or the use of aqueous amine solutions for separating CO$_2$ (15,16,17).

In addition to reacting with CO$_2$, CaO can be expected to react irreversibly with SO$_2$ deriving from the sulphur content of the fuel and thus it can be speculated that a Ca looping system could also act as a desulfurization unit. However, results presented by Manović et al. suggested that the presence of SO$_2$ had a negative effect on the reactivity of the sorbent (18). The prospect of simultaneous SO$_2$/CO$_2$ capture by Ca looping systems is thus uncertain in the case of CO$_2$ capture applications.

This process is currently being developed by several groups worldwide (19,20,21), with the largest units being able to separate the CO$_2$ from the flue gas of a 1.8MW$_{th}$ power plant (19).

**Gasification/Reforming** The use of Ca looping to promote the gasification reaction of carbonaceous materials is reported to have been initially proposed by DuMotay and Maréchal in 1867 (22). Ca looping is in fact particularly well suited for this purpose as its abilities in both heat and CO$_2$ transfer are valuable in this application. Indeed, the gasification reaction, represented by eq. 2 is endothermic and ultimately leads to the production of CO$_2$.

\[
C + 2H_2O \rightarrow CO_2 + 2H_2 \quad \Delta H^\circ = +165 \text{ kJ.mol}^{-1} \quad (2)
\]

\[
CaO + CO_2\leftrightarrow CaCO_3 \quad \Delta H^\circ = -173 \text{ kJ.mol}^{-1} \quad (3)
\]

In Ca looping gasification processes, fuel is gasified with steam in the carbonator where CO$_2$ produced by gasification, eq.2, is immediately absorbed by CaO, eq. 3, thereby releasing the heat of carbonation which drives subsequent gasification. Furthermore, the removal of CO$_2$ from the gas phase shifts the reaction equilibrium towards the production of a high proportion of H$_2$, eq. 2.

A number of Ca looping based gasification processes have been proposed in the literature (2,23,24,25), while the largest operational unit was a pilot plant gasifying up to 40 t.day$^{-1}$ of coal (26). This unit was built as a demonstration of the “CO$_2$ acceptor” process, which was aimed at converting coal into methane via gasification. A variant of this process aiming at the reforming of natural gas to hydrogen has also been proposed in the literature (27). The main difference of this process is the nature of the fuel and the need for the addition of catalysts to the Ca looping sorbent in order to promote the reforming reaction.

Similarly to the CO$_2$ capture application, CaO can be expected to irreversibly react with H$_2$S deriving from the sulphur present in the fuel to form CaS. In contrast to the CO$_2$ capture application, it was reported (28) that the formation of CaS did not affect the activity of the sorbent during cycling. These results
suggest that the Ca looping system can possibly act as a desulfurization unit when used in gasification applications.

**Ca Looping Systems**

In most cases, fluid bed technology is proposed to make use of the Ca looping cycle due to its excellent heat and mass transfer properties (2,5,14). Indeed, large scale Ca looping systems are likely to entail considerable amounts of circulating solids as well as CO₂ and heat exchange between gas and solid phases, thus making fluid bed technology a logical choice at the large scales commonly encountered in the energy sector.

While there is a wide range of different process configurations reported in the literature, making use of both bubbling and circulating fluid beds, the process most commonly selected for scale-up uses a circulating fluid bed (CFB) for both the carbonator and the calciner units, with sorbent material circulating continuously between them (19,20,21).

Thus it appears that Ca looping is an emerging technology platform with promising economics in a wide range of applications in the energy sector. The ability of Ca looping systems to both enhance energy production processes and to separate CO₂ from carbonaceous fuels put it in a unique position to contribute to resolving the principal energy challenges of the XXI century.

**Process Limitations** While each Ca looping application presents specific difficulties that must be resolved for a successful deployment of the technology, one major issue common to all these processes is the deactivation of the sorbent, leading to the incomplete conversion of the carbonation reaction (eq. 3).

Most studies dealing with cyclic calcination/carbonation of limestone have reported observing a decline in the CO₂ carrying capacity of limestone with increasing cycle number (8,29,30), which was attributed to a progressive reduction in the conversion achieved during the carbonation step (8). Figure 2a plots the conversion vs. time curves for successive carbonation steps during Ca looping cycles, as reported by Abanades et al. (29).

The carbonation reaction was found to proceed in two distinct reaction regimes, which were explained by a change in the rate-controlling step during the carbonation reaction from chemical to diffusion control (31). During the early phase of the reaction, the rate of carbonation is controlled by the chemical rate of reaction and proceeds rapidly for about three minutes as shown in Figure 2a. During this phase, a CaCO₃ layer of increasing thickness forms on the surfaces of CaO grains leading to the formation of a diffusion barrier for CO₂ that inhibits further reaction. At ≈3 min the rate of diffusion of CO₂ through this product layer becomes the rate limiting step and the carbonation reaction rapidly slows down (31).

Alvarez et al. (32) calculated that the critical thickness of the CaCO₃ layer at which the reaction becomes diffusion controlled is approximately 50 nm (+/-20%). As a result, it can be said that the pore size distribution of the sorbent plays a major role in the conversion level achieved in the fast regime. Namely, pores with a radius <100 nm will be plugged by the CaCO₃ product before diffusion takes control of the reaction kinetics, while pores larger than 100 nm will continue carbonating beyond that point. In theory, the carbonation conversion achieved in the fast regime can thus be expressed as a
function of *suitable porosity*, i.e. the volume of all pores < 100 nm and the area of all pores > 100 nm (33).

Figure 2a also illustrates that, while the time required to reach the regime transition point remains more or less constant (=3 min) with increasing cycle numbers, the conversion reached at the transition point rapidly reduces during the first few Ca looping cycles. Given that only the fast carbonation regime is likely to be useful in an industrial setting (31), the conversion reached at the transition point is often referred to as the activity of the sorbent. The decay of sorbent activity with cycle number reported in a range of studies is also plotted in Figure 2b, where it can be seen that the sorbent activity drops to about 20% of the theoretical maximum after about 15 cycles.

It is generally accepted that the decay in sorbent activity is due to the sintering of CaO which occurs as the sorbent is subjected to high temperatures during each calcination step which reduces the amount of suitable porosity available for the next carbonation step (30,31,34,35).

Freshly calcined CaO grains do not collapse into a compact structure despite having a considerably smaller molar volume (CaCO$_3$ 37 ml.mol$^{-1}$ vs. CaO 17 ml.mol$^{-1}$) (14). Instead, the departing CO$_2$ leaves behind a network of cylindrical pores of approximately 80–100 nm in diameter (14,33,36).

These pores serve as the pathway for CO$_2$ during the following carbonation and thus their formation during calcination is the very property that enables the reversibility of the calcination of CaCO$_3$ in contrast with MgCO$_3$, for example, where this is not the case.

However, at the usual temperatures of calcination (>850°C), sintering also takes place and leads to the closure of a proportion of these freshly formed pores (34,35,37) and thus to a reduction in activity in the following carbonation step. As a result, after each calcination step, the total suitable porosity is reduced by a fraction and the sorbent activity decays with the number of cycles, see Figure 2b. Naturally, conditions that enhance the rate of sintering, such as high temperature or high CO$_2$ content during calcination, also enhance the rate of activity decay (14,38,39).

Alvarez et al. (40) reported that the proportion of pores <100 nm remained very small after approximately 29 cycles, and observed a simultaneous formation of a network of macropores (400 nm) (33,40) with extended cycling. However, these large pores do not contribute significantly to the fast carbonation regime due to their low surface area/volume ratio.

An interesting exception is the case of CaCO$_3$ nanoparticles; Barker (8) reported that no activity decay was observed when ≈10 nm CaCO$_3$ nanoparticles were subjected to Ca looping cycles and that the diffusion controlled regime was entirely absent. In contrast, Florin et al. (41) reported observing the decay in activity with 40 nm particles, which they attributed to the agglomeration of particles during cycling. The use of nanoparticles has not so far been proposed for a practical use due to the difficulties associated with their use in a practical setting as they would have to be mounted on particles that can be used in fluid bed systems.
Figure 2. **a)** The evolution of carbonation kinetics (conversion vs. time) with cycle number, extracted from Abanades et al. (31). The curve $X_n$ represents the carbonation kinetics of the sorbent during the $n^{th}$ carbonation. **b)** The decay of sorbent activity with increasing cycle number in a range of conditions. The legend uses the following syntax: Reactor-Calcination Temperature/CO$_2$ concentration. TG stands for thermogravimetric apparatus, FB stands for fluidized bed. Reprinted with permission from Abanades and Alvarez (31). Copyright 2003, American Chemical Society.

Finally, as illustrated in Figure 2b, the activity of the sorbent appears to decay exponentially to a non-zero value, suggesting the existence of a stable, or “residual”, final carbonation conversion (34,42). The value of this final conversion was reported to vary between 7–15% depending on the type of limestone and the Ca looping conditions used.

**Methods for Increasing Sorbent Activity**

Economic analyses have suggested that Ca looping processes could be viable even when operating with the final carbonation conversion level ($\approx$10%) (15,17,43). However, it is clear that an increase in the average activity of the sorbent is likely to greatly enhance Ca looping economics, as it would lead to a considerable reduction in the size of the system.

As a result, many groups worldwide are developing methods for improving the average activity of Ca looping sorbents, using a variety of strategies. Some methods aim at removing the activity decay altogether while others periodically reactivate the spent sorbent, i.e. it is processed in such a way as to restore its activity. The various methods reported so far are discussed in the following paragraphs.

**Tailored Sorbents** A wide range of strategies for producing sorbents with reduced decay activity can be found in the literature, although the mechanisms of operation remains unclear in many cases.

Doping the sorbent with various dopants was found to have an effect on the decay of sorbent activity (44,45). A number of different dopants have been tested, e.g. KCl, K$_2$CO$_3$, H$_2$NO$_3$, HCl, HBr, as well as a number of different doping techniques, e.g. wet impregnation or solid mixing. Typically, very small amounts of dopant remain on the sorbent ($\approx$1%) (45), unlike what happens in methods for producing synthetic sorbents, see below. Some dopants were found to lead to an increase in activity, e.g. HBr.
improved the long-term conversion of the sorbent while others led to a reduction of the sorbent activity (KCl).

The addition of 10% aluminate cements, followed by the pelletization of the sorbent, was found to greatly improve the activity of Ca looping sorbents (46). However, harsher calcination conditions (47) and the presence of sulphur (48) in the flue gas were found to cancel to some extent the advantages of this technique. It was speculated that the aluminate cement forms an un-sinterable matrix that stabilizes the pore structure of the sorbent and thus slows down the activity decay.

A range of synthetic sorbents with high and constant CO₂ capture activities have also been proposed in the literature. The addition of CaTiO₃ (49), Calcium acetate (50) or a 20% loading of various alkali cations (Cs, Rb, Li) (51), were found to generate sorbents which were resistant to sintering, at least in the mild calcination conditions used in the laboratory. Further studies (52,53) suggest that the performance of these sorbents in harsher calcination conditions, coupled with their high cost, is not promising for their industrial application.

“CO₂ Shocking” is a sorbent reactivation method in which spent sorbent is made to react with CO₂ in the diffusion regime until reaching high conversion levels (8,54). Barker et al. reported that if a sorbent was allowed sufficient time to carbonate to 100% in the diffusion regime, the sorbent would behave like fresh limestone, i.e. the activity decay would start again as if it were fresh limestone (8).

This behaviour can be understood if one considers that upon calcination, the departing CO₂ leaves behind cylindrical pores of approximately 80–100 nm diameter in the calcined CaO (14,33), which enable the reversibility of the reaction, as discussed above. Thus, if a sintered CaO is fully carbonated through the diffusion regime and then calcined, the departing CO₂ will leave behind a network of suitable porosity and thus generate an active CaO. It can be said that fully carbonating, then calcining the spent sorbent will allow restoring a suitable pore network for further carbonations.

This reactivation method was proposed for industrial use, where spent sorbents would be periodically carbonated in 100% CO₂ for extended periods of time thereby restoring their activity (54).

An interesting corollary of this observation is that activity decay can be reduced if sorbents are left to react for extended periods of time in the diffusion regime, which was observed by a number of authors (55,56). By allowing a proportion of the previously inactive CaO to be reactivated through diffusion based carbonation, it is theoretically possible to counteract the progressive deactivation induced by the calcination reaction; this could be called “partial CO₂ shocking”. In this context, the presence of steam during carbonation was shown to slow down the rate of activity decay by increasing the rate of diffusion controlled carbonation regime (3,47).

_Hydration_ Another reactivation technique which has been widely experimented with consists in hydrating and dehydrating the spent sorbent according to reaction 4:

\[ Ca(OH)₂ → CaO + H₂O \quad \Delta H^* = 109 \text{ kJ.mol}^{-1} \]  

(4)
Hydration of CaO has been considered as a technique for reactivating CaO in desulfurization applications (57,58). The hydration of CaO is known to proceed rapidly with liquid water but also with steam (59,60,61).

Completely hydrating the spent sorbent leads to a significant expansion of the solid phase (CaO 17 ml.mol$^{-1}$ vs. Ca(OH)$_2$ 33 ml.mol$^{-1}$) followed by the formation of a suitable network of pores upon dehydration (18). In that respect the hydration-dehydration reactivation technique is similar to the CO$_2$ shocking technique, with the difference being that H$_2$O is used as the shocking agent. The advantage of H$_2$O is that typical rates of hydration are considerably higher than those of the diffusion controlled carbonation regime, despite being carried out at lower temperatures (20–400°C).

It was found that the dehydrated sorbent exhibited a large number of mesopores (in the 80–100 nm diameter range) which, as discussed above, are of the ideal size for carbonation. There are suggestions in the literature that the conditions of dehydration could affect the size and nature of the pore network generated (62), suggesting that the dehydration parameters might have an effect on the reactivation potential of this method.

The hydration-dehydration technique was tested by a number of groups in different configurations. Hughes et al. (59) reported that hydrating the sorbent as a pre-treatment reduced the sorbent’s rate of activity decay while a range of different hydration methods were found to be effective in restoring sorbent activity: using atmospheric humidity (63) at various temperatures and pressures with water and steam (18,36,55,60,61) and with additives to the water, e.g. ethanol (64). In all cases, hydrating and dehydrating the sorbent led to a considerable increase in activity for the following carbonation cycle and in some cases, to a reduced rate of activity decay in subsequent cycling (18).

A number of studies have also shown that the hydration-dehydration technique is effective when periodically employed to restore sorbent activity, i.e. the sorbent is hydrated after every $n$ Ca looping cycles. Using this approach in previous work, the author and colleagues succeeded in maintaining an average sorbent activity of 33% over 50 cycles while periodically hydrating the sorbent every three cycles in a fluidized bed (1). Fennell et al. maintained an average activity of $\approx$35% over 85 cycles while only hydrating-dehydrating the sorbent 3 times (after cycles 30, 50 and 70) in a TGA apparatus (65).

**Limitations of the Hydration Reactivation Technique** Although the conventional hydration technique was found to be very successful in maintaining a high sorbent activity, it was also found to considerably increase the friability of the sorbent, making it weaker and less resistant to mechanical stresses.

Indeed, Manović et al. (18) reported that sorbents reactivated by hydration-dehydration doubled in particle volume and appeared fragile while Blamey et al. (66) reported observing a fourfold increase in sorbent breakage after using the hydration-dehydration in a fluid bed.

The sorbent’s tendency to break (sorbent friability) is important as fluidized beds are commonly used in the implementation of Ca looping processes (3,14). In fluid beds, solid particles are subjected to extensive mechanical stresses that often result in attrition, i.e. the breakage of sorbent particles (67). The reduction in particle size inevitably leads to the loss of some particles out of the system, increasing
the cost of downstream cleaning units. Also, a reduction in particle size can affect the hydrodynamics of fluid beds disturbing their normal operation (68). Thus, the increase in the sorbent friability due to the reactivation process greatly limits the applicability of the hydration-dehydration reactivation technique.

The use of aluminate cements and the pelletization of the sorbent presents a potential solution to this issue, as it was reported that the pelletized sorbents are more resistant to attrition (69) and a combined reactivation/pelletization procedure was also proposed which could allow the use of the hydration-dehydration technique without the associated increase in sorbent friability (70).

Preliminary work undertaken by the author and colleagues at Industrial Research Ltd. (IRL) has led to the discovery of an unusual behaviour of Ca(OH)$_2$ when exposed to CO$_2$ at high temperature, which we have called Ca(OH)$_2$ superheating. We observed that thermally treating the freshly hydrated Ca(OH)$_2$ in CO$_2$ could minimize the increase in friability of the reactivated sorbent, and proposed using this method to enable reactivating the sorbents via hydration without compromising the mechanical strength of the sorbent. These results were previously published and thus are not considered part of the work presented in this thesis (1,55) but subsequent work on the superheating of Ca(OH)$_2$ and its use as a reactivation method for Ca looping sorbents is the subject of this thesis.

The following section will present those preliminary results and describe what was known about the superheating reactivation technique at the outset of this work.

**Ca(OH)$_2$ Superheating**

The existence of Ca(OH)$_2$ superheating was first demonstrated in a series of experiments, performed by the author of the thesis and the team at IRL prior to the beginning of the PhD program, where a fluidized bed of Ca(OH)$_2$, freshly prepared by steam hydrating CaO at 300°C, was heated in the presence of N$_2$ and CO$_2$ (55). Figure 3a,b plots the temperature of the bed and the partial pressure of water vapour leaving the bed as the bed is heated in the presence of N$_2$ and CO$_2$, respectively.

**Normal Dehydration** Figure 3a displays the results obtained when freshly hydrated Ca(OH)$_2$ is heated in the presence of N$_2$ as occurs in the hydration-dehydration reactivation procedure. The presence of water vapour leaving the bed between 35–43 min is due to the final stages of hydration. Namely, steam is being introduced into the fluid bed but since hydration is complete all the introduced steam leaves the reactor and is therefore detected. At min 45, the supply of steam is stopped and the bed is heated under a flow of N$_2$. As can be seen in Figure 3, water was released from the bed at 450°C, which was attributed to the onset of the dehydration reaction.

**Superheated Dehydration** An entirely different behaviour was observed when freshly hydrated Ca(OH)$_2$ was heated in the presence of 37.5% CO$_2$ in N$_2$. As above, the steam supply was stopped at min 43 but the bed was then heated in CO$_2$. A brief burst of water was observed as soon as CO$_2$ was introduced in the bed (min 43) and no more water was released until the temperature reached 618°C. Thus, the presence of 37.5% CO$_2$ was said to have increased the temperature of onset of dehydration from 450°C, the normal dehydration temperature, to 618°C, the temperature of “superheated dehydration”. It can also be said that between 450°C and 618°C, Ca(OH)$_2$ was superheated, i.e. it remained stable at temperatures above its normal decomposition temperature.
Further experiments by the author and colleagues revealed that the temperature of superheated dehydration depended on the proportion of CO$_2$ in the gas phase, but remained $\approx 620^\circ$C for any CO$_2$ concentration above 37.5% (1). In addition, as shown in Figure 3c, it was observed that superheated dehydration could be triggered by replacing the CO$_2$ containing flow with a flow of N$_2$ at 520°C (1). Indeed, dehydration occurred 7 seconds after CO$_2$ was removed from the gas and this method of triggering the superheated dehydration was termed “N$_2$ trigger”. This experiment also revealed that some carbonation did occur during Ca(OH)$_2$ superheating, as approximately 15% of the sorbent was found to have converted to CaCO$_3$ after the N$_2$ trigger.

During the course of this work, the superheated dehydration (SD) effect was also observed by Blamey et al. using a TGA apparatus coupled to a mass spectrometer (71). They observed different types of behaviour with different Ca(OH)$_2$ samples and in particular that the SD effect was not observed with ground samples or with dolomite i.e. limestone containing a large proportion of MgCO$_3$. In contrast, Montez-Hernandez et al., in a paper published during the course of this thesis, did not observe any superheated dehydration when heating Ca(OH)$_2$ in the presence of CO$_2$ (72).
Note that the absence of superheating had not been observed in the author’s laboratory under the conditions tested prior to the beginning of this work.

**Effect on Sorbent Performance** Table 2 presents data on sorbent performance, in terms of activity and attrition, measured over 48 Ca looping cycles when different hydration reactivation techniques were used after every 3 Ca looping cycles (1). The “conventional” reactivation refers to the hydration-dehydration technique, see Figure 3a, while “superheating” reactivation refers to the technique in which the spent sorbent is hydrated then superheated, Figure 3b.

**Table 2.** Performance of sorbents reactivated with hydration-based methods. Activity was calculated using a mass flow meter during each carbonation; fine levels were assessed by sieving after 48 cycles

<table>
<thead>
<tr>
<th>Over 48 capture Cycles</th>
<th>No reactivation</th>
<th>“Conventional” reactivation</th>
<th>“Superheating” reactivation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average activity</strong></td>
<td>26%</td>
<td>36%</td>
<td>63%</td>
</tr>
<tr>
<td><strong>Fines &lt; 150 µm w.%</strong></td>
<td>2.9%</td>
<td>7.4%</td>
<td>3.5%</td>
</tr>
</tbody>
</table>

The results in Table 2 clearly show the advantage of the superheating reactivation method compared to the conventional one, as both indicators of sorbent performance are improved. The average activity of the sorbent is clearly higher than both the unreactivated and conventional methods, while the attrition rates measured with the superheating reactivation method are only moderately higher than that observed when the sorbent is not reactivated at all.

Obtaining the advantages of the superheating reactivation technique was found to be dependent on achieving the Superheated Dehydration (SD) effect at 620°C and maintaining the sorbent in the superheated state for a period of time (1). However, it was also reported that after a number of cycles, the SD temperature progressively reduced, accompanied by a simultaneous increase in the rate of sorbent attrition. It was postulated that the progressive reduction in the tendency for superheated dehydration was due to some change in the physical properties of Ca(OH)₂ induced by the cycling process itself.

In another work by the author and the team at IRL, published prior to the beginning of the PhD program (55), we investigated the evolution of the microstructure of the sorbents that were subjected to cyclic carbonation/calcination/hydration i.e. to a reactivation step after every Ca Looping cycle. Although this was not known or detected at the time, the conditions used were likely to lead to the superheating of Ca(OH)₂. Note that reactivation was implemented after every Ca looping cycle in this work in order to more easily assess its long-term effects. In practical systems it is expected that reactivation would occur at greater intervals e.g. every 10 Ca looping cycles (1).

We also reported observing the expansion of the particles and the formation of vesicles or very large pores (up to 300 µm) within the particles after 53 cycles (55). Thus it can be speculated that the superheating process is likely to affect the microstructure of the sorbent to some degree.
1.3 Research Questions
To summarize, the superheated reactivation technique initially discovered by the author and colleagues prior to the beginning of this PhD program, has the potential to contribute to substantial improvements in the performance of Ca looping sorbents both from the standpoint of carrying capacity and the tendency of the sorbents to attrite. Such improvements could significantly enhance the economics of Ca looping systems if this technique could be implemented in practice.

However, the lack of understanding of the chemical and physical processes underlying the superheated reactivation technique is the first obstacle in the development of a practical reactivation method based on Ca(OH)$_2$ superheating. For example, it was observed that the extent of superheated dehydration reduces with increasing sorbent cycling (1) and that not all sorbents were able to achieve superheated dehydration (71,72). Since this phenomenon is poorly understood it is difficult to formulate solutions to remediate this issue.

Therefore, the objective of this thesis was to develop an understanding of Ca(OH)$_2$ superheating sufficient to provide a basis for the further development of a practical superheating reactivation method.

The principal aspects of Ca(OH)$_2$ superheating relevant to its practical use are explored in separate chapters; Chapter 2 focuses on the chemical aspects of superheating while Chapter 3 focuses on the physical aspects i.e. the relationship between superheating and attrition.

Each chapter aimed at answering specific research questions and was structured as a series of independent studies. The results of each study were used to guide and formulate the following one, in what might be called an “inductive-deductive” approach. This approach was used to provide guidance to the experimental work in the absence of any information from the literature.

Chapter 2 aimed at understanding why superheating occurs only with some sorbents.

The first study in this chapter (section 2.2.2) was an experimental survey performed in order to discover a method for preparing Ca(OH)$_2$ materials that do not exhibit any superheated dehydration (SD) as well as to identify material properties and process parameters affecting the SD effect.

Following observations made during the experimental survey, the second study (section 2.2.3) focussed on comparing the surface area and porosity of materials with very different tendencies for superheated dehydration.

The third study (section 2.2.4) focussed on comparing the chemical kinetics of dehydration and carbonation of materials that exhibit SD and those that do not exhibit SD at all. The aim was to establish the reaction sequence occurring during the heating of Ca(OH)$_2$ in CO$_2$ with these materials, and provide information as to reaction mechanisms.

Finally, in Section 2.3, all the data and experimental observations gathered were used to formulate a range of testable hypotheses as to the mechanism(s) underlying Ca(OH)$_2$ superheating, and the most parsimonious hypothesis for testing in further work was identified.
Chapter 3 aimed at explaining why superheating reduces the friability of reactivated sorbent. The first experimental section of this chapter (Section 3.2.1) describes the development of a novel attrition testing method, which was deemed necessary to enable a full characterization of sorbent attrition.

The second study aimed to establish the mechanism by which conventional hydration-dehydration technique weakens the reactivated sorbent, and thus allow formulating a hypothesis to explain why the superheating method leads to the absence of this weakening.

Finally, the third study aimed at testing this hypothesis by identifying which parameters of the superheated method affected the sorbent strength after reactivation.

Finally, in Chapter 4, the main findings of this work are summarized and their theoretical and practical implications are discussed. Further work is proposed to confirm the hypotheses formulated about the nature of the chemical mechanisms involved and to support the development of a practical reactivation method making use of the superheating phenomenon.
Chapter 2
Chemical Aspects of Superheating

2.1 Introduction

The ultimate objective of the work presented in this chapter is to elucidate the chemical mechanism(s) underlying the superheating reactivation technique to a degree at least sufficient to allow its control and optimization.

However, given how little was initially known about Ca(OH)$_2$ superheating, it can be said that this work is exploratory by its very nature. Indeed, it would be unreasonable to expect that a detailed, experimentally supported mechanistic description of the underlying chemical processes could be produced within the timeframe of this thesis.

Rather, this work aims to represent a first step in that direction insofar that it provides a foundation of experimental observations and a framework for understanding them that is a prerequisite to formulating and testing credible hypotheses as to the nature of the mechanism(s) underlying Ca(OH)$_2$ superheating.

Thus, the guiding question of this chapter is: Why does superheated dehydration (SD) occur with some Ca(OH)$_2$ samples only?

The first section (Section 2.1) of this chapter describes the results of a literature review on what was known at the outset of this work about Ca(OH)$_2$ superheating, about the behaviour of Ca(OH)$_2$ in the presence of CO$_2$ at high temperatures and the individual reactions thermodynamically expected to occur in these conditions.

The second section (Section 2.2) of this chapter presents data obtained during a series of experimental studies aimed at answering the question above. A series of experimental studies were conducted to establish which conditions lead to the superheated dehydration (SD) effect, and which ones lead to its absence and to a near complete conversion to CaCO$_3$. In addition, the relationship between the carbonation and superheating of Ca(OH)$_2$ was also investigated. Besides the obvious advantage of knowing which parameters lead to the SD effect, this step was important to provide experimental control over the system. Indeed, the experimental procedures used in the laboratory at the onset of this work had not allowed any observation of the absence of the SD effect.

Another series of experiments was conducted to establish whether the near complete conversion to CaCO$_3$ typically observed in the absence of superheated dehydration was the cause or a consequence of this absence. These experiments also provided a range of useful observations on the kinetics of the reaction system which provided insight into the mechanism of Ca(OH)$_2$ carbonation at high temperature.
Finally, in the third section of this chapter (Section 2.3), observations gathered during the experimental studies were used to formulate hypotheses regarding the mechanism(s) underlying the superheating reactivation technique. In addition, methods for testing these hypotheses were proposed.

2.1.1 Literature Review

When Ca(OH)₂ is heated in the presence of CO₂, a range of reactions are thermodynamically expected to occur¹, so that the reaction system under investigation can thus be written as:

\[
\begin{align*}
Ca(OH)_2 & \rightarrow CaO + H_2O \\
CaO + CO_2 & \rightarrow CaCO_3 \\
Ca(OH)_2 + CO_2 & \rightarrow CaCO_3 + H_2O
\end{align*}
\]

(1) Dehydration  
(2) “Indirect” Carbonation  
(3) Direct Carbonation

In this context, superheating is defined as an increase in the temperature of the onset of the dehydration reaction (eq. 1), while carbonation refers to the gas-solid chemical process ultimately leading to the formation of CaCO₃. Note that the CaCO₃ can form via an “indirect” route i.e. by carbonation of crystalline CaO resulting from dehydration (eqs. 1+2) or via a “direct” route i.e. by carbonating Ca(OH)₂ (eq. 3).

The literature review is composed of three distinct parts. In the first part, available information on the dehydration reaction (eq. 1) is reviewed, focussing in particular on the parameters known to affect the temperature at which it occurs. The second part presents and discusses literature information regarding the carbonation mechanism of Ca(OH)₂, both at low temperatures where the “direct” mechanism is expected to prevail and at higher temperatures, where the “indirect” mechanism can be expected to occur. Finally a number of studies in which Ca(OH)₂ was heated in CO₂ but no SD effect was observed are presented and the implications of their results discussed and used to formulate the initial research questions.

The Dehydration Reaction

The thermal disassociation of Ca(OH)₂, also called dehydration, is a reversible, multi-phase reaction, see eq. 1. Its equilibrium is entirely controlled by the partial pressure of water in the gas phase since solid solutions are not usually assumed to form and thus the activity of solids is equal to one. The relationship between the equilibrium water vapour pressure \( p_{eqH_2O} \) and temperature was calculated using HSC, a thermodynamic calculation program, and is plotted in Figure 4.

\[
\begin{align*}
Ca(OH)_2 & \rightarrow CaO + H_2O \quad \Delta H^\circ = 109 \text{ kJ.mol}^{-1} \\
K &= \frac{A_{Ca(OH)_2}}{A_{H_2O} \cdot A_{CaO}} = \frac{1}{p_{H_2O}}
\end{align*}
\]

¹ Intermediary compounds such as calcium carbonate hydrates are not expected to be observed at high temperatures.
Note that if one assumes the activity of solids to be equal to one, the progress of the reaction depends only on the partial pressure of water vapour. As a result, a temperature of dehydration onset can be defined at a given water partial pressure based on thermodynamical considerations. For example, at a water vapour pressure of 1 atm. the temperature of onset of dehydration is 520°C i.e. dehydration is not thermodynamically expected to occur at temperatures below 520°C.

**Figure 4.** Equilibrium water vapour pressure for the hydration/dehydration reaction as a function of temperature.

This reaction has been studied in some detail in the context of developing reversible thermal energy storage systems due to its simplicity, its high enthalpy of reaction (eq. 1) and its ability to operate at temperatures (300–500°C) compatible with the operation of steam cycles for power generation, see Figure 4 (11,12,73).

The dehydration process is also known to give rise to a very reactive form of CaO which was of interest to a number of researchers in the context of flue gas desulfurization processes (74,75,76). The increased reactivity was attributed to an increased specific surface area observed with dehydrated CaO, typically 5–10 times higher than that of CaO obtained by calcining CaCO₃ (37,77).

In fact, the increase in specific surface area due to dehydration is the mechanism by which the conventional reactivation technique is believed to operate, see Section 1.2 (18). In the conventional, hydration-dehydration reactivation technique, spent CaO is hydrated and water vapour is able to penetrate into the sintered core of CaO, transforming it into Ca(OH)₂. Upon dehydration, this material reverts into a porous and reactive CaO restoring the pore network that was gradually lost through the sintering which inevitably occurs during Ca looping cycles.

As discussed above, the temperature of dehydration onset, and the parameters affecting it, is of particular interest for this work. However defining this temperature is not as simple as might initially appear. Using the thermodynamical definition of this temperature (Figure 4) which seems like an obvious choice, is in reality misleading.
Indeed, based on the thermodynamical equilibrium, the onset of dehydration in a flow of industrial grade nitrogen, wherein \( \text{H}_2\text{O} < 16 \text{ ppm} \) should occur at 194°C, since the equilibrium water vapour pressure at this temperature is 1.67x10\(^{-5}\) atm. In contrast, experiments performed in these conditions show that dehydration is observed only between 300 to 450°C (1,71), more than 100°C above the “expected” temperature of dehydration based on thermodynamical considerations only.

The reason for this discrepancy is the role played by the reaction kinetics since it is the rate of dehydration that determines whether and when this reaction will be experimentally detected. As a result, the temperature of onset of dehydration is better defined as the temperature at which water is released from \( \text{Ca(OH)}_2 \) at a detectable rate in a given experimental setup. This point is henceforth referred to as the “normal dehydration temperature”.

However, as a result of this definition, the normal dehydration temperature will depend on the experimental conditions and detection methods employed. Indeed, experimental studies on the dehydration of \( \text{Ca(OH)}_2 \) typically report normal dehydration temperatures between 300–400°C (11,74,75,78) and in some extreme cases 170°C (79), 260°C (80) or 445°C (1).

However, 445°C remains the highest reported normal temperature of dehydration of \( \text{Ca(OH)}_2 \) (1), so that the SD effect cannot, \textit{a priori}, be attributed to the variations in experimental conditions as the temperature of superheated dehydration (620°C) is considerably higher. Therefore it can be said that the presence of \( \text{CO}_2 \) in the gas phase definitely affects the kinetics of dehydration either by entirely blocking this reaction or by slowing it down below the detection level (Figure 3, p.11).

While there are many studies on the kinetics of \( \text{Ca(OH)}_2 \) dehydration in the literature, there is some debate as to the interpretation of the kinetic results obtained. This is illustrated by the wide range of activation energies calculated in these studies, ranging from 34 to 190 kJ mol\(^{-1}\) (81). Furthermore, two main models have been proposed to fit the experimental kinetic data – the contracting sphere model typical of a heterogeneous mechanism with a sharp reaction interface, and a first order reaction model, typical of a homogeneous mechanism and thus implying the absence of a distinct reaction interface.

Galwey et al. attributed the variability of these results to the difficulty of establishing conditions in which the reverse reaction (i.e. hydration of \( \text{CaO} \)) did not occur (81). In an authoritative study, they have demonstrated that the rate of dehydration was sensitive to the locally prevailing water vapour pressure, so that the measured rate depends on a large number of parameters including sample porosity, packing and particle size. After discounting the effect of the reverse reaction, they found that the homogeneous model fitted the kinetic data better and postulated that dehydration does not occur through a sharp reaction interface.

Based on kinetic data, microstructural observations and previous work on the pre-reactional transformation of \( \text{Ca(OH)}_2 \), Galwey et al. postulated a mechanism for the dehydration of \( \text{Ca(OH)}_2 \) which has not been challenged in the open literature since its original publication in 1993 (82). According to this model, the rate limiting step of the dehydration kinetics is the diffusive escape of \( \text{H}_2\text{O} \) out of the
solid through thick layers of partially decomposed Ca(OH)$_2$; the latter forming a meta-stable, open structure which allows the diffusion of water molecules from the unreacted core of Ca(OH)$_2$ to the outer surfaces.

It is worth noting that a very similar mechanism was independently postulated by Freund et al. for the thermal decomposition of Mg(OH)$_2$ (82). The similarity in mechanism can be at least partly explained by the similarity in the crystal structure of these materials, which are both hexagonal, brucite-like, layered structures.

The many aspects of the proposed dehydration mechanism and the pre-reactional transformations occurring during the heat-up of Ca(OH)$_2$ and other brucite-like materials have been the subject of a focussed literature review, but for the sake of reading flow, the results of this review are presented in detail in section 2.3 where they will be used to formulate hypotheses as to the chemical mechanism(s) of Ca(OH)$_2$ superheating.

**Carbonation of Ca(OH)$_2$**

*Carbonation at low temperatures (<100°C) At temperatures below 100°C, the dehydration reaction (eq. 1) is not expected to proceed to any detectable extent so that any carbonation of Ca(OH)$_2$ occurring at this temperatures can only be expected to occur via the “direct” mechanism (eq. 3).*

The carbonation of aqueous Ca(OH)$_2$ is a well-known and rapid reaction leading to the precipitation of CaCO$_3$ out of solution. However in dry conditions the solid-gas carbonation of Ca(OH)$_2$ is reported to be extremely slow, but is reported to be catalysed by the presence of water vapour (83,84,85).

It was reported that besides the rates of carbonation, the maximum advancement of the carbonation reaction was also greatly affected by the relative humidity (RH) of the gas atmosphere during carbonation of Ca(OH)$_2$ (83,84). The RH value was found to have considerably more effect than any other factor tested e.g. temperature or partial pressure of CO$_2$. As an illustration of the importance of the RH value, Beruto et al. reported that in a carbonation test at 100°C, with RH <0.5% and pCO$_2$ =0.65 kPa the material reached 8% conversion after 48 hours of reaction. In contrast, carbonation at 20°C with RH =88% and pCO$_2$ =0.65 kPa, a conversion of 61% was reached within 12 hours.

There is consensus in the literature that the effect of increasing RH is to create a layer of adsorbed water, of increasing thickness, which catalyses the carbonation reaction (83,84,85). As both Ca(OH)$_2$ and CO$_2$ can dissolve in this water film, the reaction mechanism postulated is very similar to that of the carbonation of aqueous Ca(OH)$_2$ and the reaction sequence can be written as:

\[
\text{Ca(OH)}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^- \\
\text{CO}_2(\text{g}) + \text{H}_2\text{O}_{\text{aq}} \leftrightarrow \text{CO}_2\cdot\text{H}_2\text{O} \\
\text{CO}_2\cdot\text{H}_2\text{O} + 2\text{OH}^- \leftrightarrow \text{CO}_3^{2-} + 2\text{H}_2\text{O} \\
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3
\]
Where \( \text{CO}_2 \cdot \text{H}_2\text{O} \) represents \( \text{CO}_2 \) gaseous molecules dissolved in a thin layer of molecular water adsorbed at the surface of \( \text{Ca(OH)}_2 \), which may not necessarily behave similarly to aqueous \( \text{CO}_2 \).

Interestingly, above a certain threshold value (≈50%) the relative humidity had only a mild effect on the rate of carbonation but largely affected the maximum conversion to \( \text{CaCO}_3 \). As a result, a stalled reaction could be restarted by increasing the relative humidity of the gas, leading Beruto et al. (84) to postulate that there is a critical thickness the water film must reach in order to promote this reaction.

Furthermore, to explain the high conversions to \( \text{CaCO}_3 \) observed, they postulated that the carbonation layer is not formed as a protective, or passivating, layer. Although they did not refer to it in the original article, it is possible that this is due to the formation of amorphous \( \text{CaCO}_3 \) during carbonation at low temperatures as reported by Gillott et al. (86), who also reported that recrystallization to calcite occurred only as this material was heated, at approximately 310°C.

Beruto et al. also postulated that the expansion due to the formation of \( \text{CaCO}_3 \) (36.9 ml mol\(^{-1}\) vs. 34.5 ml mol\(^{-1}\) for \( \text{Ca(OH)}_2 \)) occurred inside the pores of \( \text{Ca(OH)}_2 \), possibly leading to pore plugging phenomena during carbonation, thus affecting the maximum conversion attainable (84).

*Carbonation at temperatures above 100°C* As the temperature increases above 100°C, water vapour saturation pressure increases rapidly (1 Mpa at 180°C) so that the RH of the gas phase is necessarily very low. As a result, it is difficult to imagine that the RH-catalysed carbonation mechanism described above can take place at temperatures above 100°C, at atmospheric pressure.

However, carbonation was observed to occur in a number of studies when \( \text{Ca(OH)}_2 \) is heated in the presence of \( \text{CO}_2 \) at temperatures above 200°C. In a study by Nikulshina et al. carbonation was found to proceed to a limited extent at 250°C in the presence of 500 ppm of \( \text{CO}_2 \) and was greatly accelerated at temperatures above 300°C (87). An increase in mass was observed and attributed to carbonation, when \( \text{Ca(OH)}_2 \) was heated in the presence of \( \text{CO}_2 \), starting at 250°C and progressively accelerating with heating (88, 89). The formation of \( \text{CaCO}_3 \) at high temperatures in the presence of dry \( \text{CO}_2 \) was also verified by infrared spectroscopy (90).

These results point to the existence of a mechanism for the direct carbonation of \( \text{Ca(OH)}_2 \) active at high temperatures and in the absence of water vapour. The nature of this mechanism and its relationship to the direct carbonation mechanism operating at lower temperature remain unclear. This high-temperature, direct carbonation mechanism can be expected to be the primary mechanism at temperatures below the normal dehydration temperature (300-400°C) while above this temperature, two broad categories of mechanisms can be imagined depending on whether \( \text{CaO} \) forms as a distinct crystalline intermediary (“indirect” mechanism – eq. 1+2) or not (direct mechanism – eq. 3) such as the high temperature direct carbonation mechanism discussed above.

Surprisingly, this distinction has not been made in previous studies on high temperature carbonation of \( \text{Ca(OH)}_2 \). No attempts were reported in the literature to address this question and the analysis of kinetics of the carbonation \( \text{Ca(OH)}_2 \) implicitly assumed that no dehydration was taking place.
independently of carbonation, despite \( \text{Ca(OH)}_2 \) being heated to temperatures above its normal dehydration temperature (72,87,88).

Furthermore, the experimental methods used in these studies (TGA, FTIR) did not allow establishing whether or not the loss of water was occurring simultaneously with the carbonation of \( \text{Ca(OH)}_2 \), which could have allowed discriminating between the “direct” and “indirect” mechanisms.

Supporting evidence can be found in the existing literature for both the “direct” and “indirect” mechanisms, but it is insufficient to conclude which mechanism is preferred. The indirect carbonation mechanism is supported by the observation that the carbonation reaction was found to accelerate as the temperature reached the normal dehydration temperature (20,21,24), which suggests that the rate of carbonation depends on the amount of CaO available and thus that carbonation proceeds via the “indirect” mechanism.

The direct carbonation mechanism is supported by the observation that the carbonation of \( \text{Ca(OH)}_2 \) in dry \( \text{CO}_2 \) proceeded significantly faster and to greater extent than the carbonation of dehydrated CaO (72,88,87). However, as illustrated by Nikulshina et al. this effect could be simply due to the presence of water vapour released by \( \text{Ca(OH)}_2 \) during the experiment, which is known to enhance the rate and extent of carbonation of CaO (87).

Thus there is no conclusive experimental evidence as to whether carbonation occurs “directly” or “indirectly”, and the possibility that both routes are active cannot be excluded either. Nevertheless, Nikulshina et al. postulated that the carbonation of \( \text{Ca(OH)}_2 \) occurs at high temperature via a direct mechanism, similar to that occurring at low temperatures insofar that adsorbed water catalysed this reaction. However, Nikulshina postulated that water was released by the carbonation reaction itself was the catalyst, so that this reaction could be said to be auto-catalytic although no experimental evidence was proposed to support this hypothesis.

In contrast, Montez-Hernandez et al. postulated a direct carbonation mechanism in which the thermal excitations would induce the mobility of the oxygen atoms from the lattice, which would then migrate to the surface and mineralize into \( \text{CaCO}_3 \) (72,90). Similarly, no experimental evidence was provided to support this hypothesis either.

2.1.2 Research Questions

The Irregular Occurrence of Superheated Dehydration

The SD effect itself was initially observed when \( \text{Ca(OH)}_2 \) was heated in \( \text{CO}_2 \) inside a bubbling fluid bed (1) and following that in a thermogravimetric analyser (TGA) for some materials (71). In contrast, several studies using a TGA apparatus reported not observing the SD effect (20,21,24).

Clearly, it can be said that the superheated dehydration effect does not occur every time that \( \text{Ca(OH)}_2 \) is heated in the presence of \( \text{CO}_2 \). This simple observation, and what can be deduced from it, has been chosen as the starting point of the experimental research work presented in this section.
In order to formulate the initial research questions which will lead us into this enquiry, it is helpful to compare the TGA profiles obtained when the SD effect is absent, Figure 5a and when it is observed, Figure 5b.

Figure 5a illustrates the mass vs. temperature profile obtained by Montez-Hernandez et al. (72) when heating a non-SD prone Ca(OH)$_2$ sample in 100% CO$_2$ at 10°C.min$^{-1}$ in a TGA. It can be seen that the carbonation reaction starts at approximately 270°C (563 K), as deduced from the beginning of the mass increase, and proceeds to a near-complete conversion to CaCO$_3$ as the temperature reaches 580°C (853 K). Note that this type of behaviour had not been observed under the conditions used in the experiments performed prior to the beginning of the PhD project.

In contrast, Figure 5b illustrates the mass vs. temperature profile obtained when a SD prone Ca(OH)$_2$ sample is heated at the same heating rate in CO$_2$. Similarly, the carbonation reaction starts at approximately 280°C (563 K) but then suddenly slows down at 390°C (663K). Furthermore, when the critical temperature of 620°C (893 K) is reached a sudden loss of mass is observed which can be attributed to the loss of water, and thus to the superheated dehydration effect. The conversion to CaCO$_3$ is considerably lower than that achieved by non-SD Ca(OH)$_2$ samples, see Figure 5a.

Since identical heating conditions were used here but the superheated dehydration was observed only with one of the materials, it can be concluded that the properties of the Ca(OH)$_2$ material itself e.g. composition, crystallinity or microstructure, have a large influence on the extent and occurrence of the SD effect.

The first major research question, addressed in Sections 2.2.2 and 2.2.3 is stated as: What material properties and/or process parameters affect the extent of the superheated dehydration?

As shown in Figure 2, the absence of the SD effect was correlated with a high conversion to CaCO$_3$ but the casual relationship between the two is not clear. Namely, it could be imagined that the high carbonation conversion is due to the absence of the SD effect since Ca(OH)$_2$ decomposes into CaO which
then carbonates (eqs. 1+2). However, it can also be imagined that the absence of the SD effect is due to the high carbonation conversion (eq. 3) since this reaction could lead to the release of water from the system before the SD temperature was reached.

Therefore the second major research question, addressed in Section 2.2.4, is stated as: *Is increased carbonation the cause or the consequence of reduced Superheated Dehydration?*

### 2.1.3 Approach

This chapter is structured as a series of independent studies where the results of each study were used to guide and formulate the following one, in what might be called an “inductive-deductive” approach.

The first study in this chapter (section 2.2.2) was an experimental survey performed in order to discover a method for preparing Ca(OH)$_2$ materials that do not exhibit any superheated dehydration (SD). Namely, while it was clear that some materials did not do any SD, methods for preparing those were unknown at the outset of this work. The characterization of the properties of such materials was expected to identify material properties that further studies should investigate in subsequent studies.

Particle surface area and porosity were identified as one of the relevant parameters during the experimental survey and were chosen for further investigation. The second study (section 2.2.3) focussed on comparing the surface area and porosity of materials with very different tendencies for superheated dehydration. In addition, the data gathered in this section was in the analysis of reaction kinetics in the following study.

The third study (section 2.2.4) focussed on comparing the chemical kinetics of dehydration and carbonation of materials that exhibit SD and those that do not exhibit SD at all. The aim was to establish the reaction sequence occurring during the heating of Ca(OH)$_2$ in CO$_2$ with these materials, and provide information as to reaction mechanisms, which were found to exhibit unusual properties.

Finally, in Section 2.3, all the data and experimental observations gathered were used to formulate a range of testable hypotheses as to the mechanism(s) underlying Ca(OH)$_2$ superheating, and the most parsimonious hypothesis for testing and quantification in subsequent work was identified.
2.2 Experimental Work

This section describes a series of experiments which were undertaken to provide answers to the research questions formulated in the previous paragraphs. The results are presented as a series of semi-independent experimental studies contained within each sub-section.

Prior to describing in detail the results leading to answering these questions, the next sections discuss the apparatus and analyses used during the experimental work reported in this chapter. The specific method used during the experimental work will be reported alongside the results of this work in each respective section.

2.2.1 Apparatus and Analyses

Fluid Bed Apparatus
A small fluid bed apparatus, 32 mm diameter and 1.3 m height, was used for the preparation of cycled and hydrated sorbents (primarily composed of CaO and Ca(OH)$_2$, respectively). The reactor was operated in the bubbling regime while the temperature was controlled via an external furnace. The conditions used in the preparation of samples were the following. Calcination reactions were performed in N$_2$ atmospheric pressure, at 850°C and for 20 min Carbonation reactions were performed in 25%CO$_2$/N$_2$ at 620–650°C for 12 min Hydration reactions were performed at in a 30% H$_2$O/N$_2$ at 250°C for 35 min.

Thermogravimetric Analysis
A TGA apparatus was especially modified for the purpose of this work to allow the injection of steam into the gas flow, enabling steam hydration of calcined sorbents in-situ.

A controlled pressure of air was used to drive a minute flow of liquid water (≈10 µl.min$^{-1}$) from a water reservoir, through a 1/16” nozzle and into the environment chamber of the TGA apparatus, which contained the CaO sample to be hydrated. A glass capillary tube was placed on the water supply line to provide a large resistance to flow and thus allow precise control of the water flow by adjusting the gas pressure over the reservoir.

In addition, the switching of gases and addition of water were entirely automated allowing for the repeatable execution of experimental procedures.

The TGA apparatus allowed continuous measurements of sample mass during the course of the different Ca looping reactions, as well as hydration and dehydration or heating in CO$_2$ of hydrated sorbent. In all cases sample mass was expressed as a percentage of the mass of the fully carbonated sample so as to allow easy comparison across experiments. In some cases (see section 2.2.4) a relative humidity probe was placed at the gas outlet of the TGA apparatus, allowing for a qualitative assessment of the rate of water release from the sample during dehydration and heating in CO$_2$ of hydrated sorbents.
**X-Ray Diffraction (XRD)**
The XRD technique was used in order to identify the crystalline phases present in a sample as well as to assess the crystallinity of each phase. A simple survey scan technique between 4–80° was performed on a Philips PW 1700 series automatic diffractometer with CoKα radiation and graphite monochromators.

**Fourier Transform Infrared (FTIR)**
Infrared Spectroscopy is typically used as a tool for detecting and measuring the presence of specific functional groups providing information on the chemical composition of the sample. With inorganic solids however, the infrared technique can also provide a wealth of information regarding the structure of the solid that is inaccessible via XRD, e.g. the distortion of molecular units at different lattice sites, the presence of compounds adsorbed at the solid surface or the presence of activated intermediary compounds.

In this work, the FTIR, Attenuated Total Reflectance (ATR) technique was used to produce IR spectra of samples of Ca(OH)$_2$ between 600–4000 cm$^{-1}$ with a 4 cm$^{-1}$ resolution, as discussed in Section 2.2.

**N$_2$ Adsorption**
The specific surface area and porosity of different samples were measured using the N$_2$ adsorption technique. N$_2$ adsorption isotherms were measured on approx. 1g samples of hydrated sorbent using a Micrometrics ASAP-2010 apparatus with helium as the carrier gas. Automated BET calculations were used to calculate surface area, pore volume and average pore size (calculated as $P_{size} = 4*V/A$). Note that due to the limitations of this technique, the area and volume of pores larger than 300 nm is typically not detected.

**2.2.2 Parameters leading to the Superheated Dehydration (SD) Effect**

**Introduction**
As discussed in the introduction, the first study in this chapter was an experimental survey focussed on establishing methods to produce sorbent with little or no SD effect and determining which material properties and process parameters affected the extent of superheated dehydration (see Section 2.1). The principal objective of this section is thus to determine which experimental conditions influence the superheating behaviour of Ca(OH)$_2$ upon heating in CO$_2$ i.e. the occurrence and extent of the SD effect as well as the carbonation conversion. Relevant experimental parameters can be divided into two broad categories: Ca(OH)$_2$ preparation parameters, which ultimately control the properties of the hydroxide and the heating parameters used during the heating in CO$_2$. In this study, Ca(OH)$_2$ material samples were prepared by hydrating cycled Ca Looping sorbents, so that the former category can be further subdivided into two sub-categories: sorbent cycling and hydration conditions. Table 3 summarizes the various experimental parameters tested in each category.
Figure 6. Schematic illustrating the experimental procedure used in this section.

Table 3. List of experimental parameters considered in this work.

<table>
<thead>
<tr>
<th>Sorbent cycling conditions</th>
<th>Hydration conditions</th>
<th>Heating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone origin and composition</td>
<td>Hydration temperature</td>
<td>Heating rates/profile</td>
</tr>
<tr>
<td>Particle size</td>
<td>Hydration time</td>
<td>% CO₂ in heating gas</td>
</tr>
<tr>
<td>Calcination/carbonation conditions</td>
<td>Water content</td>
<td></td>
</tr>
<tr>
<td>Number of Ca looping cycles</td>
<td>Steam/liquid</td>
<td></td>
</tr>
</tbody>
</table>

In this section, a TGA apparatus, described in Section 2.2.1, was used to test the effect of the parameters identified in Table 3 on the behaviour of hydrated sorbents upon heating in CO₂. As can be seen in Table 3, the number of possible parameter combinations is very large so that all possible combinations have not been tested. Instead, each parameter was varied separately while maintaining the others constant. The results are therefore presented as a series of short experimental studies on a single parameter at a time and findings from one study were often used to adjust the parameters for subsequent ones. Each study also includes a short discussion on the implications of the findings.

Materials and Methods

Materials The reference material used in this work was a raw limestone supplied by Taylor’s Agricultural Lime, New Zealand, which is a natural, high purity, calcite limestone containing approximately 1–2% silica and traces of iron oxide (0.13%) as determined by XRD and EDX analysis. The raw material had a particle size <2 mm but was subsequently sieved, and only the 300–600 μm fraction was used. Other limestones tested in this work are described in more detail in the relevant sections.

Sample Preparation Hydrated sorbent preparation was carried out by calcining a limestone sample (20–30 mg) in the TGA apparatus and subjecting it to a number of carbonation/calcination cycles as discussed in section 2.2.1. The calcined sorbent was then steam hydrated inside the TGA apparatus and largely converted to Ca(OH)₂.

Heating in CO₂ The hydrated sorbent was then heated up to 560°C in a 100% CO₂ atmosphere inside the TGA. Once that temperature was reached, the supply gas was switched from CO₂ to N₂, which triggers the sudden dehydration of the remaining Ca(OH)₂ in a similar manner to what was previously observed in fluid bed experiments (1). This method of triggering superheated dehydration is called “N₂ Trigger”.

Given that many parameters were varied in this exploratory study, parameter variations are reported alongside experimental results if different from the “reference” parameters, which are reported in
Table 4. The “reference” parameters were selected based on the conditions used in the fluid bed that were known to lead to the SD effect.

**Table 4. “Reference” conditions used for the preparation of hydrated sorbents and their heating in CO₂.**

<table>
<thead>
<tr>
<th>Sorbent cycling</th>
<th>Hydration conditions</th>
<th>Heating in CO₂ – conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>≈20mg. Taylor’s limestone 300–600μm</td>
<td>Hydration: 20 min at 380°C in 30% steam in N₂</td>
<td>Linear heating: 380°C to 560°C at 6°C.min⁻¹ in 100% CO₂ N₂ trigger at 560°C</td>
</tr>
<tr>
<td>Calcination: 5 min at 800°C in N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonation: 15 min at 620°C in CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Ca looping cycle: raw limestone is calcined, carbonated then calcined</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Sorbent composition calculation** Using the “N₂ trigger” method of dehydration enabled determination of the composition of the sorbent at the moment of the trigger, i.e. at 560°C.

This is achieved by assuming that the mass lost at the moment of the trigger is water, released from superheated Ca(OH)₂, which is then entirely dehydrated. With the knowledge of the mass of H₂O released, the mass of Ca(OH)₂ present in the sample at the moment of the trigger can be easily calculated. Once dehydration is complete, the sorbent is composed of a mixture of CaO and CaCO₃. The mass of CO₂ captured by the sorbent, and thus the proportion of CaCO₃, can be easily calculated since the mass of the fully calcined sample is known. This calculation method is illustrated in Figure 7 and discussed in more detail in the results sections.

The proportion of Ca(OH)₂ remaining at the moment of the trigger was used in this work as a quantitative measure of the extent of the SD effect, while the proportion of CaCO₃ was used to evaluate the tendency of the hydrated sorbent to carbonate when heated in CO₂. In addition, the presence of CaO above that which was present in the hydroxide, due to incomplete conversion to Ca(OH)₂ can be used to assess the tendency of Ca(OH)₂ to dehydrate.

The two types of Ca(OH)₂ behaviour upon heating identified so far (see Section 2.1.1, Figures 5a,b) should therefore be distinguishable by the proportion of Ca(OH)₂ and CaCO₃ in the sample at the moment of the trigger.

**Results**

*Description of the “reference” experiment* Figure 7a plots the mass and temperature versus time profiles obtained with the “reference” TGA experiment while Table 4 details the conditions used. Sample mass is expressed as a percentage of the mass of the starting limestone, which is fully carbonated. This is particularly convenient since the molar mass of CaCO₃ is 100 g.mol⁻¹.
Figure 7. **a)** Mass (pink) and temperature (blue) traces of Taylor’s lime, subjected to one Ca looping cycle hydrated at 380°C, heated to 560°C in 100% CO$_2$, dehydration is then triggered by replacing CO$_2$ by N$_2$, see text below. **b)** Molar composition of the sorbent sample at the moment of the trigger and standard deviation measured with repeated results **c)** calculations performed to obtain molar composition

As the temperature reaches 700°C, at approximately 40 min the sample mass starts decreasing as a result of the calcination reaction. The calcination is rapid and the final mass reached is 57% of the initial mass indicating that calcination is complete since the molar mass of CaO is 56 gmol$^{-1}$. The slightly higher reading of 57% can be attributed to the presence of impurities, which are not expected to participate in the reaction.

Calculations performed:

\[
\%	ext{hydrated} = \frac{(m_1 - m_0) \times M_{\text{CaO}}}{m_0 \times M_{\text{H}_2\text{O}}}
\]

\[
\%	ext{Ca(OH)2} = \frac{(m_3 - m_2) \times M_{\text{CaO}}}{m_0 \times M_{\text{H}_2\text{O}}}
\]

\[
\%	ext{CaCO3} = \frac{(m_2 - m_0) \times M_{\text{CaO}}}{m_0 \times M_{\text{H}_2\text{O}}}
\]

\[
\%	ext{CaO} = 100 - \%	ext{CaCO3} - \%	ext{Ca(OH)2}
\]
The freshly calcined sorbent is then subjected to one carbonation/calcination cycle: first, the temperature is reduced to 620°C and CO₂ is introduced – the exact moment of the gas switch is visible by an artefact in the mass and temperature curves – then, the previously calcined sorbent reacts with CO₂ from the gas and the sample mass increases. After the sample reaches about 85% of the original mass, the rate of carbonation reduces as it is now controlled by diffusion through the newly formed layer of CaCO₃ (31). At approximately 80 min, the gas is switched back to N₂ and the sorbent is calcined again by raising the temperature to 800°C.

After the completion of a single Ca looping cycle, the temperature is reduced to the desired hydration temperature, here 380°C, and liquid water is injected into the TGA apparatus where it evaporates and mixes with the flowing gas, so that the calcined sample is hydrated in a gas flow containing 30% steam in N₂. Hydration is accompanied by a rapid rise in sample mass at 135 min. Sample mass reaches ≈74% indicating that hydration is near complete since the molar mass of Ca(OH)₂ is 74g.mol⁻¹.

Upon completion of the hydration step, the gas is switched to CO₂ again and the hydrated sorbent is heated up to 560°C at 5°C.min⁻¹, see Figure 7a. During this step, sample mass is observed to increase, first at a very rapid rate, then as the temperature starts increasing, at an approximately constant rate throughout the heating period.

Once the temperature of 560°C is reached the gas is switched to N₂ again leading to a rapid loss of mass, attributed to the loss of water based on the observations made in a fluid bed (1). Although not shown in Figure 7a, subsequent analyses have confirmed that the loss of mass is indeed due to the release of water from the sample, see section 2.2.4.

After dehydration is triggered, the composition of the sorbent sample can be easily calculated by subtraction, as described in the methodology above. The results obtained with the reference experiment are plotted in Figure 7b, which also displays the percentage of initial Ca(OH)₂ in the hydrated sorbent sample, as well as the standard deviation of these values obtained after repeating this experiment four times.

Figure 7b shows that the sample still contained 48% Ca(OH)₂ at the moment of the trigger (i.e. at 560°C) which is nearly half of the Ca(OH)₂ initially present in the hydrated sample. Another 46% of the hydrated sample was converted to CaCO₃ during heating in CO₂. The proportion of CaO at the trigger was 2% higher than that present at the end of hydration, suggesting that dehydration of Ca(OH)₂ might have occurred to a limited extent. However, this value is near the level of experimental uncertainty, making it difficult to conclude if any dehydration to CaO had occurred. Note that the proportion of CaCO₃ formed during contact with CO₂ measured in this experiment is similar to that reported from preliminary work by the author and colleagues when the experiment was performed in a fluid bed (1).

Note that after the dehydration was triggered, the resulting material (a mixture of CaO and CaCO₃) still carbonated when contacted with CO₂, see Figure 7a. The amount of carbonation reached after the dehydration trigger was also recorded as it represents the CO₂ carrying capacity of the reactivated sorbent, although the results were not exploited in this section. This aspect is further developed in section 2.2.4.
The results presented here confirm the existence of the SD effect under conditions comparable to those of studies in which this effect was not observed (72,88). This is a novel and encouraging result. The following pages present a series of experimental studies on the various experimental parameters in the order of presentation of Table 4.

Sorbent Parameters: Limestone Origin and Composition In this experiment, hydrated sorbent samples were prepared from a range of raw limestones containing different levels of MgCO₃ and other impurities, see Table 5. All limestones were sieved prior to testing and only the 300-600 µm was used here.

The magnesium fraction of the limestones was assumed not to participate in the carbonation and hydration reactions so that composition calculations were performed on the Ca fraction only. This assumption is justified by the fact that MgO is thermodynamically stable at the carbonation and hydration conditions used here (600°C, 100% CO₂; 265°C, 30% H₂O). The results obtained with the different limestones are plotted in Figure 8.

![Figure 8](image)

**Figure 8.** Sample composition at the moment of trigger (560°C) after heating in CO₂ for hydrated sorbents derived from limestones of varying origins. Default parameters were used, cf. Table 4, with a hydration temperature of 200°C.

**Table 5.** Magnesium content of the limestones tested in this section as estimated by XRD analysis.

<table>
<thead>
<tr>
<th>Raw limestone</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taylor’s</td>
<td>High purity calcite (&gt;97%)</td>
</tr>
<tr>
<td>Omya</td>
<td>High purity calcite (&gt;97%)</td>
</tr>
<tr>
<td>Lhoist</td>
<td>95% calcite, 5% magnesite</td>
</tr>
<tr>
<td>Fembrae</td>
<td>90% calcite, 10% magnesite</td>
</tr>
<tr>
<td>Golden Bay Dolomite</td>
<td>95% dolomite (MgCa(CO₃)₂), 5% calcite</td>
</tr>
</tbody>
</table>
With all calcitic limestones, a significant proportion of Ca(OH)$_2$ (28–38%) was observed at the moment of the trigger (560°C) regardless of the magnesium content of the starting limestone. This result confirms that the SD effect is not an isolated case and is likely to occur with most hydrated sorbents derived from calcitic limestones, regardless of the impurities present.

In the case of the dolomitic limestone, calculation of the sample composition at the moment of trigger yielded obviously incorrect results as shown in Figure 8. This issue is most likely due to the fact that, in dolomitic limestones, MgO does not form a separate phase as with the other limestone samples. Instead, it is incorporated into the crystal lattice and therefore likely to at least partially carbonate/hydrate thus rendering invalid the calculation assumptions.

Nevertheless, this issue does not affect the conclusion that hydrated sorbents derived from Golden Bay dolomite limestones, exhibited less SD compared to the reference material. A similar result was also reported during the course of this thesis (71) although the methodology used does not allow for a direct comparison of SD extents observed.

On the basis of these observations it can be speculated that superheating occurs at the grain (crystallite) level. Indeed, the presence of MgO in the hydrated sorbent, in the form of separate crystallites, did not significantly affect the extent of SD observed while the inclusion of Mg into the crystal lattice clearly reduced it.

**Sorbent Parameters: Particle Size** In this experiment, a hydrated sorbent sample, prepared using the “reference” conditions, was taken out of the TGA and ground. Once reduced to a fine powder, this sample was returned to the TGA and heated using the “reference” parameters, see Table 4. The results obtained were then compared with those obtained with the hydrated sorbent in its original size (300–600 µm) in order to assess the effect of particle size; Figure 9 plots the results obtained.

Grinding the particles is expected to lead to an increase in particle surface area as well as to a reduction in the mass transfer rate of the gas out of the sample, due to a change of the packing density of the sample. An additional experiment was performed to distinguish between these two distinct factors, in which the mass of the reference sample was doubled in order to evaluate the effect of reduced mass transfer rates on the results obtained.
Reducing the particle size was found to have a significant effect on the behaviour of the hydroxide upon heating, as seen in Figure 9. Grinding the hydrated sorbent led to a reduction of the proportion of superheated Ca(OH)$_2$ at the trigger from 48% to 17% which is considerably larger than the standard deviation observed upon repeating the test with the reference sized particles, see Figure 9. This reduction was accompanied by an increase in the proportion of CaCO$_3$, formed by carbonation. The proportion of CaO was also increased beyond the uncertainty levels, so it can be concluded that a proportion of Ca(OH)$_2$ did dehydrate to CaO during the heating step.

On the other hand, increasing the sample mass was found not to affect the composition of the sorbent at the trigger, suggesting that mass transfer of water out of the sample does not have a major influence on the dehydration kinetics as was observed in previous work (81).

These results suggest that the superheating behaviour of hydrated sorbent particles is affected by particle surface area. Similar observations have been reported by Blamey et al. during the course of this work, who found that ground hydrated sorbents exhibited no superheated dehydration (71). Unfortunately, the amount of Ca(OH)$_2$ that could be prepared in the TGA was too small to allow for surface area and porosity (pore volume) measurements via the N$_2$ adsorption technique. An alternative Ca(OH)$_2$ sample production method was developed to allow this, and will be discussed in section 2.2.3.

**Sorbent Parameters: Commercial Hydroxides** Two different commercial hydroxides were tested in this work: McDonald’s slaked lime, which is a construction material industrially produced from Taylor’s limestone, while BDH Ca(OH)$_2$ is a laboratory grade reagent. Both hydroxides were acquired in a fine powder form and were dried in N$_2$ at 200°C for 20 min prior to being heated in CO$_2$, at 10°C.min$^{-1}$. The results obtained are plotted in Figure 10a, and compared to the behaviour of the ground “reference” hydroxide. Figure 10b plots the TGA profile obtained with the McDonald’s material.

**Figure 9.** Sample composition at the moment of trigger (560°C) after heating in CO$_2$ for hydrated sorbents derived from Taylor’s particles of different sizes. Default parameters were used (Table 4).
Figure 10. a) Sample composition at the moment of trigger (560°C) after heating in CO₂ for commercial hydroxides, compared with the reference material of a similar size. Default parameters were used (Table 4) with a hydration temperature of 265°C. b) TGA profile obtained upon heating McDonald’s hydroxide in CO₂, resembling that reported in studies where no SD was observed.

No Ca(OH)₂ was found to be present at the moment of the trigger for either of the commercial hydroxides, while the carbonation levels were considerably higher than those obtained with the reference material, see Figure 10a. Furthermore, the sample mass had reached a maximum before the temperature had reached 560°C and no carbonation could be achieved after the trigger point. Commercial hydroxides were thus found to behave similarly to the Ca(OH)₂ materials tested in the literature i.e. to reach high conversion of carbonate without exhibiting any SD effect (72,88).

Given the relative lack of information on the exact preparation methods of these hydroxides it is difficult to ascribe the change in behaviour to a specific parameter. For this reason, a series of analyses were performed on McDonald’s hydroxide and the reference material in order to attempt identifying measurable differences between the two hydrated sorbents.

A simple XRD survey scan of the McDonald’s hydroxide material revealed a small proportion of CaCO₃ (3%) and broader Ca(OH)₂ peaks than that of the reference hydrated sorbent, see Appendix 1. The latter suggests a smaller crystallite size for the McDonald’s hydroxide, as confirmed by calculations using the Scherrer equation. The crystallite size is thus a potential parameter affecting superheated dehydration that could be worthwhile exploring in the following studies.

Sorbent Parameters: Sorbent Cycling History The effect of the cycling history on the behaviour of the hydroxide upon heating was tested by varying the number of Ca looping cycles (1, 7 and 34) performed prior to hydration, see Figure 11 and Table 4. Subsequent hydration and heating in CO₂ were performed using the reference conditions.
An additional experiment was performed in which raw limestone was calcined and sintered for 20h at 900°C, subjected to one Ca looping cycle and finally hydrated and heated using the reference conditions. Figure 11 plots the composition of the sample at the moment of the trigger.

![Figure 11](image)

**Figure 11.** Sample composition at the moment of trigger (560°C) after heating in CO₂ for hydrated sorbents derived from Taylor’s particles with different cycling histories. Default parameters were used (Table 4).

Where the sorbent was cycled or sintered prior to hydration, the reference hydration conditions led to incomplete conversion to Ca(OH)₂ as shown in Figure 11. Hydration conversion was particularly low for the extensively cycled sorbent (30%) while surprisingly, it was relatively high for the extensively sintered sorbent (72%). It is here implicitly assumed that the incomplete conversion of the sample is due to the incomplete conversion of each individual sample grain as opposed to having some fully hydrated and some non-hydrated grains. Achieving full hydration is a requirement for maximizing the carrying capacity of the reactivated sorbent (91) and methods for achieving this with extensively cycled sorbents are investigated in section 2.2.3.

A considerable proportion of superheated Ca(OH)₂ was found at the trigger point with both the seven cycled and the extensively sintered sorbent samples. In contrast, no SD was observed with the 34 cycled sorbent. These results indicate that the presence of unconverted CaO in the hydrated sorbent does not suppress the SD effect for the hydrated portion of the grains.

Prolonged exposure to high temperatures (>800°C) is known to promote sorbent sintering and to reduce its specific surface area (37). Samples prepared by hydration of cycled and sintered sorbents can be expected to have a reduced surface area compared to the reference hydrated sorbent, which could be the origin of the different behaviour of these hydrated samples when heated in CO₂.
However, a reduction in surface area alone is not sufficient to explain the results here. Indeed, if surface area were the only factor, it could be expected that both the extensively sintered and extensively cycled material would exhibit a reduced extent of SD, which is not the case (Figure 11). One notable difference between cycled and sintered sorbents however is the pore size distribution, as cycled sorbents have been shown to exhibit a number of large pores that are absent from sintered sorbents (32,35).

This observation allows us to speculate that the microstructure of the Ca(OH)$_2$ sorbent, and in particular its pore size distribution, might play a critical role in controlling the occurrence of the SD effect. This aspect is further investigated in section 2.2.3.

Hydration Parameters: Time and Temperature In this series of experiments, the effect of hydration temperature and time was tested by changing the hydration temperature (150, 265 and 380°C) and hydration time (15, 20 and 35 min) of the reference experiment.

Figure 12. Sample composition at the moment of trigger (560°C) after heating in CO$_2$ for hydrated sorbent prepared with varying hydration temperature and times. Default parameters were used (Table 4).

Figure 12 illustrates that hydration temperature affects the extent of the SD effect more than the length of hydration. A reduction in the hydration temperature was found to lead to a decreased proportion of Ca(OH)$_2$ compared to the reference case (at 380°C) and a slightly increased tendency to carbonate, although the relationship was not found to be linear. Changing the hydration time at the reference temperature did not affect the composition of the sorbent significantly.

The temperature and time of hydration were found to have little effect on the composition of the sorbent at the trigger, although they were found to be very important factors to achieve complete hydration conversion of extensively cycled sorbents, as discussed in section 2.2.3.
Hydration Parameters: Water Stoichiometry In this series of experiments, the effect of the water content during hydration was assessed by hydrating the “reference” calcined sorbent in different concentrations of steam (15, 30 and 60%) at 265°C, while the heating step was carried out using the reference conditions.

In addition, the “reference” calcined sorbent was also hydrated in liquid water; after the final calcination, the sample pan was taken out of the TGA, a drop of water was added in the pan which was then returned to the TGA and dried at 200°C for 20 min. Thus prepared, the liquid hydrated sorbent was heated in CO₂ using reference conditions. Note that during liquid water hydration, sorbent particles were pulverized to some extent, presumably due to the high rate of the hydration reaction with liquid water. Figure 13 plots the results obtained.

<table>
<thead>
<tr>
<th>%Hydration</th>
<th>15% steam</th>
<th>30% steam (reference)</th>
<th>60% steam</th>
<th>Liquid water</th>
</tr>
</thead>
<tbody>
<tr>
<td>%CaO</td>
<td>3%</td>
<td>10%</td>
<td>25%</td>
<td>13%</td>
</tr>
<tr>
<td>%CaCO₂</td>
<td>62%</td>
<td>56%</td>
<td>74%</td>
<td>27%</td>
</tr>
<tr>
<td>%CaOH₂</td>
<td>35%</td>
<td>34%</td>
<td>1%</td>
<td>2%</td>
</tr>
</tbody>
</table>

Figure 13. Sample composition at the moment of trigger (560°C) after heating in CO₂ with varying water stoichiometry during hydration. Default parameters were used (Table 4), with varying steam content as well as a liquid water hydration.

The sorbent sample hydrated with liquid water was found to release a considerable amount of water at the trigger point (27%), as shown in Figure 13. The proportion of Ca(OH)₂ found in the sample was nevertheless lower than that obtained with the reference steam hydration conditions (30%), potentially due to the reduction in particle size induced by liquid hydration, as reported above.

The steam content of the hydrating gas was found to have a significant impact on the superheating behaviour of the hydrated sorbents (Figure 13). While the increase of hydration steam content from 15 to 30% had only a minor effect in the form of reduced carbonation, the increase from 30 to 60% steam lead to the absence of any superheated dehydration at the moment of the trigger.

This result is important as it is the first time that no superheated dehydration was observed with a particulate material (300–600 µm), as opposed to the powdered commercial hydroxide samples.
discussed above. In order to verify this result, the 60% steam hydration experiment was repeated four times (Figure 13); the SD effect was not observed in any of the repeated experiments.

An XRD survey scan of the sorbent hydrated in 60% steam was performed and is shown in Appendix 1. Similarly to the results obtained with the commercial hydroxide discussed above, broader Ca(OH)$_2$ peaks were found, and Scherrer’s equation suggests a smaller crystalline size for this material.

This result suggests that smaller crystallite size might be an important parameter since materials that exhibited no SD effect also had reduced crystallite sizes (McDonald’s, 60% steam hydrated). However, the peak broadening might be due to other effects e.g. strain or instrument broadening so that a detailed investigation is required prior to confirming this relationship.

Further differences were observed in the fine structure of the FTIR spectra of sorbents hydrated in 30% and 60% steam and that of the McDonald’s samples, suggesting some structural differences, but these could not be correlated with their superheating behaviour. Unfortunately, the amounts of hydrated sorbent generated via the TGA method were not sufficient for N$_2$ adsorption measurements, so it was not possible to compare the surface area and pore size distribution of the materials presented here. The relationship between sorbent surface area and porosity and superheating behaviour was investigated in another study, see section 2.2.3.

**Heating Parameters: Heat-up Rates/Profile** Hydrated sorbent samples, prepared in the TGA using the reference method with a 200°C hydration, were heated up to 560°C in 100% CO$_2$ at varying heating rates (1, 2 and 6°C.min$^{-1}$). An additional experiment was performed in which a 2°C.min$^{-1}$ heating rate was used and the temperature held for 2 hour periods at 350°C and 380°C. Figure 14 plots the results obtained.

![Figure 14a](image.png)

**Figure 14a.** Sample composition at (560°C) after heating in CO$_2$ for a hydrated sorbent derived from Taylor’s limestone. Default parameters were used (Table 4), with hydration performed at 200°C while the heat up-rate and profile of the heating step were varied.
Surprisingly, neither heating rate nor the additional four hour hold had any significant effect on the composition of the sample at the trigger, see Figure 14a. This is a particularly unusual result considering that the contact time between the hydrated sorbent sample and 100% CO$_2$ was increased almost nine-fold (from 60 min at 6°C.min$^{-1}$ to 520 min in the experiment with holds), suggesting that the advancement of the carbonation and dehydration reactions of Ca(OH)$_2$ in the sample during the heating step was independent of contact time.

This idea was investigated further by plotting the sample mass evolution measured in these experiments versus temperature instead of time, in contrast to the results presented in Figure 7a and Figure 10a. The result obtained is equally surprising as the mass vs. temperature curves are remarkably similar at all heating rates, see Figure 14b. In all three cases, a small “bump” in the mass profile is observed between 280–300°C; inflection points are observed at 300–320°C and 370°C and finally the mass conversion achieved at any given temperature is within 2–3% in all three cases.

It follows that with the hydrated sorbent used here, the advancement of the carbonation and dehydration reactions is independent of time and therefore can be expressed as a function of temperature only. This point is well illustrated by the TGA mass vs. time profile obtained when freshly hydrated Ca(OH)$_2$ is heated in CO$_2$ with two hour holds at 350°C and 370°C shown in Figure 15.

It can be seen that the rate of sorbent mass increase varies with the rate of heating, i.e. sorbent mass increases during heating and stops increasing during the temperature hold steps. Note that this type of behaviour was observed in over 12 repeated experiments with hydrated sorbents derived from Taylor’s limestone, involving holds at various temperatures.

**Figure 14b** TGA mass vs. temperature plot obtained during experiments with varying heat-up rates.
Figure 15. Mass vs. time profile obtained during the heating of a hydrated sorbent sample derived from Taylor’s limestone in CO$_2$ with the standard conditions. During the heating step, the sorbent was held in CO$_2$ for 2 hours at 350°C and 370°C. Note how the mass stops increasing when the temperature stops increasing.

Such behaviour cannot be explained by thermodynamical considerations of the overall reaction since carbonation of Ca(OH)$_2$ is expected to proceed to completion in the conditions of this experiment i.e. in the presence of a sweeping flow of 100% CO$_2$ at elevated temperatures. Furthermore, based on thermodynamic analysis the dehydration reaction would be expected to be occurring when the temperature is held constant, forming CaO which would then be expected to react with CO$_2$ to form CaCO$_3$. These remarks allow deducing that the advancement of the carbonation reaction is controlled by the reaction kinetics, and it is possible to speculate that the rate limiting step is temperature controlled in such a way as to lead to the time independence of the overall reaction.

The results open a new and promising research area, namely the kinetics of the high temperature carbonation of Ca(OH)$_2$. Such an unusual kinetic behaviour is very likely to provide information that can be used to formulate testable hypotheses regarding the mechanism of Ca(OH)$_2$ carbonation at high temperature as well the origin of Ca(OH)$_2$ superheating. The kinetics of the system are investigated in more detail in section 2.2.3.

Discussion and Conclusion(s)

The results presented in this work have greatly broadened the range of available observations of Ca(OH)$_2$ superheating and allowed defining areas of interest for further research.

The superheated dehydration (SD) effect was observed to occur in over 30 experiments with hydrated sorbents prepared from a range of different limestones and using a range of experimental parameters, see Figures 7 to 14. These results confirm that this effect is not an isolated case occurring in a narrow range of conditions. However, the extent of the SD effect, i.e. the proportion of superheated Ca(OH)$_2$
remaining at 560°C, was found to vary with the experimental parameters used but usually remained above 20%, if the SD effect occurred.

The total absence of the SD effect was also observed with different types of Ca(OH)$_2$ materials, e.g. with dolomitic limestones (Figure 8), commercial hydroxides (Figure 10), extensively cycled limestone (Figure 11) and sorbents hydrated in 60% steam (Figure 13). This is a new and important result as, until now, the absence of superheated dehydration had not been observed in this laboratory. Having identified the Ca(OH)$_2$ materials that exhibit no SD effect is an important practical step as it allows observing these materials more closely.

Surprisingly, heating parameters were found not to affect the extent of SD at all, see Figure 14a, and the composition of the sorbent could be expressed as a function of temperature only, see Figure 14b. This unusual behaviour opens a new area of research, which will be developed in section 2.2.4. Based on this observation, it can also be postulated that the tendency for superheated dehydration is a property of the hydrated sorbent itself and thus it can be related to some of its measurable properties such as such as composition, crystallinity or microstructure (surface area, porosity and pore size distribution).

The composition of the sorbent did not appear to be an important factor since the presence of other phases (MgO, CaO, and impurities) did not greatly affect the extent of the SD effect as shown in Figures 9 and 11. It was speculated that superheating occurs at the level of individual grains as the SD effect was not observed with dolomitic limestone, which contained Mg within the crystal grains.

The crystallinity of the sorbent was identified as a potential parameter related to the tendency to SD of the hydrated sorbent, as XRD diffractograms of sorbents which exhibited little or no Superheated Dehydration exhibited broader Ca(OH)$_2$ peaks suggesting a smaller crystallite size for these materials. However, these results were insufficient to definitely establish this relationship.

The results presented here also suggest that particle microstructure could be a key parameter affecting the occurrence and extent of the SD effect. Indeed, the parameters that influenced most the extent of the SD effect (particle size, cycling history) are known to modify the surface area and the porosity of the sorbent (32,35). However, due to the limited size of samples that could be generated in the TGA apparatus, it was not possible to obtain surface area and porosity measurements of the hydrated sorbents and relate them to the superheating behaviour.

Therefore, an additional study was undertaken, where larger amounts of Ca(OH)$_2$ were prepared to allow surface area measurements and heated inside the TGA apparatus in the presence of CO$_2$ to assess their superheating behaviour. This study is described in the following section.
2.2.3 The effect of surface area and porosity on the superheated dehydration effect

Introduction
As discussed above, the principal aim of this section of the work is to determine which parameters control the SD effect. An experimental survey, reported in Section 2.2.2 identified particle surface area and porosity (pore volume) as a potential key parameter affecting the occurrence and extent of the SD effect.

In addition, it was observed that sorbents subjected to more than one Ca looping cycle (carbonation/calcination) could not be hydrated (converted to Ca(OH)\(_2\)) to near completion (>90%) with the reference hydration conditions used in the experimental survey. Incomplete hydration of calcined sorbents made comparing superheating behaviour more difficult, and is also expected to limit the extent of sorbent reactivation.

An additional study was thus performed with a two-fold objective. The first objective was to determine the conditions in which extensively cycled sorbents could be hydrated in order to allow comparisons of their superheating behaviour and to maximise the effect of the reactivation technique. The second objective was to investigate the relationship between the surface area and porosity of the hydrated sorbent with its superheating behaviour i.e. the extent of SD and the carbonation conversion at the moment of the trigger.

In this study, a small fluid bed, described in section 2.2.1, was used to prepare 100g samples of multi-cycled sorbents (1, 7 and 37 Ca looping cycles). A range of hydration techniques was then applied to produce a range of hydrated sorbents in sufficient quantity to allow measuring their surface area and pore volume using the N\(_2\) adsorption technique. Hydrated sorbents were then heated in the presence of CO\(_2\) inside a TGA apparatus, described in Section 2.2.1, to measure the extent of the SD effect and carbonation achieved during heating. The CO\(_2\) carrying capacity i.e. activity of reactivated sorbents, was also measured.

Materials and Methods
Sample Preparation 100 g of Taylor’s limestone (300–600 µm) was charged into a fluid bed apparatus, see Section 2.2.1, calcined and then subjected to a varying number of Ca looping cycles (1, 7 and 37), using the conditions presented in Table 4. Calcination reactions were performed in a flow of N\(_2\) at 905°C for 15 min while carbonation reactions were performed in 37.5% CO\(_2\) in N\(_2\) at 600°C. Due to the absence of a cooling system, the heat released by the carbonation reaction would raise the bed temperature to approx. 640–660°C. Once the cycling was completed, cycled sorbents were discharged from the bed, as CaO, and kept in an airtight container to minimise interactions with atmospheric humidity and CO\(_2\).

Liquid Water Hydration was performed by contacting a 4 g sample of cycled sorbent (CaO) with 5 ml of water (1:4 CaO/water molecular ratio) in a stirred beaker at room temperature for 30 min. No effort was made to control the increase in the temperature of the mixture due to the heat released from the reaction. However the beaker was covered with aluminium foil to minimize water evaporation. During liquid water hydration many sorbent particles were pulverized, leading to a reduction in the average
particle size. Immediately after the hydration step, the hydrated sorbent was dried overnight in a 140°C oven prior to its heating in CO\textsubscript{2} and testing with N\textsubscript{2} adsorption.

Additional experiments were performed in which the experimental parameters were varied (stoichiometry, time and addition temperature) but they are not reported here as the results were in all cases comparable to the results obtained with the standard method described above.

\textit{Oven Steam Hydration} was performed by placing a glass vial containing a 1.5 g sample of cycled sorbent (CaO) in a loosely capped jar containing water which was then placed inside a laboratory oven. Hydration was performed at two different temperatures, at 90°C and 120°C, where the hydrating atmosphere contained saturated and unsaturated steam, respectively.

Indeed, at 90°C the equilibrium water vapour pressure is below 100 kPa so that the relative humidity in the loosely capped jar is at 100% and the jar is thus filled with saturated (or wet) steam, causing observable condensation on the inner walls of the vial containing the sample. In contrast, at 120°C the equilibrium water vapour pressure is above 100 kPa so that the relative humidity is necessarily below 100% and the loosely capped jar is filled with unsaturated (or dry) steam, as confirmed by the observed absence of condensation on the inner walls of the vial.

The progress of the hydration reaction was monitored by the expansion of the solid inside the glass vial using engraved distance markings. The conversion of hydration reaction was evaluated by the weight gain after the hydrated sorbent was dried.

\textit{TGA Hydration} was performed using the modified TGA apparatus with a flow of a 30% steam/N\textsubscript{2} mixture, for 35 min and at varying temperatures (100, 200 and 300°C).

\textit{Heating in CO\textsubscript{2}} Hydrated sorbent samples were first dried at 200°C for 20 min and then heated in 100% CO\textsubscript{2} at 15°C.min\textsuperscript{-1} up to 520°C. Once that temperature was reached, superheated dehydration was triggered using the N\textsubscript{2} trigger described previously by switching the gas to N\textsubscript{2}. The composition of the sample at the moment of the trigger was calculated using the method described in Materials and Methods, section 2.2.2.

\textit{SEM analyses} Due to the inability of the N\textsubscript{2} adsorption method to detect pores larger than \(\approx\)100 nm, the existence of such pores was investigated using Scanning Electron Microscopy (SEM) for 120°C steam hydrated (Ca(OH)\textsubscript{2}) sorbent samples of different cycling histories.

Sample particles were cut with a razor blade and metal coated with Au/Pd for 120 seconds. SEM images were taken on a Quanta 450 SEM equipped with a tungsten filament. The secondary electron images were acquired operating the SEM at 20 keV using a spot size of 3. The SEM beam was pointed at clean fracture surfaces. It was possible to identify such areas since outer surfaces of the particle were distinguishable from inner surfaces as they were covered with residual fines from the sieving process. For each sample, the beam was focused on several zones of 2-3 different particles and images were taken at different scales.
Results

Surface area and Porosity of Spent Sorbents  

$\text{N}_2$ adsorption isotherms of the spent sorbents, i.e. prior to hydration, were measured and are plotted in Appendix 2, while the results of BET calculations of surface area and pore volume are shown in Table 6.

The results presented in Table 6 confirm that the surface area and pore volume are considerably reduced with increasing cycle numbers, as expected. The average pore size, as calculated by the BET method ($4V/A$) is also somewhat reduced, although less than either the pore volume or surface area.

All the isotherms obtained were of type IV with a hysteresis loop, suggesting that tested materials were mesoporous. This can also be deduced from the result of BJH calculations, which are plotted in Appendix 2 and show a bimodal pore size distribution for spent sorbents with peaks at 3 and 20-40 nm pore diameter size. BJH plots were calculated from the adsorption branch because calculations using the desorption branch exhibited artefact peaks at ≈20-40 nm due to the rapid closure of the hysteresis loop.

It is worth noting at this point that the $\text{N}_2$ adsorption technique is unable to detect pores larger than approximately 100-300 nm, and that extensively cycled sorbents are known to develop a substantial amount of pores in the 400–500 nm size range (32), suggesting that our measurement of pore volume via $\text{N}_2$ adsorption is not entirely representative of the porosity of the extensively cycled sorbent.

Table 6. Surface area and porosity of spent sorbents as a function of number of Ca looping cycles.

<table>
<thead>
<tr>
<th></th>
<th>Surface area (m$^2$.g$^{-1}$)</th>
<th>Pore volume (cm$^3$.g$^{-1}$)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Cycle</td>
<td>8.1</td>
<td>0.08</td>
<td>38.1</td>
</tr>
<tr>
<td>7 Cycles</td>
<td>3.8</td>
<td>0.03</td>
<td>30.5</td>
</tr>
<tr>
<td>37 Cycles</td>
<td>1.8</td>
<td>0.01</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Achieving Full Hydration  

Hydration conversions achieved with the different methods employed and the time required to achieve them are plotted in Figure 16a. As can be seen, hydration conversion was high (>85%) for all sorbents and all hydration methods as long as the temperature remained below 200°C. However the time required to reach the final hydration conversion varied considerably from approximately 30 min for the liquid water and the TGA 100°C steam hydration up to 270 min for the unsaturated steam hydration. Extensively cycled sorbent samples were typically slower to hydrate; at 90°C it took 170 min to hydrate the once-cycled sorbent samples, while 270 min were needed to hydrate the 37 cycled sorbent samples.

Figure 16b plots the relationship between the carbonation capacity of the sorbent after SD reactivation against the hydration conversion of the spent sorbent. As expected, this figure illustrates that incomplete hydration (<80%) always leads to a low carbonation capacity of the reactivated sorbent (<40%). On the other hand, when hydration conversion is high (>80%) the resulting carbonation capacity is always >60% but interestingly, when reactivated, the sorbents that experienced more cycles (7, 37 cycles) achieved higher carbonation levels than the once-cycled sorbent.
These results suggest that a hydration conversion >80% is desirable in practical systems to achieve high reactivation levels. Reducing the temperature of hydration is a feasible method to achieving such hydration conversion even with extensively cycled sorbents. However, reducing the temperature also leads to longer hydration steps, so that a trade-off must be made between conversion and rate.

![Figure 16](image1.png)

**Figure 16.** a) Hydration levels reached with different hydration methods b) Final carbonations observed as a function of the extent of hydration reached.

*Surface area and pore volume vs. SD and Carbonation Extent* Figure 17 plots the composition at the N\textsubscript{2} trigger point obtained with the various hydrated sorbent samples upon heating in CO\textsubscript{2}. In addition, Table 7 shows the results obtained by N\textsubscript{2} adsorption measurements for these hydrated sorbents. Note that in all cases a high hydration conversion was achieved (>80%), making these results directly comparable.

![Figure 17](image2.png)

**Figure 17.** Sample composition at the moment of the trigger (560°C) after heating in CO\textsubscript{2} of hydrated sorbents with different cycling histories produced via a range of hydration techniques.
Table 7. Surface area and porosity data for hydrated sorbents reported in Figure 17.

<table>
<thead>
<tr>
<th></th>
<th>BET area (m².g⁻¹)</th>
<th>Pore volume (cm³.g⁻¹)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1C – Liquid</td>
<td>34.4</td>
<td>0.20</td>
<td>19</td>
</tr>
<tr>
<td>1C – Sat. steam</td>
<td>10.6</td>
<td>0.10</td>
<td>32</td>
</tr>
<tr>
<td>1C – Unsat. steam</td>
<td>11.3</td>
<td>0.09</td>
<td>27</td>
</tr>
<tr>
<td>7C – Liquid</td>
<td>32.9</td>
<td>0.20</td>
<td>20</td>
</tr>
<tr>
<td>7C – Sat. steam</td>
<td>9.5</td>
<td>0.07</td>
<td>28</td>
</tr>
<tr>
<td>7C – Unsat. steam</td>
<td>7.5</td>
<td>0.06</td>
<td>27</td>
</tr>
<tr>
<td>37C – Liquid</td>
<td>25.5</td>
<td>0.16</td>
<td>22</td>
</tr>
<tr>
<td>37C – Sat. steam</td>
<td>7.2</td>
<td>0.06</td>
<td>31</td>
</tr>
<tr>
<td>37C – Unsat. steam</td>
<td>8.1</td>
<td>0.06</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure 17 shows that the cycling history greatly affected the SD extent of hydrated sorbents. With the extensively cycled sorbent (37 cycles), no SD effect was observed at the trigger point regardless of the hydration method employed. In contrast, with the least cycled sorbent (one cycle), superheated dehydration occurred with all hydration methods employed. The seven-cycled sorbent exhibited an intermediary behaviour, with little SD observed when it was hydrated with liquid water and high levels of SD occurring with 120°C steam hydration.

The extent of carbonation followed the opposite trend; it was high when the extent of SD was low and vice-versa. The formation of CaO, which can be attributed to the dehydration of Ca(OH)₂, remained below 10% and did not follow any obvious pattern. Surface area and pore volume, as measured by N₂ adsorption, did not match the extent of SD of the sorbent pattern, see Table 7. The particle surface area and volume were mostly affected by the type of hydration used rather than particle history, i.e. sorbents hydrated in liquid water had surface areas between 25–35 m².g⁻¹ while the surface area of steam hydrated sorbents was much lower (7–11 m².g⁻¹).

The pore size distribution of the hydrated sorbents was found to be remain bimodal with principal peaks at 3 and 20-40 nm. The breadth and relative height of the peaks was found to vary with the hydration technique used but no relevant pattern was detected, see Appendix 2. The average pore size as measured by the BET technique was found to vary with the type of hydration used regardless of the history of the sorbent i.e. 19-22 nm for liquid, 28-32 nm for saturated steam and 25–27 nm for unsaturated steam hydration (Table 7) although the difference is not large.

Discussion

The results obtained in this work suggest that reducing the hydration temperature is the key to ensuring that high hydration conversions can be reached even in the case of extensively hydrated sorbents, see Figure 16. However in practical processes, this temperature should be as high as possible in order to minimize the energy penalty associated with cooling and heating the sorbent (71,91). Based on the

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2 Refers to the proportion of CaO in excess of that present in the original hydroxides, which must have formed during the heating stage and thus have been formed via dehydration.
results obtained here, 200°C can be suggested as an initial guess for an optimal hydration temperature since high conversions (>80%) were reached in a reasonable timeframe (35 min).

The results presented here raise an important contradiction regarding the relationship between sorbent specific surface area and the SD effect. Namely, the extent of the SD effect was observed to decrease with increasing specific area/volume in several cases, such as when the 1C and 7C were hydrated in liquid water as seen in Figure 17 and Table 7, or when the hydrated sorbent was ground prior to heating in CO₂ (Figure 9 in section 2.2.2). This implies that a low specific surface/volume should lead to a high extent of SD. Yet, the SD effect was not observed at all with the 37C hydrated sorbent, which had the lowest surface area of all three sorbents tested regardless of the hydration method used.

A possible solution to this apparent contradiction could be to also consider the pore size distribution of the hydrated sorbent and the limitations of the N₂ adsorption method used here. Repeated Ca looping cycles are known to lead to the formation of bimodal pore size distribution structure with peaks at 90 nm and 400–600 nm (32), although the mechanism by which this occurs remains unknown. The total volume of the large pores (400–600 nm) was reported to grow with the cycling number and exceed the volume available in the smaller pores after the 29th cycle.

As discussed above, pores larger than 300 nm are not detected in with the N₂ adsorption. As a result, the results presented in Table 7 do not accurately represent particle pore volume, as the presence of undetected large pores would considerably increase total pore volume but not the total surface area.

In order to assess the existence of large pores a SEM was used to observe the fracture surfaces of spent sorbent particles (1 and 37 cycles) hydrated in steam at 120°C; the micrograms obtained are shown in Figure 18. In the case of the once-cycled sample, Ca(OH)₂ grains appear composed of an agglomeration of small crystallites leaving between them a network of small pores, see Figure 18a. In contrast, with the 37 cycled sample, these crystallites are considerably larger and the existence of large pores (> 300 nm) can be observed, see Figure 18b.

Figure 18. a) SEM image of a fracture surface of a) a once-cycled, steam hydrated Ca(OH)₂ particle b) a 37 cycle, steam hydrated Ca(OH)₂ particle. Scale bar: 4μm
On the basis of this observation it is possible to postulate that the key parameter affecting the extent of SD observed is in fact the presence of large pores within the particle. It can be imagined that the expansion of the newly formed CaCO$_3$ into the pore network of the particle is able to plug the smaller pores and thus promote the inhibition of the dehydration reaction, while this does not happen with the largest pores. This hypothesis would explain many of the experimental observations that have been presented so far:

1. The SD effect was not observed with extensively cycled sorbents (37C) under any hydration regime because they have developed a significant network of large pores during cycling (Figure 18b). In contrast to cycled sorbents, the pore size of extensively sintered sorbents is considerably lower (100–200 nm) so that they are not expected to exhibit the SD effect, as observed and reported in section 2.2.2.

2. Grinding of hydrated sorbent leads to the decrease in the extent of SD as it increases the surface area of the particle exterior; in a sense, external solid surfaces can be considered surfaces in pores of infinite dimensions, so that an increase in the external surface area is equivalent to an increase in the area of large pores in the context of this hypothesis.

3. The least cycled sorbent (1C) is thought not to have developed a network of large pores at all (Figure 18a) so that superheated dehydration occurs regardless of the hydration technique applied.

This hypothesis can be used to explain the observations made in preliminary work by the author and colleagues (1) that the extent of the SD effect reduces with repeated reactivation steps, discussed in Section 1.2. Indeed, they observed that after 5 superheating reactivation steps, the temperature of onset of superheated dehydration was reduced from 620°C to 550°C.

As discussed in Section 1.2, in another work (55) they also reported observing the formation of large pores, visible by Scanning Electroscope Microscopy, within the particles after only 7 superheating steps. In this context, using the hypothesis formulated above, it can be postulated that it is the formation of large pores that occurred during repeated superheating (55) that lead to the progressive reduction in the extent of the SD effect observed (1).

Using mercury intrusion porosimetry instead of N$_2$ adsorption, in order to obtain a direct measurement of the volume and area of large pores within these particles, could easily allow testing this hypothesis. However, no suitable apparatus was identified within New Zealand and the practical limitations of this project did not permit this experiment. This experiment should clearly be the next step to identifying the key parameters for achieving superheated dehydration.

**Conclusion**

The objective of this section was to determine which experimental parameters affect the absence and presence of the SD effect.

The experimental survey revealed that the SD effect can be observed over a broad range of conditions, with Ca(OH)$_2$ derived from calcitic limestones. On the other hand, with all commercial Ca(OH)$_2$ materials tested, the SD effect was absent and high levels of carbonation were reached instead. Since most
studies reported in the literature used commercial hydroxides it is not surprising that the SD effect was not observed earlier.

It was observed that heating rate and profiles did not affect the extent of SD or that of carbonation. Indeed, sorbent mass was found to be dependent on temperature only during the heating phase. This simple and unusual observation has important implications. Namely, if heating parameters do not affect the extent of SD or that of carbonation, then it is only the properties of the hydroxide that affect SD so that it can be said that the tendency to SD is a property of the hydrated sorbent itself.

Three main properties of hydrated sorbents were considered in this work: composition, crystallinity and microstructure (surface area, porosity and pore size distribution). The presence of compounds other than Ca(OH)$_2$ in the particles, e.g. MgO, CaO or impurities, was found not to affect the hydrated sorbent’s tendency for superheated dehydration (SD). However, inclusion of Mg atoms in the lattice, as found in dolomitic limestones, lead to a non-SD hydrated sorbent.

Crystallinity was identified as a parameter with a potential effect on the presence of SD, as hydroxides with little or no tendency to SD also exhibit broader XRD diffraction peaks than the reference material. This result suggests that a smaller crystallite size for non-SD materials although a detailed XRD study would be required to confirm this relationship as the observed peak broadening can be due to other effects.

Surface area and pore volume were found to affect the presence of SD, although the relationship between the two is complex. While parameters known to affect the surface area and porosity of the hydrated sorbent were also found to greatly affect the extent of SD, no direct relationship was observed between pore area/volume, as measured by N$_2$ adsorption, and the extent of SD or carbonation.

To explain this observation, it was postulated that the area/volume present in pores larger than 300 nm is the key parameter leading to the presence or absence of the SD effect. Note that the area of external surfaces also affects the SD effect, since these surfaces can be assimilated to surfaces in very large pores. Indeed, large pores are known to be formed in extensively cycled sorbents and for this purpose external surfaces can be assimilated to pores of a large diameter (32,33). Such pores cannot be detected with N$_2$ adsorption technique, suggesting that alternative porosimetric techniques need to be used for further investigations in this area.

In any case, the absence of the SD effect was always found to be accompanied by a high conversion to CaCO$_3$. As discussed in the introduction to this chapter, TGA data alone is insufficient to determine whether the absence of SD is the cause or the consequence of the high carbonation levels that accompany it. This question is the focus of the following section.
2.2.4 Chemical Kinetics of the High Temperature Carbonation of Ca(OH)\textsubscript{2}

Introduction

The experimental survey reported in Sections 2.2.2 and 2.2.3 aimed at identifying the main factors leading to observing the SD effect. Several types of Ca(OH)\textsubscript{2} which did not exhibit any SD effect were identified; e.g. dolomites, commercial hydroxides, and extensively cycled hydrated sorbents. In all cases, the absence of SD was accompanied by a high carbonation conversion.

This section focuses on understanding the relationship between the absence of the SD effect and the carbonation reaction. In order to clarify this question it is necessary to consider the chemical reactions involved in this system:

\[
\begin{align*}
Ca(OH)_2 & \rightarrow CaO + H_2O & (1) \text{ Dehydration} \\
CaO + CO_2 & \rightarrow CaCO_3 & (2) \text{ “Indirect” Carbonation} \\
Ca(OH)_2 + CO_2 & \rightarrow CaCO_3 + H_2O & (3) \text{ Direct Carbonation}
\end{align*}
\]

Note that equations 1–3 are simply “stoichiometric” equations and not representative of the actual chemical mechanisms involved. In this context, eq. 1 represents the dehydration reaction of Ca(OH)\textsubscript{2} to a distinct crystalline phase of CaO, while eq. 2 represents the carbonation of that CaO. In contrast, eq. 3 represents the direct carbonation reaction of Ca(OH)\textsubscript{2}, i.e. without the formation of a distinct crystalline CaO phase. As a result, eqs. 1+2 (“indirect” route) and eq. 3 (“direct” route) describe two distinctly different carbonation routes, which can be expected to have significantly different kinetic behaviour.

The high carbonation levels achieved when a non-SD prone Ca(OH)\textsubscript{2} is heated in the presence of CO\textsubscript{2} can be explained in two equally plausible ways. It can be imagined that the absence of SD is the cause of the high carbonation. Indeed, if Ca(OH)\textsubscript{2} did not superheat, reaction (1) would not be inhibited and the material would convert to CaO which would then be carbonated to form a large proportion of CaCO\textsubscript{3} during the heating step (eqs. 1+2).

However it can also be imagined that the absence of SD is the consequence of the high carbonation conversion. In this case, if Ca(OH)\textsubscript{2} did superheat, i.e. reaction (1) was inhibited but the direct carbonation of Ca(OH)\textsubscript{2} (eq. 3) proceeded to a very high level, all the water would be released before the temperature reached 560°C and superheated dehydration would not be observed.

Thus, establishing the preferred carbonation route is the key to answering the key question identified through the literature review (section 2.1.1), namely whether the absence of superheating leads to the high carbonation conversion (“indirect” route) or vice-versa (“direct” route).

In this study, water release patterns and the carbonation kinetics observed when SD and non-SD Ca(OH)\textsubscript{2} samples are heated in CO\textsubscript{2} (eq. 3) were compared with those measured when these samples were dehydrated prior to carbonation (eqs. 1+2).
In addition, it was reported in section 2.2.2 that the rate of carbonation reaction was dependent on the rate of temperature increase, so that it essentially stopped when the temperature was held constant but began again when the temperature was increased, Figure 15, section 2.2.2. As a result, the advancement of the carbonation reaction could be expressed as a function of temperature only.

Although this unusual kinetic behaviour has so far only been observed with only one type of hydrated sorbent it appears as an interesting area of study, likely to provide useful insight into the chemical mechanism of carbonation and possibly superheating. In this study, the generality of this observation was tested by heating different hydrated sorbents in CO₂ using sawtooth-like temperature profiles. Furthermore, data obtained in section 2.2.3 is reanalysed here to investigate the relationship between surface area and pore volume with the kinetics of carbonation.

Materials and Methods
Materials Two calcium hydroxide materials were used in this study. High purity commercial hydroxide (>95% Ca(OH)₂) was purchased from McDonald’s Lime, New Zealand. This material was prepared by water-based industrial slaking techniques, and had experienced some carbonation (<3%) during its storage.

A vapour-hydrated calcium hydroxide was prepared from raw limestone using a bubbling fluid bed described in detail in section 2.2.1. The raw limestone was supplied by Taylor’s Agricultural Lime, New Zealand, and is a natural, high purity, calcite limestone, with approximately 1–2% silica and traces of iron oxide (0.13%) as determined by XRD and EDX analysis. The raw material had a particle size <2 mm but was subsequently sieved and only the 300–600 µm fraction was used.

In the bubbling bed the Taylor’s raw limestone was calcined for 15 min at 905°C, carbonated in 27% CO₂ for 25 min at 620°C then calcined again at 905°C and finally steam hydrated for 40 min at 320°C at an absolute humidity of 30% in N₂. The hydration reaction was found to be complete and the vapour hydrated calcium hydroxide was sieved between 300–600 µm and used in this study.

Method Samples of 15–20 mg of calcium hydroxide were heated under N₂ or CO₂ in a Stanton Redcroft STA1500 thermogravimetric analyser (TGA). Table 8 summarizes the conditions used and the temperature profile is plotted alongside the results in each figure. Note that the temperature profile used included a final carbonation step after the trigger in order to assess the CO₂ carrying capacity of the reactivated sorbent. In additional heating experiments under CO₂, and in order to investigate the carbonation kinetics, the temperature profile of step 2 was modified to resemble a sawtooth with peaks at 300, 350, 400 and 500°C as described in Figure 21.
Table 8. Heating profile conditions used in the thermo gravimetric analyser.

<table>
<thead>
<tr>
<th>Step</th>
<th>Heating rate (°C.min⁻¹)</th>
<th>Temperature (°C)</th>
<th>Hold time (min)</th>
<th>Gas</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>200</td>
<td>10</td>
<td>N₂</td>
<td>Drying</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>560</td>
<td>5</td>
<td>N₂ or CO₂</td>
<td>Heating</td>
</tr>
<tr>
<td>3</td>
<td>n/a</td>
<td>560</td>
<td>15</td>
<td>N₂</td>
<td>Drying</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>620</td>
<td>25</td>
<td>CO₂</td>
<td>Carbonation</td>
</tr>
<tr>
<td>5</td>
<td>n/a</td>
<td>620</td>
<td>10</td>
<td>N₂</td>
<td>Line Purge</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>850</td>
<td>5</td>
<td>N₂</td>
<td>Calcination</td>
</tr>
</tbody>
</table>

The relative humidity of the gas leaving the TGA was measured with a relative humidity probe at room temperature. The humidity probe reading varied somewhat with the gas flow (N₂ - 35 ml.min⁻¹; CO₂ - 27 ml.min⁻¹) and therefore changed when the gases were switched. The humidity readings were imprecise and were used only qualitatively to determine at which point water was released from the sample.

**Results**

As in previous sections, the sample mass in the TGA profiles is expressed as a percentage of the theoretical mass of the entirely carbonated sample. This is a convenient way to display results since the molar mass of CaCO₃ is 100 g.mol⁻¹. Thus, the initial mass percentage of fully hydrated sorbents is always 74%. Also, the mass percentage of fully dehydrated Ca(OH)₂ would be 56%.

*McDonald’s Hydroxide* Figure 19 displays the TGA and humidity profiles of the outlet gas during the heating of McDonald’s Ca(OH)₂ in N₂ and in CO₂.

When McDonald’s Ca(OH)₂ was heated in N₂, Figure 19a, a mass decrease was observed starting at 355°C corresponding to the dehydration of calcium hydroxide, eq. 1, illustrated by a sudden increase in the humidity of the gas leaving the sample chamber. Dehydration was completed in 15 min, when the material reached 442°C. A smaller mass loss was observed as the temperature approached 620°C during step 3 (Table 8). The origin of this mass loss is unknown as it was not observed in experiments with the other material, see Figure 19b, and it is assumed that it is due to the calcination of small amounts of CaCO₃ (approx. 3%) formed during the production and storage of McDonald’s calcium hydroxide. Upon carbonation, the dehydrated sorbent reached a mass percentage of 85% corresponding to a carbonation conversion of 66%.
A marked difference in behaviour was observed when McDonald’s hydroxide was heated in CO₂. As shown in Figure 19b, a mass increase, attributed to the carbonation of Ca(OH)₂, eq. 3, was observed as soon as CO₂ was introduced in the TGA (step 2, Table 8). Carbonation noticeably accelerated when the sample reached 340°C and proceeded to a mass percentage of 95% as the material was heated to 560°C. No sudden release of water corresponding to the dehydration of Ca(OH)₂, eq. 1, was observed at the expected temperature, around 355°C. Instead, some water release was detected by the humidity probe as soon as CO₂ was introduced and water was released throughout the heating phase (step 2), with a peak at 500°C. While the water released in the 200–355°C temperature range can be attributed to the direct carbonation of Ca(OH)₂, eq. 3, it is not possible to say whether water released in the 355–560°C temperature range comes from the reactions of dehydration (eq.1) or direct carbonation (eq.3). In either case, some Ca(OH)₂ must have superheated, i.e. remained stable at temperatures higher than the normal decomposition temperature (355°C in these experiments), since water was still being released at 500°C.

No further changes were observed as the material was dried (step 3, Table 8) and returned to the CO₂ capture loop (steps 4-6). The material had reached a maximum mass percentage (95%) upon heating in CO₂ (step 2), corresponding to a carbonation conversion of 89%.

The carbonation conversion attained when dehydration (eq. 1) is performed as a separate step (66%), Figure 19a, was lower than that achieved during heating in CO₂ (89%), Figure 19b.

Taylor’s Hydroxide Figure 20 shows the TGA and humidity profiles during the heating of Taylor’s calcium hydroxide in N₂ or CO₂.

The N₂ heating experiment proceeded similarly to that of McDonald’s hydroxide – dehydration started at 360°C and was completed in 16 min. Upon carbonation of the dehydrated material (step 4), simulating the return to the CO₂ capture loop, the sample reached a mass percentage of 77%, corresponding to a carbonation conversion of 47%.
When Taylor’s hydroxide was heated under CO₂ a different pattern emerged. As soon as CO₂ was introduced (step 2) carbonation was also observed but proceeded more slowly than in the McDonald’s experiment, reaching only 80% mass at the end of step 2. Once the heating phase was complete (step 2), CO₂ was replaced by N₂ (step 3) and a sudden increase in the humidity reading was observed, attributed to the dehydration of Ca(OH)₂, eq. 1. This observation implies that a large proportion of Ca(OH)₂ (57% molar) superheated, i.e. remained stable above its decomposition temperature, up to 560°C. After dehydration of the superheated Ca(OH)₂ at 560°C, the CaO was returned to the CO₂ loop and carbonated again, ultimately reaching 85% mass, corresponding to 66% carbonation conversion.

Once again, the carbonation conversion attained when dehydration (eq. 1) is performed as a separate step (47%), Figure 20a, and was significantly lower than that achieved during heating in CO₂ (66%), as shown in Figure 20b.

**Sawtooth Experiments** The unexpected kinetic behaviour initially observed in section 2.2.2 was confirmed in experiments where the temperature profile of the heating step (step 2) was modified to resemble a sawtooth. Figure 21 shows TGA and humidity profiles recorded during these experiments.

In both cases, every time that the temperature was reduced, both the mass increase and water release appeared to stop. This indicates that none of the reactions 1–3 are proceeding to any appreciable extent. The absence of mass increase indicates that the carbonation of either Ca(OH)₂, eq. 3 or CaO, eq. 2 stopped when the temperature was reduced, while the absence of water release indicates that dehydration of Ca(OH)₂, eq. 1, was not occurring either. However, when the temperature was increased again, both the mass increase and water release resumed as soon as the temperature exceeded the temperature at which the heating had been stopped.

This behaviour was observed in numerous repeat experiments with a number of hydrated sorbents and using a wide range of heating profiles, suggesting that it might be a general property of Ca(OH)₂ containing materials.
Figure 21. TGA and humidity profiles for hydrated sorbent samples heated in CO$_2$ with a sawtooth profile
a) McDonald’s hydroxide b) Taylor’s hydroxide.

An important implication of this result is that Ca(OH)$_2$ superheating in fact occurs with all hydrated sorbents regardless of the extent of the SD effect observed at 560°. This can be deduced since Ca(OH)$_2$ was found to remain stable for extended periods of time at temperatures above its normal decomposition temperature, here at 400°C and 500°C for 20 min at a time, see Figure 21a and Figure 21b. The difference between the different sorbents is thus simply the proportion of Ca(OH)$_2$ that remains at any given temperature.

The high temperature stability of Ca(OH)$_2$ observed in these tests suggests that direct carbonation is the preferred carbonation route, given that eq. 1 is not found to proceed separately even at temperatures above the normal dehydration temperature.

**Reactivation Experiments** The importance of the preferred carbonation route (direct/indirect) route for the activity of the reactivated sorbent was tested in a multicycle experiment with Taylor’s limestone. The TGA profiles obtained during this experiment are reported in Figure 22. During the initial seven carbonation/calcination cycles, the carbonation activity of the sorbent decreased as reported in the literature. After the eighth calcination, the sorbent was cooled to 160°C and steam hydrated in the TGA. In one experiment, Figure 22a, the hydrated sorbent was heated in N$_2$ as in the experiment reported in Figure 20a. In the other, the hydrated sorbent was heated in CO$_2$, as reported in Figure 20b.

In both experiments, the mass percentage reached 74% indicating that hydration was complete. The TGA profiles after hydration follow the patterns reported in Figure 20 for N$_2$ and CO$_2$ hearing of Taylor’s hydroxide, respectively. After reactivation, the sorbent was subjected to three more CO$_2$ capture cycles. The activity of the sorbent after reactivation was considerably higher when the hydrated sorbent was heated in CO$_2$ rather than under N$_2$. 
Figure 22. TGA profiles of a multi-cycle experiment with different reactivation techniques: seven Ca Looping cycles, reactivation then three Ca Looping Cycles.  

a) using the hydration-dehydration technique  

b) using the superheating technique.

Mass vs. Temperature Profiles The hypothesis that carbonation conversion can be essentially expressed as a function of temperature only, was tested by plotting the mass vs. temperature curves measured during the heating in CO₂ (200–560°C) using a straight and a sawtooth profile for both the McDonald’s and Taylor’s hydroxide. The sawtooth experiment is recognizable by the irregular shape of the curve at the temperatures where the sorbent is held.

It can be seen in Figure 23 that the mass vs. temperature curves are very similar despite the doubling of the contact time and the change in the shape of the temperature profiles. In the case of the Taylor’s sorbent the two curves are almost identical, while in the case of the McDonald’s sorbent, there is a small difference between the two curves, essentially above 450°C.

Figure 23. Mass vs. temperature profiles obtained during heating in CO₂ of two hydrated sorbents, using a straight and a sawtooth heating profile.
It would be expected that sorbent surface area would play an important role in the advancement and rates of carbonation. Surface area and pore volume data obtained by N₂ adsorption for both hydrated sorbents tested is shown in Table 9 and indeed suggests that the higher degree and rate of carbonation of the McDonald’s sorbent could be due to a much larger surface area.

**Table 9. Surface area and pore volume measurements obtained via N₂ adsorption and BET analysis.**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>BET area (m²·g⁻¹)</th>
<th>Pore volume (cm³·g⁻¹)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>McDonald’s</td>
<td>13.8</td>
<td>0.08</td>
<td>23</td>
</tr>
<tr>
<td>Taylor’s</td>
<td>3.7</td>
<td>0.04</td>
<td>42</td>
</tr>
</tbody>
</table>

However, as discussed in section 2.2.2, it was shown that considering surface area alone was not sufficient to understand the superheating behaviour of the sorbent. In order to further investigate the relationship between Surface area and pore volume and carbonation kinetics, the results obtained in section 2.2.3 are analysed from a different perspective.

**The Effect of Surface Area on Carbonation Kinetics** As described in detail in section 2.2.2, sorbent samples with different cycling histories (one, seven and 37 cycles) were hydrated with different methods (water, 90°C and 120°C steam hydration) and then heated in CO₂. The surface area of hydrated sorbent samples was measured using BET and shown in Table 10, while the mass vs. temperature profiles obtained during their heating in CO₂ are plotted in Figure 24.

**Figure 24.** Mass vs. temperature profiles of hydrated sorbent samples made from Taylor’s lime **a)** after one Ca looping cycle using different hydration methods **b)** with different cycling histories, hydrated in Steam at 90°C.

**Table 10. Porosity data for the comparisons made in Figure 24.**

<table>
<thead>
<tr>
<th>BET area (m²·g⁻¹)</th>
<th>Pore volume (cm³·g⁻¹)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Figure 24a</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c – liquid</td>
<td>34.4</td>
<td>0.20</td>
</tr>
<tr>
<td>1c – steam 90°C</td>
<td>10.6</td>
<td>0.10</td>
</tr>
<tr>
<td>1c – steam 360°C</td>
<td>3.7</td>
<td>0.04</td>
</tr>
<tr>
<td><strong>Figure 24b</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c – steam 90°C</td>
<td>10.6</td>
<td>0.10</td>
</tr>
<tr>
<td>7c – steam 90°C</td>
<td>9.5</td>
<td>0.07</td>
</tr>
<tr>
<td>37c – steam 90°C</td>
<td>7.2</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Figure 24a plots the mass vs. temperature profiles of three hydrated sorbents with very different values of surface area, ranging from 3.7–34.4 m².g⁻¹ (Table 10). Regardless of their surface area, all three sorbents exhibited three distinct phases of carbonation; a slow phase between 200°C and 350°C followed by a faster phase between 350–420°C and finally a slower phase again above 420°C. Interestingly, with all three sorbents a “bump” can be observed at 290°C, similarly to what was observed with the sorbents hydrated in the TGA, section 2.2.2, as well as in the work of Montes-Hernandez et al. (72)

In the 200–350°C range, the rate of carbonation was found to increase with increasing surface area, see Figure 24 and Table 10. In contrast, the tenfold increase in the surface area had little effect on the carbonation rates observed >420°C, which were similar for all three sorbent samples. The carbonation rate in the 350–420°C range was found to be highest with the sorbent having the medium surface area (1c-Steam 90°C).

In contrast, Figure 24b plots the mass vs. temperature profiles of three hydrated sorbents with very similar values of surface area (7–10 m².g⁻¹) as measured by N₂ adsorption, see Table 10. It can be seen that carbonation rates are very similar until the temperature reaches 450°C, after which a significant difference is observed as the mass of the once-cycled sorbent slows down and stops increasing while that of the more cycled sorbent samples (7c, 37c) continues rising. Furthermore, with the most cycled sorbent (37c) the inflexion at 420°C is almost imperceptible.

No obvious relationship between final carbonation conversion and measured surface area was detected in either experiment, see Figure 24a and b and Table 10.

In order to make sense of these results it is necessary to consider that the N₂ adsorption method can only detect pores that are smaller than 300 nm, while cycled sorbents are known to have a significant volume of pores in the 400–600 nm range, as discussed in section 2.2.3.

These results therefore suggest that the surface area available in small pores only affects the early stages of carbonation (<350°C) while the surface area available in large pores has an effect on the later stages of carbonation during heating in CO₂ (>450°C).

Such behaviour could be explained by a pore plugging phenomena, since the molar volume of crystalline CaCO₃ (37 ml.mol⁻¹) is larger than that of crystalline Ca(OH)₂ (33 ml.mol⁻¹). As a result, smaller pores would be likely to become plugged in the early stages of carbonation, while the larger pores would remain open throughout the carbonation process, leading to an increased proportion of Ca(OH)₂ being carbonated during heating in CO₂.

**Discussion**

As discussed in the introduction, determining the preferred carbonation route is essential to explaining the cause of the absence of the SD effect with some hydrated sorbents. To achieve this it is useful to sequentially consider the behaviour of the hydrated sorbent both before and after the normal dehydration temperature.
Below the Normal Dehydration Temperature (<350°C) The dehydration reaction (eq. 1) is not expected to occur to any appreciable extent (Figures 19a and 20a) meaning that only the direct carbonation of Ca(OH)$_2$ (eq. 3) can take place. As discussed in section 2.1.1, direct carbonation of Ca(OH)$_2$ is known to be catalysed by the presence of adsorbed water on the surface of the particles and thus to proceed extremely slowly when the relative humidity (RH) is low.

However, in this work carbonation was observed to proceed at detectable rates between 200–350°C for all hydrated sorbents tested, as evident in the mass increase profiles plotted in Figure 19a and Figure 24a. Given that Ca(OH)$_2$ is stable in this temperature range (Figure 19a and Figure 20a) it must be concluded that the direct carbonation of Ca(OH)$_2$ (eq. 3) is in fact occurring between 200–350°C, despite RH ≈0.

These results suggest the existence of a high temperature mechanism of direct Ca(OH)$_2$ carbonation that allows for relatively rapid conversion even in a dry atmosphere. During the course of this work, this observation was confirmed by an in-situ IR study reported by Montez-Hernandez et al. (90) They reported that in the absence of humidity and at 110°C no carbonation of Ca(OH)$_2$ was observed in 5 h contact time, yet the reaction proceeded at a detectable rate when the temperature was raised to 300°C, even in dry conditions.

In the 200–350°C temperature range, reducing the temperature led to an immediate halt of the carbonation reaction with all hydrated sorbents tested as shown in Figure 21a and Figure 21b. Thus it appears that this unusual kinetic behaviour is an inherent property of the high temperature mechanism of the direct carbonation of Ca(OH)$_2$.

Above the Normal Dehydration Temperature (>350°C) As soon as the temperature reaches the normal dehydration temperature, the rate of carbonation rapidly increases while water is simultaneously released (Figure 19b and Figure 20b). It is difficult to prove without ambiguity which is the preferred carbonation route at temperatures above the normal dehydration temperature: the direct carbonation mechanism (eq. 3) or the dehydration/carbonation sequence (eq. 1 + eq. 2).

Nevertheless, a number of observations presented in this work would be better explained by postulating that the preferred route is the direct carbonation of Ca(OH)$_2$ via the high temperature mechanism which was observed to take place at temperatures below the normal dehydration temperature.

First, the unusual kinetic behaviour initially observed at low temperature persists at temperatures above the normal dehydration point. For all hydrated sorbents tested (Figure 21a and Figure 21b) both the dehydration and carbonation of Ca(OH)$_2$ stop advancing as soon as the temperature is reduced during one of the sawteeth, even when the temperature is above the normal dehydration temperature. This behaviour would be very difficult to explain if carbonation was occurring via the sequence of eqs. 1+2.

Second, the carbonation capacity of the reactivated sorbent is significantly lower if the dehydration is performed as a separate step as seen in Figure 19 and Figure 20. Given that the extent of carbonation is
largely controlled by the microstructure of the sorbent, see Section 1.2, it is difficult to understand why this would be the case if carbonation was occurring via the sequence of eqs. 1+2.

Third, the synchronicity of the rates of water release and mass increase suggest that dehydration and carbonation are kinetically linked rather than distinct mechanisms. If carbonation was indeed occurring via the sequence of eqs. 1+2, we would have to postulate that reaction 2 is very fast in the 200–560°C range in order to explain this observation. This is inconsistent with existing reports of the carbonation rates of CaO although the presence of water vapour is known to greatly accelerate this reaction (87,88).

Finally, this postulate is also supported by in-situ XRD work published during the course of this PhD programme by Molinder et al. (30). They reported that the formation of CaO was not observed when Ca(OH)$_2$ was carbonated at temperatures in the 200–500°C range.

As a result, it is postulated in this work that the majority of CaCO$_3$ formed during heating in CO$_2$ derives from the direct carbonation mechanism, although this hypothesis does not preclude the occurrence of reaction 1 to a limited extent, as was observed in section 2.2.2. A number of relevant points naturally flow from this postulate.

*Consequences of this Postulate* In this context, the absence of the SD effect observed with certain hydrated sorbents should not be interpreted as the absence of superheating, i.e. the inhibition of the dehydration reaction (eq.1), but rather as an increased tendency to directly carbonate via the high temperature Ca(OH)$_2$ carbonation mechanism. Indeed, if it is assumed that carbonation largely occurs without forming CaO as an intermediate, it follows that the proportion of superheated Ca(OH)$_2$ remaining in the hydrated sorbent at any given temperature depends on its tendency to carbonate. Therefore, the absence of SD can be said to be the consequence of the high carbonation conversion observed.

It can therefore be said that the presence of CO$_2$ has a dual and contradictory role in regards to Ca(OH)$_2$ at high temperatures. On one hand, the presence of CO$_2$ during heating increases the stability of Ca(OH)$_2$ while on the other it drives the removal of water by direct carbonation.

In fact, results observed so far do not exclude the possibility that superheating is an effect induced by the direct carbonation mechanism considering in particular that carbonation starts at temperatures lower than the normal dehydration temperature of Ca(OH)$_2$ and thus has the potential to inhibit this reaction.

Indeed, it could be imagined that the initial interaction between CO$_2$ and Ca(OH)$_2$, occurring below the temperature of dehydration, blocks the dehydration process from occurring at the normal temperature, perhaps by forming a physical barrier to the egress of water or interfering with a key step in the dehydration process. Thus stabilized, the Ca(OH)$_2$ would continue reacting with CO$_2$ according to this high temperature mechanism.

In any case, it can be said the direct carbonation mechanism of Ca(OH)$_2$ at high temperature is a major part of Ca(OH)$_2$ superheating. However, very little is known about its nature. The kinetic results
presented in this work preclude a simple kinetic mechanism as it would be difficult to explain most of the unusual features observed, such as the time-independence of the advancement of carbonation (Figure 23) or the complex effect of porosity and surface area on the carbonation kinetics (Figure 24).

Flowing from the direct carbonation hypothesis it is possible to understand the effect of porosity on the advancement of carbonation and therefore on the extent of the SD effect. Indeed, the formation of CaCO$_3$ leads to at least a 10% expansion of the solid phase and the product CaCO$_3$ is expected to grow inside the pore structure of the Ca(OH)$_2$. In hydrated sorbents with no large pores, carbonation would lead rapidly to the plugging of pores in the early stages of carbonation which would then limit the available solid gas contact surface and therefore the extent of carbonation. However, large pores would be able to accommodate the product CaCO$_3$ and remain open throughout the heating step, thus leading to a high conversion to CaCO$_3$ and therefore to a low extent of superheated dehydration.

In addition, postulating a direct carbonation mechanism for Ca(OH)$_2$ allows explaining the difference in reactivation levels achievable with the superheating technique compared to that achieved with the hydration-dehydration technique, see Figure 19.

As discussed in the case of CO$_2$ shocking, see Section 2.1.1, converting spent sorbents to CaCO$_3$ restores their CO$_2$ capture activity in subsequent cycles. Indeed, upon calcination of the newly formed carbonate a suitable network of pores is formed again.

Since carbonating Ca(OH)$_2$ directly allows achieving a higher conversion to CaCO$_3$ than indirectly carbonating Ca(OH)$_2$ (i.e. dehydrating prior to carbonation) it is natural that the sorbent reactivated by superheating would be more active during subsequent cycles. This observation suggests that carbonation via the direct route is preferred in practical applications as it allows a higher carbonation conversion and thus a more active reactivated sorbent.

The higher carbonation conversion achieved during superheating can be understood by considering that the direct carbonation route would not have the same limitations as the indirect route, since CaO would not be formed as an intermediary during the direct carbonation mechanism. Thus it can be expected that the final conversion to CaCO$_3$ achievable would be different for each route. This observation further supports the hypothesis that carbonation occurs via the direct route during superheating.

**Conclusion**

The results presented in this work have confirmed the existence of a direct carbonation mechanism for Ca(OH)$_2$ which could proceed at detectable rates at very low relative humidity and at temperatures >200°C. This carbonation mechanism was found to exhibit the unusual property that the rate of carbonation was dependent on the rate of temperature increase, so that the carbonation reaction would stop if the temperature were reduced.

Although insufficient to prove beyond doubt, the results obtained in this section strongly suggested that the largest proportion of CaCO$_3$ formed during heating of Ca(OH)$_2$ in CO$_2$ is formed via the high temperature direct carbonation mechanism for Ca(OH)$_2$.
The implication of this postulate is that the absence of SD observed with some hydrated sorbents is in fact due to an increased tendency to carbonate via this direct mechanism. In this context, gaseous CO$_2$ can be said to play a dual and contradictory role vis-a-vis Ca(OH)$_2$ – on one hand its presence stabilizes it by inhibiting the dehydration reaction (superheating) while on the other its presence leads to its transformation to CaCO$_3$ via the direct, high temperature, carbonation mechanism.

This postulate also allowed explanation of the relationship between pore size and the extent of the SD effect and carbonation. Due to the 10% expansion of the solid induced by the formation of CaCO$_3$, smaller pores become plugged during the early stages of carbonation. Carbonation of small pores is thus self-limiting as the advancement of carbonation would lead to the plugging of pores which would block further advancement of carbonation. In contrast, larger pores remain open throughout the heating process, leading to a high level of carbonation and thus a low extent of the SD effect.

The following section focuses on formulating hypotheses regarding the chemical mechanisms of both the superheating and the direct carbonation of Ca(OH)$_2$, and using the data gathered in this and previous sections to test them.


2.3 Hypotheses Formulation

Introduction
As discussed in section 2.1.1, the lack of experimental observations regarding Ca(OH)$_2$ superheating was a major obstacle to explaining its origin. For this reason, the first step of the work presented in this thesis consisted of performing an experimental survey in order to identify some of the major characteristics of this phenomenon and to allow the formulation of coherent hypothesis as to the origin and mechanism of superheating, which is the objective of this section.

This preliminary work, reported in sections 2.2.2 and 2.2.3, has highlighted the dual role of CO$_2$ towards Ca(OH)$_2$ at high temperatures. On one hand, the presence of CO$_2$ was found to increase the stability of Ca(OH)$_2$ by inhibiting the dehydration reaction (superheating) while on the other it was found to lead to the conversion of Ca(OH)$_2$ to CaCO$_3$ (carbonation). The carbonation and superheating of Ca(OH)$_2$ were found to be interrelated to the point of allowing the possibility that they are causally related, see section 2.2.4. In addition, a number of defining and unusual features of both aspects were identified, which will have to be taken into account when formulating hypothetical mechanisms. These points are summarized below.

Superheating The presence of at least 10% CO$_2$ in the gas phase was found to inhibit the dehydration reaction (eq. 1) in the normal dehydration temperature range (>350°C). This inhibition was manifested by the maintenance of a distinct Ca(OH)$_2$ crystalline phase for prolonged periods of time at temperatures well above the normal decomposition temperature as established in section 2.2.4.

Superheated dehydration occurred if the temperature exceeded a critical value which was found to depend on the percentage of CO$_2$ in the gas phase. This temperature was at approx. 620°C if CO$_2$ content exceeded 37.5%. Also, dehydration could be triggered by removing CO$_2$ from the gas atmosphere at 560°C in a method referred to as the “N$_2$ trigger”

Superheating was found to occur with all calcitic limestones tested (section 2.2.2) although in most cases small amounts of CaO (3–10%) generated by the dehydration reaction were detected. In some cases (cycled sorbents, commercial hydroxides) the reactivity of superheated Ca(OH)$_2$ towards CO$_2$ was such that it was entirely carbonated before reaching the superheated dehydration temperature (section 2.2.3), leading to the erroneous conclusion that superheating did not occur with these materials.

Direct Ca(OH)$_2$ Carbonation The existence of a direct Ca(OH)$_2$ carbonation mechanism occurring at high temperatures and in dry conditions was demonstrated in section 2.2.4. It was postulated that this mechanism was the principal mechanism by which CaCO$_3$ was formed when Ca(OH)$_2$ was heated above the normal dehydration temperature. This assumption was justified since the dehydration of Ca(OH)$_2$ to CaO is largely inhibited by the presence of CO$_2$ in the gas phase. The direct carbonation mechanism of Ca(OH)$_2$ presents a number of unusual characteristics.

In section 2.2.4 it was shown that the rate of carbonation depends on the rate of temperature increase, i.e. carbonation slows down considerably when the temperature stops increasing. As a result of this
behaviour the advancement of the carbonation reaction can be expressed as a function of temperature only.

Secondly, the maximum conversion to CaCO$_3$ was found to be very dependent on the size and cycling history of the sorbent prior to hydration. It was postulated that the presence of large pores (>400 nm) and increased external surface area was the main parameter controlling the maximum extent of carbonation, see section 2.2.3. This behaviour was attributed to pore plugging, resulting from the expansion of the solid as it transforms into CaCO$_3$ (37 ml.mol$^{-1}$ vs. 33 ml.mol$^{-1}$).

In this section a literature review is undertaken in order to provide the basis required to formulate a hypothesis on the mechanism(s) of superheating and direct carbonation of Ca(OH)$_2$. Given the lack of information on either topic in the open literature, a particular approach was chosen, based on the reasoning described as follows.

In order to inhibit the dehydration reaction, the presence of CO$_2$ in the gas phase must interfere with one of the steps of the normal dehydration mechanism. Identifying each one of these steps should therefore provide insight into the potential mechanisms by which CO$_2$ can interfere with them.

This extensive literature review on the normal dehydration mechanism of Ca(OH)$_2$ allows identification of the various steps involved in the normal dehydration process. Based on this review, a range of hypotheses on the chemical mechanism of superheating were formulated and methods of testing these hypotheses proposed.

**Theoretical Considerations**
The thermal decomposition of Ca(OH)$_2$, called dehydration, is a reversible solid-gas reaction, see eq. 1. Solid solutions are typically not assumed to form so that the activity of the solid phases is considered equal to unity and thus the equilibrium constant is dependant only on the partial pressure of water vapour in the gas phase, see eq. 1.

\[
Ca(OH)_2 \rightarrow CaO + H_2O \quad \Delta H^\circ = 109 \text{ kJ.mol}^{-1} \quad (1)
\]

\[
K = \frac{A_{Ca(OH)_2}}{A_{H_2O} \times A_{CaO}} = \frac{1}{p_{H_2O}}
\]

As discussed in the Introduction (section 2.1.1) reaction kinetics determine the normal dehydration temperature, which is defined as the temperature at which dehydration starts proceeding at detectable rates in the experimental conditions used. As a result, a range of normal dehydration temperatures is reported in the literature, typically between 300–400°C.

On the basis of the information gathered during the literature review, the dehydration process can be divided into three principal steps, which occur sequentially as the temperature of the solid increases. These can be written as follows (note that temperature ranges are only indicative as they vary somewhat amongst sources):
1. Formation of H\textsubscript{2}O within the lattice. (>120°C)
2. Migration of H\textsubscript{2}O out of the grains/recrystallization to CaO. (>170°C)
3. Migration of H\textsubscript{2}O out of the particles (>250°C)

1. **Formation of H\textsubscript{2}O Within the Lattice**

Freund et al. have conducted an extensive study on the pre-reactional transformations of brucite-like materials (Ca(OH)\textsubscript{2}, Al(OH)\textsubscript{3} and Mg(OH)\textsubscript{2}) using thermal conductivity and polarization measurements as well as FTIR analysis (79,92).

These authors reported that all three hydroxides started exhibiting a measurable proton conductivity at a certain temperature; 80, 120 and 170°C for Ca(OH)\textsubscript{2}, Al(OH)\textsubscript{3} and Mg(OH)\textsubscript{2}, respectively. This behaviour was attributed to the thermal activation of hydroxyl protons, which become mobile following eq. 2:

\[
\text{OH}^- + \text{OH}^- \leftrightarrow \text{O}^{2-} + \text{HOH}
\]

As shown in eq. 2, this reaction leads to the formation of a lattice site with an excess proton (HOH) and a lattice site with a proton defect (O\textsuperscript{2-}). Both the proton excess and proton defects are mobile, thus giving rise to the ability of the material to conduct protons as demonstrated by proton conductivity and thermopotential measurements reported in this study.

It was also reported that the proton conductivity was significantly reduced once the temperature was increased above a certain temperature (120°C for Ca(OH)\textsubscript{2}), which they attributed to the transformation of the HOH precursor into molecular water within the lattice. The formation of molecular water was observed via infrared spectroscopy in the case of Mg(OH)\textsubscript{2} and it was postulated that this behaviour is general to all three hydroxides.

Using neutron and X-ray diffraction methods, Chaix-Pluchery et al. observed that strain in the basal plane (00l) of Ca(OH)\textsubscript{2} increased with increasing temperature, which was attributed to the appearance of molecular water precursors (HOH) as well as the accompanying proton defects (93). Furthermore, a threshold temperature (130°C) was observed at which the rate of strain diminished and it was postulated that this was due to the formation of water molecules and their subsequent segregation into water rich and water poor zones.

Moreno et al. have performed an NMR study on the proton dynamics in Ca(OH)\textsubscript{2} in the -110°C to 120°C range (94). They also observed the formation of mobile, delocalized protons, starting at approximately 70°C. At the highest temperatures tested (120°C) they reported that the large majority (>90%) of the protons were mobile and delocalized. At the same temperature, an unidentified transformation in the dynamic behaviour of the remaining, localized, protons was observed. Although not stated in this study, it is possible to postulate that this transition corresponds to the formation of water.

It can then be deduced that molecular water is likely formed within the crystal lattice of Ca(OH)\textsubscript{2} at temperatures well below the normal dehydration temperature (∼120°C). Furthermore, there is evidence
in the literature suggesting that species present in the gas phase can exchange protons with the crystal lattice and thereby have a significant effect on the temperature of water formation.

Galwey et al. reported observing significant proton exchange when Ca(OH)$_2$ was contacted with D$_2$O under vacuum (81). After five hours of contact at 70°C, they observed that 24% of the hydrogen atoms in Ca(OH)$_2$ had been replaced by deuterium, confirming the existence of interaction between the gas phase species and the crystal via the proton mobility mechanism discussed above.

Freund et al. reported that the presence of chemisorbed species on the surface of the hydroxides does affect the proton conductivity of the hydroxides (79). The presence of adsorbed acetic acid, a proton donor, was found to greatly increase the maximum proton conductivity, and increased the temperature of water formation by approximately 10°C, as demonstrated by thermopotential measurements. Unfortunately the effect on the final dehydration temperature was not measured.

Chaix-Pluchery et al. also observed that the presence of adsorbed D$_2$O (1.76 Torr) led to an increase in the characteristic temperature of peak sharpening, which they attributed to the formation and ordering of molecular water, from 130°C to 170°C (93). This change was also accompanied by an increase in the dehydration temperature from 215°C to 307°C. They attributed this increase to the injection of excess protons into the crystal lattice due to the presence of D$_2$O adsorbed on the surfaces.

Thus, it can be postulated that the presence of proton donor species can lead to a significant delay in the temperature of dehydration of Ca(OH)$_2$. Although CO$_2$ is an acidic species it is not a proton donor of itself so that it is necessary to postulate an additional mechanism by which CO$_2$ leads to the injection of protons into the Ca(OH)$_2$ lattice, thereby delaying the temperature of dehydration. This postulate is further elaborated into the “liquid layer” hypothesis and discussed in detail below.

2. Migration of H$_2$O Molecules to the Grain Surface

No detailed experimental studies on the mobility of the H$_2$O molecules immediately upon their formation in the crystal lattice were found. However, it can be deduced from the literature that the newly formed H$_2$O molecules are not very mobile, since they are formed at least 50°C prior to the beginning of the dehydration reaction. Indeed, if these water molecules were mobile, hydration would be expected to start occurring immediately.

Chaix-Pluchery et al. postulated that molecular water was initially formed in ordered, discrete, water rich zones which at some point coalesce to provide a network of fast diffusion pathways through the crystal, thus triggering the onset of rapid dehydration (93). It was suggested that this was the primary pathway for water diffusion out of the crystal, however, no experimental evidence was provided to support this hypothesis.

In contrast, Galwey et al. proposed quite a different mechanism for the migration of molecular water from the core to the surface of the grains (81). This mechanism is based on the claim that when the first water molecules leave the crystal, the recrystallization to CaO does not occur immediately. Rather, there exists for a period of time a highly deficient crystal structure which can be written as Ca(OH)$_{2-x}$O$_{x/2}$O$_{x/2}$.
where △ designates a neutral anion-sized lattice vacancy. This structure is sometimes referred to as a pseudo-lattice, suggesting that the material is chemically CaO but crystallographically retains the hexagonal structure typical of Ca(OH)$_2$ (82).

According to Galwey et al. this defect structure is sufficiently open so as to allow the diffusion of water through it, thus providing a pathway for molecular water to diffuse out of the grain core (81). The departure of the first water molecules from the outermost layers of the grain, results in the formation of a “reaction rim” which allows the departure of water from the layers beneath, providing an effective mechanism for the migration of water molecules from the core to the surface of each grain. As the reaction progresses, the thickness of this “reaction rim” would increase leading to a decrease in the observed dehydration rate and thus explain the progressive deceleration of this reaction.

The existence of the defect structure was also postulated for Ca(OH)$_2$ by Glasson et al., who observed that there was a substantial time lag between the decomposition of Ca(OH)$_2$, as measured by TGA data, and the increase in its specific surface as measured by N$_2$ adsorption (75). Furthermore, they reported that XRD diffractograms of partially decomposed Ca(OH)$_2$ still showed a pattern corresponding to 100% Ca(OH)$_2$. The existence of such a structure can also be deduced from in-situ XRD data, where it was reported that the start of dehydration preceded the formation of CaO by 25°C (93). Similar observations were made in the case of Mg(OH)$_2$ where the formation of this defect structure was observed via x-ray diffraction (82,95).

Freund et al. postulated an identical mechanism for the dehydration of Mg(OH)$_2$ (82). In addition, they postulated that once a critical temperature, or “reaction rim” thickness, was reached the defect structure would collapse and recrystallize as MgO. The contraction caused by the recrystallization of the “reaction rim” (approximately 50%) would then lead to the exposure of fresh Mg(OH)$_2$ surfaces where the whole process could repeat itself.

It should be noted that in contrast, Beruto et al. concluded that such a defect structure did not form, based on in-situ XRD data obtained during dehydration of Ca(OH)$_2$ (77). They claimed that a normal crystallographic transformation took place as they observed no induction period and a linear increase in the proportion of CaO during the dehydration process. However, given that they had no measure of the moment at which water departed from the solid, the results presented are insufficient to conclude as to the non-existence of the defect structure.

The presence of CO$_2$ could be postulated to interfere with the migration of water out of Ca(OH)$_2$ grains in at least two different ways. First, the presence of CO$_2$ can be expected to lead to the carbonation of the outer grain surfaces, thus potentially forming a passivating layer that would slow down, or even entirely block, the diffusion of water out of the grains. Such behaviour was observed in the case of high temperature carbonation of Mg(OH)$_2$ where a layer of MgCO$_3$ was reported to have been formed (96,97). This postulate was developed into the “passivating layer” hypothesis which is discussed in more detail in below.

Second, the presence of CO$_2$ in the gas phase could also interfere with the defect structure composing the “reaction rim”. Glasson et al. reported that the presence of traces of chemisorbed CO$_2$ or water
inhibited the recrystallization of the defect structure to CaO, as deduced from the lower surface area for the same amount of decomposition for materials dehydrated in air (75). Furthermore, if this defect structure is open enough to allow diffusion of water through it, it could be postulated that CO₂ is able to penetrate and diffuse through it as well. As a result, the “reaction rim” would become a reaction interface for the simultaneous dehydration and carbonation of Ca(OH)₂. This postulate is developed into the “reaction interface” hypothesis and discussed in detail below.

3. Mass Transfer of Water Vapour out of the Particle

Once water has been released into the gas phase through the outer surface of a grain, it has to make its way to the outside of the particle, which implies travelling through the particle’s pores. Depending on the particle’s pore network structure, this process can be quite slow and thus lead to large variations in the local water vapour pressure. Increased water vapour pressure can in turn lead to the appearance of the reverse reaction (hydration) and thus considerably complicate the kinetic analysis of the system. Galwey et al. attributed most of the difficulties in establishing the kinetic parameters of the dehydration reaction to the occurrence of the reverse reaction (81).

The presence of CO₂ in the gas phase clearly has the potential to interfere with this step. Indeed, it can be expected that the external surfaces of Ca(OH)₂ particles will be rapidly carbonated during the heating in CO₂. Given that CaCO₃ has a higher molar volume than Ca(OH)₂, the carbonation of the outer surface of the particle can lead to the development of a CaCO₃ shell around the particles that acts as a barrier for the transfer of gases to/from the particle interior. This hypothesis was initially proposed by Blamey et al. in a paper confirming the existence of the SD effect, and is discussed in more detail below (71).

Based on review of the relevant literature, three principal means by which the presence of CO₂ could inhibit the dehydration have been identified. They correspond to the interference of CO₂ with the three elementary steps of the dehydration reaction. These are that:

1. The presence of CO₂ can delay the formation of molecular water, by virtue of injecting excess protons into the Ca(OH)₂ lattice;
2. The presence of CO₂ could slow down or block the diffusion of water from the grain to the surface, either by forming a passivating layer or interfering with the “reaction rim”; 
3. The presence of CO₂ could slow down or block the mass transfer of water vapour out of the particles by forming a shell of CaCO₃, which acts as a physical barrier.

In the following paragraphs, these possibilities are developed into hypotheses and attempts are made to use them to explain the other observations made in the experimental survey. Finally, methods of testing each hypothesis are proposed.

**Blocking the Formation of Water (Step 1)**

*The proton Injection Hypothesis* The presence of proton donor species adsorbed on the surface of the hydroxide can introduce excess protons into the crystal lattice and thereby increase the temperature of water formation (step 1 of dehydration), as discussed above. As a result, the temperature of onset of dehydration could be significantly increased, as discussed above.
However, molecular CO₂ is not a proton donor so that an additional element is needed, and here it is postulated that this is the interaction between CO₂ and H₂O, which leads to the release of excess protons according to eqs. 8 and 9 shown below. Although a number of modes of CO₂/H₂O interaction could be imagined, here it is postulated that a thin layer of water molecules exists on the Ca(OH)₂ grain surfaces. The dissolution of gaseous CO₂ in this layer leads to the release of protons into the lattice (eqs. 8 and 9), and the subsequent increase in the temperature of dehydration.

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+ \quad (8)
\]

\[
\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \quad (9)
\]

In order to explain the presence of a thin water layer on the surface of the hydroxide it is postulated that there also exists a slow dehydration mechanism, with H₂O molecules slowly diffusing out of the lattice. It is this process that leads to the formation of the surface water layer which would be dynamic insofar that it is continuously supplied with water molecules arriving from the lattice and drained by evaporation of water into the gas phase. The principal elements of the proton injection hypothesis are illustrated in Figure 25.

**Figure 25.** Schematic illustrating of the proton injection hypothesis.

Having formulated the hypothesis above, let us consider how it can explain the experimental observations made so far:

a) Superheated dehydration at 620°C can be explained by considering that the number of proton defects rises rapidly with temperature and that at 620°C, the number of protons injected is not sufficient to block dehydration any further.

b) The N₂ trigger can be explained by considering that the removal of CO₂ from the gas phase would stop the proton injection from the CO₂ dissolved in the water layer, thus triggering the onset of dehydration.

c) The direct carbonation mechanism of Ca(OH)₂ can be explained considering that the presence of water on the surface of Ca(OH)₂ would be expected to catalyse the direct carbonation reaction.
as discussed in section 2.1.1. It follows that the carbonation reaction is auto-catalytic as one of its products (water) is its catalyst.

d) The unusual kinetics of carbonation can be explained by the auto-catalytic properties of the water released by the carbonation reaction, although the details of how exactly this could happen remain unclear.
e) The dependence of SD and carbonation extent on porosity can be explained by considering that as carbonation progresses the smaller pores become filled with the expanded CaCO$_3$ while larger pores remain open even when carbonation is well advanced, as discussed in detail in section 2.2.4.

**Testing the Hypothesis** The formation of molecular water within the crystal lattice should be detectable by infrared spectroscopy. Indeed, Freund et al. reported observing the formation of molecular water when Mg(OH)$_2$ particles were heated to 250°C with an in-situ FTIR apparatus (92). Therefore, it can be expected that the formation of molecular water can also be detected during the heating of Ca(OH)$_2$, providing a method of testing this hypothesis.

By comparing the temperature at which molecular water is formed in the Ca(OH)$_2$, both in the presence and the absence of CO$_2$, it is possible to test the hypothesis that CO$_2$ leads to superheating of Ca(OH)$_2$ by delaying the temperature of formation of molecular water.

Furthermore, the presence of surface water films can usually be detected by IR spectroscopy and it would be expected that the spectrum of the carbonate ions would also be modified by the interaction with liquid water.

Preliminary tests, described in Appendix 3, were undertaken which lend some credibility to this hypothesis insofar that it was observed that the presence of molten boric acid, a proton donor, could lead to an 80°C increase in the temperature of the onset of dehydration.

**Blocking Migration of H$_2$O out of the Grains (Step 2)**

*The Passivating Layer Hypothesis* It can be imagined that in the presence of CO$_2$, the outer surfaces of Ca(OH)$_2$ grains rapidly carbonate leading to the formation of a layer of CaCO$_3$ which separates the remaining Ca(OH)$_2$ from the gas phase, i.e. a passivating layer, see above. The presence of the passivating layer would naturally reduce the diffusion rates of H$_2$O out of the grain as well as those of CO$_2$ entering the grain, thus effectively inhibiting both the dehydration and carbonation reactions. This hypothesis is illustrated in Figure 26.
Let us consider how it can be used to explain the experimental observations made so far:

a) In order to explain superheated dehydration occurring at 620°C, it would be necessary to postulate a sudden acceleration of the diffusion phenomena or the appearance of a new dehydration mechanism at these temperatures.

b) In order to explain the N$_2$ trigger it would be necessary to postulate that some calcination of the passivating layer occurs, since the trigger was performed at 560°C in N$_2$ and calcination is thermodynamically favoured in these conditions.

c) In order to explain the direct carbonation of Ca(OH)$_2$ and the unusual kinetic behaviour observed in the experimental survey, an additional mechanism must be postulated since the presence of the passivating layer is in fact the consequence of the direct carbonation of Ca(OH)$_2$.

d) The unusual kinetics of carbonation are a property of the direct carbonation mechanism of Ca(OH)$_2$ which must be postulated separately from the passivating layer hypothesis.

e) The dependence of SD and carbonation extent on sorbent porosity is difficult to explain with this hypothesis. It would be expected that reduced specific surface area would lead to a larger extent of carbonation, which has observed not to be the case, section 2.2.3, Figure 17.

Testing the Hypothesis This hypothesis could be falsified with a series of TGA experiments. Namely, if this hypothesis was correct, heating a Ca(OH)$_2$ sample in CO$_2$ to a temperature considerably higher than the normal dehydration temperature, say 450°C, should lead to the formation of a passivating layer of CaCO$_3$, sufficient to block the dehydration reaction at these temperatures.

If the same sample was then cooled to ambient temperature and heated again in air, the passivating layer should still be able to block the dehydration reaction until at least 530°C, which is the temperature at which the calcination of CaCO$_3$ is thermodynamically expected to occur in air.
This test is designed to falsify the hypothesis rather than confirm it. If the hypothesis were to pass this test, an additional series of experiments would need to be undertaken to confirm that it is indeed the passivating layer that is responsible rather than some other mechanism.

**Blocking Migration of H₂O out of the Grains (Step 2)**

*The Reaction Interface Hypothesis* An alternative hypothesis can be developed by postulating that the CO₂ from the gas phase can penetrate into the defect structure left behind by the departing water which is believed to serve as the main pathway for the diffusion of water out of the grain cores in the normal dehydration process, see above.

In this hypothesis, the intrusion of CO₂ would not immediately lead to the formation of crystalline CaCO₃. Rather, this defect Ca(OH)₂ structure would remain open, thus becoming an interface region through which H₂O molecules from the core can diffuse out of the grains while CO₂ molecules from the gas phase can diffuse into the grain core. The rates of diffusion of the two species are interrelated as every molecule of H₂O leaving creates some space for CO₂ to enter. The thickness of this interface region would increase with time, leading to a progressive reduction of the rates of both the carbonation and dehydration reactions. The reaction interface hypothesis is illustrated in Figure 27.

![Figure 27. Schematic illustrating the reaction interface hypothesis.](image)

Let us consider how it can be used to explain the experimental observations made so far:

a) Superheated dehydration at 620°C can be explained by considering that the stability of the defect structure reduces with increasing temperature, so that at 620°C the defect structure would immediately collapse to CaO occurs upon dehydration and the superheating effect stops occurring.

b) The N₂ trigger can be explained by considering that CO₂ molecules in the defect structure would be mobile, unlike the carbonate ions in crystalline CaCO₃. As a result, if CO₂ is removed from the gas phase then the mobile CO₂ molecules would be able to migrate out of the defect structure, leading to the opening of the reaction interface (or “rim”) and the acceleration of the dehydration reaction.
c) The direct carbonation mechanism of Ca(OH)$_2$ is explained considering that the defect structure acts as an interface region allowing the simultaneous and in-depth dehydration and carbonation of Ca(OH)$_2$ grains, without the formation of a crystalline CaO intermediary. The existence of such a structure and exhibition of an increased tendency to carbonate was observed in the case of Mg(OH)$_2$ (96).

d) The unusual kinetics of the direct carbonation mechanism can be explained by considering that, in this model, as long as no recrystallization into CaCO$_3$ occurs, the reaction rate will slow down as the thickness of the interface region increases. As a result, when the temperature is kept constant or reduced, the reaction rate would slow down significantly, as observed in section 2.2.4. Recrystallization of the defect structure into CaCO$_3$ would occur at some critical temperature/thickness leading to exposure of fresh Ca(OH)$_2$ surfaces and thus to the restarting of the reaction when the temperature is increased again.

e) The dependence of the carbonation and SD extent on sorbent porosity can be explained in a similar manner to the liquid film hypothesis above. As carbonation progresses, the smaller pores become filled with the expanded CaCO$_3$ while larger pores remain open even when carbonation is well advanced, as discussed in detail in section 2.2.4.

**Testing the Hypothesis** In-situ FTIR analysis appears to be the technique of choice to test this hypothesis. Water hydroxyl groups present in the defect structure should give a distinct IR absorption peak, and the carbonate ions would be in an environment significantly different to that encountered in CaCO$_3$. Depending on the thickness that this reaction interface reaches, in-situ XRD experiments could also allow observing its existence.

**Blocking the Mass Transfer of H$_2$O out of the Particles (Step 2)**

*The Carbonate Shell Hypothesis* It can be imagined that the presence of CO$_2$ could lead to the formation of a CaCO$_3$ shell on the outer surfaces of Ca(OH)$_2$ particles (as opposed to grains), thus blocking the departure of water molecules out of the particles. This hypothesis was initially proposed by Blamey et al. (71).

In this case, dehydration would occur normally but water vapour released in the pores would be unable to escape the particles since the pathways are blocked by the CaCO$_3$ shell. As a result, an internal overpressure of water vapour would be created with a partial pressure equal to the equilibrium value, see equation 1.
Let us consider how this hypothesis can explain the experimental observations made so far:

a) Superheated dehydration at 620°C can be explained by considering that with increasing temperature, the pressure of water vapour inside the pore system increases until it becomes sufficient to break the outer CaCO$_3$ shell (536 kPa at 620°C), triggering the dehydration of the material.

b) The N$_2$ trigger can be explained by considering that the calcination of the CaCO$_3$ shell is thermodynamically favoured at 560°C in N$_2$ so that the replacement of CO$_2$ by N$_2$ at 560°C could lead to at least a partial calcination and weakening of the CaCO$_3$ shell, which then leads to the sudden and complete dehydration of the remaining Ca(OH)$_2$.

c) In order to explain the direct carbonation of Ca(OH)$_2$ observed in the experimental survey, an additional mechanism must be postulated since the presence of the carbonate shell is in fact the consequence of the direct carbonation of Ca(OH)$_2$.

d) The unusual kinetics of carbonation are a property of the direct carbonation mechanism of Ca(OH)$_2$, which must be postulated separately from the passivating layer hypothesis.

e) The dependence of the carbonation and SD extent on sorbent porosity would have to be explained as part of the unspecified direct carbonation mechanism of Ca(OH)$_2$.

**Testing the Hypothesis** This hypothesis could be tested using TGA in a manner similar to that described for the passivating layer hypothesis. However, as with that example, this test is designed to falsify the hypothesis rather than to confirm it, which would be much more difficult.

**Discussion and Conclusion**

Three elementary steps of the dehydration reaction were identified in this study, namely:

1. The formation of molecular H$_2$O inside the Ca(OH)$_2$ lattice
2. The migration of H$_2$O out of the grain cores
3. The diffusion of H$_2$O out of the Ca(OH)$_2$ particles.
It was postulated that the presence of CO$_2$ must interfere with one of these steps in order to cause the inhibition of the dehydration reaction. Four distinct hypotheses were formulated regarding the nature of the interaction leading to the inhibition of the dehydration reaction in the presence of CO$_2$.

In the *proton injection hypothesis* CO$_2$ interacts with a layer of molecular water on the Ca(OH)$_2$ surface which leads to the injection of protons into the lattice and the inhibition of the formation of molecular water inside the Ca(OH)$_2$ lattices (step 1). This water layer also provides a mechanism for the direct carbonation of Ca(OH)$_2$.

In the *passivating layer hypothesis* direct carbonation of Ca(OH)$_2$ leads to the formation of an impermeable layer around the grains, which slows down the diffusion of water out of the grains (step 2).

In the *reaction interface hypothesis* CO$_2$ interacts with an open and defective Ca(OH)$_2$ structure which greatly slows down the migration of H$_2$O out of the grains (step 2) and provides an interface for the simultaneous dehydration and carbonation of Ca(OH)$_2$.

In the *CaCO$_3$ shell hypothesis* the direct carbonation of Ca(OH)$_2$ leads to the formation of a physical barrier to the egress of water from the particles (step 3).

When the compatibility of each hypothesis with the results observed during the experimental survey was assessed only the proton injection and the reaction interface hypotheses were found to provide explanations to all the phenomena observed in the experimental survey. The passivating layer and carbonate shell hypothesis required postulating an additional mechanism for the direct carbonation of Ca(OH)$_2$ to explain the unusual kinetics and pore-size dependence of the carbonation reaction.

Based on existing evidence and information, the reaction interface hypothesis appears the most credible as it is able to explain all of the experimental observations while requiring making fewer assumptions than in the proton injection hypothesis since the defect structures postulated have been reported in the literature. Subsequent work should therefore be directed to investigating this hypothesis further.

Naturally, it cannot be excluded that more than one mechanism is involved and contributes to the inhibition of the dehydration reaction. Additional experimental results would be required before dismissing any of the hypotheses proposed here.

In situ FTIR analysis was identified as a promising technique for further investigation of the superheating and direct carbonation of Ca(OH)$_2$. Simple TGA experiments were also devised to test the passivating layer and CaCO$_3$ shell hypotheses.
2.4 Conclusion

The investigative work reported in this chapter has greatly expanded the understanding and control of the chemical mechanisms occurring when Ca(OH)$_2$ is heated in CO$_2$. At the outset of this work, conflicting reports were found in the literature regarding the behaviour of Ca(OH)$_2$, when heated in the presence of CO$_2$ to temperatures above its normal dehydration temperature$^3$.

Prior to the beginning of this PhD program, the author and colleagues reported observing partial carbonation of Ca(OH)$_2$ and an inhibition of the dehydration reaction manifested by an absence of water release until either the temperature reached 620°C or CO$_2$ was removed from the gas phase; the latter effect was termed superheated dehydration (1). On the other hand, several authors observed a near-complete conversion to CaCO$_3$ and observed no evidence of the inhibition of dehydration or a sudden release of water near 600°C.

The first part of this study focussed on establishing which experimental parameters led to the two different types of behaviour reported in the literature. It was established that the microstructure of Ca(OH)$_2$ particles played a major role in this respect, section 2.2.3. Furthermore, it was postulated that the existence of a significant volume of pores larger than 300 nm is the critical parameter controlling the behaviour of Ca(OH)$_2$ when heated in the presence of CO$_2$.

The second part of this study focused on explaining the absence of the SD effect with some of the hydrated sorbents tested by observing the kinetics of the chemical reactions involved in the system. First, the existence of a high temperature direct carbonation mechanism for Ca(OH)$_2$ with an unusual kinetic behaviour was observed. Second, it was established that the dehydration of Ca(OH)$_2$ is inhibited in the presence of CO$_2$ regardless of the presence or absence of the SD effect, see section 2.2.4. Finally, it was postulated that the majority of CaCO$_3$ formed during heating in CO$_2$ resulted from the “direct” carbonation of Ca(OH)$_2$, i.e. without the formation of crystalline CaO as an intermediary.

As a result it can be said that CO$_2$ plays a dual role vis-à-vis Ca(OH)$_2$ at high temperatures. On one hand, the presence of CO$_2$ maintains the stability of Ca(OH)$_2$ through superheating, while on the other the presence of CO$_2$ drives the removal of Ca(OH)$_2$ through direct carbonation.

While superheating, i.e. the inhibition of the dehydration reaction, was found to occur with all hydrated sorbents. The absence of the SD effect with some hydrated sorbents can be attributed to their increased tendency to carbonate, which leads to the release of water before the temperature of SD is reached.

Thus, it appears that the mechanism of high temperature carbonation of Ca(OH)$_2$ is the very core of the superheating reactivation technique, and that superheating is in reality inseparable from it. In that sense the superheating effect is perhaps best understood as a side-effect of the direct, high temperature, carbonation mechanism of Ca(OH)$_2$. This shift in perception is possibly the most important result of this chapter.

$^3$ The temperature of onset of rapid dehydration in the absence of CO$_2$, see Section 2.1.
Further work in this area should focus on elucidating the mechanism of the direct, high temperature carbonation of Ca(OH)$_2$. This carbonation mechanism was found to present a number of unusual and defining features that need to be taken into account when providing an explanation for this mechanism.

First, it was repeatedly observed that the rate of reaction was closely linked to the rate of temperature increase, so that if the temperature was held constant or reduced, the reaction would not proceed.

Secondly, and as a result of the previous point, the advancement of the reaction could be expressed as a function of temperature only (\( \alpha = f(T) \)) as seen in section 2.2.3. The nature of this function was found to depend in particular on the pore size distribution of the hydrated sorbent, and it was postulated that the presence of a significant volume of large pores (>400 nm) ultimately controlled the final conversion to CaCO$_3$. Such behaviour could be explained by pore plugging phenomena, where the carbonation conversion was limited by the volume available in the existing pore system to accommodate for the expansion of the solid as it transforms to CaCO$_3$ (Ca(OH)$_2$ 33 ml.mol$^{-1}$; CaCO$_3$ 37ml.mol$^{-1}$).

Finally, four hypotheses on the mechanisms underlying the chemical behaviour of the system were formulated and their compatibility tested with the experimental observations made in this work. A hypothesis in which the simultaneous dehydration and carbonation were postulated to occur through a defective Ca(OH)$_2$ structure, called the “reaction interface”, was found to be the most parsimonious hypothesis. Methods for testing or falsifying all the proposed hypotheses were proposed.
Chapter 3 Superheating and Attrition

3.1 Introduction

The objective of this chapter is to identify the mechanism(s) by which the superheating of Ca(OH)$_2$ generates a reactivated, attrition-resistant sorbent in order to enable optimization and control of the superheating reactivation method.

The friability (tendency to break) of the sorbent is a very important parameter since fluid bed reactors are expected to be used in most proposed Ca looping systems (14). In such reactors, sorbent particles are subjected to mechanical stresses inevitably leading to attrition phenomena (breakage) which has nefarious consequences on the operation of fluid bed reactors.

The conventional hydration-dehydration technique is known to be able to restore sorbent activity but also to weaken the sorbent particles, greatly increasing their friability (66). The resulting increase in sorbent attrition in fluid beds is likely to offset any gains made by increasing the activity of the sorbent, thus limiting the value of the hydration-dehydration reactivation method.

In contrast, prior to the beginning of the PhD program, the author and colleagues have shown that when Ca(OH)$_2$ is superheated instead of being dehydrated the reactivated sorbent was found to be only slightly more friable than un-reactivated sorbents (1). Thus the guiding question of this chapter is: How does superheating reduce the friability of the reactivated sorbent, compared to the hydration-dehydration technique?

Naturally, being able to measure sorbent friability is essential to conducting this research, which is a surprisingly difficult task. This is discussed in the first section of this chapter where the information gathered during a literature review is used to discuss the limitations of existing attrition testing methods when applied to measuring the friability of Ca looping sorbents.

The second section of this chapter presents a novel attrition testing method developed during this work and designed to overcome some of those limitations. In this section, a prototype apparatus is used to validate the new method by measuring the friability of un-reactivated Ca looping sorbents and comparing the results to those obtained in the literature.

The third section describes a study in which this novel attrition testing method is applied to investigate the friability of conventionally reactivated sorbents. The aim of this study is to identify the source of increased sorbent friability when the conventional, hydration-dehydration technique is used. It is expected that understanding the origin of increased friability of conventionally reactivated sorbents can provide insight into how the superheating technique can avoid this weakening.

Finally, the fourth section describes a study aimed at identifying which steps of the superheating technique are critical to minimizing the friability of the superheated sorbent. This study has both a practical and a theoretical aspect as the knowledge of which aspects of the superheating technique
affect the friability of the superheated sorbent is likely to allow optimizing this method as well as provide insight into the mechanism(s) involved.

3.1.1 Literature Review

Introduction to Attrition and Friability

Any process involving the use and transport of particulate materials inevitably subjects the particles to mechanical stress, usually resulting in particle breakage to some extent. This phenomenon is referred to as comminution or attrition. Although the distinction is somewhat blurry, “comminution” is generally used in cases where the breakage is intentional and desired while “attrition” is preferred when the breakage is accidental and/or undesirable (68).

In the context of fluidized beds in general and Ca looping in particular, attrition is the most commonly used term since particle breakage has a number of negative consequences on the process (67). Attrition often leads to the generation of very small particles, called fines, which cannot be kept within the system, causing loss of material and creating the need for additional filtration systems. Furthermore, attrition also leads to a reduction in the size of the particles remaining in the system, called mother particles.

Since particle size distribution is a key parameter for the hydrodynamic behaviour of fluidized beds, attrition phenomena can have a profound influence on these processes. Some authors even claim that “fluidized beds with attritable materials cannot be designed and simulated appropriately until the attrition activity is quantified” (68).

However, quantifying attrition is a complex and difficult endeavour. Attrition is by its very nature a statistical phenomenon only measurable for a large number of particles since each individual particle and each mechanical stress exerted on it are unique (67). Furthermore, attrition occurs via a variety of mechanisms, dependent on a multitude of factors ranging from the shape of the particles to the geometry of the process.

These complexities make a theoretical approach very difficult and most reported work in the literature is empirical in nature (67). As a general rule, the more accurately a test is able to describe and quantify attrition, the more fundamental it becomes which limits its applicability. On the other hand the more closely a test approaches the conditions of particle use, the more limited it becomes in scope and the more arbitrary are its results (68).

Attrition Mechanisms A number of mechanisms, or modes, of attrition have been identified in the literature. The primary division reported is between the abrasion and fragmentation mechanisms, or modes, shown in Figure 29, with the main difference being the size of the fragments generated.

The abrasion mode is characterized by the surface wear of mother particles, leading to a removal of asperities from the particle surface. The mother particles remain of a similar size but get progressively rounded, creating a large number of very small fines, see Figure 29.
In contrast, the fragmentation mode is characterized by a significant reduction in the size of mother particles (Figure 29), and the formation of large fragments. Furthermore, a number of fragmentation sub-modes are also mentioned in the literature, e.g. chipping, splitting or disintegration, which are depicted in Figure 29. Given that it has the lowest energy of activation, abrasion is the only attrition mode that can be observed independently. Above a certain stress level, fragmentation occurs simultaneously to abrasion.

The dominance of a particular fragmentation sub-mode over others, Figure 29, largely depends on the type of particles and intensity of mechanical stress involved. Scala et al. suggested that soft materials such as lime typically follow a disintegration pattern during fragmentation, while brittle and semi-brittle materials, such as limestone, tend to chip at lower stress and split at higher stress levels (99).

The vocabulary used in the literature to describe attrition modes varies considerably; in some references the term attrition is used to describe abrasion only and is used as opposed to fragmentation. Furthermore, fragmentation is sometimes used to refer only to splitting, while chipping is called “surface fragmentation” or used to refer to abrasion. Figure 29 provides a guide for the vocabulary used in this work and an illustration of the effect of these different attrition modes on the particle size distribution.

**Figure 29.** Nomenclature, illustration and signature probability density function distributions of various attrition mechanisms after a single impact. Adapted with permission from Scala et al. (99); Copyright 2007 American Chemical Society.

**Attrition in Fluid Beds** In bubbling or circulating fluidized beds, the main sources of mechanical stress leading to attrition are impacts between particles as well as impacts of particles against walls. These stresses are generally recognized to be most significant in three distinct zones (67,98):

1. The distributor region, where high velocity gas jets penetrate into the bulk of the bed causing high velocity particle-particle impacts that can potentially lead to fragmentation.

2. The bulk bubbling bed, where a very large number of low velocity particle-particle impacts can lead to significant abrasion. The presence of internal features in the bed such as heat exchanger tubes or baffles also leads to attrition by particle-wall impacts.
3. The cyclone, where high velocity particle-wall impacts causing fragmentation are followed by the spiralling downwards of solids against the cyclone walls causing abrasion.

Furthermore, the distinction between primary and secondary attrition has to be made (100). Primary attrition occurs immediately after the injection of the particles in the bed as a consequence of thermal shock, decrepitation (breakage due to internal overpressure) and initial rounding off of the particles. This primary attrition includes elements of both fragmentation and abrasion modes, and the extent of attrition is largely dependent on particle properties and history, e.g. structure, shape, hydration level, grinding history, etc.

After a certain time, “particle memory” fades out and a steady state is reached, i.e. the attrition rate becomes constant. After this point, attrition phenomena are called secondary attrition and can include elements of abrasion and fragmentation. The rate of attrition in this phase is dependent on process conditions as well as the particle properties but it is expected to be independent of the time the particles have spent in the process. The steady state attrition rate is possibly the most representative value of attrition and friability in a given situation.

**Measuring Attrition**

The extent of attrition is often assessed by the change in the particle size distribution, e.g. using the change in average particle size of the sample after the test. Knowing the change of the average particle size is particularly useful for assessing the effect that attrition will have on the hydrodynamics of the bed.

Another commonly used approach is to define the size under which particles are considered “attrited” or “fines” and express the extent of attrition as a percentage of bed material smaller than the given size. This approach is useful when considering loss of material from the process; in any fluid bed process, particles smaller than a given size will be lost (elutriated) from the bed. The exact value of the cut size depends on the specific process considered. As a result, a commonly used quantifier of attrition in practical, continuous, systems is the elutriation rate; the rate of loss of materials under the cut-size from the system considered.

**Measuring Friability**

The tendency of a material to undergo attrition upon mechanical stress is referred to as the friability of the material. Methods to measure friability consist of measuring the extent of attrition occurring when a controlled mechanical stress is applied to the sample particles.

Obviously no single method can be appropriate due to the variable response of materials to different stresses, as illustrated by the following quote from Pell et al. (101); “If we rubbed diamond and rubber on abrasive paper we would conclude that diamond is more resistant; if we hit them with a hammer we would conclude that rubber is more resistant”. Attrition is a result of the interaction of particles and stress – an appropriate test should at least reproduce the dominant stresses expected in the process considered.

Although one can distinguish three types of stresses, namely compression, impact and shear (67), impact-based attrition testing methods are mostly used in the context of Ca looping as impact stresses
are expected to be the only significant type in fluidized beds, as discussed above. A number of impact-based attrition testing methods have so far been reported in the literature (67).

The impact plate method is commonly used to measure sorbent friability. It consists of firing sample particles at an impact plate under a controlled velocity and measuring the particle size distribution of the resulting fragments. Such methods have been used to compare the relative friability of Ca looping sorbents when subjected to particle-wall impacts (99,102,103) as well as for more fundamental investigations into attrition mechanisms (104) with other materials. Such methods allow easy correlation of the intensity of stress with the level of attrition allowing one to draw “friability profiles” describing the evolution of sorbent friability with increasing impact velocity.

Another common category of tests are the so-called submerged jet tests, where gas jets are fired into the bulk of a bubbling bed inducing high velocity particle-particle impacts. Such methods aim to simulate attrition conditions prevailing in the distributor region, and have been used to compare the friability of Ca looping sorbents (105,106). Abrasion was the dominant attrition mechanism in these circumstances and attrition proceeded very slowly, with tests extending over 100 hours.

Finally, a number of tests aiming to simulate the stresses occurring in the cyclone are reported in the literature. These tests are usually carried out in cyclones themselves (107) or in Grace-Davidson jet-cup type apparatus. However, no measurements using such tests have been reported for Ca looping sorbents.

Furthermore, a number of authors use an “integral” approach to measuring friability, using an actual fluidized bed to perform Ca looping and measure particle attrition in some form. Abrasion was found to dominate in bubbling fluid bed experiments (65,66) while some fragmentation was observed in circulating fluidized beds (108,109). Although this approach is most representative of the actual process, particles are subjected to such a variety of mechanical stresses in the different regions of the reactor that it is difficult to correlate stress intensity to the extent of attrition. Furthermore, extrapolation of data from a laboratory bed to a pilot plant can only be done if they are similarly designed.

**Friability of Ca Looping Sorbents**

The sorbent enters the Ca looping process as raw limestone but experiences considerable structural changes during its working life in the Ca loop. Namely, the sorbent composition and crystal structure vary repeatedly between CaCO$_3$, CaO and Ca(OH)$_2$. The physical structure of the sorbent is also repeatedly modified by changes in molar volume (CaO – 16.9cm$^3$.mol$^{-1}$, CaCO$_3$ – 36.9cm$^3$.mol$^{-1}$, Ca(OH)$_2$ – 33.1cm$^3$.mol$^{-1}$) as well as sintering phenomena (section 1.2).

It is to be expected that sorbent friability will vary greatly throughout its working life in the Ca loop, primarily with the chemical composition but also with the time spent in the process, i.e. the number of cycles it has been subjected to. In order to get a complete picture of the Ca looping friability, it is necessary to measure it at different moments in the cycle. For this reason, literature data on Ca looping sorbent friability is ordered here based on cycle number.
The First Cycle: Raw Limestone has a number of properties that set it apart from other forms of the sorbent. First, it is fully carbonated and second, it is expected to experience primary attrition due to the initial thermal shock, decrepitation and rounding off of the particles as they are injected into the bed. This phenomenon was indeed observed in a number of studies both in repeated impact tests (102,106) as well as in circulating fluid beds (98,110,111).

The existence of primary attrition suggests that a large variability of attrition rates for raw limestones from different sources can be expected. These differences arise from variations in particle history, grinding type and hydration state but also the microstructure of the limestone, which varies from quarry to quarry. Scala et al. confirmed this observation by testing five different limestones in single impact tests (103). They observed that the friability of raw limestones varied considerably and attributed a part of these large variations at least to primary fragmentation since the extent of attrition was found to reduce and stabilize upon repeated impacts. This was further corroborated by the observation that pre-calcination in a bubbling fluid bed prior to testing reduced the variations in friability of the raw limestones.

Scala et al. proposed that limestone displays fragmentation patterns typical of brittle materials (99); impact generates cracks on the particles’ peripheries, which eventually propagate into the particles. At low impact velocities the cracks remain near the surface and chipping is the main mechanism. At high impact velocities, the cracks extend throughout the particle and splitting is the main mechanism. It is worth noting that Ray et al. (98) suggested that “materials, such as coal or limestone ... attrite into fines of a characteristic size distribution, referred to as “natural grain size”. This idea has found some support in experimental evidence with a number of studies reporting a preponderance of 70–150 µm fines amongst the fragments produced by abrasion and/or chipping of either limestone or calcined lime (98,99,102,111). However, petrographic analysis suggests this is most likely a simplification as there is considerable variation in the grain size of natural limestones, which can range from 1 µm up to about 1000 µm (113).

The activation of attrition mechanisms for raw limestone has been experimentally observed by a number of authors, using single impact tests. Chen et al. reported observing the activation of the chipping fragmentation mode at particle impact velocities of 8.5–9 m.s\(^{-1}\) (102). Scala et al. reported observing the activation of the splitting fragmentation mode for a number of raw limestones at an impact velocity of about 25 m.s\(^{-1}\) (99,103). Furthermore, Chen et al. observed a reduction in friability with increasing temperature up to 560°C (102).

It is worth noting that in a fundamental study of monocrystal attrition, Ghadiri and Zhang reported that repeated impact led to a reduction in the activation velocity of fragmentation due to the hardening of the sample particles upon impact (104). Upon repeated impacts, they reported observing the transition between abrasion (which they call chipping) and chipping (which they call fragmentation) at a range of velocities between 10–18 m.s\(^{-1}\) for different materials.

The First Cycle: Calcined Limestone is obtained by the calcination of raw limestone, and is expected to be 100% CaO as calcination generally proceeds to completion, see section 1.2. In a number of studies in
fluidized beds, the rate of attrition of calcined limestone was initially very high and decayed exponentially to a steady state \((98,108,109,111)\). It is not clear whether this is due to primary attrition or some other phenomena, such as decrepitation due to the release of \(\text{CO}_2\) from the limestone particles \((100)\).

In any case, all studies report that the calcined limestone is much more friable than raw limestone. Calcination was found to lead to a threefold increase in attrition rates after calcination in a fluidized bed \((102)\) and a tenfold increase in the proportion of fines generated at high velocities in single impact apparatus \((99)\).

The lack of separate measurement of primary and secondary attrition creates some confusion regarding the friability of calcined limestone. For example, Scala et al. reported that for some materials, daughter calcined particles were less friable than their parent limestones \((103)\). This result is most likely due to the methodology used – primary fragmentation was included in the measurement of the parent limestone but not in that of the daughter calcined limestone.

This issue illustrates well the advantages and limitations of the single impact plate method for measuring friability in Ca looping sorbents. While these methods allow easy plotting of friability profiles and thus identification of the attrition mechanisms and their activation thresholds, it is difficult to distinguish between primary and secondary attrition. To achieve this, it would be necessary to perform repeated impacts. Although it can be done with impact plate methods \((112)\), it is very labour intensive as the apparatus must be disassembled after each impact.

Scala et al. proposed that the main fragmentation mode for calcined sorbent particles is disintegration, see Figure 29, and that the friability profile would follow a power law \((99)\), although the latter statement is not well justified either experimentally or by way of reference. Scala et al. reported observing the activation of the disintegration mechanism at 12 m.s\(^{-1}\) for both calcined sorbents tested \((110)\).

**Beyond the First Cycle** Recarbonated sorbents are never fully carbonated due to the formation of an impervious \(\text{CaCO}_3\) layer on the outer surfaces of the parent calcium oxide grains \((31)\), see section 1.1. This layer limits the kinetics of carbonation, inducing a slow diffusion controlled regime that ultimately limits the \(\text{CO}_2\) carrying capacity of the sorbent. As a result, recarbonated sorbents typically exhibit a shell and core structure, where the shell is composed of \(\text{CaCO}_3\) while the core remains sintered \(\text{CaO}\).

Very few studies have been performed on the friability of recarbonated sorbents. Scala et al. have reported single impact friability profiles for the carbonated sorbent after one Ca looping cycle, i.e. limestone that was calcined and recarbonated once \((99,103)\). They reported that the recarbonated sorbent had an intermediate behaviour between raw and calcined limestones. At velocities below the activation threshold for the splitting mechanism, the friability of the recarbonated sorbent was comparable to that of the parent limestone. However, above this threshold value, the friability of the recarbonated material was substantially higher than that of raw limestone as shown in Figure 30.

These results were explained by postulating that the shell, i.e. the outer layer of \(\text{CaCO}_3\), acts as a shield for the core of \(\text{CaO}\) at velocities below the threshold value, so that the recarbonated material behaves
like the raw limestone (99). At higher velocities, however, the impact is sufficiently strong to break the shell of CaCO$_3$ and the cracks extend into the softer CaO core which disintegrates, leading to friability higher than that of raw limestone.

Interestingly, sulphated sorbents that also exhibit a shell (CaSO$_4$) and core (CaO) structure exhibit very similar behaviour to the recarbonated sorbent. A similar explanation was proposed for such materials (99,103).

![Figure 30](image)

**Figure 30.** Friability profiles of Ca based sorbents, as measured in single impact friability tests, adapted with permission from Scala et al. (99); Copyright 2007 American Chemical Society.

*Beyond the First Cycle* All the studies reported in the literature concerning the friability of Ca looping sorbents beyond the first cycle were performed in actual fluidized beds, generally at a pilot scale. Fluid beds facilitate this type of study as both sample preparation and friability testing can be performed in the same apparatus, considerably reducing the work required compared to single impact apparatus.

Most studies reported high rates of attrition during the first two cycles both in bubbling fluid beds where mainly abrasion is expected (65) and circulating fluid beds where fragmentation can also occur (109). The initial period was generally followed by a reduction in the rate of attrition as the cycling progressed (44).

However, in some cases, the attrition rates did not reduce with cycling – Fennell et al. found that Cadomin limestone sorbents would remain quite friable during at least 30 cycles (65), while Lu et al. found that the attrition rate did not reduce after the first two cycles in their fast bubbling bed calciner (114). No explanations were proposed for this observation, although such discrepancies could be explained by postulating that in the latter case the system was subjecting particles to impact velocities above a threshold level at which extensive attrition occurs, i.e. the splitting mechanism. However it is difficult to ascertain the actual impact velocities that the particles are experiencing in the many components of a pilot fluid bed, e.g. bulk bed, cyclone or transfer lines.

These observations highlight the advantages and disadvantages of using fluid beds to measure sorbent friability. They allow easy distinction between primary and secondary attrition as well as rapid measurement of the evolution of sorbent friability. However, it is difficult to correlate attrition with a
specific impact velocity and thus explain variations between the attrition observed in different apparatus.

Hydrated and Reactivated Sorbents A number of authors have reported that sorbents reactivated with the conventional, hydration-dehydration methods appeared fragile and presented a large increase in volume (1,115). However, there have been only two experimental studies regarding the attrition of conventionally reactivated sorbents during Ca looping for CO₂ capture (1,66) both of which were carried out in bubbling fluid beds and therefore with low velocity impacts.

Both studies observed an increase in attrition when reactivation methods were used but conclusions drawn from these experiments were contradictory. Blamey et al attributed the increase in attrition to the breakage of Ca(OH)₂, and developed a theoretical model to describe it (66), while in preliminary work, the author and colleagues concluded that the source of increased friability of the sorbent could not be the hydration step since it was possible to minimize attrition if freshly hydrated Ca(OH)₂ was superheated (1).

The friability of hydrated sorbents upon high velocity impact was also studied in the context of reactivation of sulphated sorbents for further sulphur capture. Montagnaro et al. hydrated and dehydrated sulphated sorbents prior to attrition testing, arguing that it is the dehydrated form that will be exposed to the mechanical stresses in the process (57). They reported that, after dehydration, sorbents initially hydrated in steam were very fragile and prone to disintegration while those hydrated in water were more robust and tended to chip or split.

Conclusion
This literature review has illustrated that the study of attrition and friability of particulate materials is a remarkably complex field. This is due in particular to a number of difficulties associated with measuring, quantifying and assessing attrition and sorbent friability. These difficulties have led to a rather fragmented and partial understanding of attrition in Ca looping cycles.

The first difficulty resides in experimentally defining friability, since the extent of attrition can be measured and expressed in a number of equivalent ways, e.g. by the change in average particle size of the sample; by the proportion of particles elutriated out of the test system or by the amount of fines created during the test. This difficulty could be resolved if the attrition testing method allowed measurement of both change in particle size and proportion of particles elutriated.

A second difficulty arises from the fact that attrition proceeds via a range of mechanisms that are activated at increasing impact velocities and shown in Figure 29 above. Friability profiles, i.e. friability vs. impact velocity curves, are typically non-linear (99,103,104) and present sudden changes when new mechanisms are activated such that their interpretation requires knowledge of the mechanisms involved. A single friability value obtained at a single impact velocity is of limited use for comparing sorbents or process design and operation as particles in the process will be subjected to impacts in a range of velocities, as discussed above.
This difficulty can be overcome by measuring sorbent friability over a range of velocities to produce friability profiles. This is easily done in impact plate type apparatus as the impact velocity can be precisely controlled. On the other hand, this is a difficulty for fluid bed apparatus as particles are exposed to a range of impact velocities and it is difficult to associate a friability measurement with a specific impact velocity. In the case of fluid beds, this issue can lead to results that are quite difficult to interpret, such as the case of Hughes et al. who reported that in their fluid bed a constantly high rate of attrition was observed in contrast to most other apparatus (116). This behaviour could be explained by the presence of a high velocity impacts in some part of the system (i.e. transfer line), as discussed above.

A third difficulty arises due to the fact that sorbent friability is dependent on the number of impacts experienced. As discussed above, attrition phenomena are divided in two broad categories – primary and secondary attrition (100). Primary attrition is associated with transient phenomena occurring upon particle injection in fluid beds, such as thermal shock and initial rounding of particle edges. After a certain time period, a steady state is usually reached and attrition occurring then is called secondary attrition. When comparing sorbent friability it is essential to compare the tendency for primary and secondary attrition separately for the comparison to be meaningful. Furthermore, from the perspective of a fluid bed designer/operator, primary and secondary attrition need to be quantified separately. For primary attrition it is the extent i.e. the proportion of fines generated that should be measured as it occurs only for a short period; for secondary attrition it is the rate that must be measured since it is expected to occur over the entire working life of the particles.

This difficulty can be overcome by subjecting the sorbent sample to repeated impacts which allows observation of the establishment of steady state attrition and thus discerning between primary and secondary attrition. This is easily done in a fluid bed apparatus as particles are constantly subjected to impacts. On the other hand this is a difficulty for impact plate apparatus as the sample particles must be manually discharged/recharged after every impact, which is impractical even when a modest number of impacts (10–20) are performed. The number of impacts particles are likely to experience in their working life is most likely in the order of tens of thousands.

The inability to distinguish between primary and secondary attrition can lead to results that are difficult to interpret, as discussed above. For example, most friability tests suggest that calcined limestone is more friable than raw limestone at all velocities. However, using single impact tests, Scala and Salatino observed one raw limestone sample for which the reverse was true. This could indeed be an anomalous limestone but it is also possible that the limestone sample was simply very prone to primary attrition, for example due to the angular shape of the particles. The calcined limestone sample particles would have been rounded during calcination in the bubbling bed and therefore appear less friable than the parent limestone. However, the difficulty of performing repeated impacts in single impact apparatus limits the ability of testing such a hypothesis.

Finally, in most methods reported in the literature (67,99,102,105,111), the entirety of the sample must be discharged from the apparatus to measure sorbent friability for each impact velocity. The effort required to establish sorbent friability profiles with existing methods has limited the scope of reported studies, and no friability profiles have been reported for sorbents beyond the first Ca Looping cycle.
3.1.2 Research Questions

As discussed in section 3.1.1, this chapter aims answering the following question: how does superheating reduce the friability of the reactivated sorbent, compared to the hydration-dehydration technique? The information gathered during the literature review has allowed formulating a range of sub-questions that need to be answered in order to provide an answer to the question above.

First, it has become apparent that there is a clear need to develop a low-effort attrition testing method able to provide meaningful friability data for Ca looping sorbents. Such a method was indeed developed during the course of this work and it is presented in section 3.2.1. The proof of concept and validation of this method was carried out by measuring the friability of un-reactivated Ca looping sorbents and comparing it to the results obtained in the literature.

Second, little information was found in the literature about the friability of reactivated sorbents. Based on existing information, it can only be said that the using the hydration-dehydration technique increases the friability of the reactivated sorbent while using the superheating technique avoids this increase.

Therefore, in order to answer the question above, it is first necessary to understand how does the hydration-dehydration technique induce an increase in friability of the reactivated sorbent? This question is addressed in section 3.2.2 in which the step and the mechanism by which friability is increased during conventional reactivation is identified.

Establishing the friability increase mechanism during hydration-dehydration is expected to shed light on the difference between the two techniques that lead to the improved friability after superheating and allow answering the question: how does the superheating technique avoid increasing sorbent friability? This question is addressed in section 3.2.3 in which the effect of the primary parameters of superheating on the friability of the reactivated sorbents is investigated.
3.2 Experimental Work

This section describes a series of experiments which were undertaken to provide answers to the research questions formulated in the previous paragraphs. The results are presented as a series of semi-independent experimental studies contained within each sub-section.

Given that all experiments were carried out using a custom built apparatus, using methods developed during this work, there is no separate Apparatus and Analysis section in this chapter. Instead, the first section (3.2.1) describes this novel apparatus and testing methods.

3.2.1 A Low-Effort Attrition Testing Method for Ca Looping Sorbents

Introduction
Existing attrition testing methods have been found to be inappropriate for the study of attrition and sorbent friability in Ca looping. The principal issue was the amount of effort required in obtaining a friability profile for a sorbent sample, which is critical in the case of Ca looping since a large number of measurements must be made to characterize the evolution of sorbent friability throughout cycling.

As a result, a new attrition testing apparatus was devised to overcome the limitations of existing friability testing methods and to allow rapid and practical measurement of sorbent friability over a range of velocities. This new apparatus allows control of the impact velocity while repeatedly impacting particles using an internal circulating fluid bed (ICFB) design. In addition, friability can be evaluated simply by measuring the amount of material elutriated from the bed, avoiding the need to discharge the sample after each measurement.

The objective of this work was to investigate the feasibility and the potential of the proposed attrition testing apparatus in the context of Ca looping. In this work a prototype ICFB attrition testing apparatus was built and validated by measuring the friability of raw and calcined limestone. Once the basic method was validated, the prototype apparatus was used to measure the friability of Ca looping sorbents after one and six calcination/carbonation cycles.

Materials and Methods
The operating principle of the apparatus developed here is illustrated in Figure 31a. Sample particles are continuously aspirated from the bottom of a reservoir, entrained along a central tube and projected tangentially against a circular wall. Upon impact, large particles return to the top of the reservoir by spiralling downwards against the circular wall (similarly to what occurs in a cyclone) while small fragments generated are entrained and elutriated out of the bed. Sorbent friability can be simply evaluated by measuring the mass of elutriated fragments, while particles returning to the reservoir are recirculated (repeatedly impacted against the circular wall). The temperature and atmosphere in the apparatus can be set by controlling the furnace temperature and changing the supply gas composition.

Materials Raw limestone used in this study was McDonald’s Agricultural Limestone, containing >95% CaCO₃, with particle size in the 400–800 µm range. Carbonated cycled sorbents were produced in a bubbling fluid bed, by subjecting 1.2 kg batches of raw limestone to one and six calcination–carbonation cycles. Calcinations were performed in air at 870–900°C for 80 min, while carbonations were performed
in 25% CO₂ in air at 650–710°C for 20 min After discharge from the bubbling bed, the sorbents were sieved and only the 500–600 µm fraction was used.

Calcined sorbents were produced by in-situ calcination of raw limestone and of recarbonated sorbents inside the prototype attrition tester, immediately prior to an attrition test. Calcination in the attrition tester was performed at 940°C for 70 min with a purge flow of air so that particles were not circulating during calcination. This calcination method was tested and found to lead to full calcination of raw limestone, as measured by thermogravimetric analysis.

The sample size used varied with sorbent form – 17 g for calcined samples and 21 g for carbonated samples in order to keep the molar amounts relatively constant.

***Figure 31. Schematic of the proposed attrition testing apparatus a) operation principle b) prototype apparatus. M represents the solid state microphone.***

**Prototype Apparatus Description** A prototype ICFB attrition testing apparatus was designed and built for this study, which was composed of three tubes, as shown in Figure 31b. The body of the apparatus is a 6 cm-diameter tube and is referred to as “the vessel”. A 1.27 cm-diameter tube extends into the vessel and is referred to as the “central tube”. The central tube also extends out of the vessel and was used as a discharge line, to discharge the sample at the end of an experiment. Concentric with the central tube is a 0.63 cm-diameter tube with 0.08 cm nozzle at the end, referred to as the “nozzle tube”. The temperature in the apparatus is controlled with an electric furnace, and supplying different gases controls the gas composition.

Gases were preheated to 450°C prior to feeding into the tester and their flows were controlled using rotameters. The composition of gases and vessel temperature used during experiments varied with the form of material tested (calcined or carbonated). Carbonated samples were tested at 650°C in an atmosphere containing at least 12% CO₂, in order to avoid calcining the samples, while calcined samples
were tested in air both at 650°C and 940°C. Carbonation of the calcined samples is not thermodynamically expected to occur at 650°C in air.

Compressed air was fed into the nozzle tube and used to induce and control solid circulation in the apparatus. The gas jet exiting the nozzle tube creates a depression (via the Venturi effect), which aspirates particles from the reservoir, entrains them along the central tube and finally projects them tangentially onto the vessel wall, as described above and shown in Figure 31a and Figure 31b. Larger particles are returned to the reservoir and subsequently recirculated, i.e. subjected to further impacts, while smaller fragments are elutriated out of the bed and recovered in a settling pot, Figure 31b. Sorbent friability was evaluated in two different ways: by measuring the mass of elutriated particles and by analysing the particle size distribution of the entire sample (elutriated + remaining in bed) after a test.

The rate of solid circulation and therefore the frequency of impact could not be directly measured in the prototype apparatus used in this study. Data in the literature regarding particle entrainment in grid jets suggest that the rate of circulation should vary linearly with gas velocity and provides an order of magnitude estimate for the impact frequency in this apparatus at 10–50 impacts.min⁻¹. In this work, a solid-state microphone, Figure 31b, was used to provide qualitative measurement of circulation rates, which were found to increase approximately linearly with gas velocity.

Upon completion of an experiment, particles remaining in the vessel were discharged by blowing compressed air in the reverse direction, as illustrated in Figure 31b. During the experiments, however, a small “purge flow” of gas (air/CO₂) was fed through the discharge line directly into the central tube in order to prevent backflow of solids.

Mass balances were always close to at least 95% except in two cases where were calcined in-situ when the closure was at 90%. It is believed that the missing particle were lost during discharge into a blind section of pipe.

Particles discharged from the bed and those recovered in the settling pot after the experiment, were sieved separately. As a complementary measure, sorbent friability was also assessed by measuring the amount of fines created during the experiment, both elutriated and remaining in the bed. Fines are defined here as particles passing through a 125 µm sieve.

**Methods** During this work two different attrition testing methods using the prototype apparatus were used, each providing a complementary perspective on sorbent attrition and friability.

**Method One** The “friability profile” method aimed at establishing the friability of a sorbent sample over a velocity range, generating a friability vs. gas velocity curve i.e. a friability profile.

After charging (and in-situ calcination for calcined samples) the sorbent samples were circulated at low velocity (7.1 m.s⁻¹ for carbonated samples, 5.2 m.s⁻¹ for calcined samples) for ten minute periods until the mass elutriated per period became constant. This indicated that primary attrition was completed and that effects due to particle history would not interfere with further measurements.
After primary attrition was complete, the samples were circulated in the apparatus for ten minute periods at increasing gas velocities. During this time, the vessel was periodically tapped to release the fines potentially adhering to vessel walls. At the end of a ten minute period, circulation was stopped and the mass of particles elutriated was measured by weighing the tarred settling pot. Sorbent friability at a given gas velocity was evaluated by the % mass elutriated during ten minutes of circulation.

\[
\% F_e = \frac{m_{elutriated \ in \ 10 \ min. \ period}}{m_{in \ bed \ at \ beginning \ of \ period}}
\]

Given that the prototype apparatus used in this work did not allow direct measurement of the particle impact velocity, the friability of the sorbent is plotted against the velocity of the gas used to induce circulation.

**Method Two** The “constant velocity” method allowed investigating the dominant attrition mechanism at a given gas velocity and provided a complementary measure of sorbent friability which did not rely on elutriation.

After charging, the sorbent samples were circulated at low velocity until primary attrition was completed as described above. The sorbent samples were then circulated at a constant velocity for a period of time sufficient to elutriate 1-2 g of fragments for further analysis, with times required ranging from 35 to 300 min in the extreme cases. At the end of the experiment, particles remaining in the bed were discharged and sieved. Elutriated particles recovered in the settling pot were sieved separately. Mass balances were always close to at least 90%.

The particle size distribution of the entire sample (elutriated + remaining in bed) after the experiment was then used to provide a complementary evaluation of sorbent friability, defined as the rate of fine creation per ten minutes:

\[
\% F_e = \frac{\% fines}{t_{circulation}}
\]

The particle size distribution of the sample after the experiment was also used to identify the attrition mechanisms present at a given gas velocity. A probability density function (PDF) was used to express this distribution, which offset the distorting effect of unequal size bins. For particles found in the X µm to Y µm size bin, the PDF at size \((X+Y)/2\) is expressed in g.µm^{-1} as the mass of particles found in a size bin is divided by the width of the bin.

\[
PDF_{(X+Y)} = \frac{m_{XYbin}}{(X + Y)}
\]

The particle size distribution data, conveniently expressed in terms of PDF, was then used to identify attrition mechanisms using the key presented in Figure 29. This figure was adapted from Scala et al. and describes the attrition mechanisms encountered in this work, the nomenclature used to describe them and the effect of each attrition mechanism on the particle size distribution of the sample in ideal conditions.
circumstances, i.e. when only one mechanism is active. Note that in real experiments several attrition mechanisms are simultaneously active and that repeated impacts would lead to a less clear outcome.

Results
The objective of this section of the work was to validate the proposed apparatus and associated methods. This was achieved by establishing that the apparatus provides meaningful and repeatable friability measurements; that it is able to distinguish between primary and secondary attrition and that it is able to produce friability results compatible with existing knowledge on Ca looping sorbent attrition and friability.

The proposed method was then tested by measuring the friability profiles of raw and calcined limestones over a range of velocities. In addition, constant velocity tests were performed to identify the attrition mechanisms involved and provide a complementary measurement for sorbent friability.

Suitability of Elutriation for Measuring Friability The elutriation efficiency and the size of elutriated particles were measured by sieving both the particles elutriated and those remaining in the bed after a sorbent sample had been circulated in the apparatus using the constant velocity method. Figure 32 plots the cumulative size distribution curves of elutriated particles obtained at different velocities with raw and calcined limestone, respectively. Gas velocities tested correspond to the velocities used in friability profiles as seen in the legend of Figure 32.

As could be expected, the size of particles elutriated during the experiment was found to vary with the gas velocity used for circulation and sorbent form (calcined or carbonated). Nevertheless, in all but one case more than 98% of the particles elutriated were fragments (<500um) and ≈90% were smaller than 225µm, indicating that the elutriated mass is indeed indicative of the amount of fragments created. However, at a gas velocity of 9.5m.s⁻¹, larger particles were also elutriated out of the bed suggesting that interpretation of elutriation data obtained at this velocity should be carried out with caution.

![Figure 32. Cumulative particle size distribution of elutriated particles after circulation with a range of gas velocities, see legend; a) raw limestone b) calcined sorbent.](image)

Primary and Secondary Attrition The extent of primary attrition was found to be low with the raw limestone used in this work. This was evaluated by repeating the lowest velocity measurement until the elutriation rate was found to be stable, as shown in Figure 33. With raw limestone, primary attrition was complete within ten minutes, after approximately 1.5% of the material had elutriated. With calcined
limestone, little or no primary attrition phenomena were observed – elutriation rates did not vary significantly with time, as illustrated in Figure 33b.

![Figure 33. Evolution of the attrition rate with time during constant velocity experiments with a) raw limestone b) calcined limestone.](image)

**Figure 33.** Evolution of the attrition rate with time during constant velocity experiments with a) raw limestone b) calcined limestone.

**Repeatability/Robustness** Figure 34a plots the friability profiles of raw limestone as measured in repeated tests at 650°C. The average fine creation rate measured during constant velocity tests at selected velocities is also plotted for comparison. Figure 34b plots the friability profiles of calcined limestone measured at 940°C, immediately after in-situ calcination.

The repeatability and robustness of the friability profile method with both materials is apparent in Figure 34. Although not represented here, most operating parameters (time period, preheat temperatures, purge flow levels, sample amount) were also varied during the development of the method and none affected the friability measurement significantly.

![Figure 34. Friability profile obtained with a) raw limestone, tested at 650°C b) calcined limestone, tested at 940°C, immediately after in-situ calcination.](image)

**Figure 34.** Friability profile obtained with a) raw limestone, tested at 650°C b) calcined limestone, tested at 940°C, immediately after in-situ calcination.

**Interpretation of Friability Profiles** Transition points in the friability profiles were observed with both materials. A threshold value of gas velocity, at 8 m.s⁻¹ for raw limestone and 6.5 m.s⁻¹ for calcined limestone can be seen in Figure 34, above which the elutriated mass increased rapidly with gas velocity. The fine creation rate measured in constant velocity experiments also exhibited a similar behaviour, suggesting that the rapid increase in elutriated mass effectively corresponds to increased fine creation and cannot be explained only by improved elutriation.

Threshold gas velocities at which sorbent friability is found to rapidly increase with impact velocity have been reported in the literature and are usually attributed to the activation of a new attrition
mechanism. For natural limestones, Chen et al. reported a threshold impact velocity at 8.5 m.s\(^{-1}\) using single impact tests, which was attributed to the activation of the chipping mechanism (102), while Scala et al. observed a threshold impact velocity at 25 m.s\(^{-1}\), at which the splitting attrition mechanism was activated. For calcined limestones in single impact tests, Scala et al. reported a threshold impact velocity of 12 m.s\(^{-1}\), which they attributed to the appearance of the disintegration mode. However, no investigations of attrition mechanisms were reported for calcined limestone in the velocity range investigated here (5-9 m.s\(^{-1}\)).

The possibility that the threshold velocity observed in this work is due to the appearance of a new attrition mechanism was tested by examining the particle size distribution of samples after constant velocity tests. Figure 35a and Figure 35b plot the PSD data for samples after circulation at a velocity below the threshold value (7.1 m.s\(^{-1}\) for raw, 5.2 m.s\(^{-1}\) for calcined limestone) and a velocity above the threshold value (9.5 m.s\(^{-1}\) for raw, 7.1 m.s\(^{-1}\) for calcined limestone).

When gas velocity exceeded the threshold value a considerably larger proportion of fragments in the 85–150 µm range was generated compared to when gas velocity was lower than the threshold value.

In addition, in the case of the raw limestone, a lower proportion of the smallest fragments (<66 µm) was also generated and the remaining mother particles were smaller when the velocity exceeded the threshold value.

All the observations described above can be explained by the activation of the chipping attrition mechanism at the threshold velocity. Chipping is triggered once the impact velocity reaches a threshold value at which the subsurface lateral cracks generated upon impact propagate far enough to reach the surface of the particle. As a result, larger fragments are separated than in the case of abrasion, which predominates at lower velocities, see Figure 29.

The appearance of the chipping mechanism would thus be expected to lead to increased fine creation and elutriation rates and an increased size of fragments generated, as was observed in these experiments and shown in Figure 34 and Figure 35, respectively.

Interestingly, the typical size of limestone chipping fragments has been reported to be in the 80–150 µm range (99,102), similar to what was observed in this work (Figure 35a). The preponderance of this size

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Figure 35. PSD distribution of the entire sample at the end of constant velocity tests a) raw limestone b) calcined limestone.
population was explained in their work by postulating that this size corresponded to the natural grain size of the parent material (98) although this statement is not experimentally supported.

A subtle difference can be observed in the case of calcined limestone, Figure 35b. Tests at both velocities lead to the generation of a significant proportion of the smallest fragments and a notable reduction in the size of the mother particles. However, at velocities above the threshold the proportion of 80–150 µm fragments is increased, suggesting increased chipping. These results suggest that the mechanisms are not as neatly separated as in the case of raw limestone, i.e. that some chipping occurs below the threshold velocity and abrasion occurs above the threshold velocity.

In summary, the friability profile method using the proposed apparatus was found to be valid. It could distinguish between primary and secondary attrition, it was repeatable, and friability data obtained was compatible with existing knowledge. Furthermore, the friability profile tests required little effort and were completed in less than 1 hour for raw limestones. Calcined limestone was successfully produced in-situ and tested within 2 hours of charging the limestone sample. In addition, the use of the constant velocity method provided a complementary measure of sorbent friability and allowed identification of the attrition mechanisms involved at the different gas velocities used.

**Evolution of Sorbent Friability with Cycling** The friability profile method was subsequently used to investigate the evolution of sorbent friability with cycling. Cycled sorbent samples, in their carbonated form, were prepared by subjecting raw limestones to one and six calcination/carbonation cycles in a bubbling fluid bed. The friability profiles of these carbonated sorbent samples, and their calcined counterparts (prepared in-situ) were then measured. In addition a sintered, calcined, sorbent sample was prepared by subjecting raw limestone to 940°C in the attrition tester for 20 hours to assess the effect of sintering on the friability of calcined sorbents.

![Figure 36. Friability profiles of calcined and carbonated samples with varying cycle number, as measured in the novel ICFB apparatus.](image)

Figure 36 plots the friability profiles obtained for all the sorbent samples tested, and a number of observations can be made regarding the results presented. First, the calcined forms of the sorbent were found to be more friable than the carbonated forms at all velocities tested. However, the difference between the friability of the carbonated and calcined sorbents varied with the gas velocity used. This
result underlines the importance of testing for attrition over a range of velocities when comparing sorbent friability.

Second, Figure 36 shows that the friability of calcined sorbents did not vary significantly with cycle number but was greatly increased by extended sintering. This new result suggests that, contrary to what might be expected, sintering of the sorbent actually decreases its mechanical resistance to impacts.

Third, the friability profiles of cycled carbonated sorbent samples exhibited threshold values at 8 m.s\(^{-1}\), despite containing large proportions of calcium oxide (30% CaO for one cycle and 80% CaO for six cycles). Both cycled carbonated sorbent samples were more friable than raw limestone but only at velocities near and above the threshold value (8 m.s\(^{-1}\)). Furthermore, there was no significant difference in friability between the cycled carbonated sorbent samples despite the large difference in the proportion of CaO.

The increased friability of cycled carbonated sorbents after one calcination/carbonation cycle was also observed by Scala et al., and explained by the core and shell structure of cycled carbonated sorbents. The core of such sorbents is composed of unreactive CaO while the shell is composed of CaCO\(_3\) (31). As discussed above, the impact velocity of the chipping mechanism is dependent on the composition of the particles’ surface. In the case of cycled carbonated sorbents, given that the shell is composed of CaCO\(_3\), the threshold value is similar to that of the raw limestone. However, once the threshold velocity is exceeded, cracks generated upon impact can propagate into the calcium oxide core of the particles; this leads to increased attrition compared to raw limestone at velocities above the threshold. The new result presented here demonstrates that the friability of carbonated sorbents was not affected by the ratio of core (CaO) to shell (CaCO\(_3\)), as seen in Figure 36, as both the once-cycled sorbent (70% CaCO\(_3\); 30% CaO) and the six-cycled sorbent (20% CaCO\(_3\); 80% CaO) have very similar friability profiles.

**Calcination Induced Attrition** The apparatus developed in this work was also used to investigate the friability of the sorbent samples during calcination, as opposed to the friability of the calcined sorbent samples after calcination. It was suggested in the literature (100) that transient phenomena occurring during calcination can be a source of additional attrition, e.g. transformations of the crystal lattice or local overpressures of CO\(_2\).

To achieve this, a raw limestone was charged in the apparatus at 940°C and circulated at 5.2 m.s\(^{-1}\) for 70 min, while the calcination reaction was taking place. The attrition rate measured was compared to that obtained when a calcined limestone sample was circulated at 5.2 m.s\(^{-1}\) after calcination was completed without any circulation, as described in the methods section.

There was no apparent difference between the two measured fine creation rates, at 0.95%.(10 min)\(^{-1}\) suggesting that the transient phenomena associated with calcination did not cause additional attrition.

**Discussion and Conclusion**

The proposed attrition testing apparatus was found to be a suitable tool for measuring the friability of Ca looping sorbents as well as for investigating the attrition mechanisms involved. The apparatus
developed fulfilled all the criteria required for a good friability testing method; it allowed for representative and repeatable multi-impact attrition tests at controlled gas velocities.

The attrition testing apparatus subjected the particles to mechanical stresses representative of stresses expected in fluid beds, see Figure 31; particle-particle impacts occurred when the sorbent sample was entrained from the reservoir, particle-wall impacts occurred when the particles were projected onto the vessel walls, as well as the abrasive mechanical stress typical of cyclones when particles were returned to the reservoir.

In addition, tests could be performed at temperatures typical of the Ca looping process (650–940°C) as well as during the Ca looping reactions, as discussed in the results section. The latter ability can be used to investigate attrition induced by the reactions themselves and was used here to show that the process of calcining the sorbent did not contribute to additional attrition.

The apparatus subjected the sample to repeated impacts due to continuous solid circulation and it was possible to discern between primary and secondary attrition. With the limestone used in this work, primary attrition was found to be very low – the elutriation rate stabilized after 0.5% of the sample had elutriated.

The apparatus was able to rapidly measure friability profiles (friability vs. velocity curves) of sorbent samples and identify velocity thresholds at which attrition mechanisms were activated. The importance of this aspect is clear when one considers the data presented in Figure 36; had the tests been performed at a constant velocity, e.g. 5, 7 or 9 m.s\(^{-1}\), different conclusions as to the relative friability would have been made. In addition the apparatus, using the constant velocity method, was used to identify the activation of the chipping attrition mechanism above the threshold gas velocities which were observed to be ≈8 m.s\(^{-1}\) for carbonated sorbents and ≈6.5 m.s\(^{-1}\) for calcined sorbents.

Using the prototype apparatus built during this study, the measurement of a single friability profile was achieved within only 2 hours, which allowed characterization of the evolution of sorbent friability during the first six calcination carbonation cycles within days. With the limestone used in this study (McDonalds agricultural limestone), it was found that the friability of calcined sorbent did not vary significantly with the cycle number while, in contrast, friability was greatly increased by extended sintering. The friability of recarbonated sorbents was independent of the extent of carbonation but was higher than that of raw limestone, see Figure 36.

However, the prototype apparatus used in this work did not allow measurement of the frequency of impacts and the actual impact velocities that the particles were subjected to. As a result, the numerical values obtained here, such as the threshold velocities, cannot be generalized. Only relative comparisons of sorbent friability can be made based on the results obtained with this prototype. For example, based on the results shown in Figure 36, it can be stated that extended sintering increased the friability of the calcined sorbent or that the friability of recarbonated sorbents is a little higher than that of raw limestone at high velocities. Further embodiments of this attrition testing apparatus should include a means of measuring particle impact velocities and frequency.
With further improvements, the proposed attrition testing apparatus concept could become an important tool for the development of Ca looping processes. Its ability to rapidly provide a full assessment of the friability of the many forms of Ca looping sorbents could be used to provide the information required for both the scientific and engineering aspects of the development of Ca looping processes.

For example, the use of this apparatus would have allowed clarification of the problems of anomalous behaviour of natural limestones discussed in the Introduction. In the case of the single impact tests (112), use of the apparatus presented here would have allowed comparing raw and calcined limestones on an equal basis by easily discerning between primary and secondary attrition and thus pointing to the origin of the anomalous behaviour. In the case of fluid beds (65,116), the friability of different limestones could have been compared over a range of velocities, thus allowing to test the hypothesis that the variation in behaviour is due to a reduced chipping threshold or establishing an optimal gas velocity to minimize sorbent friability and thus attrition.

The proposed attrition testing apparatus naturally has wider applications than those explored in this work. The prototype was designed to investigate the attrition behaviour of relatively large Ca looping sorbent particles (300–600 µm), elutriating fragments smaller than <125 µm in the 5–10 m.s⁻¹ gas velocity range. The operating parameters (gas velocity, sample particle size, elutriated particle size) of the apparatus can be modified by adjusting the diameters of the three tubes composing the apparatus, allowing the use of this attrition testing concept in any application involving the circulation of solid particles.

In the following sections, the newly developed attrition method is used to explore the effects of hydration based reactivation methods on sorbent friability. In section 3.2.2 this method is used to identify the cause of increased sorbent friability when the hydration dehydration method is used, while section 3.2.3 focuses on identifying which aspect of the superheating method allows avoiding this increase.

### 3.2.2 The Origin of Increased Sorbent Friability after Hydration-Dehydration

#### Introduction

As discussed in Chapter 1, one of the major limitations of all Ca Looping processes is the progressive decay in the CO₂ carrying capacity of Ca looping sorbents during cycling, i.e. repeated carbonation/calcination cycles. The CO₂ carrying capacity, or activity, of the sorbent rapidly decays over the first 10 Ca looping cycles, ultimately stabilizing at around 10–20% of its theoretical capacity (at 0.78 gCO₂·gCaO⁻¹). The sorbent is then said to be “spent”. The decay in sorbent activity has been attributed to progressive loss of suitable porosity via sintering which occurs when the sorbent is exposed to high temperatures (800-900°C) during every calcination step (30,31).

Although Ca Looping processes operating at such low activity levels were estimated to be cost effective (15,17,43), improvements in sorbent activity are nevertheless expected to considerably improve the economics of Ca Looping processes (53). A number of methods for increasing sorbent activity have been proposed in the open literature (115). These methods include using synthetic or modified CaO-based
sorbents instead of limestone, e.g. sorbents produced by pelletization (46), doping and precipitation (51,89), pre-treating limestone prior to cycling (e.g. by deep sintering (56)) and periodically reactivating spent sorbent after a number of carbonation/calcination cycles (e.g. by hydration (18,65) or CO₂ shocking (54).

This work focuses on steam hydration reactivation techniques which have been shown to be effective at restoring the activity of spent sorbents in a variety of conditions. Hydration with water vapour at room temperature was found to increase the activity of spent sorbent activity from ≈15% to 30–50% of the theoretical maximum for CaO (65,66), while Manović et al. have shown that spent sorbents, steam hydrated at 200°C, actually performed better over ten Ca looping cycles than the original limestone (117). In work completed prior to the start of this PhD programme, it was also shown by the authors and colleagues that steam hydration can be repeatedly used to restore sorbent activity both in bubbling beds and thermogravimetric apparatus (1,55).

The conventional reactivation technique consists of two steps (38). The first step consists of contacting the spent calcined sorbent (CaO) with water vapour to form a hydrated sorbent (Ca(OH)₂). The second step consists of dehydrating the Ca(OH)₂ formed in the first step, yielding a dehydrated sorbent (CaO) that is considerably more active than the spent calcined sorbent (CaO); the spent sorbent is then said to be reactivated and is used to perform more Ca looping cycles. This method is also referred to as the hydration-dehydration technique.

Hydrating and dehydrating the spent sorbent was found to restore some of the porosity lost during the initial Ca looping cycles and thus restore CO₂ carrying capacity. Water vapour is able to penetrate into the particles’ core, enabling high conversions to Ca(OH)₂ even with sintered and spent sorbents (38,117). The formation of Ca(OH)₂ leads to considerable expansion (38,55,66) of the particles due to its higher molar volume (Ca(OH)₂ – 33.1 cm³.mol⁻¹, CaO – 16.9 cm³.mol⁻¹). The expansion is not entirely reversible, so that the dehydrated sorbent (CaO) is considerably more porous and thus more active than the spent sorbent before reactivation. These aspects are discussed in detail in Section 2.1.

However, the hydration-dehydration reactivation technique was also reported to considerably increase the friability, or tendency to break, of the sorbent thus greatly limiting the practicality of this technique (1,66). Indeed, most proposed Ca looping processes involve circulating the sorbent between two fluid bed reactors (14) in which it is inevitably subjected to mechanical stresses eventually leading to the breakage, or attrition, of sorbent particles. In this context, a major increase in sorbent friability will lead to a major increase in sorbent attrition which is particularly nefarious for the operation of fluidized beds; the small fragments (fines) generated by attrition are usually lost by elutriation while the reduction in the size of the particles remaining in the system can profoundly modify the hydrodynamic behaviour of the fluid bed.

The extent of attrition induced by the conventional reactivation technique was measured by subjecting reactivated sorbents to Ca looping cycles in bubbling fluid beds (1,66). Even in those relatively gentle conditions a significant increase in attrition was observed after sorbent reactivation. Blamey et al. reported a five to tenfold increase in elutriation over 13 cycles after reactivating the sorbent by
hydration at room temperature (66). In preliminary work, the author and colleagues reported a threefold increase in the rate of fines creation over 19 Ca looping cycles (1), where the sorbent was reactivated in the bubbling bed every three cycles by steam hydration at 300°C.

Thus, the advantage gained by increasing sorbent activity via the conventional reactivation technique appears to be negated by the increased friability of the conventionally reactivated sorbent. However, the mechanism by which sorbent friability is increased during reactivation by hydration-dehydration is not well understood which limits the ability of remediating this problem.

Understanding exactly how conventional reactivation increases sorbent friability could lead to production of a non-friable reactivated sorbent or improving existing ways of doing so, such as the superheating reactivation method (1).

Unfortunately, relevant experimental data is scarce and limited in scope. The friability of the reactivated sorbent has so far been evaluated in only two different studies (1,66) by measuring the amount of fines generated when it is subjected to Ca looping cycles in a bubbling bed. This measurement method is not well adapted to the problem at hand; for example, it was not possible to say at which point the sorbent friability increased and which attrition mechanisms were responsible for the increased attrition.

As a result, explanations proposed so far are not well experimentally supported. Both existing studies attributed increased friability of the reactivated sorbent to particle strains and cracks created during hydration, suggesting that dehydration and superheating would relieve these stresses. Yet, no measurement of the friability of the hydrated or dehydrated sorbent has been reported.

The first step in understanding the cause of attrition increase is thus to provide a more comprehensive set of experimental data on the evolution of sorbent friability during and after the reactivation step, which is the objective of this work.

In this work, the friability profiles of a hydrated and a dehydrated sorbent were measured to establish at which step the increased friability appeared. Furthermore, the friability of sorbents reactivated by the conventional and superheated technique was also measured and compared to that of an un-reactivated sorbent. Dominant attrition mechanisms were established in all cases.

This work focused on identifying the step at which sorbent friability was increased and the mechanism by which increased attrition occurs. These results allowed testing the existing hypothesis, which was found to be incomplete. A new hypothesis was proposed that takes into account new evidence brought to light by the experiments carried out in this work.

Materials and Methods

Sample Preparation High purity limestone (>96% CaCO₃) from Te Kuiti was supplied by McDonald’s Agricultural Lime. A bubbling fluid bed was used to prepare sorbent samples for attrition tests, starting with 1.2 kg batches of raw limestone and using the conditions summarized in Table 11. Figure 37 illustrates the preparation pathways for all samples tested in this work as well as the names used to refer to them.
An un-reactivated sorbent was produced by subjecting limestone to six calcination/carbonation cycles in the bubbling bed; TGA analysis showed that this sample contained 17% of CaCO$_3$ in CaO.

A hydrated sorbent was made by producing un-reactivated sorbent as above, but replacing the final carbonation with steam hydration at 250°C in 25% H$_2$O in N$_2$; TGA analysis indicated that this sample contained 92% of Ca(OH)$_2$ in CaO.

A superheated sorbent was produced by preparing a hydrated sorbent as above and then heating it to 500°C under 100% CO$_2$ and holding it at that temperature for 25 min. At the end of the hold time at 500°C, CO$_2$ was replaced by air which leads to the dehydration of the “superheated” Ca(OH)$_2$, i.e. the fraction of the superheated sorbent that remained in the Ca(OH)$_2$ form despite being heated to temperatures above the normal decomposition point of Ca(OH)$_2$. Carbonation also occurred during superheating, as TGA analyses showed that this sample contained 56% CaCO$_3$ in CaO.

In all cases, gas flow was sufficient to ensure fluidization of sorbent particles throughout the production process. Upon discharging from the bubbling bed, sorbent particles were sieved and only the 500–600 µm fraction was used for attrition testing.

Furthermore, the attrition testing apparatus, described below, was used for further conversions of the three samples produced in the bubbling bed. 25 g of the sample were charged in the attrition tester and calcination, carbonation and dehydration, as required, were performed in-situ and immediately prior to testing, using conditions described in Table 11.

\textbf{Table 11. Conditions used in the preparation of attrition testing samples. Note that since the bed was not actively cooled, exothermic reactions (hydration, carbonation) raised the bed temperature.}

<table>
<thead>
<tr>
<th>Bubbling bed conversions</th>
<th>Attrition tester conversions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td><strong>Calcination</strong></td>
</tr>
<tr>
<td></td>
<td>870–900</td>
</tr>
<tr>
<td><strong>Gas composition</strong></td>
<td>Air</td>
</tr>
<tr>
<td><strong>Time (min)</strong></td>
<td>80</td>
</tr>
</tbody>
</table>

\textbf{Figure 37. Schematic of the samples tested for friability in this work and methods of preparation.}
**Apparatus** The Internal Circulating Fluid Bed (ICFB) apparatus, described in section 3.2.1, was used for attrition testing in this study. The operating principle of the proposed apparatus is illustrated in Figure 31. Sample particles are continuously aspirated from the bottom of a reservoir, entrained along a central tube and projected tangentially against a circular wall. Upon impact, large particles return to the top of the reservoir by spiralling downwards against the circular wall (similarly to what occurs in a cyclone) while small fragments generated are entrained and elutriated out of the bed and captured in the settling pot. This apparatus is illustrated in Figure 31b in section 3.2.1.

Sorbent friability can be simply evaluated by measuring the mass of elutriated fragments, while particles returning to the reservoir are re-circulated, i.e. repeatedly impacted against the circular wall. The temperature and atmosphere in the apparatus can be set by controlling the furnace temperature and changing the supply gas composition.

**Method** Only the friability profile method, described in detail in section 3.2.1 was used in this study. After charging (and in-situ reactions where required), the sorbent samples were circulated at the lowest possible velocity (between 3–6 m.s\(^{-1}\)) for ten minutes in order to minimize the effect of primary attrition on the measurement. This procedure was skipped for the most fragile sorbents as it would result in the loss of a large proportion of sample before the start of the test. As in previous results, see Section 3.2.1, the extent of primary attrition, where measured, was negligible at ≈1%.

After primary attrition was complete, the samples were circulated in the apparatus for ten minute periods at increasing gas velocities. During this time, the vessel was periodically tapped to release the fines potentially stuck on the vessel walls. At the end of the ten minute period the circulation was stopped and the mass of particles elutriated was measured by weighing the tarred settling pot. Sorbent friability at a given gas velocity was evaluated by the percentage of mass elutriated in ten minutes.

At the end of the experiment, particles remaining in the vessel were discharged, mixed with those elutriated during the test (recovered from the settling pot) and sieved. Sieving allowed obtaining the particle size distribution (PSD) of the entire sample after the attrition test. The particle size distribution of the sample after test used to identify the attrition mechanisms present at a given gas velocity, using a probability density function (PDF) to express this distribution, as discussed in section 3.2.1, and shown in Figure 29. Note that in this work, the PSD of the sample was measured after attrition testing over a range of velocities while different attrition mechanisms were active. It can therefore be expected that the results obtained here will be a superposition of the typical PSD distributions depicted in Figure 29.

As discussed in section 3.2.1, the repeatability and robustness of the friability measurement method were found to be satisfactory and results obtained with raw and calcined limestone were in line with observations made in the literature. However, with the apparatus used here it was not possible to measure the particle impact velocity or frequency so that the numerical results obtained here cannot be easily extrapolated to other apparatus. However, general conclusions deriving from relative comparisons and analysis of attrition mechanisms remain valid.
Results

Attrition during Reactivation: Hydrated and Dehydrated Sorbents Sorbent friability was measured after each step of the conventional reactivation technique (hydration and dehydration) with the aim of identifying the step at which sorbent friability is increased and which mechanisms were responsible for the increased attrition.

The ICFB apparatus was used to measure the friability of a hydrated and dehydrated sorbent at 300°C over a range of velocities; Figure 37 illustrates the details of sample preparation. The test temperature of 300°C was chosen to ensure the stability of the hydrated sorbent. Figure 38a plots the elutriation vs. gas velocity curves, or friability profiles, generated during these experiments as well as the friability profile of a calcined limestone at 300°C for reference.

Figure 38. a) Mass elutriated during 10 minutes of circulation in the ICFB apparatus at 300°C as a function of gas velocity for hydrated and dehydrated sorbents as well as a calcined limestone measured at b) Particle size distribution of samples after the test. Figure 37 shows details on sample preparation.

Figure 38a shows that at all velocities tested in this work the order of sorbent friability could be stated as dehydrated ≥ hydrated ≥ calcined. However, the relative difference in sorbent friability varied greatly in the velocity range tested, in particular when the velocity exceeded 5 m.s⁻¹, above which the mass elutriated increased rapidly with velocity for the dehydrated sorbent and calcined limestone. Note that the hydrated sorbent did not present such sudden changes over the range of velocities tested.

Threshold velocities in friability profiles are usually associated with the activation of a new attrition mechanism such as those presented in Figure 29 in section 3.2.1. In this case, the threshold velocity observed in Figure 38a was attributed to the activation of the chipping mechanism, which can be deduced from the analysis of PSD data of the samples after attrition testing, plotted in Figure 38b.

In the case of both calcined and dehydrated sorbents, the most common fragment size generated during the test was 80–125 µm; such fragments are typically produced by the chipping attrition mechanism, as defined here and shown in Figure 29. Given that the vast majority of fragments were created at velocities above the threshold, Figure 38a, and that the largest proportion of fragments resulted from chipping, it can be deduced that the threshold velocity is that of the activation of the chipping mechanism. This is particularly apparent in the case of the dehydrated sorbent where the high proportion of chipping fragments (80–125 µm) is consistent with a remarkable increase in friability above the velocity threshold.
This explanation also corresponds well with previous observations that the appearance of the chipping mechanism was observed at 6.5 m.s\(^{-1}\) for calcined limestone tested at 650°C, see section 3.2.1.

In the case of the hydrated sorbent, fragments generated were in a more broad size range (0–150 µm), with a peak size below 85 µm. Very small fragments are typically generated by the abrasion mechanism, although the breadth of the peak is indicative of the presence of other mechanisms such as chipping or disintegration in a smaller proportion. The lack of sudden changes in the hydrated sorbent’s friability profile coupled with these observations suggests that the hydrated sorbent was largely attrited by abrasion over the entire velocity range tested.

In summary, the hydrated sorbent was found to be more friable than its parent calcined limestone. However, this difference in friability reduced with increasing velocity as the calcined limestone started chipping while the hydrated sorbent did not, see Figure 38a. In contrast, the dehydrated sorbent was found to be the most friable sorbent form. It was found to be remarkably prone to attrition via chipping above the threshold velocity (5 m.s\(^{-1}\)).

It can be said that sorbent friability was greatly increased during the dehydration step leading to increased attrition via the chipping mechanism above the chipping threshold velocity.

**Friability of Conventionally Reactivated Sorbents** The friability profiles of conventionally reactivated sorbent samples were measured and compared with that of superheated and un-reactivated sorbent samples. Both forms of reactivated sorbent (calcined and carbonated) were tested and compared separately to their unreacted and superheated counterparts, to allow valid comparisons. The objective was to establish whether the increased friability appearing during the dehydration step is transmitted to the reactivated sorbent in either form.

**Reactivated Carbonated Sorbents** The friability profiles of conventionally reactivated carbonated sorbent samples were measured at 650°C and compared to that of un-reactivated and superheated carbonated sorbents as well as raw limestone, for reference. Figure 39a plots the friability profiles obtained while Figure 39b plots the PSD data of the sample measured after completion of the friability tests. Details about sample preparation can be found in Figure 37.

![Figure 39](image)

**Figure 39.** *a) Friability profiles of various carbonated sorbent samples as well as raw limestone measured at 650°C b) Particle size distribution of sorbent samples after the test. Figure 37 shows details on sample preparation.*
Figure 39a illustrates that the conventionally reactivated carbonated sorbent was more friable at all velocities tested than both the un-reactivated and superheated carbonates, resulting in a two to six-fold increase in elutiated mass throughout the velocity range tested. In contrast, the un-reactivated and superheated sorbent samples were similarly friable and exhibited a threshold velocity at 8 m.s\(^{-1}\), which was previously attributed to the activation of the chipping mechanism as seen in section 3.2.1.

The PSD data presented in Figure 39b suggest that the conventionally reactivated carbonated sorbent was considerably more prone to attrition by chipping, as illustrated by the large proportion of chipping fragments (80–150 µm). The absence of a threshold velocity in the friability profile, Figure 38a, suggests that the chipping mechanism was active throughout the range of velocities tested. In contrast, both the un-reactivated and superheated carbonates present a PSD with a considerably lower proportion of chipping fragments.

**Reactivated Calcined Sorbents** The friability of the conventionally reactivated calcined sorbent samples was measured at 650°C over a range of velocities and compared to that of un-reactivated and superheated calcined sorbents as well as that of calcined limestone, for reference. In addition, the effect of extended sintering on sorbent friability was tested by calcining a conventionally reactivated sorbent sample in-situ at 940°C for 20h. Figure 34a plots the friability profiles obtained for these sorbents as well as the friability profile of the dehydrated sorbent measured at 650°C, for reference. Details on sample preparation can be found in Figure 37.

As shown in Figure 40a, the reactivated calcined sorbent was found to be more friable than both the cycled and superheated calcines at all velocities resulting in a two- to five-fold increase in elutriated mass. The friability of the reactivated calcined sorbent sample (CaO) was found to be comparable to that of its parent dehydrated sorbent (also CaO). Thus, carbonating and calcining the dehydrated sorbent did not lead to any strengthening effect as might have been expected. Furthermore, extended sintering did not strengthen the sorbent either and instead led to a significant increase in the friability of the reactivated calcined sorbent (Figure 40).

Examination of the PSD data presented in Figure 40b indicates that chipping was the principal attrition mechanism for the conventionally reactivated and sintered calcined sorbent samples. It can be
concluded that the tendency of the dehydrated sorbent to attrite by chipping has been “transmitted” to the calcined reactivated sorbent and that sintering enhances this tendency further.

Surprisingly, despite a considerably lower overall friability, the PSD of the superheated oxide after the test suggest that some chipping might have taken place resulting in a high proportion of fragments in a narrow range (85-115 µm). In addition, large fragments (250-300 µm) were observed suggesting that some splitting had taken place during the attrition test. These results suggest that some weakening might also be introduced during superheating, possibly in the proportion of Ca(OH)$_2$ that is dehydrated to CaO.

In summary, both the carbonated and calcined forms of the conventionally reactivated sorbent were found to be prone to chipping and as a consequence, were more friable than their un-reactivated counterparts. It can be said that the tendency to attrite by chipping, which appeared after the dehydration step, was transmitted to the conventionally reactivated sorbent. The observation that sintering led to an increase in sorbent friability suggests that the further carbonation/calcination cycles are not likely to remediate this problem.

**Comparison of Reactivation Techniques** The friability profile data presented in the previous sections are re-plotted in Figure 41 to facilitate the comparison of the friability of un-reactivated, conventionally reactivated and superheated sorbents.

While the conventionally reactivated sorbent in both forms is considerably weaker than its un-reactivated and superheated counterparts, it is the calcined form that is remarkably more friable. In contrast, the friability of superheated sorbents was comparable to that of the un-reactivated sorbents, with only a moderate friability increase observed in the case of the calcined superheated sorbent. In all cases, however, the carbonated form of the sorbents was less friable than the calcined form.

![Figure 41](image.png)

**Figure 41.** Comparison of friability profiles for samples of a conventionally reactivated sorbent, a superheated sorbent and an un-reactivated sorbent in both calcined (circles) and carbonated (triangles) forms. Figure 37 shows details on sample preparation.
Discussion and Conclusions

As previously observed, the conventionally reactivated sorbent was found to be more friable than the un-reactivated sorbent in this work. In addition, the methodology used in this work has allowed gathering a much more detailed set of experimental observations, which can be used to formulate an explanation as to the origin of increased friability of conventionally reactivated sorbents.

It was established that the friability of both forms of the sorbent (calcined and carbonated) was affected by the reactivation process, as both the reactivated calcined and carbonated sorbents were found to be more friable than their un-reactivated counterpart, as seen in Figure 39a and Figure 40a. However, reactivation did not affect the relative friability of sorbent forms, i.e. the reactivated carbonated sorbent remained stronger than the reactivated calcined sorbent, compare Figure 39a and Figure 40a.

The reactivation process was also found to increase the sorbent’s tendency to attrite via the chipping mechanism. With both forms of the reactivated sorbent, the chipping mechanism was activated at ≈5 m.s⁻¹ while for their un-reactivated counterparts, chipping was not observed until 6.5 m.s⁻¹ (calcined) and 8 m.s⁻¹ (carbonated), as shown in Figure 39a,b and Figure 40a,b.

The intensity of the chipping mechanism was also increased for both forms of the conventionally reactivated sorbent, since the large majority of fragments created during the attrition tests were found to be the products of chipping (85–115 µm) for both forms of the conventionally reactivated sorbents, compare Figure 39b and Figure 40b.

The increased tendency to chip, characteristic of the conventionally reactivated sorbent, was first detected after the dehydration step (Figure 38a,b). The dehydrated sorbent, although composed of CaO, was found to be considerably more prone to chipping than un-reactivated or superheated calcined sorbents which are also composed of CaO (Figure 40a,b).

In contrast, the hydrated sorbent was not prone to chipping. It was found to mostly attrite by abrasion and the chipping threshold velocity was not observed at the velocities tested (Figure 38a,b). This data can also be used to disprove the hypothesis proposed in the literature (1,66) that cracks and strains introduced in the particles by the hydration reaction are the cause of the increased friability of the conventionally reactivated sorbent.

According to this hypothesis, the hydrated sorbent is in a highly stressed state which can be relieved by dehydration or superheating. Results shown in Figure 38 are contrary to those predictions as the hydrated sorbent was only moderately more friable than calcined limestone and did not chip at any of the velocities tested while the calcined limestone started chipping at 5 m.s⁻¹. Furthermore, contrary to the prediction, dehydration led to an increase in sorbent friability and in particular to the increased tendency for chipping which was identified as the main pathway leading to the increased friability of conventionally reactivated sorbents.

The increased tendency to chip was not observed with the superheated sorbent, Figure 39b. The friability of both forms of the superheated sorbent was comparable to that of the un-reactivated sorbent, Figure 39a and Figure 40a. The contours of an alternative hypothesis can be drawn when one
considers that, during superheating, a large proportion (=50%) of the hydrated sorbent is directly carbonated, as discussed in Chapter 2, and therefore the weakened, dehydrated CaO is never formed.

It is here proposed that the increased friability of conventionally reactivated sorbent is in fact due to the formation of a “weakened” calcium oxide during the dehydration step of conventional reactivation. The nature of this “weakness” is such that further carbonation/calcination cycles or sintering are not able to remediate it. As a result, this “weakness” is transmitted to all sorbent forms deriving from the dehydrated sorbent, leading to increased friability of the reactivated sorbent long after the dehydration step was completed.

Although the nature of the “weakened” dehydrated CaO remains unclear, it could be postulated that its origin lies in the collapse and subsequent contraction of the calcium hydroxide grains to form dehydrated calcium oxide grains (Ca(OH)$_2$ 33.1 cm$^3$.mol$^{-1}$ vs. CaO 16.9 cm$^3$.mol$^{-1}$). This contraction could lead to the formation of intergranular cracks propagating into the particle core which would greatly facilitate the chipping mechanism. With a large network of pre-existing cracks, only a moderate energy impact would be sufficient to connect some of these cracks and induce attrition by chipping.

An immediate corollary of this hypothesis is that avoiding the dehydration step should lead to avoiding the increased tendency to chip and thus the friability increase. This was indeed observed in the case of the sorbent prepared by superheating, during which a large proportion (=50%) of the hydrated sorbent is directly carbonated and thus not dehydrated. The superheated sorbent exhibited similar friability levels compared to the un-reactivated sorbent and a considerably reduced tendency to chip compared to the conventionally reactivated sorbent, see Figure 32b and Figure 35.

However, the evidence presented here cannot rule out the possibility that superheated dehydration can lead to a less “weakened” calcium oxide since it occurs in different circumstances i.e. at a higher temperature than normal dehydration, as was suggested in the initial work on this topic by the author and colleagues (1).

Naturally, the hypothesis presented here is only speculative since the observations it is based upon have only been made with sorbents prepared from a single natural limestone. Further experiments should focus on establishing the generality of the observations made here with different starting limestones and particle sizes. Additionally, comparative structural analysis of calcined and dehydrated calcium oxide could provide insight into the origins of the “weakness” postulated in this work.

The following section focuses on establishing which aspect of the superheating method, i.e. direct carbonation or superheated annealing of Ca(OH)$_2$, affects the friability of the superheated sorbent most.
3.2.3 The Effect of Superheating Parameters on Sorbent Friability

Introduction
In the previous section, the increased friability of conventionally reactivated sorbents was attributed to the dehydration step, which introduced a structural “weakness” in the sorbent particles. Further Ca looping cycles or sintering could not remediate this issue and all subsequent sorbent forms were found to be very friable and prone to attrition by chipping.

However, when the freshly hydrated Ca(OH)\(_2\) was heated in CO\(_2\), i.e. superheated, no such weakening of the sorbent was observed. Clearly, some aspect of the superheating reactivation method allows avoiding the generation of this “weakness”.

In the previous section it was proposed that the direct carbonation of Ca(OH)\(_2\), which occurs during superheating, see Section 2.2.3, could allow avoiding the dehydration induced weakening. Indeed, it can be imagined that since a large proportion of Ca(OH)\(_2\) is directly carbonated during superheating, that proportion is effectively never dehydrated to form CaO so that the sorbent would be less weakened. If this hypothesis were correct it would be expected that the friability of superheated sorbents would depend on the extent of carbonation occurring during superheating.

An alternative explanation was also initially proposed by the author and colleagues (1), in which the absence of weakening was explained by the thermal treatment of superheated Ca(OH)\(_2\), which led to the annealing of cracks and defects generated during hydration (1). If this hypothesis was correct it would be expected that the friability of the superheated sorbent would depend on the amount of time spent annealing in the superheated state.

Some experimental evidence gathered during multi-cycle Ca looping runs in a bubbling fluid bed was presented in support of the latter hypothesis (1). However, this evidence is insufficient to distinguish between the two hypotheses presented here. Indeed, levels of carbonation achieved during superheating were not measured and the cyclic nature of these experiments makes it difficult to attribute the improvement in sorbent friability to a particular aspect of superheating.

In this study, the novel attrition testing method developed in section 3.2.1 was used to measure the friability profiles of a range of sorbents immediately after superheating. The superheating parameters were varied to achieve different carbonation levels and annealing times, thus allowing assessment of their effect on friability of superheated sorbents and distinguishing between the two hypotheses presented above.

Materials and Methods
Sample Preparation
A bubbling fluidized bed apparatus was used in this work to produce samples for attrition testing, starting with high purity calcitic raw limestone (>97% CaCO\(_3\)) with traces of quartz (≈2%) and iron oxide (≈0.2%) provided by Taylors Agricultural Lime Ltd.

Batches of 1.2 kg of raw limestone were calcined and then subjected to five more carbonation-calcination cycles. Calcination was carried out in air at 870–900°C for 80 min while carbonation was
carried out under 25% of CO$_2$ in air at 650–700°C for 20 min. After this initial cycling the calcined sorbent was hydrated in a gas flow containing 20% of H$_2$O in N$_2$ for 60 min. Based on previous experiments, see section 3.2.2, hydration conversions were expected to be above 92% using such conditions.

After hydration, samples were heated to either 410°C or 550°C in the presence of 100% CO$_2$, and annealed, i.e. held at that temperature for either 5 or 40 min. After reaching the desired temperature and end of the annealing period, CO$_2$ was replaced by a flow of air in order to trigger the dehydration reaction, see section 2.2.1. Note that when the lower temperature of 410°C was used the bed was further heated to 550°C after dehydration in order to accelerate the dehydration reaction.

Upon dehydration, the material was discharged from the reactor and its composition was tested by thermogravimetric analysis (TGA). The material was sieved and only the 500–600 µm fraction was used for attrition testing, with the friability profile method described in section 3.2.1. The primary attrition of superheated sorbent samples was evaluated and found to be low in all cases (<1%).

The naming system for samples prepared in this way and their composition as measured by TGA analysis is presented in Table 12. Note that the carbonation conversion of the samples heated to the same temperature was very similar, due to the unusual kinetic behaviour of the direct carbonation reaction of Ca(OH)$_2$ discussed in detail in section 2.2.3.

<table>
<thead>
<tr>
<th>Temperature/time</th>
<th>No annealing</th>
<th>40min annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>420°C</strong></td>
<td>Low C-N (19% CaCO$_3$)</td>
<td>Low C-A (15% CaCO$_3$)</td>
</tr>
<tr>
<td><strong>550°C</strong></td>
<td>High C-N (52% CaCO$_3$)</td>
<td>High C-A (54% CaCO$_3$)</td>
</tr>
</tbody>
</table>

The unusual temperature dependence of the direct carbonation of Ca(OH)$_2$ was exploited to prepare a set of sorbent samples with varying levels of carbonation conversion and annealing time during superheating. Indeed, due to this behaviour the carbonation level of the superheated sorbent remains stable during the annealing period and as a result, sorbent samples with similar carbonation levels but different annealing times can be produced. This method was found to be satisfactory, as samples heated to the same temperature had reached similar levels of carbonation regardless of the time spent annealing, as shown in Table 12. However, this dependence also means the annealing temperature used and the carbonation levels are inseparable; these can only be varied by changing the porosity of the hydrated sorbent, see section 2.2.2.

This sample set was chosen to allow evaluation the separate effects of direct carbonation and annealing of superheated Ca(OH)$_2$ on the friability of the superheated sorbent. Indeed, comparing the friability of superheated sorbents with similar carbonation levels (Low C-N vs. Low C-A and High C-A vs. High C-N) but using different annealing times allows assessment of the effect of annealing at different
temperatures. On the other hand, comparing samples with an identical annealing time (Low C-N vs. High C-N and High C-A vs. Low C-A) allows the assessment of the effect of direct Ca(OH)$_2$ carbonation.

**Results**

Figure 42a presents the friability profiles of superheated carbonates with different carbonation levels and annealing times, as discussed above. The friability profile of the raw limestone used to prepare these samples is also plotted for reference. Figure 42b illustrates the particle size distribution of the samples after the attrition test and allows identification of the dominant attrition mechanisms involved, as discussed in sections 3.2.1 and 3.2.2.

![Figure 42. a) Friability profiles of different superheated carbonates b) Particle size distribution of samples after the test.](image)

As with the results obtained in previous sections, the friability profiles of all measured sorbent samples also exhibited a threshold velocity, at $\approx 7.5 \text{ m.s}^{-1}$, above which the elutriation rate rapidly increased. In previous sections (3.2.1 and 3.2.2) it was shown that this threshold velocity corresponds to the activation of the chipping attrition mechanism.

However, the threshold value of the raw limestone used here ($7.5 \text{ m.s}^{-1}$) is somewhat lower than that measured for the raw limestone used in previous sections ($8 \text{ m.s}^{-1}$). In addition, in the raw limestone used in this section the measured elutriation rates were found to be considerably lower than those measured for samples of raw limestone from the previous sections. The limestone came from the same quarry, but from a different bag of limestone. The measurements were repeatable, suggesting that there can be considerable variation in the friability of limestone within a single quarry site. This is understandable considering that limestone forms in a given site over geological time periods and that limestone microstructure can vary considerably even within the same quarry (113) which could have a considerable effect on sorbent friability.

Nevertheless, all the samples prepared in this section were derived from the same batch of parent limestone so that the natural variations of limestone are not expected to affect the conclusions obtained by comparing the friability of these superheated sorbent samples.

Increasing the annealing time did not have a significant effect on the friability of the superheated sorbent, regardless of temperature/carbonation levels. Superheated sorbents with varying annealing time (Low C-A, Low C-N and High C-A, High C-N) exhibited very similar friability levels and velocity thresholds.
In contrast, increasing the carbonation level had a considerable effect on the friability of the superheated sorbent. Sorbents with a low level of direct carbonation (Low C-A, Low C-N) were found to be more friable than sorbents with a high level of direct carbonation (High C-A, High C-N) at velocities both below and above the threshold velocity, see Figure 42a. In addition, the threshold velocity was found to be reduced with the less carbonated samples (6.5 m.s\(^{-1}\)) when compared to the more carbonated samples or raw limestone (7.5 m.s\(^{-1}\)). Note, in addition, that the friability of superheated sorbents with high levels of direct carbonation was very similar to that of the raw limestones.

The PSD data presented in Figure 42b suggests that the carbonation level reached during heat-up also affected the dominant attrition mechanism during these tests. Samples with a low level of carbonation exhibited an increased tendency for chipping, illustrated by in increased proportion of fragments 80–120 µm. Such behaviour is typical for sorbents that have been “weakened” by the dehydration reaction, see section 3.2.2. In contrast, samples with a low level of carbonation exhibited a PSD profile similar to that obtained with un-reactivated sorbents, see section 3.2.1, suggesting that the direct carbonation of Ca(OH)\(_2\) allowed avoiding the weakness induced by the dehydration reaction. Annealing time was found to have little or no effect on the dominant attrition mechanisms, see Figure 42b.

**Discussion and Conclusion**

It can be concluded that annealing of superheated Ca(OH)\(_2\) is not the principal mechanism by which the dehydration-induced weakening of the sorbent is avoided during superheating. The results presented in this study clearly indicate that varying the annealing time did not have any noticeable effect on the friability of the superheated sorbent.

However, as discussed in the Introduction, there is evidence that time spent in the superheated state does affect sorbent attrition in bubbling fluid beds over a number of cycles (1). This observation suggests that there might be other mechanisms leading to increased attrition whose effects become apparent only with repeated hydration-superheating steps. For example, when subjected to repeated hydration-carbonation-calcination cycles the morphology of the particle was reported to evolve slowly to generate weakened, sponge-like structures after 55 cycles (55).

In regards to a single reactivation step, it can be said that the carbonation level achieved during superheating has a large effect on the friability of the superheated sorbent, Figure 42. When the carbonation level was high, no dehydration-induced weakening was observed, but when the carbonation level was low, the increased friability and tendency to chip typical of dehydration-induced weakening were observed.

This behaviour is specific to superheated sorbents as the level of carbonation does not have a strong effect on friability in un-reactivated sorbents. Indeed, the friability profiles of raw limestone (100% CaCO\(_3\)) and that of the cycled sorbent (20% CaCO\(_3\)) were very similar, see section 3.2.1

These observations support the hypothesis that the direct carbonation of Ca(OH)\(_2\) allows avoiding the formation of the dehydration-induced weakness in the sorbent particles. By converting Ca(OH)\(_2\) to CaCO\(_3\) without transition through dehydrated CaO, the superheating method avoids the dehydration-induced weakness.
At the moment of the trigger a proportion of the sorbent is effectively dehydrated, although it is done so at superheated temperatures. Although less likely, it could be imagined that the CaO formed by dehydration of Ca(OH)$_2$ at superheated temperatures is less weak than the normal dehydrated Ca(OH)$_2$. Due to the inherent coupling of temperature and carbonation levels it is difficult to separate these two parameters.

As proposed in the previous section, a detailed study of the microstructure of calcined and dehydrated CaO should be conducted to identify the structural causes for the increased friability. If these can be identified, the observation of the superheated sorbents microstructure should allow discerning between these two hypotheses.

In any case, it can be said that the maximizing the extent of direct carbonation of Ca(OH)$_2$ is likely to minimize the friability of the superheated sorbent, given that high carbonation levels during superheating also increase the activity of the sorbent, see Section 2.2.2. Thus, high levels of direct carbonation are desirable from a practical perspective as they improve sorbent performance from both the perspective of friability and activity.
3.3 Conclusions

Maintaining a low sorbent friability is one of the key parameters required for the successful operation of Ca looping systems (3), due to the widespread utilization of fluid bed technology in its application. Existing methods for measuring sorbent friability were found not to be well suited for the investigation of Ca looping sorbent friability.

A novel method for measuring friability using an internally circulating fluidized bed was developed during this work. This method combines the principal advantages of existing techniques: the ease of operation and sample preparation of fluid bed methods with the precise velocity control of impact plate apparatus.

A prototype apparatus was built to demonstrate the feasibility of this approach. It was found to be very practical and produce repeatable and meaningful results that were in line with literature reports, thus effectively validating this approach. Although the prototype built had a number of limitations, e.g. inability to precisely measure particle impact or frequency, the results obtained here are extremely encouraging for further development of this apparatus. Naturally, the applications of such a device extend far beyond the scope of Ca looping as it could be tailored to allow measuring the friability of other particles encountered in fluid bed reactors, e.g. cracking catalysts, sand in fluid bed combustors or O₂ carriers in chemical looping combustion processes.

This apparatus was used to investigate the friability of the sorbent during and after hydration-based reactivation methods, with the aim of understanding how the superheating reactivation technique allowed reactivating sorbents without compromising their friability.

It was observed that, contrary to existing hypotheses (1,66) the origin of increased friability of conventionally reactivated sorbents does not lie in the hydration step, as the hydrated sorbent was found not to be particularly friable. In contrast, once the sorbent was dehydrated, it became prone to chipping at low impact velocities and its friability was considerably increased. Further Ca looping cycles did not reduce the sorbent friability or tendency to chip and as a result, it was said that the dehydration reaction introduced a structural “weakness” into the sorbent.

A possible explanation for the microstructural nature of this weakening was proposed. Namely, dehydration is accompanied by substantial contraction of the crystal structure (CaO – 18 cm³.mol⁻¹; Ca(OH)₂ – 37 cm³.mol⁻¹), which could lead to the formation of intergranular cracks that propagate within the particles. Although there is no evidence for this explanation it can be used to explain the increased tendency for chipping of a dehydrated sorbent.

The observations made in this work were derived using one parent limestone only. Further studies should focus on repeating these experiments with several parent limestones in order to ensure the generality of these observations. In addition, comparative observations of dehydrated (weakened) and calcined (non-weakened) CaO, using SEM and XRD, could enable identifying the microstructural causes of the weakening and thus provide further insight into this issue.
A new hypothesis, using results obtained in Chapter 2, was formulated to explain the absence of weakening when the superheating technique is used. During superheating, a large proportion (≈50%) of Ca(OH)$_2$ is directly carbonated to CaCO$_3$, see Chapter 2, so that dehydration to CaO and thus sorbent weakening is avoided. This hypothesis is in contrast to the existing hypothesis (1), which claimed that the absence of weakening was due to the annealing of superheated Ca(OH)$_2$.

A series of experiments were conducted to discern between these two hypotheses and it was concluded that annealing did not play a significant role in reducing the dehydration-induced weakening, while the friability of the reactivated sorbent was directly related to the level of carbonation achieved during superheating. These results support the hypothesis that direct carbonation of Ca(OH)$_2$ is responsible for the absence of weakening during superheating.

Nevertheless, even during superheating a relatively large proportion of Ca(OH)$_2$ is ultimately dehydrated, albeit at higher temperatures than normal. The role of the dehydrated fraction of the superheated sorbent remains unclear, and further studies should focus on establishing if the dehydration process also weakens this fraction. If the origin of dehydration-induced weakening was identified, as discussed above, this could be simply established by SEM or XRD observations.
Chapter 4
Discussion and Conclusion

4.1 Introduction

At the outset of this work, an unusual chemical behaviour of \( \text{Ca(OH)}_2 \), called superheating, was identified as a promising route for the development of a new reactivation method for Ca looping sorbents (1). The primary advantage of this method is the ability to reactivate sorbents without compromising their mechanical strength, which typically occurs when conventional, hydration-based techniques are used (1,66). The successful development of such a reactivation method has the potential to enhance the economics of Ca looping processes in a range of energy conversion applications and thus contribute to meeting the energy challenges of industrial societies of the XXI century (3).

However, the existence and the potential of the superheating effect were demonstrated only very recently so that extremely little information about the nature and the causes of this effect were available at the outset of this work. This knowledge gap represented a major barrier to the development of a reactivation process based on \( \text{Ca(OH)}_2 \) superheating. The research work presented here aimed to fill this gap by exploring chemical and physical aspects of \( \text{Ca(OH)}_2 \) superheating in order to provide a foundation for further detailed mechanistic investigations and process development. In that respect, this work had both a practical and a theoretical aspect.

This thesis has presented a range of exploratory studies that have established the basic phenomenology of the superheating effect and have led to a considerable shift in the perception of its nature. Each study focussed on a particular aspect of the superheating phenomenon, with both practical and theoretical considerations, with the primary research questions formulated as follows:

A. Which key sorbent properties lead to observing the superheated dehydration effect?

B. What is the relationship between superheating and the carbonation of \( \text{Ca(OH)}_2 \)?

C. What is the relationship between superheating and the friability of the reactivated sorbent?

The results collected here have answered these questions and also allowed formulation of a range of testable hypotheses for further research work. The central tenet of these hypotheses is the existence of a direct carbonation mechanism of \( \text{Ca(OH)}_2 \) at high temperature, which has been used to explain the nature of the superheating effect and the mechanisms by which it improves sorbent activity and friability. In turn, this improved understanding allowed contemplation of basic design principles for the reactivation process and definition of avenues for further research required for the development of a practical reactivation method.
4.2 Key Findings

Key Sorbent Properties
The wide applicability of Ca(OH)$_2$ superheating was clearly established in this work as the superheated dehydration (SD) effect was observed with hydrated sorbents produced with a wide variety of different conditions from a range of parent limestones (Section 2.2.1). Typically, 30–40% of Ca(OH)$_2$ present in the sorbent would remain stable at temperatures up to 560°C, which is considerably above the normal dehydration temperature (355°C).

However, with some Ca(OH)$_2$ materials the superheated dehydration (SD) effect was not observed or was considerably reduced, e.g. with commercial Ca(OH)$_2$ or Ca(OH)$_2$ deriving from dolomitic limestones and extensively cycled sorbents. It was postulated that pore size distribution, and in particular the presence of large pores (>300 nm) in the sorbent, determines if the SD effect would be observed (Section 2.2.2).

This hypothesis could not be verified within the framework of this PhD programme because of instrumentation limitations, and this should be the focus of further experimental work. Nevertheless, this hypothesis is compatible with reported literature data and provides an explanation for the evolution of the extent of SD during repeated reactivation by superheating.

Carbonation and Superheating
The common characteristic of all non-SD Ca(OH)$_2$ materials was that they all achieved a high conversion to CaCO$_3$ when heated in the presence of CO$_2$. The causal relationship between high carbonation conversion and the absence of the SD effect was not clear: which is the consequence of the other?

A kinetic study of the reaction system revealed that in the presence of CO$_2$ the dehydration and carbonation reactions of Ca(OH)$_2$ were closely coupled. The dehydration of Ca(OH)$_2$ to CaO was found not to proceed independently in the presence of CO$_2$, even with non-SD Ca(OH)$_2$ materials. This result suggests the existence of a high temperature, direct, carbonation mechanism for Ca(OH)$_2$ in which CaO is not formed as an intermediary (Section 2.2.3). In this context, the absence of the SD effect with some sorbents can be understood as a result of their increased tendency to carbonate via this mechanism.

This direct carbonation mechanism of Ca(OH)$_2$ exhibited a particularly unusual kinetic behaviour. Carbonation conversion was independent of contact time and was found to depend on temperature only, at least within the reaction times tested (=4–6 hours). As a result of this, the composition of Ca(OH)$_2$, when heated in CO$_2$, could be expressed as a function of temperature only. The exact relationship between carbonation conversion and temperature was found to be related to the pore size distribution of the sample (Section 2.2.3). The carbonation conversion achieved at 420°C was found to be dependent on the available porosity in the 0–300 nm pore size range diameters, while carbonation conversion achieved above 420°C appeared dependent on sorbent porosity >300 nm.

Superheating and Friability
To allow investigation of the relationship between superheating and sorbent friability, a new attrition testing method was developed and validated in this work (Section 3.2.1). This development was
required to overcome the limitations of existing methods which were time-consuming and limited the feasibility of comprehensive studies on the friability of Ca looping sorbents.

Using this novel method it was established that, during the conventional reactivation process, sorbent friability was first increased after the dehydration step. This friability increase manifested as an increased tendency for chipping of the sorbent at low impact velocities (Section 3.2.2). No further treatment was able to restore sorbent friability to pre-reactivation levels, so it was concluded that the dehydration step induced a structural weakness into the sorbent particles. The increase in friability was attributed to the contraction of Ca(OH)$_2$ grains during dehydration although the microstructural origin of this induced weakening was not identified through experimentation.

In contrast, superheated sorbents exhibited only a moderate increase in friability compared to pre-reactivation levels, even at high impact velocities (Section 3.2.2). It was observed that the extent of direct carbonation that occurred during superheating was the key parameter affecting the friability of the superheated sorbent, as opposed to previous assertions that claimed annealing in the superheated state was essential to reduce sorbent friability (Section 3.2.3).

4.3 Implications and Outlook

Theoretical Implications

The key discovery presented in this thesis is the existence of a high temperature direct carbonation mechanism of Ca(OH)$_2$ (Section 2.2.3). While the possibility of carbonating Ca(OH)$_2$ at elevated temperatures and in the absence of humidity had been reported earlier, see section 2.1, this work has greatly extended knowledge in this area and has identified a range of anomalies deserving further investigation.

First, it was observed that carbonation and superheating of Ca(OH)$_2$ at high temperature were two inseparable phenomena that occur with all materials tested in different proportions. It was therefore concluded that Ca(OH)$_2$ superheating is best understood as a side-effect or one of the anomalies of the high temperature carbonation mechanism. This discovery represents a major shift in perception from the starting point of this work, when the increase in the temperature of onset of dehydration to 620°C was the only definition of superheating. As a result, it was believed that only some Ca(OH)$_2$ sorbents could superheat (1,71), which was disproved in Section 2.2.3.

Another unusual property of this mechanism is the time-independence of the carbonation conversion and its relationship with the microstructure of Ca(OH)$_2$, see Section 2.2.3. This property suggests a complex and highly specific reaction mechanism that cannot be adequately described by typical solid gas reaction models, e.g. the shrinking core or the nucleation and growth models. To the author’s knowledge, such kinetic behaviour had not been so far reported for other solid-gas reactions.

It is clear that these unusual properties (superheating, reaction kinetics) represent essential clues to the nature of the high temperature carbonation mechanism under scrutiny. Drawing on existing literature and the results obtained here, a range of testable hypotheses were formulated in this work in order to explain these properties, and methods to test these hypotheses were also suggested (Section 2.3). This
outcome represents a considerable advance on knowledge at the outset of this work, when it was only possible to speculate about the origin of superheating and the existence of a high temperature carbonation mechanism for Ca(OH)$_2$ (71,90).

The direct carbonation of Ca(OH)$_2$ was found to play a central role in generating an active, non-friable sorbent which is the purpose of the superheating reactivation technique. Carbonating Ca(OH)$_2$ via this mechanism allowed conversion of a large proportion of the sorbent to CaCO$_3$, thereby bypassing the limitations associated with the carbonation of CaO (31). Achieving a high carbonation conversion during the superheating step automatically leads to the generation of an active sorbent, like what occurs in the “CO$_2$ shocking” approach (54) (Section 2.2.2).

In addition, it was postulated that the direct carbonation of Ca(OH)$_2$ at high temperatures allowed maintaining sorbent mechanical strength by avoiding the dehydration to CaO of a significant proportion of the hydrated sorbent. Indeed, the results presented here indicate that dehydration to CaO is the critical step that leads to the increased friability of conventionally reactivated sorbents (Section 3.2.2). However, the range of materials tested remains insufficient to generalize this conclusion to all hydrated sorbents and further work should focus on establishing the generality of this relationship.

This result is contrary to previous speculations (1,66) in which the hydration-induced particle expansion was claimed as the cause of the increased friability of the conventionally reactivated sorbent (1,66). Use of an improved methodology has enabled observation of the phenomena in finer detail and different conclusions from those presented in the literature. Indeed, the novel attrition method developed during this work has allowed collection of friability measurements of the sorbent after each step of the reactivation process, as opposed to previous measurements made after a number of Ca looping cycles (Section 3.2.2).

The research work presented here clearly represents a first step forward in expanding the knowledge about the chemistry of Ca(OH)$_2$ at high temperature. Further work is necessary to consolidate the findings on the chemical and physical aspects of Ca(OH)$_2$ superheating reported here. Further research should focus on testing the hypotheses regarding the mechanisms of superheating and carbonation of Ca(OH)$_2$ formulated in this work. The first difficulty in achieving this will be gaining access to appropriate equipment, e.g. a mercury porosimeter should be used to confirm the relationship between large pores carbonation/superheated dehydration; in-situ XRD or in-situ FTIR analyses should be carried out to test the hypotheses formulated in Chapter 3.

The postulated hypothesis regarding the friability of conventionally reactivated sorbents was confirmed for one type of sorbent only; its generality should be further explored by testing a wider range of hydrated sorbents derived from different natural limestones. Furthermore, an SEM survey of microstructural changes occurring during conventional and superheating reactivations is likely to provide insight into the mechanisms by which these reactivation techniques affect sorbent friability.

Finally, the similarities between Ca(OH)$_2$, Mg(OH)$_2$ and Al(OH)$_3$, in terms of structure and dehydration mechanism (79), suggest that other brucite materials could be susceptible to superheating and direct carbonation at temperatures above the normal dehydration temperature. While it is difficult to imagine
what practical applications this might have, it is certainly another interesting research area uncovered
by this work.

**Practical Considerations**

The wide applicability of the superheating phenomenon demonstrated in this work is encouraging for
the development of a practical reactivation process as it suggests that superheating can in theory be
achieved with hydrated sorbents derived from any calcitic limestones (Section 2.2.1).

As discussed above, the proportion of direct carbonation and superheated dehydration experienced by
hydrated sorbents when heated in \( \text{CO}_2 \) is dependent on the microstructure of the hydrated sorbent
rather than the conditions of superheating. Therefore, in order to be able to control the superheated
reactivation process it is essential to control the microstructure of the hydrated sorbent.

However, the microstructure of the hydrated sorbent is a result of a relatively large number of
parameters, many of which are outside the reactivation process itself and cannot be assumed to be
controllable by the reactivation process designer, e.g. particle size, type of limestone or the calcination
and carbonation conditions in the main Ca loop. From this analysis two principal design parameters that
can be controlled emerge: the frequency of reactivation and the hydration conditions.

As illustrated in section 2.2.3, varying these two parameters allowed control of the proportion of
carbonation and superheated dehydration observed upon heating in \( \text{CO}_2 \). Of these two parameters the
frequency of reactivation was found to be more important, as varying the hydration technique to modify
the proportion of \( \text{CaCO}_3 \) formed during superheating was found to be effective only on moderately
cycled sorbents (seven Ca looping cycles prior to reactivation).

Furthermore, the results obtained here suggest that achieving a high carbonation conversion during
superheating is desirable as it improves both the activity and the mechanical strength of the
superheated sorbent. However, some uncertainty remains in this regard as, in this work, the properties
of the superheated sorbent were measured after one superheating step only. It cannot be ruled out that
other mechanisms exist that become apparent only when the superheated technique is implemented on
a periodical basis, as was suggested in previous work on superheating (1,55).

Further work on the practical aspects of the superheating reactivation process should investigate the
evolution of sorbent properties with repeated reactivation by superheating. The focus should be on
establishing the optimal proportions of direct carbonation and superheated dehydration when
superheating reactivation is implemented on a periodic basis.

Although not strictly related to superheating, the feasibility of a new attrition testing method, capable of
producing meaningful friability data with comparatively little effort was demonstrated in this work. Such
a method clearly has the potential to introduce a step change in the field of attrition measurement for
particulate solids beyond the field of Ca looping. It is hoped that further development of this method
could lead to its acceptance by other research and industrial groups.
4.4 Final Remarks

The research work presented here has successfully developed the basic understanding of Ca(OH)$_2$ superheating required for further development of the superheating reactivation method. A considerable shift in perception has taken place during the course of this research as it became apparent that a new Ca(OH)$_2$ carbonation mechanism played a central role in the superheating reactivation method.

A range of promising research areas have opened as a result of this work, both from theoretical and practical perspectives. Further research on the detailed mechanism of the direct, high temperature carbonation of Ca(OH)$_2$ is of clear theoretical interest while the findings presented here represent important developments in the search for an economic method for the reactivation of Ca looping sorbents.
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Appendix 1 – Comparison between hydroxide materials

XRD comparisons

![XRD diffractogram of three different hydroxide powders. Black: McDonald's hydroxide. Red: Reference Hydroxide. Green: Hydroxide hydrated in 60% steam.](image)

The XRD diffractogram was consistent with the database diffractogram for portlandite i.e. Ca(OH)$_2$ (blue). A small proportion of calcite (red) was detected in the case of the McDonalds material, presumably due to carbonation occurring in air.

The integral Breadth of Ca(OH)$_2$ peaks were measured and the results are reported in the table below. It can be seen that the peaks corresponding to the (001), (011), (012), (111) were found to be broader in the case of the McDonalds and 60% steam hydroxide. These results suggest a smaller crystallite size for these materials, although peak broadening could be due to other effects i.e. strain or instrumental broadening.

<table>
<thead>
<tr>
<th>Peak</th>
<th>McDonalds</th>
<th>Reference</th>
<th>60% steam</th>
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<tr>
<td>(001)</td>
<td>0.55</td>
<td>0.39</td>
<td>0.43</td>
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<tr>
<td>(011)</td>
<td>0.62</td>
<td>0.45</td>
<td>0.64</td>
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<tr>
<td>(012)</td>
<td>0.73</td>
<td>0.6</td>
<td>0.77</td>
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<tr>
<td>(110)</td>
<td>0.44</td>
<td>0.42</td>
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<tr>
<td>(111)</td>
<td>0.57</td>
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FTIR Comparisons


All three spectra present a similar structure, with a principal peak at 3641 cm\(^{-1}\) and smaller peaks at 3931, 3784, 3722 and 3300 cm\(^{-1}\). There are some differences in the finer structure of the spectra e.g. a small peak at 3695 cm\(^{-1}\) is observed only with the commercial hydroxide while the shoulder at 3664 cm\(^{-1}\) is present with the two prepared hydroxides but not the commercial material. However these differences do not correlate well with the differences in superheating behaviour since both the commercial material (green) and the material hydrated in 60% steam exhibit no SD effect.
Appendix 2 – N₂ adsorption data

N₂ adsorption data, plotting the pore size distribution of sorbents with different cycling histories (1, 7, 37 Ca Looping cycles) and hydrated using different hydration techniques (saturated steam, unsaturated steam and water hydrated).

Cycled Sorbents (prior to hydration)

1 Cycle – Spent Sorbent

7 Cycles – Spent Sorbent
1 cycle - hydrated sorbents

1C - Saturated steam hydrated
1C - Unsaturated steam hydrated

1C - Water hydrated
7 cycle sorbents

7C - Saturated steam hydrated

7C - Unsaturated steam hydrated
37 cycle sorbents

7C – Water hydrated

37C – Saturated steam hydrated
37C – Saturated steam hydrated

37C – Water hydrated
Appendix 3 – The effect of additives on the temperature of Ca(OH)₂ dehydration

Introduction

It was postulated in Section 2.4 that the presence of proton donor species on the surface of Ca(OH)₂ could affect the temperature of dehydration. In order to test this possibility experiments were undertaken where Ca(OH)₂ was heated in the presence of a proton donor species (Boric Acid - H₃BO₃) and sodium hydroxide Na(OH) and the temperature of dehydration was determined.

Material and Methods

Samples of a commercial non-SD Ca(OH)₂ (McDonalds, see section 2.2.2) were intimately mixed with Boric Acid (H₃BO₃), a proton donor, or Na(OH), a proton acceptor species. The mixture was then heated inside a TGA apparatus to 500°C at 5°C under N₂. The temperature of the onset of dehydration was defined as the temperature at which the sorbent mass was first observed to reduce. The temperature at which the rate of dehydration became rapid and constant was also recorded, see figure below.

![TGA profile of the dehydration of Ca(OH)₂ with no additives. Pink : sample mass Blue : Temperature. The recorded temperatures are indicated 1: onset of dehydration 2: Rapid Dehydration](image)

In preliminary TGA experiments, boric acid was determined to be melted and in the form of H₃B₂O₇ up to 347°C, where it slowly started to lose more water and form B₂O₃. This was deduced from the weight change of the material, and the fact that it was melted was inferred from the appearance of the resulting material.

In preliminary TGA experiments sodium hydroxide was found to melt at 318°C and did not lose weight during the heat up.

Thus both proton donor and acceptor additives are expected to be liquid at the temperatures of dehydration (≈400°C). The amount of additive was chosen after several preliminary tests to give the best signal.
Results and Discussion

The results obtained are shown in the table below. It can be seen that the addition of Boric Acid, a proton donor lead to an increase in the both the temperature of onset of Ca(OH)$_2$ dehydration of (by 80°C) and the beginning of the rapid dehydration phase (by 45°C) . In contrast the addition of sodium hydroxide, Na(OH), did not significantly affect the temperature of onset of Ca(OH)$_2$ dehydration but lead to a reduction in the temperature of the beginning of the rapid dehydration phase.

<table>
<thead>
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<th>Recorded temperatures of dehydration with different additives.</th>
<th>onset of dehydration</th>
<th>rapid dehydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>No addition</td>
<td>329°C</td>
<td>396°C</td>
</tr>
<tr>
<td>50% Boric</td>
<td>409°C</td>
<td>440°C</td>
</tr>
<tr>
<td>18% NaOH</td>
<td>326°C</td>
<td>362°C</td>
</tr>
</tbody>
</table>

It seems likely that the presence of a molten salt such as boric acid or sodium hydroxide can affect the kinetics of the dehydration reaction and thus lead to a modification of the onset temperature without exchanging protons with the sample. However, the different salts affect the temperature of dehydration in the opposite direction, i.e. boric acid, a proton donor increases it while sodium hydroxide, a proton acceptor decreases it in accordance of what was suggested in the literature (79,93).

Although the results presented here do not allow us to conclude unequivocally that proton exchange between the additives and Ca(OH)$_2$ is responsible for the modifications of the dehydration temperature, they lend some credibility to the proton donor hypothesis presented in Section 2.4.
Appendix 4 –Co-authorship Forms

Co-Authorship Form

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work.** Completed forms should be included in all copies of your thesis submitted for examination and library deposit (including digital deposit), following your thesis Acknowledgements.

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Results from Section 2.2.2 were published as:


| Nature of contribution by PhD candidate | Design of the experiments, analysis and interpretation of the data, preparation of the figures and the manuscript. |
| Extent of contribution by PhD candidate (%) | 75% |

**CO-AUTHORS**

<table>
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<tr>
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<tbody>
<tr>
<td>Margaret Hyland</td>
<td>supervision, discussion, advice</td>
</tr>
<tr>
<td>Mark Jones</td>
<td>supervision, discussion and advice</td>
</tr>
<tr>
<td>Bryan Northover</td>
<td>Execution of the experimental program</td>
</tr>
</tbody>
</table>

**Certification by Co-Authors**

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate’s contribution to this work, and the nature of the contribution of each of the co-authors; and
- in cases where the PhD candidate was the lead author of the work that the candidate wrote the text.

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<thead>
<tr>
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<tr>
<td>Margaret Hyland</td>
<td>[Signature]</td>
<td>1/05/2014</td>
</tr>
<tr>
<td>Mark Jones</td>
<td>[Signature]</td>
<td>1/05/2014</td>
</tr>
<tr>
<td>Bryan Northover</td>
<td>[Signature]</td>
<td>22/04/2014</td>
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</tr>
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<tbody>
<tr>
<td>A large part of section 2.2.4 was published in 2011 as an article in Industrial and Engineering Chemical Research as an article entitled &quot;High Temperature Carbonation of Ca(OH)2&quot;</td>
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<table>
<thead>
<tr>
<th>Nature of contribution by PhD candidate</th>
<th>Design and execution of the experiments, lead in the writing of article.</th>
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<tr>
<td>Extent of contribution by PhD candidate (%)</td>
<td>70%</td>
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<tr>
<th>Name</th>
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<tr>
<td>Stuart I. Smedley</td>
<td>Assistance in writing</td>
</tr>
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**Name**

- Stuart I. Smedley

**Signature**

- [Signature]

**Date**

- June 17, 2013
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Results from Section 3.2.1 were published as: Materić V.; Holt R.; Hyland M.M.; Jones M.I., An internally circulating fluid bed for attrition testing of Ca looping sorbents Fuel 127, p.116-123, 2013.

<table>
<thead>
<tr>
<th>Nature of contribution by PhD candidate</th>
<th>Design and execution of the experiments, analysis and interpretation of the data, preparation of the figures and the manuscript.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of contribution by PhD candidate (%)</td>
<td>85%</td>
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</table>

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<tr>
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Results from Section 3.2.2 were published as: Matic V.; Hyland M.M.; Jones M.I.; Holt R. Investigation of the friability of Ca looping sorbents during and after hydration based reactivation, Fuel 127, p.70-77, 2013

**Nature of contribution by PhD candidate**
Design of the experiments, analysis and interpretation of the data, preparation of the figures and the manuscript.

**Extent of contribution by PhD candidate (%)**
90%

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