Reactivation Mechanism Studies on Calcium-Based Sorbents and its Applications for Clean Fossil Energy Conversion Systems

DISSERTATION

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By

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Abstract

As our nation moves to increase the usage of hydrogen as an energy carrier, the ability to produce hydrogen as a primary product will depend on new technologies that will provide greater efficiency and lower overall cost. In addition, the ability to use America’s most abundant energy resource, coal, as the source for hydrogen production will become extremely important as moving towards more energy self-sufficient. Moreover, the growing interest in finding ways to provide with lower emissions of greenhouse gases, in particular carbon dioxide makes a technology such as Calcium-Based Looping technologies for hydrogen production well suited to further investigation and demonstration, because it generates a nearly pure, sequestration-ready CO₂ stream while capturing sulfur impurities. With the potential for capturing CO₂ and sulfur, while simultaneously producing high purity hydrogen at a very high efficiency from the input coal feedstock, this process translates to an attractive technology to pursue further.

Limestone is abundant and cheap materials and calcium oxide (CaO) derived from naturally-occurring limestone are microporous in nature. However, due to the high calcination temperature, pore filling and pore closure of the sorbents limit the CO₂ sorption capacity for long term uses. To date, steam/water hydration is found to be capable of
restoring the reactivity and durability of calcium-based sorbents for multiple calcination-carbonation reaction cycles. The calcination-hydration-carbonation scheme has been demonstrated successfully using calcium-based sorbents for multiple cycle operation at the 120 kWth coal combustion facility based on the Calcination-Carbonation Reaction (CCR) process. This thesis is intended to systematically explore the fundamental mechanism underlining reactivation of calcium-based sorbents through hydration with water. The CO$_2$ sorption characteristics of calcium-based sorbents before and after the hydration, from a given calcination condition, are examined using a Thermogravimetric Analyzer (TGA). Further, the changes in morphological properties of calcium-based sorbents are characterized by Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). It is found that the hydration changes not only the macrostructure of calcium-based sorbents but also their microstructure. CaO sorbents with a higher surface area, a higher pore volume and a predominantly mesoporous structure are obtained after the hydration. The concentrations of a CaO (111) plane and a CaO (100) plane of CaO sorbents are found to increase simultaneously after the hydration. The changes in sorbent properties at both macroscopic and microscopic levels are considered to be responsible ultimately for the superior and sustained activities of the sorbents for the CO$_2$ capture.
The influence of reactivation by hydration on the performance of a high-purity limestone during the CO$_2$ capture cycle is further investigated in the study. Of particular interest is the variation of the microstructural properties for CaO obtained from hydrated lime. A density functional theory (DFT) calculation to illustrate the behavior of CO$_2$ adsorption on the CaO surface is conducted. Three dominating planes of the CaO surface, i.e. CaO (100), CaO (110) and CaO (111), are considered in the calculation. It is shown that the most stable adsorption configuration on a given surface for CO$_2$ molecules is that the adsorption takes place with the C atom of CO$_2$ molecules adsorbed on the O lattice sites of CaO with the O atom of CO$_2$ molecules pointed to the Ca atoms of CaO. That is, the CO$_2$ molecule does not adsorb either via the O atom of CO$_2$ molecules or on the Ca sites of CaO. Further, the results show that the CO$_2$ adsorption is more favorable on a CaO (100) surface and a CaO (111) surface compared to a CaO (110) surface based on their corresponding adsorption energy. These calculation results are consistent with the experimental XRD studies.

Besides, the high-pressure carbonation kinetics of calcium oxide (CaO) derived from three calcium-based sorbents, i.e. limestone (CaCO$_3$), calcium hydroxide (Ca(OH)$_2$) and Precipitated Calcium Carbonate (PCC), being used in the Calcium Looping Process (CLP) system, were studied using a Magnetic Suspension Balance (MSB) analyzer.
Different total pressures (1000~15000 torrs) and concentrations of CO$_2$ (10~30\%) were tested to determine their effects on the carbonation reaction rate. The carbonation reaction rate was found to increase with an increase in the concentrations of CO$_2$ at a constant total pressure. However, the total pressure has an effect on the carbonation reaction rate only at lower pressures. With a 20\% CO$_2$ stream, the reaction rate was observed to increase until the pressure reached 4000 torrs but after that an increase in total pressures has a negligible effect on the rate of carbonation reaction of CaO derived from all three precursors. Further, the carbonation reaction has a different reaction order with respect to the partial pressure of CO$_2$. It was found that the reaction is first-order at lower CO$_2$ partial pressures but changes to zero-order when the CO$_2$ partial pressure exceeds 800 torrs. In addition, the reaction rate of the carbonation conducted at high pressures is greater as compared to that at atmospheric pressure, under cyclic testing. The results also showed that there is no significant difference in the behavior of the carbonation reaction of CaO at elevated pressures regardless of different precursors.
This document is dedicated to my family and friends whom I love.
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CHAPTER 1

Towards Zero or Negative Emission Carbonaceous Fuel Conversions –
A Review on the Activation Strategies for Calcium-Based CO₂ Sorbents

1.1. Introduction

Energy, the power that sustains the human civilization and the impetus that advances the technological development, is still one of the most significant topics in the 21st century. Prior to the 18th century, use of energy was constrained into limited applications such as residential heating and cooking, ancient metallurgical activities, and etc. Due to the lack of advanced mining and energy conversion technology as well as sophisticated practical needs, energy was primarily obtained from naturally-available sources with or without preliminary pretreatment, and global energy consumption was at negligible levels compared with today ¹. However, the UK-oriented Industrial Revolution stormed the entire world, which gradually transformed the traditional small-scale manual-labor-based and draft-animal-based economy into modern large-scale machine-based manufacturing. With this transition, a large number of modern industries emerged in the followed decades, e.g. textile, aviation, and chemical industries. Large-scale
manufacturing and advancement in technology brought long-term economic prosperity and worldwide population growth \(^2-^3\). With the tremendous change in almost every single aspect in human society, the needs for stable and abundant energy supplies turned out to be indispensable. Due to the immature alternative-energy technology and relatively high availability, conventional combustion of fossil fuels, \textit{i.e.} coal, natural gas, and petroleum, possessed the unshakable position in world’s energy supply throughout the 18\(^{\text{th}}\), 19\(^{\text{th}}\), and 20\(^{\text{th}}\) centuries \(^4\). When the easy access to these carbon-based fossil fuels was taken for granted, no potential related issues but resource depletion was predicted until the late 20\(^{\text{th}}\) century \(^5\).

In 1975, the concept of “global warming” was first proposed by Prof. Broecker in his paper to describe the global temperature increase due to the CO\(_2\) emission from burning chemical fuels \(^5\). In the followed decades, many researches and debates were surrounding this specific issue which might bring the modern civilization to the end \(^6-^{12}\). Despite of minor doubts and debates, consensus is widely accepted that reducing anthropological CO\(_2\) emission is the key solution to the worsening global warming \(^13\).

Due to the fact that a large portion of anthropological CO\(_2\) emission is contributed by the fossil fuel burning for energy demands, a lot of research efforts and governmental subsidy are put onto the development of renewable energy, especially carbon-free energy \(^14-^{15}\). Hence, in the past decade, share of carbon-free renewable energy, such as solar
energy, geothermal power, and wind power, experienced worldwide rapid growth. However, due to the inadequate technology accumulation and/or relatively low supply capacity, most carbon-free renewable energies either suffer from low cost efficiency and technological bottle-neck or cannot meet the vast and soaring market demand. Therefore, in the near future, complete replacement of fossil fuels from the global energy supply chain by renewable energy is not possible.

Given this situation, in the recent years, a lot of attention has been attracted to the modification of existing energy conversion technologies as well as development of new technologies/processes with CO₂ Capture and Storage (CCS), which are ideally of high energy utilization efficiency. This CCS refers to two major issues: (1) to separate CO₂ during fossil fuel conversion with minimal energy penalty; (2) to compress, inject, and store the CO₂ into geological strata in a safe and efficient manner. With respect to the CO₂ separation during fossil fuel conversion, most processes applied in industry or under R & D can be categorized into “oxy-fuel combustion”, “wet processes”, or “dry processes”. Oxy-fuel combustion refers to direct combustion of carbonaceous fossil fuels with pure O₂ instead of air (in conventional combustion processes). This novel process produces a N₂-free stream after combustion, which significantly reduces the energy and hardware requirements for downstream CO₂ purification. However, in order to provide the vast quantity of O₂, a large air separation unit is needed. Moreover,
because the direct combustion with pure O$_2$ is a strong exothermal reaction, it requires stringent safety management and additional capital and operating costs. Most wet processes aim at CO$_2$ scrubbing from post-combustion flue gas using liquid alkaline solutions, *e.g.* MEA. Although wet process is the most commercially successful technology to date in CO$_2$ separation, its intrinsic disadvantages, such as low energy and cost efficiency, solvent instability at high temperature, and undesired solvent reactions with certain compounds in flue gas, would hinder its future application in industry $^{20-21}$. Unlike the liquid solution and oxy-fuel combustion, solid sorbents/oxygen-carriers can perform at wider operating conditions with higher efficiency and the related process operation does not require excessive safety management. Two major reaction schemes of dry processes are under intensive development, including direct capture and release of CO$_2$ by sorbents through cyclic carbonation-calcination reaction (CCR) and indirect CO$_2$ separation through the reduction-oxidation (REDOX) cycles of oxygen-carriers $^{15}$.

As one of the most promising dry CO$_2$ separation processes, calcium-based looping process has attracted a lot of research attention and effort, which not only shares the common advantages of other chemical looping processes with CCR but also benefits from the high availability and low cost of the naturally-occurring limestone $^{22}$. The calcium-based looping process can achieve *in-situ* and/or post-combustion CO$_2$ capture in carbonation step and release the CO$_2$ for sequestration in calcination step. A number of
such processes have been proposed and under intensive study, e.g. OSU Calcium Looping Process (CLP)\textsuperscript{23}, Zero Emission Coal Alliance (ZECA) Process\textsuperscript{24}, Hydrogen Production by Reaction Integrated Novel Gasification (HyPr-RING) Process\textsuperscript{25-26}, the ALSTOM Hybrid Combustion Gasification Process\textsuperscript{27}, the GE Fuel-Flexible Process\textsuperscript{28}, and the CO\textsubscript{2} Acceptor Process\textsuperscript{29}. After years of development, general process-design and reaction-parameter related issues have been well studied. The current challenges and research effort mostly focus on the unit scaling-up as well as sorbent optimization. Over the past decades, some processes have been successfully demonstrated at sub-pilot scale, while some others are still at the transitional stage from bench-top to larger scale.

The result of testing a naturally-occurring limestone obtained from Graymont (from quarry at Pleasant Gap, Pennsylvania) is shown in Figure 1.1. It can be seen that the CO\textsubscript{2} sorption capacity decreases over multiple cycles. The CO\textsubscript{2} sorption capacity can be defined as follows:

\[
\text{Weight Capture (\%) } = \frac{(W_f - W_o)}{W_o} \times 100
\]  

(1.1)

It is widely reported that CO\textsubscript{2} capture capacity of calcium-based sorbents decreases over multiple carbonation-calcination cycles\textsuperscript{30-31}. High calcination
temperatures used for the sorbent regeneration has deteriorating effect on the reactivity and recyclability of these sorbents, which is attributed to the sintering of the sorbents.\textsuperscript{30-38} The carbonation reaction can be considered as several elementary reaction steps such as CO\textsubscript{2} adsorption and CaCO\textsubscript{3} formation. Both macrostructural and microstructural properties of a CaO sorbent have effects on its reactivity to a certain extent, including surface area, pore volume and pore structure as well as orientation of the CaO surface. Although the initial properties of sorbents are important, how to maintain or recover such properties after regeneration step plays a much more significant role on the performance of sorbents for the carbonation reaction.

In order to improve initial sorbent properties and/or restore those properties of deactivated sorbents, a number of approaches have been proposed and tested, including synthesis/modification of sorbents, doped and supported sorbents, and steam/water hydration, some of which shows promising results while others need further work to prove their viability in future commercial applications. This chapter addresses these procedures and materials with view of enabling commercially competitive CO\textsubscript{2} capture technologies using calcium-based sorbents. The results of these investigations are described in the following sections. In addition, the challenges for further implementation into an existing process are presented as well.
1.2. Synthesis of the Calcium-Based Sorbents from Different Precursors

The rapid decay of the CO₂ sorption capacity of CaO derived from naturally-occurring sources drove the development of synthetic CaO sorbents from different precursors. Apparently, calcium precursors play an important role on the CO₂ capture performance of their derived CaO sorbents. These investigations aim at retaining high surface area and a stable pore structure of the sorbents for cyclic use. It is believed that a higher surface area of sorbents is favorable for gas-solid reaction and bigger pore volume of sorbents facilitates the gas molecule diffusion and the fast formation of calcium carbonate (CaCO₃).

Precipitated calcium carbonate (PCC) with a high surface area was synthesized by bubbling CO₂ through Ca(OH)₂ slurry in the work of Gupta et al. Since the theoretical conversions could not be achieved during the carbonation of CaO, this work attempted to alter sorbent morphology using an anionic dispersant (N40V), with the goal of achieving better performance. The synthesized PCC was found to have a unique mesoporous structure (5-30 nm) with a maximum pore diameter at 15 nm and thus its derived CaO was able to maintain high reactivity over several cycles. This was further explored by obtaining CaO from commercially available inorganic and organometallic precursors in the work of Lu et al. The precursors included calcium oxide (CaO), calcium
hydroxide (Ca(OH)$_2$), calcium carbonate (CaCO$_3$), calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$·4H$_2$O), calcium acetate (Ca(CH$_3$COO)$_2$), calcium propionate (Ca(C$_2$H$_5$COO)$_2$), calcium acetylacetonate (Ca(CH$_3$COCHCOCH$_3$)$_2$), calcium oxalate (Ca(COO)$_2$), calcium 2-ethylhexanoate (Ca(C$_7$H$_{15}$COO)$_2$), calcium D-gluconate monohydrate, etc.

As can be seen from Table 1.1, the CaO derived from calcium acetate, calcium propionate and calcium D-gluconate monohydrate possessed a higher CO$_2$ capture capacity due to its mesoporous and macroporous structures and larger surface area and pore volume. On the other hand, calcium oxalate-derived CaO was microporous and consequently, a poor performer. All these studies indicate the importance of sorbent morphology in relation to CO$_2$ capture capacity. Recent studies with more exotic calcium precursors have also confirmed this\textsuperscript{41}. The surface area and pore volume of CaO derived from these precursors are given in Table 1.2.

While studies continue to be carried out to find better precursors, other researchers have also applied the technique of modifying natural precursors by chemical treatment. Li \textit{et al.} modified CaO obtained from naturally-occurring limestone with ethanol/water solutions\textsuperscript{42}. No major difference in the carbonation conversion of sorbents was found in the first cycle but CaO sorbents modified with ethanol solution showed a
higher conversion over subsequent cycles. In addition, higher concentration of ethanol in the solution resulted in better pore structure. It is hypothesized that presence of ethanol improves H$_2$O molecule affinity and penetrability to CaO, yielding a change in pore structure and particle size of CaO sorbents. Additionally, the limestone gave a better performance of the carbonation conversion over 100 cycles compared to that of sorbents derived from the original limestone, when modified with acetic acid solution. Similar results were obtained with dolomite. As can be seen from Figure 1.2, modification by acetic acid or ethanol/water solution can delay or prevent the sintering to maintain the pore structure of sorbents over cycles, yielding better durability of sorbents.

Alternatively, many novel CaCO$_3$ structures have been investigated, including platelets, hollow spheres, hexagonal plates, rodlike particles and multibranched hierarchical structures with presence of organic additives or templates. CaCO$_3$ with these structures has not been tested as a high temperature CO$_2$ adsorbent and therefore Yang synthesized a novel CaO-based sorbent with a hollow structure, denoted as CaO nanopads. This sorbent was prepared by bubbling CO$_2$ through Ca(OH)$_2$ slurry in the presence of the triblock copolymer surfactant, P123 (PEO$_{20}$PPO$_{70}$PEO$_{20}$). This approach is similar to the one taken by Gupta and Fan; however nano-pores are targeted here instead of mesopores, as in the former. The presence of P123 was found to stabilize CO$_2$ bubbles, causing the tailored CaCO$_3$ to appear as hollow pod containing numerous
nanosized CaCO₃ platelets. This unique structure yielded a superior performance on CO₂ sorption capacity of 39.3 % after 50 cycles.

Even though sorbents with higher surface area and a predominately pore structure can be obtained using above methods, the effects of high regeneration temperatures, like the ones encountered in commercial calciners, have not been investigated. Further, most studies have been conducted in a Thermogravimetric Analyzer (TGA) at milder reaction conditions for limited cycles and thus the scope of using such sorbents in a realistic application, is limited at best.

1.3. Doped or supported Calcium Oxides

Many researchers have proposed to maintain the CO₂ removal capacity by tuning the morphology of sorbents by doping or addition of supports instead of changing CaO precursors. The strategy is to use dopants or supports to prevent or delay sintering and consequently improve sorbent recyclability for extended use. However, some dopants have found to enhance the sintering of the sorbents.

The effect of doping CaO with NaCl and Na₂CO₃ was investigated in the work if Salvador et al. for specific application in fluidized bed combustion (FBC) systems. It
was shown that the addition of NaCl retained the CO$_2$ capture capacity of the sorbents at 0.4 over 10 cycles due to favorable changes in the pore structure and surface area of the sorbent while the addition of Na$_2$CO$_3$ did not have significant effect on the extent of carbonation as shown in Figure 1.3. Previously conducted studies, for enhancing SO$_2$ capture using calcium sorbents modified with sodium salts, hypothesize that the presence of salt induces structural rearrangement which results in optimum pore size distribution. However, the performance of these calcium oxides with NaCl or Na$_2$CO$_3$ differs significantly in the FBC environment as compared to TGA results. When the doped sorbents were tested in the fluidized bed, both NaCl and Na$_2$CO$_3$ caused a decrease in the CO$_2$ sorption capacity of the sorbents which might be attributed to a coating formed over the surface of the sorbents in the calcination stage, leading to pore blockage. These findings prove that interpreting these results for large-scale systems is likely to be complicated.

Encouraging results from sodium-doped CaO have led to investigations with other group 1A elements. An independent study has linked the performance of alkali metal-doped CaO to the electropositivity of the metal on the CO$_2$ capture capacity. It is observed that a Cs-doped CaO sorbent with 20% Cs/CaO has the highest sorption capacity at 50 wt % in the first cycle compared to CaO doped with other alkali metals, including Li, Na, K, Rb, and Cs. The improvement of the CO$_2$ capture capacity resulted...
from an increase in basic sites on the surface. The authors also report an enhancement in the rate of CO$_2$ adsorption due to doping with Cs.

Since higher surface area of the sorbent has been linked to better CO$_2$ capture capacity, a new method of synthesizing calcium-based nanosorbents with a wide range of refractory dopants (Si, Ti, Cr, CO, Zr, and Ce) by flame spray pyrolysis (FSP) has also been explored. Though all the doped-CaO showed lower CaO conversion compared to nascent CaO in the first cycle due to less CaO content, the durability of the doped sorbents is improved. Zr-doped CaO exhibited the best CO$_2$ sorption capacity under similar operational conditions among all the dopants. With a Zr/Ca molar ratio of 0.3, the sorbents were capable of resisting the sintering agglomeration, leading to 50 wt % reactivity after 100 cycles. The surface area of all the FSP-made sorbents was two times as that of PCC, leading to faster and higher CO$_2$ uptake capacity as shown in Table 1.3. 

Recently, supports like aluminum oxide (Al$_2$O$_3$), cement (contains CaO and Al$_2$O$_3$), magnesium oxide (MgO), and silica have also shown to improve the durability of CaO sorbents. A new regenerable calcium-based sorbent, CaO/Ca$_{12}$Al$_{14}$O$_{33}$, was tested at the mild (850 °C, 100% N$_2$) and severe (980 °C, 100% CO$_2$) calcination conditions. It was observed that this new sorbent can attain the reactivity of 41 wt % after 50 cycles.
under mild conditions and 22 wt% after 56 cycles under severe conditions \(^5^7\). The Al\(_2\)O\(_3\)
reacted with CaO to form Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) in the calcination step, yielding a stable structure
among CaO micrograins, and thus retarding the sintering of CaO. However, the
Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) transitions to Ca\(_3\)Al\(_2\)O\(_6\) when the calcination temperature exceeds 1100 °C.
Further, CaO/Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) derived from different precursors — Ca(OH)\(_2\) and
Ca(CH\(_3\)COO)\(_2\) — were studied by Martavaltzi and Lemonidou \(^5^8\) and the results obtained
from this study are in agreement with the results of Li and co-workers \(^5^6^\)-\(^5^7\). Alternatively,
CaO-based pellets prepared from hydrated lime (Ca(OH)\(_2\)) and calcium aluminate
cements were tested for calcination/carbonation cycles \(^5^9\). It was found the pellets
exhibited a similar trend as powders, maintaining a high residual capacity of 22% after
1000 cycles. The durability of various CaO sorbents with Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) is summarized in
Table 1.4. It can be concluded that the formation of Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) results in a stable
framework within CaO sorbents to impede the sintering of CaO sorbents.

A mixture of 26 wt % MgO with CaO was observed to maintain 45 wt % CO\(_2\)
removal capacities over 100 calcination-carbonation reaction cycles \(^6^0\). Albrecht \emph{et al.}
also reported that CaO with 20 wt % MgO can maintain 24 wt % CO\(_2\) capacities after
1250 cycles \(^6^1\). Li \emph{et al.} have claimed that the method of introduction of MgO in CaO
plays an important role in determining its effectiveness. It is well-known that dolomite-
derived CaO performs better than limestone-derived CaO over multiple cycles because of
the presence of MgO which limits the sintering. However, it is reported that the performance of synthetically prepared MgO-doped CaO is superior than CaO derived by calcining dolomite.

Nano-CaCO₃, which has been widely used in plastic as packaging materials, is composed of a better morphological properties compared to micro-CaCO₃ and the CO₂ capture capacity of CaO from nano-sized CaCO₃ was first conducted by Barker in the application of energy storage. Further, nano-CaCO₃ precursor was mixed with Al₂O₃, yielding a stable adsorption ratio of 68.3% after 15 cycles. Basically, this approach combines the concepts of nano-sorbent and aluminum doing highlighted before. It was found that nano-CaCO₃ reacted with Al₂O₃ at a lower temperature of 800 °C compared to micro-CaCO₃ to form Ca₁₂Al₁₄O₃₃. Besides Al₂O₃, nano-CaO sorbent has been coated with TiO₂ and transformed to CaTiO₃/nano-CaO in the work of Wu et al. The CaTiO₃/nano-CaO showed a higher CO₂ capture capacity after 40 cycles compared to that of nano-CaO. It is likely that CaTiO₃ has high thermal stability and thus provided a stable structure at elevated temperatures.

More recently, it was shown that the addition of KMnO₄ using wet impregnation methods can improve CO₂ sorption capacity of calcium-based sorbents for long term calcination/carbonation cycles. It is claimed that KMnO₄ helps to maintain particle
stability by holding the surface area and pores within a specific range. Novel CaO/La$_2$O$_3$ sorbents have also been developed by different methods, including dry physical mixing, wet chemistry and sol gel combustion synthesis, in the work of Luo et al$^{68}$. The well-dispersed La$_2$O$_3$ can prevent the agglomeration of CaO, leading to a carbonation conversion of 65% after 50 cycles. Unlike MgO, which acts as an inert material, La$_2$O$_3$ reacts with CO$_2$ and forms La$_2$O$_2$CO$_3$ simultaneously in the carbonation reaction and decomposes back to La$_2$O$_3$ during the calcination reaction.

Mesoporous silicates (MCM-41 and SBA-15) have been recognized as a new class of inorganic materials$^{69}$. The MCM-41 represents a hexagonal ordering of cylindrical channel with amorphous silica with pore diameter in a range of 1.5 to 10 nm. SBA-15 contains a larger pore (> 30nm) compared to MCM-14, yielding better stability. Due to high surface areas and well-defined pore structures, these materials have been incorporated with CaO to capture CO$_2$ at high temperatures. The calcium-based sorbents on SBA-15 for CO$_2$ adsorption have been studied by Huang et al$^{70}$. SBA-15 mesoporous sieve provides a stable framework for supporting CaO and is composed of very high surface area and pore volume as given in Table 1.5. It is found that the stable structure of CaO sorbents with SBA-15 prohibited the sintering of CaO over cyclic testing. The results showed that the sorbents possessed 63% of the capture capacity after 40 cycles.
The CO₂ capture capacity of the sorbent with various supports under long series testing is given in Table 1.6.

The dopants or supports are capable of providing more stable structure under cyclic testing. Though they perform better over many cycles, the overall CO₂ capture capacity can suffer due to lesser CaO content. The impact on the process material and energy balances also needs to be considered due to the additional material (inerts) that will be circulated in the loop. The cost of these sorbents is also higher and thus their performance needs to be extremely robust in order to maintain the economics of the process relative to natural limestone or other technologies such as the conventional amine solution for the CO₂ capture.

1.4. Reactivation through Steam/Water Hydration

An intermediate step, reactivation using hydration, has been suggested as a path to overcome the problem of decay in reactivity of calcium-based sorbents and seems to be the most promising among the various alternatives that exist. This idea was first suggested by Argonne National Laboratories in 1980 to improve the utilization of CaO sorbents for SO₂ capture in FBC systems ⁷¹. In this case, the formation of Ca(OH)₂, which has a higher molar volume than CaO, leads to particle expansion and cracking on the
CaO surface. This allows the unconverted CaO in the interior to react with SO₂. Similarly, studies were also conducted during that period to compare the performance of CaO derived from different naturally occurring precursors and it was observed that Ca(OH)₂-derived CaO performed better than the one derived from CaCO₃. Besides hydration, the “melting technique” was also employed to improve acceptor properties in the development of the CO₂ Acceptor Process. Curran et al. were able to correlate the concentration of Ca(OH)₂ in the melts to the sorbent activity. They also report that the activities of the melts were independent of the precursor used in the preparation of the melts – fresh or deactivated limestone. The conversion of inactive CaO to Ca(OH)₂ was reported to be the key to success of this technique. It was probably these findings that have encouraged the application of CaO hydration for improving long-term CO₂ capture and experimental evidence clearly indicates that this can be a viable alternative.

The addition of steam during carbonation has also been investigated in the work of Manovic and Anthony. In this case, the steam does not actually react with CaO, but enhances carbonation conversion via solid state diffusion in the product layer. Similarly, Ramkumar and Fan report that use of steam during calcination reduces the extent of sintering and results in the production of CaO with higher reactivity. However, these results seem contradictory to the findings of Borgwardt. Though promising, these strategies may not be as effective as independent hydration of CaO. Since the reactor
design in calcium-based CO$_2$ capture systems will rely on the fast reaction regime during carbonation, the enhancement of carbonation conversion in the slow reaction regime (diffusion limited) due to presence of steam is not particularly advantageous. The inconclusive results obtained for calcination further limit the application of this concept.

Hydration of CaO is a fast and exothermic reaction as shown in the following:

$$\text{CaO} + \text{H}_2\text{O} \leftrightarrow \text{Ca(OH)}_2 \quad (1.1)$$

Two options exist for hydrating CaO – using water or steam. Both have been studied by several researchers. The high temperature and pressure steam hydration of CaO was investigated by Kuramoto et al. for specific application in the HyPr-RING Process developed in Japan, and it was reported that the sorbent was more durable in repetitive CO$_2$ sorption$^{76}$. Since the calcium sorbent and steam are directly added to the gasifier in the HyPr-RING Process, the hydration of CaO is inevitable at the operating conditions. It is important to note that the operating conditions are such that both hydration and carbonation of CaO can occur. Ultimately, the hydrated CaO also reacts with CO$_2$ to form CaCO$_3$. The advantage of such a scheme is that it does not require a separate hydration reactor and the heat of hydration can balance the endothermic gasification. However, direct interaction of coal minerals and ash with the calcium
sorbents in the gasifier can negatively affect CO\textsubscript{2} capture capacity. Also, controlling the extent of hydration is a challenge.

Hughes \textit{et al.} also confirmed the positive effect of high pressure steam hydration – an increase in surface area of the sorbents\textsuperscript{77}. They suggest that hydration causes cracks to be formed in CaO particles, creating channels extending to the interior of the particles and thus improving CO\textsubscript{2} capture. While most studies have investigated the use of hydration treatment after the calcination reaction and prior to the carbonation reaction, steam reactivation of spent sorbents in the form of calcium carbonate (CaCO\textsubscript{3}) has also been investigated\textsuperscript{78-79}. However, it has been proved that hydration of the sorbents derived from the calciner in the form of calcium oxide (CaO) would be better. Zeman has suggested performing hydration at 300 °C and an atmospheric pressure to avoid the extra costs associated with high pressure steam reactors\textsuperscript{80}. On the other hand, Fennell \textit{et al.} have studied regeneration of spent CaO sorbents by reaction with humid air\textsuperscript{81}. The study by Han \textit{et al.} shows that steam hydration is more effective than water hydration for 6 cycles\textsuperscript{82}; however, single cycle tests conducted at OSU indicate otherwise\textsuperscript{15}.

The mechanism of hydration of CaO has been extensively studied by researchers in the period 1950-1960. These studies do not focus on improving the CO\textsubscript{2} capture
capacity of the sorbents as this area has gained prominence only recently. Nonetheless, they still provide valuable insights:

- The mechanism can differ depending on the calcination time and temperature used to obtain CaO. Water hydration predominantly occurs ‘through solution’. In this mechanism, supersaturated solutions with respect to crystalline calcium hydroxide are formed and this facilitates the formation and growth crystals in the pores and spaces previously occupied by CaO. This leads to decrease in the pore volume and pore size.

- The ‘advancing interface mechanism’ has also been proposed for hydration by both water and water vapor. In this case, the hydration proceeds inwards from outside of each CaO crystallite. The product is formed at the original sites of the reactant and it is accompanied by overall expansion because specific volume of the products is much greater (1.98x).

The surface area of CaO derived by calcining Ca(OH)$_2$ (or hydrated CaO) is usually higher as compared to CaO obtained by calcining limestone. However, Mikhail points out that surface area of CaO is also a function of temperature of decomposition of Ca(OH)$_2$ and atmosphere of decomposition and there is an optimum temperature where the area is maximum (tip of an inverted U-shaped curve). According to this study, there
are two opposing effects – recrystallization and sintering. While recrystallization leads to increase in surface area, sintering creates products of smaller surface area and larger grain size. This hypothesis has also been put forward in an independent study by Ghosh-Dastidar et al. In addition to temperature and atmosphere of calcination, this study introduces residence time as one of the important variables – shorter the time scale, more is the domination of the calcination (recrystallization) kinetics over sintering kinetics and vice versa.

The importance of hydration in calcium-based CO$_2$ capture systems can be gauged by the number of studies that have been published recently highlighting different aspects. While there is a unanimous agreement on improvement in CO$_2$ capture capacity over multiple cycles, the attrition or break up of the hydrated particles can pose a challenge for operating the hydrator as a fluidized bed reactor. Strategies like using fixed-bed reactors and pelletization have been put forward to deal with particle attrition. Since hydration of CaO is a highly exothermic reaction, fixed-bed reactor may not be ideal for heat transfer. Also, issues like buildup of pressure in such reactors can also pose difficulties. Though pelletization should help reduce attrition effects, the hydration over multiple cycles might ultimately induce friability and break the strength of these pellets. The frequency of hydration has also been a matter of debate, though relatively high frequency should be beneficial. A scheme where only a fraction of the
sorbent is hydrated has also been suggested to minimize steam consumption. Theoretically, this can be accomplished by either splitting the calcined sorbent into two streams and hydrating only one or hydrating the entire calcined sorbent periodically, once in few cycles. While this strategy is likely to reduce steam consumption, higher solids circulation will be required to achieve the same % CO$_2$ removal since full potential of hydration is not being exploited. Additionally, the detail mechanism of reactivation through hydration is still lack of studies and to incorporate hydration into existing calcium-based looping technologies is still a challenge.

1.5. Concluding Remarks

The United States government has identified hydrogen as a potential fuel to replaced hydrocarbon based fuels. Unfortunately, hydrogen must be produced from materials that contain hydrogen such as water, hydrocarbon or coal. Hydrogen can be produced from coal gasification and the yield of hydrogen can be increased if the syngas is treated in a Water-Gas-Shift (WGS) reaction. However, when hydrocarbon based materials such as coal are processed, they produce carbon dioxide as well as hydrogen. Further, even with the use of a WGS catalyst, the amount of hydrogen produced is limited by the equilibrium concentration. This limits the conversion efficiency.
The calcium-based looping process has been identified as a promising technology for hydrogen production. This process is based on continuous removal of CO₂ from the product stream with calcium-based sorbents. CO₂ concentration can be lowered down to ppm levels by the carbonation reaction, thereby maximize the production of hydrogen from carbon by the WGS reaction. The spent sorbents can be regenerated separately to yield a pure CO₂ stream, which can then be compressed and liquefied for its transportation to sequestration sites. The CaO sorbents so formed can be recycled to capture CO₂ in the next cycle so on. Since the calcium-based processes for post-combustion and pre-combustion CO₂ capture face a common challenge – decreasing CO₂ capture capacity of sorbents over multiple cycles – lots of recent work has focused on this aspect. Researchers have investigated different techniques to overcome this obstacle and each approach has its own merits and drawbacks.

Sorbents with improved morphology can be obtained by using modified precursors, which leads to higher CO₂ capture capacities at the first place but most of them are fail to maintain the reactivity after several carbonation-calcination cycles. Additionally, most studies have been conducted in a TGA at milder conditions and hence caution needs to be exercised while interpreting these results with respect to actual conditions which are likely to be harsher and complicated by other unforeseen variables. Doped and supported sorbents have the disadvantage of carrying more inert material in
the loop. Though superior performance of these sorbents at TGA-scale suggests that operation at lower sorbent feeding rates might be possible, this advantage can be nullified if the percentage of inert (performance-enhancing elements) is too high. The mass production of such sorbents is also likely to be prohibitively expensive.

Though limited, some of the available evidence suggests that modified or doped-supported sorbents may not perform well in actual systems. If this is indeed the case, and these sorbents lose reactivity quickly, they will not offer any advantage over naturally obtained CaO, unless the pretreatment procedures are carried out multiple times in between cycles. Apart from unfavorable economics, feasibility of such a scheme is highly doubtful.

As far as practicality and economics are concerned, hydration seems to be the most promising solution. The integration of a separate reaction vessel – hydrator – would also provide high quality heat due to the exothermicity of the reactivation reaction. The operation of the hydrator can be very flexible – all or only a fraction of the calcined CaO can be hydrated. Also, hydration can be performed in every cycle or once in a few cycles. However, further investigation on the detail mechanism is highly desired and it is crucial to address key issues – operating conditions (temperature, pressure, etc.) and reactor configuration.
A study of the published literature reveals that all this work has closely followed the trend in sorbent enhancement methods suggested in the period 1980-2000 for improving utilization of calcium sorbents in SO₂ capture in fluidized bed combustion (FBC). Despite technical merits, most of these methods were not implemented commercially due to economic reasons and the research efforts that followed were directed toward overcoming these limitations. Similar hurdles are expected in the case of CO₂ capture; nonetheless previous experience will be helpful in dealing with them.

In this thesis, the details studies on reactivation mechanism of calcium-based sorbents are presented. As the particles employed in these processes are mainly in solid form and the success of the chemical looping technology applications depends strongly on the performance of the sorbents, Chapter 2 is devoted entirely to the subjects of kinetic investigation of high-pressure carbonation reaction in the context of the calcium looping process (CLP), which converts gaseous fuel such as syngas and light hydrocarbons. Chapter 3 further discusses the deactivation mechanism and possible reactivations strategies in the Calcium Looping Process (CLP). Several methods are conducted, including CaO sorbents with supports in the form of pellets, thermal pretreatment and hydration. It is found that hydration is the most promising method among all. The detail mechanism of reactivation through hydration is discussed in Chapter 4. Chapter 5 further investigates the hydration mechanism using Density Function Theory (DFT) calculation.
Integration of hydration into CLP, conclusion and future recommendations are presented in Chapter 6.
1.6. Notations

\( t: \) Time (min)

\( W_0: \) The initial weight of sorbent (g)

\( W_t: \) The weight of sorbent at given time (g)
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<td>P&lt;sub&gt;CO₂&lt;/sub&gt; (atm)</td>
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</tr>
<tr>
<td>Ca(CH₃COCHCOCH₃)&lt;sub&gt;2&lt;/sub&gt;-CaO&lt;sup&gt;40&lt;/sup&gt;</td>
<td>700</td>
<td>300</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca(COO)&lt;sub&gt;2&lt;/sub&gt;-CaO&lt;sup&gt;40&lt;/sup&gt;</td>
<td>700</td>
<td>300</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca(C₁₇H₁₅COO)&lt;sub&gt;2&lt;/sub&gt;-CaO&lt;sup&gt;40&lt;/sup&gt;</td>
<td>700</td>
<td>300</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca d-gluconate monohydrate-CaO&lt;sup&gt;41&lt;/sup&gt;</td>
<td>650</td>
<td>30</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 1.1 The CO₂ capture capacity of CaO obtained from various precursors.
<table>
<thead>
<tr>
<th>Precursor</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC-CaO</td>
<td>12.8</td>
<td>0.027</td>
</tr>
<tr>
<td>CaCO₃-CaO</td>
<td>5.3</td>
<td>0.08</td>
</tr>
<tr>
<td>Ca(OH)₂-CaO</td>
<td>13.9</td>
<td>0.15</td>
</tr>
<tr>
<td>CaO-CaO</td>
<td>4.2</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca(C₂H₅COO)₂-CaO</td>
<td>15.0</td>
<td>0.18</td>
</tr>
<tr>
<td>Ca(CH₃COO)₂-CaO</td>
<td>20.0</td>
<td>0.22</td>
</tr>
<tr>
<td>Ca(CH₃COCHCOCH₃)₂-CaO</td>
<td>12.0</td>
<td>0.09</td>
</tr>
<tr>
<td>Ca(COO)₂-CaO</td>
<td>5.9</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca(C₇H₁₅COO)₂-CaO</td>
<td>9.3</td>
<td>0.015</td>
</tr>
<tr>
<td>Ca D-gluconate monohydrate-CaO</td>
<td>17.0</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 1.2 The surface area and pore volume of CaO from different precursors.
<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSP Si/Ca (1:10)</td>
<td>78</td>
<td>0.34</td>
</tr>
<tr>
<td>FSP Ti/Ca (1:10)</td>
<td>61</td>
<td>0.38</td>
</tr>
<tr>
<td>FSP Cr/Ca (1:10)</td>
<td>74</td>
<td>0.39</td>
</tr>
<tr>
<td>FSP Co/Ca (1:10)</td>
<td>80</td>
<td>0.42</td>
</tr>
<tr>
<td>FSP Ce/Ca (1:10)</td>
<td>89</td>
<td>0.42</td>
</tr>
<tr>
<td>FSP Zr/Ca (1:10)</td>
<td>74</td>
<td>0.23</td>
</tr>
<tr>
<td>FSP Zr/Ca (1:5)</td>
<td>67</td>
<td>0.23</td>
</tr>
<tr>
<td>FSP Zr/Ca (3:10)</td>
<td>71</td>
<td>0.24</td>
</tr>
<tr>
<td>PCC ²²</td>
<td>38</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 1.3 BET surface area and pore volume of various sorbents by FSP ³³.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Carbonation</th>
<th>Calcination</th>
<th>Cycles</th>
<th>CO₂ capture Capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>t (min)</td>
<td>P&lt;sub&gt;CO₂&lt;/sub&gt; (atm)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>CaO/(\text{Ca}<em>{12}\text{Al}</em>{14}\text{O}_{33})(^{57})</td>
<td>700</td>
<td>30</td>
<td>0.2</td>
<td>850</td>
</tr>
<tr>
<td>CaO/(\text{Ca}<em>{12}\text{Al}</em>{14}\text{O}_{33})(^{57})</td>
<td>650</td>
<td>30</td>
<td>0.2</td>
<td>980</td>
</tr>
<tr>
<td>Ca(OH)&lt;sub&gt;2&lt;/sub&gt;/(\text{Ca}<em>{12}\text{Al}</em>{14}\text{O}_{33})(^{58})</td>
<td>690</td>
<td>30</td>
<td>0.15</td>
<td>850</td>
</tr>
<tr>
<td>Ca(CH&lt;sub&gt;3&lt;/sub&gt;COO)&lt;sub&gt;2&lt;/sub&gt;/(\text{Ca}<em>{12}\text{Al}</em>{14}\text{O}_{33})(^{58})</td>
<td>690</td>
<td>30</td>
<td>0.15</td>
<td>850</td>
</tr>
<tr>
<td>Ca(OH)&lt;sub&gt;2&lt;/sub&gt;/calcium aluminate cement(^{59})</td>
<td>800</td>
<td>10</td>
<td>0.5</td>
<td>800</td>
</tr>
</tbody>
</table>

Table 1.4 The long series of CO₂ capacity of various CaO sorbents with \(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}\).
<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>659</td>
<td>0.83</td>
<td>5.27</td>
</tr>
<tr>
<td>CaO/SBA-15ᵃ</td>
<td>367</td>
<td>0.667</td>
<td>5.05</td>
</tr>
<tr>
<td>CaO/SBA-15ᵇ</td>
<td>155</td>
<td>0.432</td>
<td>4.75</td>
</tr>
</tbody>
</table>

Table 1.5 The morphological properties of various samples ⁷⁰.

ᵃ: solvent was removed by filtration.

ᵇ: solvent was removed by evaporation.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Carbonation</th>
<th>Calcination</th>
<th>Cycles</th>
<th>CO₂ capture Capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO/CaO 60</td>
<td>T (°C)</td>
<td>t (min)</td>
<td>P&lt;sub&gt;CO₂&lt;/sub&gt; (atm)</td>
<td>T (°C)</td>
</tr>
<tr>
<td></td>
<td>758</td>
<td>30</td>
<td>1</td>
<td>758</td>
</tr>
<tr>
<td>MgO/CaO 61</td>
<td>750</td>
<td>20</td>
<td>0.25</td>
<td>750</td>
</tr>
<tr>
<td>Al₂O₃/nano-CaO 65</td>
<td>600</td>
<td>40</td>
<td>0.33</td>
<td>800</td>
</tr>
<tr>
<td>CaTiO₃/nano-CaO 66</td>
<td>600</td>
<td>10</td>
<td>0.2</td>
<td>750</td>
</tr>
<tr>
<td>TiO₂/nano-CaO 66</td>
<td>600</td>
<td>10</td>
<td>0.2</td>
<td>750</td>
</tr>
<tr>
<td>KMnO₄/CaO 67</td>
<td>700</td>
<td>20</td>
<td>0.15</td>
<td>850</td>
</tr>
<tr>
<td>La₂O₃/CaO 68</td>
<td>650</td>
<td>15</td>
<td>0.15</td>
<td>850</td>
</tr>
<tr>
<td>La₂O₃/CaO 68</td>
<td>650</td>
<td>15</td>
<td>0.15</td>
<td>950</td>
</tr>
<tr>
<td>SBA-15/CaO 70</td>
<td>700</td>
<td>60</td>
<td>1</td>
<td>910</td>
</tr>
</tbody>
</table>

Table 1.6 The long series of CO₂ capacity of CaO sorbents with different supports.
Figure 1.1 Loss of reactivity during multiple CCR cycles testing of Graymont limestone in TGA, 700°C, calcination in N\textsubscript{2} for 30 min, carbonation under 10\% CO\textsubscript{2} (balanced with N\textsubscript{2}) for 30 min.
Figure 1.2 BET surface area and pore volume for sorbents calcined at 920 °C with and without modification.\textsuperscript{42-44}
Figure 1.3 Comparisons of CO₂ capture capacity for Havelock limestone with additions.
CHAPTER 2

Kinetic Study of High-Pressure Carbonation Reaction of Calcium-Based Sorbents in the Calcium Looping Process (CLP)

2.1. Introduction

With rising energy demand and concerns over global warming, it is desirable to develop clean and efficient energy conversion systems. Hydrogen, a clean and carbon free fuel, has been regarded as one of the ideal energy carriers. Thus, hydrogen generation using highly efficient processes will be crucial. Large-scale hydrogen production is dependent on the conversion of carbonaceous fuels processes, such as steam methane reforming, coal gasification, catalytic cracking of natural gas, and partial oxidation of heavy oils. The gases obtained from these reactions are then sent to the downstream water-gas-shift (WGS) reactors to enhance the hydrogen production. An effective technique to improve the hydrogen productivity through the WGS reaction is to remove CO₂ in-situ from the reaction mixtures. The continuous removal of the CO₂ product from the WGS reactor would incessantly drive the equilibrium-limited WGS reaction in the forward direction. Thus, it will allow this exothermic reaction to be carried out at high temperatures and high pressures leading to faster kinetics in the forward
direction. The efficiency of a hydrogen production process of this nature will be significantly higher compared to the current processes, especially when the CO₂ sequestration is integrated.

In the recent years, a number of novel processes have been proposed in the literatures, which aim at high efficiency hydrogen production with CO₂ capture. Among these processes, that are calcium-based looping processes include the Zero Emission Coal Alliance (ZECA) Process ²⁴, the Hydrogen Production by Reaction Integrated Novel Gasification (HyPr-RING) Process ²⁵-²⁶, the CO₂ Acceptor Process ²⁹, ⁹⁸, the ALSTOM Hybrid Combustion Gasification Process ²⁷ and the GE Fuel-Flexible Process ²⁸. Despite the varied schemes in the reactions of the processes, in essence, these processes involve the use of calcium-based sorbents to remove CO₂ in producing high-purity hydrogen. These systems usually operate at very high pressures and require excess steam to produce hydrogen ²⁵-²⁹. The Calcium Looping Process (CLP) system ¹⁵, ²³, ⁹⁹, which is being developed at the Ohio State University, integrates several reactions in one single reactor, including the WGS reaction, CO₂ capture, and sulfur and halide removal at high temperatures, resulting in process intensification. This process is composed of two main reactors, carbonator and calciner. The carbonator can be operated at 550-700 °C and different pressures depending upon the purity of hydrogen required. The calciner is operated at 800-1000 °C at atmospheric pressure for spent sorbent regeneration while
producing sequestration ready CO$_2$. The major reactions occurring in the CLP are as follows:

**Carbonator:**

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO}_2 & (2.1) \\
\text{CaO} + \text{CO}_2 & \rightarrow \text{CaCO}_3 & (2.2) \\
\text{CaO} + \text{H}_2\text{S} & \rightarrow \text{CaS} + \text{H}_2\text{O} & (2.3) \\
\text{CaO} + \text{COS} & \rightarrow \text{CaS} + \text{CO}_2 & (2.4) \\
\text{CaO} + 2\text{HCl} & \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} & (2.5)
\end{align*}
\]

**Calciner:**

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

(2.6)

With growing interest in CO$_2$ capture, calcium-based sorbents have been gaining special attention. Extensive studies have been conducted on the calcination reaction. Fuertes *et al.* have shown that the calcium carbonate decomposes at a definite boundary between CaO and CaCO$_3$\textsuperscript{100}. Dennis and Hayhurst found a slower calcination reaction rate at a higher system pressure even without CO$_2$ in the bulk gases \textsuperscript{101}. The effects of CO$_2$ concentration and total pressure on the calcination reaction were also investigated in the work of Garcia-Labiano \textsuperscript{102}. They found that increasing CO$_2$ partial pressure or
increasing total pressure would decrease the calcination reaction rate. They developed a model to predict the calcination reaction behavior over a wide range of CO$_2$ concentration, total pressures, particle sizes and temperatures. The kinetic studies on carbonation reaction have been extensive; little, however, has been carried out under elevated pressure conditions. Von Nitsch found that the initial carbonation reaction has the zero activation energy at 800-850 °C$^{103}$. Bhatia and Perlmutter employed the random pore model to illustrate their experimental results and zero activation energy was obtained using an atmospheric thermogravimetric analyzer$^{35}$. Sun et al. and Chen et al. found that an increasing in partial pressure of CO$_2$ can enhance the carbonation reaction rate$^{104-105}$. Further investigation of the carbonation reaction under high total pressures and high partial pressures of CO$_2$ over wider ranges is necessary.

Bench-scale testing of the CLP has shown that a pure hydrogen stream (> 99.9%) can be obtained at a moderate operating pressure of 15000 torrs$^{15,23,99}$. In addition, the CLP system yields an efficiency of 63% (based on High Heating Value (HHV) similar to existing state-of-art processes that generate hydrogen at extremely higher pressures, but without CO$_2$ capture$^{19}$. Thus, the study of the carbonation kinetics of calcium-based sorbents for the CLP at elevated pressures is important.
The objective of this chapter is to investigate the effect of partial pressure of reacting gases and total pressure on the carbonation reaction rate of CaO obtained from different precursors, including CaCO$_3$, Ca(OH)$_2$ and PCC. The pressure effect on the carbonation reaction rate with number of cycles is also investigated.

2.2. Experimental Section

2.2.1. Particle and Pellet preparation

Calcium-based sorbents were prepared in the form of powders and pellets. Naturally-occurring limestone and calcium hydroxide were obtained from Graymont Inc. The PCC was prepared according to the procedure described by Agnihotri et al.\textsuperscript{106}. In addition, raw powders were manually pressed into cylindrical pellets (a diameter of 5 mm and a height of 2 mm).

2.2.2. Particle Reactivity and Recyclability

The Magnetic Suspension Balances (MSB) analyzer was used in this study to test the performance of calcium-based sorbents at elevated pressures. Figure 2.1 shows the
apparatus of the MSB which consists of a set of mass flow controllers conveying the reaction gas mixture into a high pressure reactor enclosed in a high temperature furnace. The measuring accuracy, pressure tolerance, and maximum temperature of the system can be up to 1µg, 22,000 torrs and 1000°C, respectively.

Powdered samples and pelletized samples have been examined in this study. Before each experiment, 0.3-0.5 g of the sample was loaded into a quartz crucible. Next, the MSB was purged with nitrogen to introduce an inert atmosphere. The crucible was then heated to the desired calcination temperature, 700 ºC with sufficient time of 30 min to fully calcine the samples to CaO. In addition, to assure the proper calcination rate, the calcination reaction is conducted at 1000 torrs under nitrogen environment. In order to compare the reaction rate of various calcium-based sorbents, about 120 ml/min of reacting gases, comprising 10-30% CO₂ balanced with nitrogen, were introduced to the MSB at 700 ºC and different total pressures after completion of calcination. The weight change of the sample was continuously recorded as a function of time for further analysis. The initial rate of carbonation is mainly related to the concentration of CO₂ and the total pressures. Hence, these two parameters are used to characterize the effect of pressures on the carbonation reaction.
The sorbent reactivity (weight capture %) and carbonation reaction rate are defined as follows:

Weight Capture %: \( C = \frac{(W_t - W_0)}{W_0} \times 100 \) (2.1)

Carbonation Reaction Rate of CaO (%/min) = \( \frac{dC}{dt} \) (2.2)

It is known that the carbonation reaction can be considered for two regimes with the first regime involving a rapid chemical reaction which is followed by the second regime of a slow reaction characterized by the CaCO\(_3\) layer formation that impedes the reactant gas diffusion. In this study, the carbonation reaction rates for various sorbents were compared for the first regime of the reaction. Moreover, in order to study multiple calcination-carbonation reaction cycles, the gases introduced to the MSB are switched between inert gases and reacting gases every 30 min for five cycles. Both carbonation and calcination reaction are conducted at 700\(^\circ\)C with 120 ml/min gas flow rate. The calcination reaction was conducted at 1000 torrs but the carbonation reaction was conducted at 5000 torrs with 10 % CO\(_2\) stream (balanced with N\(_2\)). The change in weight is then monitored across cycles in order to evaluate the recyclability.
2.3. Results and Discussions

2.3.1. Buoyancy effect of MSB

The high-pressure MSB analyzer can be used to test the gas sorption capacity of solid sorbents and to study more industrially relevant temperature and pressure reaction conditions. Unlike an atmospheric thermogravimetric analyzer, the MSB analyzer is operated at elevated pressures and thus the weight measured from the system is much sensitive to the buoyancy effect. In order to offset this sensitivity, the weight buoyed needs to be accounted for. An empty quartz crucible was used to test the buoyancy effect. Next, the MSB was run under several pressures ranging from 1000 torrs to 15000 torrs using helium as an inert gas. The results are given in Figure 2.2. The buoyancy effect is indicated by the decreasing weight of the empty quartz crucible with an increase in operating pressures.

Using the gas law equation, the weight buoyed by the flowing gas due to the increasing operating pressures can be obtained. Hence, the weight of the empty quartz crucible would be adjusted by the following equation:
It can be seen from Figure 2.3 that the weight of empty quartz crucible is stable after correction. Once the buoyancy effect was considered, the calcium-based sorbents were tested in different total pressures with a constant CO\textsubscript{2} concentration and at different CO\textsubscript{2} molar fractions with fixed total pressures.

2.3.2. Carbonation Reaction Rate with Different Fractions of CO\textsubscript{2} at a Fixed Total Pressure

In CLP, desirable calcium-based sorbents should have the properties of being good in reactivity and recyclability which would reduce the reactor size and optimize the reactor design. In addition, a high reaction rate between CO\textsubscript{2} and the calcium-based sorbents is also necessary to design the reactor in a reasonable size. The syngas compositions are highly dependent on the type of gasifiers and the carbonation reaction rate is highly dependent on CO\textsubscript{2} partial pressure. The typical partial pressure of CO\textsubscript{2} from the gasifiers is 300 to 3200 torrs\textsuperscript{15, 23, 101}. Therefore, it is important to study the effect of different CO\textsubscript{2} molar fractions on the carbonation reaction rate at elevated pressure conditions. As the residence time of the sorbents in the CLP system is in an order of
seconds, the first regime of the carbonation reaction is of primary interest. Thus, in this study, the effect of CO$_2$ partial pressures on the rate of carbonation reaction was first investigated with the total pressure fixed. Several calcium-based sorbents were tested in different fractions of CO$_2$ with a fixed total pressure of 5000 torrs. Four representative fractions were used, 10%, 15%, 20%, and 30%.

As expected, the initial rate of carbonation was found to increase with an increase in the CO$_2$ fraction due to the higher driving force for the carbonation reaction as shown in Figure 2.4. It shows the weight capture versus time curves for the three calcium-based sorbents at different CO$_2$ fraction in the figure. An increase in the partial pressure of CO$_2$ produced a clear increase in the carbonation rate. That is, increasing CO$_2$ fraction in the system causes a shift in equilibrium and drives the reaction forward faster. As can be seen from Figure 2.4, the highest carbonation reaction rate occurs at 30% CO$_2$ fraction with a fixed total pressure for each sorbent.

The effect of CO$_2$ partial pressures at a constant system pressure on the reaction rate of three calcium-based sorbents is plotted in Figure 2.5. The carbonation reaction rate can be simply expressed as following:

\[
\text{Reaction rate} = k \cdot (P_{CO_2})^n
\]  

(2.4)
The reaction order can be obtained by linearly fitting Eq (2.4) with experimental data. As can be seen from Figure 2.5, the carbonation reaction is of a first-order reaction for all three calcium-based sorbents (n=1).

In addition, based on the grain model, the reaction rate for a CaO-CO\textsubscript{2} system under the first regime can also be expressed as a specific rate as given below:

\[
R' = \frac{dx}{dt(1-X)} = 3r(1-X)^{-1/3} = 56k_s(P_{CO_2}-P_{CO_2,eq})^nS
\]  
(2.5)

At initial time, t= 0, the surface area is S\textsubscript{0} and the reaction rate is r\textsubscript{0}, Eq. (2.5) becomes

\[
R' = \frac{dx}{dt} = 3r_0 = 56k_s(P_{CO_2}-P_{CO_2,eq})^nS_0
\]  
(2.6)

\[
\ln(r_0) = n\ln(P_{CO_2}-P_{CO_2,eq}) + \ln(S_0) + \ln\left(\frac{56k_s}{3}\right)
\]  
(2.7)

At a given temperature, k\textsubscript{s} and S\textsubscript{0} are constant. The equilibrium partial pressure of CO\textsubscript{2} can be calculated by following equation\textsuperscript{108}.

\[
P_{CO_2,eq} = 7.5 \times 10^{(-8308/T+9.079)}
\]  
(2.8)
Therefore, the order of the CaO-CO$_2$ reaction can be determined by the slope of a $\ln(r_0)$ vs $\ln[(P_{CO_2} - P_{CO_2,eq})/100]$ plot. Such plots are shown in Figure 2.6. It can be clearly seen from the figure that the CaO-CO$_2$ reaction is the first-order reaction for all three calcium-based sorbents.

The carbonation reaction can be considered as two elementary steps, adsorption/desorption and reaction steps, based on the Langmuir mechanism.

$$\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaO} \cdot \text{CO}_2 \rightarrow \text{CaCO}_3$$ (2.7)

Assume that rate constants for the adsorption, desorption and reaction are $k_1$, $k_{-1}$ and $k_2$, respectively. Let CaO, CO$_2$, and CaO · CO$_2$ be denoted as S, A, and AS. The reaction rate can be expressed as follows:

$$r = -\frac{dc_A}{dt} = \frac{k_1 k_2 c_A c_S}{k_1 c_A + k_{-1} + k_2}$$ (2.9)

At total pressure of 5000 torrs, the adsorption step is most likely to be the rate-limiting step, hence, $k_2 \gg k_1 c_A, k_{-1}$ and the reaction rate is given by the following:

$$r = k_1 c_A c_S$$ (2.10)
Based on Eq (2.10), the reaction is of first-order which is shown in Figure 2.6.

It can also be seen from Figure 2.5 that at any given CO\textsubscript{2} partial pressures, the CaO obtained from PCC (PCC\textsubscript{CaO}) has the highest carbonation reaction rate followed by the Ca(OH)\textsubscript{2} derived CaO (Ca(OH)\textsubscript{2}\textsubscript{CaO}) and limestone-derived CaO (CaCO\textsubscript{3}\textsubscript{CaO}). For example, the carbonation reaction rate of PCC\textsubscript{CaO} is almost twice as much as CaCO\textsubscript{3}\textsubscript{CaO} at a CO\textsubscript{2} partial pressure of 1500 torrs, corresponding to 30\% CO\textsubscript{2} at a total pressure of 5000 torrs. The reasons for the different performance of sorbents can be explained by the different morphological properties of their precursors and CaO derived from them.

Surface area and pore volume of three calcium-based sorbents and their precursors are given in Table 2.1. CaCO\textsubscript{3}\textsubscript{CaO}, Ca(OH)\textsubscript{2}\textsubscript{CaO} and PCC\textsubscript{CaO} were obtained by calcining their respective precursors at 700 °C for sufficient time. From the table it can been seen that PCC has higher surface area and pore volume than limestone and Ca(OH)\textsubscript{2}. In addition, the PCC has a unique pore size distribution with maximum pore volume at 30 nm as shown in Figure 2.7. The unique specific mesoporous structure and higher surface area and pore volume in the precursor enables favorable kinetics of carbonation reaction for PCC\textsubscript{CaO} even though it arrives at less surface area and pore volume after calcination \textsuperscript{39}. Unlike the PCC precursor, the CaCO\textsubscript{3} and Ca(OH)\textsubscript{2} are
composed of microporous structure are given in Figure 2.7. Most of the pores of CaCO$_3$ and Ca(OH)$_2$ lie in the diameter range of 5 nm. With the absence of a unique structure from the precursor, the performance of their derived sorbents would be determined by their surface properties such as surface area and pore volume, instead. As can be seen from the Table 2.1, the Ca(OH)$_2$-CaO has a higher surface area and a pore volume than does CaCO$_3$-CaO. Hence, the Ca(OH)$_2$-CaO exhibits a better CO$_2$ capture capacity and initial reaction rate.

The use of fine powder sorbents over multiple calcination and carbonation cycles may be hampered due to difficulty in the separating the sorbents from other fine powders. Hence, limestone was tested in the form of pellets as well. The experiment was conducted at 10%, 15%, 20%, and 25% CO$_2$ with the total pressure of 3800 torrs. A notable increase in the carbonation reaction rate with increasing CO$_2$ partial pressure can also be observed in Figure 2.8(a). It can be seen from Figure 2.8(a) that the fastest reaction rate occurred at 25% CO$_2$. Moreover, the carbonation of CaCO$_3$-CaO in the pellet form is also a first-order reaction as shown in Figure 2.8(b). Even though, the particles are in different forms, they display a similar performance with respect to the partial pressure of CO$_2$ at the fixed total pressure. Hence, the morphological structure differences in different calcium-based sorbents are believed to be responsible for the
difference in performance instead of their physical form, either in the powder or pellet form.

2.3.3. Carbonation Reaction Rate with Different Total Pressures at a Constant CO$_2$ Molar Fraction

To examine the effect of total pressures on CaO, the three precursors were calcined at 1000 torrs and 700 °C under 120 ml/min of the nitrogen flow. The CaO generated was then exposed to the reactant gas mixture comprising of CO$_2$ and N$_2$ at the desired carbonation pressure in the range of 1000 to 15000 torrs at 700 °C under 120 ml/min of the reacting gas flow condition. All the experiments were conducted under a constant molar fraction (20%) of reacting gas CO$_2$ balanced with N$_2$. Since an increase in the operating pressure also represents an increasing in the reacting gas partial pressure, an increase in the reaction rate would be expected. The curves of weight capture versus time at selected total pressures are plotted in Figure 2.9. As shown in the figure, however, the carbonation reaction rate was found to increase with an increase in the total pressure from 1000 to 4000 torrs but began to decrease when the total pressure exceeded 4000 torrs for all three calcium-based sorbents. When the total pressure is 15000 torrs, the initial carbonation reaction is slightly slower compared to the reaction when the totals pressure of 4000 torrs.
The effect of different total pressures on the carbonation reaction rate of CaO obtained from the three precursors is plotted in Figure 2.10. The retardation of the carbonation reaction rate at the higher total pressures higher than 4000 torrs is similar to that of sulphidation reaction for the calcium-based sorbents. There are several effects that contribute to this behavior: total pressure, partial pressure and gas dispersion. Increasing the total pressure of the system leads to lower volumetric and linear velocities of the gas. Lower gas velocities will result in increased external mass transfer resistance which impedes the reaction between CO$_2$ and CaO. In other words, the decrease in reaction rate at higher pressure is likely to result from the increased mass transfer resistance.

The plot of $ln(r_0)$ vs $ln[(P_{CO_2}-P_{CO_2,eq})/100]$ for various calcium-based sorbents at different total pressures is shown in Figure 2.11. As can be seen, the carbonation reaction is a first-order reaction at lower partial pressures of CO$_2$ but becomes a zero-order reaction at higher pressures. The transition point occurs at corresponding partial pressures of CO$_2$ between 600-800 torrs. This is in good agreement with the results shown in Figure 2.10. The total pressure of 4000 torrs is taken as an approximation for the transition. The first-order reaction was only found for partial pressure of CO$_2$ ($P_{CO_2}$) less than 800 torrs, above which a zero-order reaction was observed. The changes in the carbonation reaction order in the first regime was also found in the study of Sun et al; the
transition point of this study, however, differs significantly from their work. They observed that the carbonation reaction rate was not further enhanced when $P_{CO_2}$ was over 75 torrs. Bhatia and Perlmutter conducted the carbonation reaction at $P_{CO_2}$ less than 75 torrs at 615 °C and found the reaction is of a first-order reaction. However, Kyaw et al. performed the carbonation reaction at higher $P_{CO_2}$ (>150 torrs) and a total pressure of 750 torrs and observed a zero-order reaction for both limestone and dolomite.

The change in the reaction order could also be explained by Eq (2.9). Once the rate-limiting step becomes the reaction step, $k_2 \ll k_1 C_A, k_{-1}$ and reaction rate is given by

$$r = -\frac{dC_A}{dt} = \frac{k_1 k_2 C_A C_S}{k_1 C_A + k_{-1}} = \frac{k_1 k_2 C_A C_S}{k_1 C_A + 1}$$

(2.11)

$$K_1 = \frac{k_1}{k_{-1}}$$

(2.12)

At a lower total pressure, it yields

$$r = K_1 k_2 C_A C_S$$

(2.13)

At a higher total pressure, it yields

$$r = k_2 C_S$$

(2.14)
Thus, Eq (2.13) reflects a first-order reaction with respect to specie A at lower total pressures while Eq (2.14) reflects a zero-order reaction with respect to A at higher total pressures since the $C_s$, $K_1$ and $k_2$ are constant at a given temperature condition.

2.3.4. Multiple cycles testing

The CaO sorbents undergo carbonation to form CaCO$_3$, which is regenerated by calcination to form CaO, releasing a pure CO$_2$ stream. For commercial viability, the spent calcium-based sorbents must be regenerated for multiple cycles to successfully maintain consistent reactivity. As can be seen in Figure 2.12, even the reaction rate for different calcium-based sorbents decreases with increasing number of cycles, the carbonation reaction rate at higher pressures is greater as compared to one at atmospheric pressure in each cycle.

In addition, it can be seen in Figure 2.13 that the reactivity decays with increasing cycles for various calcium-based sorbents under higher carbonation pressures as well. Though the kinetics of the carbonation reaction can be improved by conducting the reaction at higher pressures, the spent sorbents still need to be regenerated at elevated temperatures. Higher calcination temperatures will induce the thermal sintering and
hence the effect of sintering would cause the porosity deterioration and affect the CO$_2$ sorption.

The size of the reactor can be reduced by conducting the reaction under pressures. The information on CaO carbonation reaction kinetics at high pressures is not available in the literature. The results obtained in this work can thus be helpful for the analysis and design of pressurized calcium-based looping systems.

2.4. Conclusions

The calcium looping process (CLP) is a novel chemical looping process that efficiently converts syngas into hydrogen. The production of high purity hydrogen from the fuel gas, obtained from coal gasification, is limited by equilibrium relationship of WGS reaction. However, with the assistance of calcium-based sorbents, for in-situ removal of CO$_2$ and other pollutants, the extent of the hydrogen production in the WGS reactor is significant enhanced while the overall scheme for the syngas conversion to produce hydrogen is appreciably simplified. The CLP is operated at elevated pressures to ensure pure hydrogen production while enhancing the thermal efficiencies of the CLP simultaneously. In this study, experimental data for high-pressure carbonation were obtained at a temperature of 700 °C using MSB analyzer with three calcium-based
sorbents, i.e. CaCO$_3$, Ca(OH)$_2$ and PCC. The carbonation reaction can be considered for two regimes with the first regime involving a rapid chemical reaction which is followed by the second regime of a slow reaction characterized by the CaCO$_3$ layer formation that impedes the reactant gas diffusion. The effects of the total pressures and the CO$_2$ partial pressures on the carbonation reaction in the first regime were investigated. The results indicate that the rate of carbonation reaction linearly increases with CO$_2$ partial pressures and exhibits a first order reaction at a constant total pressure. However, the rate of carbonation reaction initially increases with increasing total pressures up to 4000 torrs, beyond which the total pressures does not further enhance the reaction rate for all the calcium-based sorbents used. The difference in the reaction order of the carbonation reaction can be explained by the Langmuir mechanism. In addition, the carbonation reaction was found to be of the first-order at lower total pressures but change to zero-order at higher total pressures. The difference in the reaction order of the carbonation reaction can be explained by the Langmuir mechanism. Further, the carbonation reaction rate under pressurized conditions decays slower than that under atmospheric conditions in the multiple cycle tests. The high-pressure kinetics data obtained in this work will be useful in the understanding the behavior of calcium-based sorbents in pressurized CLP.
2.5. Notations

\( C_A \): Concentration of CO\(_2\)

\( C_A \): Concentration of intermediate complex \( CaO \cdot CO_2 \)

\( C_S \): Total numbers site of CaO

\( k \): Rate constant \( \left( \frac{1}{\text{min} \cdot (\text{torr})^{-n}} \right) \)

\( k_1 \): Rate constant of adsorption

\( k_{-1} \): Rate constant of desorption

\( k_2 \): Rate constant of reaction

\( k_s \): Rate constant \( \left[ \frac{\text{mol}}{m^2 \cdot s \cdot (\text{torr})^{-n}} \right] \)

\( M \): Molecular weight (mol/g)

\( n \): Reaction order (-)

\( P \): Pressure (torr)

\( P_{\text{CO}_2} \): Partial pressure of CO\(_2\) (torr)

\( P_{\text{CO}_2,eq} \): Equilibrium of partial pressure of CO\(_2\) at given temperature (torr)

\( r \): The reaction rate in grain model (1/s), [the slope of \((1-(1-X)^{1/3})\) vs t]

\( r_0 \): Reaction rate at \( t=0 \) (1/s)

\( R \): Gas constant \((62.36 \ L \cdot \text{torr} / K \cdot \text{mol})\)

\( R' \): The specific rate (1/s)

\( R'_{0} \): Specific reaction rate at \( t=0 \) (1/s)
S: Specific surface area (m$^2$/g)

$S_0$: Specific surface area at $t=0$ (m$^2$/g)

$t$: Time (min)

T: Temperature (K)

V: Volume (L)

$W_0$: The weight of the sample after completion of calcination (g)

$W_t$: The weight of the sample at any given time $t$ (g)

X: Conversion of CaO (-)

Z: Compression factor (-)
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<td>PCC_CaO⁰</td>
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Table 2.1 The surface area and pore volume of the precursors and the derived CaO.

(⁰: Obtained from its representative precursor by calcining at 700 °C).
Figure 2.1 MSB Apparatus.
Figure 2.2 The effect of pressure on the weight measured in the MSB with inert gas.

$y = -4E-07x + 1.0909$

$R^2 = 0.9917$
Figure 2.3 The variation in the weight of the quartz crucible with pressure.
Figure 2.4 Effect of CO\textsubscript{2} fractions on the carbonation reaction rate with a fixed total system pressure of 5000 torrs:

(a) CaCO\textsubscript{3}\_CaO (b) PCC\_CaO (c) Ca(OH)\textsubscript{2}\_CaO (Carbonation temperature: 700 °C, total flow rate: 120 ml/min).
Figure 2.5 The carbonation reaction rate at different partial pressure of CO$_2$ of PCC$_\text{CaO}$, CaCO$_3$$_\text{CaO}$, and Ca(OH)$_2$$_\text{CaO}$ (Carbonation temperature: 700 °C and carbonation pressure: 5000 torrs).
Figure 2.6 Reaction order plot with varying CO$_2$ partial pressure at a constant total system pressure of 5000 torrs: (a) CaCO$_3$ - CaO (b) PCC - CaO (c) Ca(OH)$_2$ - CaO (carbonation temperature: 700°C, total flow rate: 120 ml/min).
Figure 2.7 Pore size distributions for different calcium-based sorbents before and after calcination.
Figure 2.8 (a) Effect of CO$_2$ fractions on the carbonation reaction rates of limestone pellet_CaO. (b) Reaction order plot with varying CO$_2$ partial pressures at a constant total system pressure. (Carbonation temperature: 700 °C and carbonation pressure: 3800 torr).
Figure 2.9 Effect of total system pressure on the carbonation reaction rates with a 20% CO₂ stream: (a) CaCO₃-CaO (b) PCC_CaO (c) Ca(OH)₂-CaO (Carbonation temperature: 700 °C and total flow rate: 120ml/min).
Figure 2.9 Continued.
Figure 2.10 The effect of different total system pressures on carbonation reaction rate of PCC_CaO, CaCO$_3$_CaO, and Ca(OH)$_2$_CaO (Carbonation temperature: 700 °C and CO$_2$ percentage: 20%).
Figure 2.11 Reaction order plot with varying CO\textsubscript{2} partial pressure corresponding to different total system pressures with a 20% CO\textsubscript{2} stream: (a) CaCO\textsubscript{3}CaO (b) PCC_CaO (c) Ca(OH)\textsubscript{2}CaO (carbonation temperature: 700°C).
Figure 2.12 The reaction rate of multiple cycles testing for PCC\_CaO, CaCO\textsubscript{3}\_CaO and Ca(OH)\textsubscript{2}\_CaO. (Carbonation temperature: 700 °C, carbonation pressure: 5000 torrs, CO\textsubscript{2} fraction: 10\%, and carbonation time: 30 min). (p: denoted as high pressure; a: denoted as atmospheric pressure).
Figure 2.13 The reaction rate of multiple cycles testing for PCC_CaO, CaCO$_3$-CaO and Ca(OH)$_2$-CaO. (Carbonation temperature: 700 °C, carbonation pressure: 5000 torrs, CO$_2$ fraction: 10%, and carbonation time: 30 min).
CHAPTER 3

Study the Deactivation Mechanism of Calcium-Based Sorbents and Reactivation Strategies in Calcium Looping Process (CLP)

3.1. Introduction

Hydrogen holds great promise as a source of environmentally friendly energy. Besides using hydrogen to produce energy through fuel cells or gas turbines, it can also be utilized for the production of liquid fuels and chemicals. Hydrogen production from coal gasification is considered as a promising technology due to large coal reserves, especially in the United States. The state of Ohio has a rich source of coal that has not been fully exploited yet. However, with conventional technologies, to remove impurities for produced hydrogen requires a large amount of energy, which poses a heavy burden on the cost of hydrogen production and subsequently lowers the overall efficiency.
The Calcium Looping Process (CLP) developed at the Ohio State University can enhance hydrogen production from the typical coal gasification by integrating the water gas shift (WGS) reaction with *in-situ* CO₂, sulfur and hydrogen halide removal at high temperature into a single stage reactor, leading to decrease the cost of hydrogen production and increase the overall process efficiency. The principle of enhancing hydrogen production by calcium-based sorbents is very simple but there exists some practical challenges, especially the loss in reactivity of sorbents. That is, the process requires calcium-based sorbents to be of high reaction capacity and have good regeneration ability while maintaining viability of the sorbents for over hundred or more cycles of usage.

The spent sorbents usually need to be fully regenerated at a very high temperature above 900 °C. The high regeneration temperature causes a severe sintering of sorbents and hence reduces the reactivity of sorbents over cycles. It is believed that sintering of sorbent is the main cause of deactivation by changing the surface texture properties. During sintering, the surface usually has growing macro
pores and shrinkage of smaller pores which reduces the CaO microporosity while increasing the macroporosity of CaO. These result in reducing surface area and pore volume which limits the CO$_2$ diffusion. This phenomenon usually occurred in the intermediate stage of sintering$^{116}$. The carbonation reaction could be divided into two stages, a fast reaction stage followed by a slow diffusion stage. The micropores contribute to the fast stage which stops when the micropores get plugged due to the increase of molar volume of formation of CaCO$_3$ layer. Although the larger pores (mesopores and macropores) could have more void space for the formation of CaCO$_3$, the formed CaCO$_3$ layer can then cause drastically increasing resistance of CO$_2$ diffusion. Therefore, this leads to a reduced fast carbonation reaction zone, and hence, decreases in CO$_2$ capture capacity of CaO sorbents over multiple cycles$^{116}$. The loss in reactivity of different calcium-based sorbents can be seen in Figure 3.1.

To be commercially viable, the improvement of sorbent reactivity is necessary and critical because sorbent replacement strongly influences the overall process such as sorbent cost, solid handling and the energy carried away by the purged sorbents.
These techniques undermine the main advantage of using natural limestone, which is cheap and abundant. For the past few years, many reactivation methods have been studied. Currently, hydration, support addition and thermal activation appear to be promising methods for restoring the reactivity.

Firstly, performance of CaO sorbents on the CO₂ capture could be improved by hydration using steam at the ambient pressure. The effect of steam hydration on the CO₂ capture capacity has been widely studied and the increase in reactivity of sorbents was confirmed. Hughes achieved 60-70 % reactivity after four cycles through hydration. On the other hand, the sorbents was observed to be reactivated by moisture as well. Fennll et al. showed the reactivity of limestone was restored to ~55 % by humid air at ambient temperature. Secondly, Manovic et al. showed that the reactivity of limestone increased with an increasing number of cycles after grinding and thermal treatment. The results showed the reactivity of sorbents reached to ~50% in the 30th cycles when sorbents were pretreated at temperature of 800-1100 °C. Finally, Sun et al. studied the reactivity of sorbents with different
dopants such as Al-, Si-, Ti-, Zr- and Mg- containing support. CaO sorbents with Al₂O₃ additions showed fairly reasonable results which maintained above 80% conversion after 15 cycles ¹¹⁹. Furthermore, it is found that the nano-CaO/Al₂O₃ exhibited a good performance over 50 cycles. The reactivity of sorbents became stable after 15th cycles and maintained at 60% in 50th cycle ⁶⁵.

However, these studies are incomplete and lack of a longer cycle testing and strong theoretical supports. Most of them only provided experimental results and are not suitable for any kind of calcium-based sorbents. From the theoretical point of view, more fundamental studies are necessary. This chapter would be based on these three methods to get more detail deactivation mechanism and have more understanding on these reactivation strategies. By doing so, the deactivation of the sorbents may be prohibited or hindered by these pretreatments or the reactivity of sorbents can be restored with a useful reactivation method in optimal conditions. By integrating these reactivation methods to the overall process, the efficiency and economics can be further increase.
Different reactivation methods will be investigated in this chapter which includes support addition, thermal activation and hydration. An ideal strategy is to successfully inhibit the deactivation of sorbents or effectively reactivate of sorbents and hence the overall process can be further modified. The integrated process depicts the potential to achieve higher system efficiencies and lower cost by combining different process units in one stage using sorbents with longer life cycle.

3.2. Experimental Sections

3.2.1. Pellet Preparation with Support Addition

Calcium-based sorbents were made in the form of pellets with Precipitated Calcium Carbonate (PCC), lime (CaO), limestone (CaCO₃) and calcium hydroxide (Ca(OH)₂) with 10 to 30 wt % inert supports, such as Al₂O₃, TiO₂ and Ash. The composite particles are cylindrical with 5 mm in a diameter and 2 mm in a height. For
the thermal pretreatment experiments, PCC in the forms of powders and pellets with different supports were pretreated at 900 °C for 24 hour before the reactivity testing.

In order to test the effect of hydration, the CaO sorbents were tested in the forms of powders and pellets. The CaO powders and pellets were exposed to humid air for 24 hour at room temperature to assure that the samples can be partially hydrated. Further, the hydration with excess water was applied to the sorbents after multiple calcination and carbonation cycles to further test the effect of the hydration in different levels of sintering.

3.2.2. Particle Reactivity and Recyclability

A Perkin Elmer Thermogravimetric Analyzer (TGA Pyris 1) is used to characterize the reactivity and recyclability of different samples. The schematic of the experimental setup is shown in Figure 3.2. The sensitivity of the TGA balance weighing mechanism is of the order of 0.001 mg. Pellets and powders samples are
directly used in the TGA. Before each experiment, around 20 mg of particle are loaded into a quartz crucible. Next, the TGA is purged with N₂ to introduce an inert atmosphere with 120 ml/min gas flow rate. The crucible is then heated to the desired calcination temperature of 700 ºC for 20 min to ensure the completion of the calcination reaction. After that, the temperature is lower to 650 ºC for the carbonation reaction. Unless otherwise mentioned, the calcination temperature is 700 ºC and carbonation temperature is 650 ºC in throughout study.

The extent of carbonation is identified by the weight gain of the sample in flowing reacting gas into TGA. To compare the reactivity of various calcium-based sorbents, about 120 ml/min of reactant gas, composed of 10% CO₂ (balanced with N₂) is introduced to the TGA. The weight change of the sample is recorded as a function of time, and the experiment is stopped after the carbonation reaches the second region. This point corresponds to the completion of first stage of carbonation under a given condition. To simulate carbonation and calcination cycles, the inert and reacting gases are alternately introduced to the TGA. Each of the carbonation-calcination steps
was conducted for 30 min. The change in reactivity is then monitored across cycles to evaluate sorbent recyclability.

3.2.3. Characterization of Morphological Properties

Physical characteristics of the particles are determined include the specific surface area, pore volume and pore size distribution. Such properties can be carried out by using low temperature nitrogen absorption technique (BET apparatus-NOVA 4200E). BET analysis is a non-destructive measurement of pore properties and only require small amounts (~0.2 g) of well-mixed samples. The BET surface area, pore volume and pore size distribution were measured at -196 °C using nitrogen as the adsorbent. All samples were vacuum degassed at 300 °C for 4 hour prior BET analysis.
3.3. Results and Discussions

3.3.1. The Reactivity and Recyclability of Calcium-Based Sorbents with Support Additions

The calcination reaction is an endothermic reaction and hence the spent sorbents is required to be regenerated at a higher temperature above 900 °C. However, the effect of sintering becomes severer when the calcination temperature increases. It has been shown that the sintering is resulted in the pore closure, particle aggregation or decreasing in surface area and pore volume. Therefore, the preservation of the morphology of sorbents is found to be an important factor under cyclic testing since it affects the reactivity and recyclability of the calcined sorbents. In this chapter, the inert supports are added and are expected to provide a stable structure in order to maintain acceptable reactivity of sorbents over multiple cycles.
First of all, the PCC powders mixed with 10-30 % of TiO$_2$ or Al$_2$O$_3$ were made in the form of pellets. It is shown in Figure 3.3 that the PCC pellets with different percentages of support show a similar conversion. That is, there is no clearly difference in the conversion of PCC pellets in terms of concentration of additions. Similar trend is obtained for both PCC pellets with TiO$_2$ and Al$_2$O$_3$ additions. This can be explained by their surface properties listed in Table 3.1. As can be seen, the PCC pellets with various percentages of different supports, TiO$_2$ or Al$_2$O$_3$, contained the similar surface area and pore volume. In addition, the pore size distribution for different sorbents displayed a similar profile at a given condition. It can be seen from the Figure 3.4 to Figure 3.7 that the PCC pellets with various fractions of TiO$_2$ supports contain a maximum pore diameter at 30 nm before and after calcination. Additionally, the PCC pellets with various fractions of Al$_2$O$_3$ supports have most pores lied at 5 nm before and after calcination. Maximum pores of PCC pellets with TiO$_2$ or Al$_2$O$_3$ are both located at a mesoporous range which has been proved to be favor in the carbonation reaction. However, the sorbents with the additions have a predominately pore structure at the first place, this structure cannot sustain after
several calcination and carbonation cycles. It is shown in Figure 3.8 that the reactivity of PCC pellets with 20% TiO$_2$ or Al$_2$O$_3$ dropped to a half value after 60 cycles compared to that at the first cycle. This is likely that the strength of the composite pellets is not strong enough and thus the structure of sorbents is difficult to retain after multiple calcination and carbonation reaction cycles.

Alternatively, the reactivity of naturally-occurring calcium-based sorbents with support additions was also tested, including CaCO$_3$, Ca(OH)$_2$ and CaO. As can be seen from Figure 3.9, there is no clear difference in the reactivity of CaO sorbents obtained from CaCO$_3$ regardless of its physical form, pellets or powders, or the kind of inert supports. Limestone pellets with 10% Al$_2$O$_3$, TiO$_2$ or ash have a similar performance on the CO$_2$ capture capacity over ten cycles as well as pure limestone powders and pellets. Additionally, the reactivity of pure Ca(OH)$_2$ in the form of powders and pellets, and Ca(OH)$_2$ with 10% Al$_2$O$_3$ in the form of pellets was shown in Figure 3.10. It can be seen that all Ca(OH)$_2$ sorbents have the similar reactivity at first three cycles, however, the reactivity of Ca(OH)$_2$ powders decays much faster.
among all three sorbents after that. Further, it is found that the reactivity of lime in the form of powders and pellets is the lowest among all three precursors but the reactivity of sorbents can be significantly improved by adding the inert supports.

It can be stated that making the calcium-based sorbents in the form of pellets with support additions is not guarantee to improve the durability of sorbents. Further, the material cost could be increase by support additions and hence the detail economic analysis is desired and further development of sorbents is required, such as how to increase the strength of the sorbents and how to maintain certain reactivity longer.

### 3.3.2. Thermal Pretreatment

In order to provide the calcium-base sorbents with stronger and persistence morphology structure, Manovic proposed a methodology which is called self-reactivation by thermal pretreatment. Four Canadian limestones were used in the work of Manovic et al.\textsuperscript{117-118} The samples were heated for 24 hour in 100% N\textsubscript{2} at different
temperature from 800-1200 °C. It is observed that the reactivity is better for those pretreated at 800-1000 °C. The samples with pretreatment at 1000 °C can maintain 50% carbonation conversion after 30 cycles.

This method is further proved with CaO sorbents in a different physical form and the combining effect of thermal pretreatment and support additions is also investigated in the following. It can be seen from Figure 3.12 that the pure PCC pellet with thermal pretreatment at 900 °C for 24 hour exhibited much lower reactivity at the first few cycles compared to that without pretreatment, however, the sorbents were reactivated by themselves and have a higher reactivity after 10 cycles.

In addition, PCC pellets with 20% TiO₂ or Al₂O₃ can also be reactivated by thermal pretreatment and it is found that the reactivity becomes stable after 10 cycles as shown in Figure 3.13. However, the reactivity of sorbents with supports does not recovery to higher state compared to that without pretreatment, especially for the PCC pellets with 20% Al₂O₃.
Similar as the effect of support additions, the thermal pretreatment is capable of recovering the reactivity. However, its practical applications in a real system still need to be further investigated.

### 3.3.3. Hydration

To date, hydration is considered as the most promising method to reactivate the sintered CaO sorbents. The partially hydration can possibly reduce the effects of sintering and change the surface properties of the spent sorbents. For the hydrated lime, the molar volume is closer to limestone but the molar mass is closer to lime. Therefore, the hydrated lime has lower density. The hydrated lime creates “popcorn” effect on the particle which increases surface area and thus enhances the reactivity of CaO sorbents. As can be seen from Figure 3.14, it is clear that the diameter of the lime pellet after partial hydration swelled two times as much as that of an initial pellet. This is likely that lime pellet reacted with the moisture in the air to form the calcium hydroxide. The hydration reaction is as following:
In the Figure 3.15, it is showed that the CO₂ capture capability of lime sorbents significantly improved by the hydration, in particular of pure lime powder. Furthermore, the lime pellets with inert supports have the similar trend while the partially hydration is applied. These sorbents were only hydrated once before the TGA test but the reactivity can be maintained over 10 cycles.

Additionally, the hydration was applied to Graymont limestone after 15 calcination and carbonation cycles to further investigate the effect of hydration. The hydration by water was conducted after the 15th, 16th, 17th, 18th, 19th and 35th cycle. It is shown in the Figure 3.16 that the reactivity decreased from 61% to 32% after first 15 cycles; however, the reactivity is gradually recovered to its original value while reacting with water. As can be seen, it is indicated that the reactivity of sorbents was recovery to 60% at 20th cycles. Furthermore, it is found that the decay rate of the sorbent reactivity is slower once the hydration is applied. It also can be seen from
Figure 3.16, the durability of sorbents derived from Ca(OH)$_2$ is better compared to that of sorbents obtained from CaCO$_3$.

Based on the above investigations, it is found that hydration is the most promising reactivation among all three. Hence, the detail mechanism of the hydration will be studied in the following chapters.

### 3.4. Conclusions

Hydrogen can be utilized in many different applications such as generating electricity, producing liquid fuel, and using in fuel cell. It has been shown that enhancing hydrogen production by calcium-based sorbents is a promising technology; however, the decay of sorbents reactivity is the main problem for all the calcium-based processes. Due to the sintering, the reactivity of calcium-based sorbents decays because of reducing surface area and pore volume. Based on the results obtained from this chapter, all three methods, support additions, thermal pretreatment, and hydration,
can increase or reactivate the reactivity of sorbents. These reactivation steps can substantially reduce the decay in carbonation capacity; however it is essential to better understand all the mechanisms responsible for the low conversion of the materials at extended number of cycles and thoroughly study the deactivation mechanism and reactivation strategy. Even though the reactivation step can improve the performance of the sorbents, the benefit of the very low cost of natural limestone may be lost. Therefore, comprehensive consideration of cost and performance is important. More detailed investigation about deactivation mechanism and reactivation strategy is required. While the deactivation mechanism is somewhat understood and useful reactivation method is identified, it would be able to utilize the calcium based sorbents along with the development of optimal strategy to improve both the process efficiency and economics.
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</table>

Table 3.1 The surface area and pore volume with PCC pellet with various supports.
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CHAPTER 4

Reactivation of Calcium-Based Sorbents through Hydration

4.1. Introduction

An increasing energy demand and growing concerns over the CO$_2$ emission have led to the development of efficient energy conversion systems that can also capture CO$_2$. In the recent years, the concept of calcium-based looping processes, i.e. calcination and carbonation reactions, has been considered to be viable for CO$_2$ separation in process systems involved in post combustion $^{114, 120-122}$ or in pre combustion $^{29, 123-125}$ and the enhancement of hydrogen production from gasification $^{25-26, 126-127}$ or steam methane reforming $^{128}$. The principle of these processes is simple and is based on the following reversible reaction:

$$\text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g) \quad (4.1)$$
Naturally-occurring limestone is abundant. For processes using calcium-based sorbents, the economic feasibility of the process is closely associated with sorbent recyclability. CaO derived from natural sources, however, fails to achieve complete reconversion to CaCO$_3$ and exhibit a rapid decay in the reactivity when undergoing cyclic reactions and regenerations $^{52, 129}$. More fresh sorbents are required eventually for the processes, which in turn increases the overall operational costs with more spent sorbents discharged causing another environmental concern $^{15}$. The decay of calcium-based sorbents is likely due to thermal sintering at high regeneration temperatures leading to degradation in surface area, pore volume, and pore structure $^{30}$. In general, the spent sorbents require an elevated temperature above 900 °C to be fully regenerated. During the sintering, the surface area and pore volume of the sorbents reduces, resulting from the porosity transformation in that the micropores decrease while the macropores increase. Typically, the carbonation reaction occurs in two steps, i.e. a fast reaction take places initially followed by a slow reaction due to the formation of CaCO$_3$ layer. The work of Sun et al. indicated that the carbonation reaction mostly occur in the smaller pores as a result of the less surface area of the
larger pores. The fast reaction step stops when smaller pores are plugged resulted from the formation of CaCO₃ layer. The increasing thickness of CaCO₃ layer drastically increases the resistance of CO₂ diffusion and decreases the CO₂ capture capacity.

Improving sorbents reactivity and recyclability is thus necessary and crucial to commercial viability of the calcium-based technology for CO₂ capture. Considering various calcium-based sorbents, hydrated lime (Ca(OH)₂) has been commonly used in industry for in-duct injection in SO₂ removal from the flue gas stream in coal combustion. For CO₂ removal from the flue gas stream in coal combustion, the first test of industrial hydrated lime was carried out in a 120 KWth sub-pilot coal combustor in the Carbonation-Calcination Reaction (CCR) process developed at the Ohio State University (OSU) in 2008. In this sub-pilot demonstration utilizing coal at 20 pounds per hour along with natural gas with Ca(OH)₂ as the sorbents for CO₂ capture, over 90% CO₂ capture and near 100% SO₂ capture was achieved on a once through basis at a Ca:C mole ratio of 1.3. At this molar ratio, the sorbent
reactivity could be maintained over multiple carbonation-calcination-hydration cycles \(^{95,120}\). It is recognized to date that for a process using calcium-based sorbents for high temperature \(\text{CO}_2\) capture, like \(\text{SO}_2\) capture, \(\text{Ca(OH)}_2\) is considered to be the most promising sorbent. The mechanism for the effectiveness of the \(\text{SO}_2\) and/or \(\text{CO}_2\) capture is of great interest. For \(\text{SO}_2\) removal, it is believed that during the hydration, the water molecules can easily permeate into the \(\text{CaSO}_4\) layer and then react with the unreacted \(\text{CaO}\) to form \(\text{Ca(OH)}_2\). \(\text{Ca(OH)}_2\), which has a larger molar volume than \(\text{CaO}\), swells and causes crack on the external shell of sulfate \(^{130}\). The expansion at the outer surface of \(\text{CaSO}_4\) would allow more \(\text{SO}_2\) to diffuse into the interior and hence further improve the sorbent utilization. The hydration is expected to diminish the effect of sintering because it can change some of the molar properties of the sorbents particles, including surface area, pore volume and pore structure. For \(\text{CO}_2\) capture, Zeman indicated that the molar volume of \(\text{Ca(OH)}_2\) is close to that of \(\text{CaCO}_3\) but its molar mass is similar to \(\text{CaO}\) and hence results in a lower density after the hydration \(^{80}\). The study assumed that the remainder of a unit volume in \(\text{Ca(OH)}_2\) is filled with pore surfaces and those pore surfaces are proportional to the surface area. That is, the
relative drop in density could produce a popcorn effect on the particle and create new surface areas for the carbonation reaction. Further, Gullet and Bruce found that the changes occur in chemical and physical properties of calcium-based sorbents upon intermediate hydration. However, those studies only show the effect of the hydration which is the improvement of CO$_2$ sorption capacity. The detailed reactivation mechanism through hydration is still sketchy up to date.

The purpose of this chapter is to conduct a systematic investigation of the characteristics of the spent sorbents before and after the hydration, in particular with respect to their unique characteristics after reactivation. The behavior of the spent sorbents and reactivated sorbents is used to further probe the reactivation mechanism for its application in the calcium-based looping processes.
4.2. Experimental Sections

4.2.1. Materials

Among various calcium-based materials, naturally-occurring limestone offers several advantages including low cost and widespread availability. In order to minimize the uncertainty factors from the precursors, Graymont limestone from Pleasant Gap is used throughout study. The composition of Graymont limestone is given in Table 4.1. As can be seen, the Graymont limestone is high pure calcium carbonate (97.8%) with about 0.8 % silica, 1.2 % magnesium carbonate and traces of iron oxide and aluminum oxide. Additionally, CO$_2$ and N$_2$ used for carbonation and calcination reaction are 99.99 % and 99.999 % pure, respectively.
4.2.2. Particle Preparation

Graymont limestone is calcined at different temperatures from 800 to 1100 °C for different time durations, 1, 4, and 16 hour, respectively, to produce samples with various levels of sintering (denoted as sintered_CaO sorbents) under N$_2$ environment. Then, sintered_CaO sorbents are reactivated through hydration by excess water at room temperature for a constant reaction time to form Ca(OH)$_2$. The current study shows that water hydration at room temperature is a rapid process and almost complete hydration can be achieved in about 5 min, even for highly sintered samples. Once the hydration reaction is complete, the samples are heated to 200 °C to remove excess water. After that, Ca(OH)$_2$ is dehydrated at 700 °C under N$_2$ environment to form reactivated samples (denoted as hydrated_CaO sorbents). The experimental procedures are shown in Figure 4.1 and the corresponding reactions are listed as follows:

Calcination:\quad \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad (4.2)
Hydration: \[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \] (4.3)

Dehydration: \[ \text{Ca(OH)}_2(s) \rightarrow \text{CaO}(s) + \text{H}_2\text{O}(g) \] (4.4)

4.2.3. Chemical Characterization of Samples

The performance of CaO obtained from assorted conditions before and after the hydration towards the carbonation reaction is tested in Perkin Elmer Thermogravimetric Analyzer (Pyris TGA 1). Based on the previous kinetics study, the optimal temperature of carbonation is 650 °C and hence the carbonation reaction is conducted at this temperature in all experiments. Before each experiment, a small amount of samples (about 20 mg) is loaded into a quartz crucible and is heated up to desired reaction temperature with 120 ml/min inert gas (N₂). Once the temperature reaches to 650 °C, the samples are subjected to carbonation with a 10% CO₂ stream balanced with N₂ for 20 min. The total gas flow rate during carbonation is 120 ml/min as well. The sample weight is continuously recorded for further analysis. The weight gain of the sorbents will be used to determine the amount of calcium carbonate in the
sample. The sensitivity of the TGA balance weighing mechanism is of the order of 0.001 mg.

The weight capture (%) is defined as followed:

\[
\text{Weight capture \% (g-CO}_2\text{/g-sorbents)} = \left( \frac{W_f - W_o}{W_o} \right) \times 100
\]  

(4.1)

4.2.4. Physical Characterization of Samples

The characterization of morphological properties such as surface area, pore volume and pore size distribution are determined by the Brunauer-Emmett-Teller (BET) methods based on the adsorption and/or desorption curve, using NOVA 4200e analyzer (Quantachrome Company). BET analysis is a non-destructive measurement of pore properties and only require small amounts (~0.2 g) of well-mixed samples. The BET surface area, pore volume and pore size distribution are measured at -196 °C
using N$_2$ as the adsorbent. All samples are vacuum degassed at 300 °C for 4 hours prior to BET analysis. Moreover, not only the macroscopic properties are matter but also the microscopic properties. The surface morphologies of the sorbents before and after the hydration are examined by Scanning Electron Microscopic (XL-30 ESEM). Further, to associate the crystal structures of the sorbents obtained from various conditions to the CO$_2$ sorption capacity, XRD patterns are identified and quantitatively analyzed using X-Ray Diffraction (XRD) (Scintag XDS2000).

4.3. Results and Discussions

4.3.1 Physical and Chemical Characterizations of Various CaO Precursors

The physical properties of different calcium-based precursors, including Graymont lime (CaO), Graymont limestone (CaCO$_3$) and Graymont quick lime (Ca(OH)$_2$), are given in Table 4.2. It can be seen that CaO and Ca(OH)$_2$ contain only
one crystal structure, i.e. a cubic crystal structure and a hexagonal crystal structure, respectively, but CaCO$_3$ has three different crystal structures, including a trigonal crystal structure (Calcite), an orthorhombic crystal structure (Aragonite), and a hexagonal crystal structure (Vaterite).

A surface area and a pore volume of the precursors and their derived CaO are given in Table 4.3. As can be seen, Graymont lime exhibits relatively low reactivity compared to CaCO$_3$-CaO and Ca(OH)$_2$-CaO. It is likely that this is due to higher surface area and pore volume of CaCO$_3$-CaO and Ca(OH)$_2$-CaO, which is three to four times as much as lime. Pore size distributions of various calcium compounds are shown in Figure 4.2. As can be seen, CaO, CaCO$_3$ and Ca(OH)$_2$ are microporous in nature but CaCO$_3$ and Ca(OH)$_2$ become mesoporous after calcination. Such mesopores (5-20 nm) have been proved to be less susceptible to pore closure and sintering, leading to better CO$_2$ sorption capacity.$^{132}$ The detail effect of surface area, pore volume and pore size distribution on CO$_2$ sorption capacity of CaO obtained from different calcination conditions will be discussed in the following sections.
As a reference, XRD is performed on the CaO derived from all three precursors. From Figure 4.3, it is seen that all three derived sorbents show similar XRD spectra with the characteristics of CaO. That is, there is no difference in terms of position of each peak. However, there are significant changes in the intensity of XRD spectra before and after the hydration. These changes will be investigated with respect to CO$_2$ capture capacity in the following sections as well.

4.3.2. Chemical Characterization of Sintered_CaO Sorbents and Hydrated_CaO Sorbents

The performance of sintered_CaO sorbents and hydrated_CaO sorbents are first tested in TGA. As shown in Figure 4.4, the reactivity of sintered_CaO sorbents decreases with increasing calcination temperatures and/or calcination times but the original reactivity can be restored after the hydration. At a given calcination temperature, sintered_CaO sorbents have higher reactivity when calcination times are shorter and it is observed that their reactivity decreases with increasing times. For the
calcination temperature of 800 °C, the reactivity decreases from 43.81 % to 23.78 % when the calcination time increases from 1 hour to 16 hour. Once the calcination conducted at 1100 °C for 16 hour, the reactivity decays to less than 5%. Despite the reactivity of as low as only 3.08 % under such severe sintering condition, the sorbents can still be effectively reactivated through hydration with excess water at room temperature. It should be noted that there is no obvious difference in the reactivity of various hydrated_CaO sorbents, irrespective of extent of deactivation, as shown in Figure 4.4. Hence, it can be stated that the hydration can effectively reactivate the spent sorbents of various degree of sintering.

Numerous studies show that CO$_2$ capture by calcium-based sorbents is governed by the surface morphology and the texture of the sorbents$^{133-136}$. For the carbonation reaction, the effective surface area and pore volume are necessary to allow the adsorption of CO$_2$ molecules on the surface and the formation of calcium carbonate. The surface area and pore volume of CaO before and after hydration are given in Figure 4.5 and Figure 4.6. It is seen, as expected, that sintered_CaO sorbents
have comparatively less surface area and pore volume. The surface area and pore volume decrease with an increase in calcination times and/or calcination temperatures. In addition, a higher calcination temperature increases the reduction rate of the surface area and the pore volume. The original sorbent has a surface area of 20.21 m$^2$/g and a pore volume of 0.152 cm$^3$/g. Using the calcination temperature of 800 °C as an example, the surface area decreases from 7.81 m$^2$/g to 4.11 m$^2$/g and the pore volume decreases from 0.0465 cm$^3$/g to 0.0106 cm$^3$/g when the calcination time increases from 1 hour to 16 hour. However, the step of hydration can recover the surface area and the pore volume of sintered_CaO sorbents. As can be seen from Figure 4.5 and Figure 4.6, hydrated_CaO sorbents from various deactivated samples can even retain higher surface area and pore volume which is 1.7 times as much as those of the original sorbent. It can be concluded that the hydration has a notable effect on the deactivated sorbents in that it not only increases the surface area but also the pore volume. The surface area, pore volume and reactivity of sintered_CaO sorbents and hydrated_CaO sorbents are summarized in the Table 4.4.
Using BET analysis, the effects of the varying calcination times and temperatures on pore size distribution are investigated and are depicted in Figure 4.7. In all sintered_CaO sorbents, the mesoporosity is reduced with an increase in calcination times at a given temperature. The pore size distribution for deactivated sorbents peaks at the diameter of 5 nm. However, hydrated_CaO sorbents exhibit a bimodal distribution which peaks at 5 nm and 20 nm corresponding to microporous and mesoporous regimes respectively. It is clearly shown in Figure 4.7 that a strong presence of the 20 nm pores in hydrated_CaO sorbents which is believed to govern the performance of calcium-based sorbents on CO₂ sorption capacity. It can thus be inferred that the hydration results in a predominately mesoporous structure and an increase in surface area and pore volume.

Enhancement in the surface area, the pore volume and the pore structure through the hydration path is clearly evidenced; so is its close linkage to a high performance of hydrated_CaO sorbents on the CO₂ sorption capacity. In order to further understand the effect of the hydration on CO₂ sorption capacity, the reactivity
data for the original sorbent, sintered_CaO sorbents and hydrated_CaO sorbents with respect to the variation of surface area or pore volume is given in Figure 4.8. Surprisingly, the reactivity is directly proportional to the surface area or the pore volume only at lower values, but there is little reactivity variation at higher values. That is, hydrated_CaO sorbents have considerable higher surface area and pore volume than do the

It is likely that the exothermic hydration reaction results in inner-pore expansion and intra-particle attrition. Considerable heat is released once the water reacts with CaO, creating cracks and forming a porous structure on the outer surface. Those cracks are able to create channels extending toward the interior of the particle. In the BET analysis, the N₂ is used as an adsorbent to measure the surface area and the pore volume and such inert gas can easily penetrate the interior of particles without restraint. However, during the carbonation reaction, the CaCO₃ layer is formed simultaneously while the CO₂ molecules are adsorbed on a CaO surface. The formation of carbonate layer prohibits the diffusion of CO₂ molecules into the interior
of sorbents. Thus, the high surface area of locally available pores, created due to the hydration, is not accessible once the carbonate layer is formed on the outer surface as shown in Figure 4.9.

Surface morphologies of sorbents before and after the hydration are examined using the SEM. Due to the sintering; particles lose their individual identity and agglomerate together as shown in Figure 4.10. Additionally, it can be seen that the particles break into smaller particles and large cracks are found on the surface. The hydration results in the superior macrostructural properties, a high surface area, a high pore volume and a predominately mesoporous structure; however, during the hydration, massive microstructural changes occur simultaneously with macrostructural changes as a result of a complex interplay of the carbonation reaction. In the following sections, the changes at microscopic levels before and after the hydration are investigated.
The crystal structure is a unique arrangement of atoms in a crystalline solid and governs many of its physical properties. CaO, CaCO₃ and Ca(OH)₂ are composed of different crystal structures as shown in Figure 4.11. Due to the nature of CaCO₃, it contains three different kinds of crystal structure. In order to minimize the uncertainty in the carbonation product, the crystal structures of derived CaCO₃ obtained from the carbonation reaction of sintered_CaO sorbents and hydrated_CaO sorbents are detected using XRD. As can be seen from Figure 4.12, the spectra of these CaCO₃ are similar with the characteristics of calcite. No vaterite or aragonite is detected from the spectra. Despite different sources of CaO, i.e. sintered_CaO sorbents and hydrated_CaO sorbents, only CaCO₃ in the form of calcite is obtained. This is predictable since the calcite is the most stable polymorph of CaCO₃. The other two are in the metastable phase of calcium carbonate at ambient conditions and vaterite is even more unstable. Aragonite changes to calcite at 470 °C and vaterite change to calcite at low temperature or aragonite at high temperature (~ 60 °C) once it is exposed to water.
Eliminating the possibility of different polymorphs resulting from the carbonation reaction, XRD is performed on different sintered_CaO sorbents and hydrated_CaO sorbents. The samples are prepared by homogenizing powders on the holder with non-diffraction pattern and the spectrum is detected over the angular range 25°-70° (2θ) in 0.03° and 1.8 s per step. These results are shown in Figure 4.13 to Figure 4.16. As can be seen, there is no distinct difference in terms of peak positions between sintered_CaO sorbents and hydrated_CaO sorbents at a given calcination temperature and/or a calcination time. This implies that the CaO structure is not changed before and after the hydration. Hence, it is stated that the crystal structure does not play a chemical role in the CO₂ capture.

However, it is known that crystals are composed of many crystallographic planes. Each plane has a specific interplanar distance and will give rise to a characteristic angle of diffracted X-rays. The relationship between wavelengths (λ), atomic space (d) and angle (θ) can be expressed by Bragg’s Law as follows:
On the other hand, each peak in the XRD pattern can represent a specific crystallographic plane. The first five planes in the CaO surface are a CaO(111) plane, a CaO(200) plane, a CaO(220) plane, a CaO(311) plane and a CaO(222) plane. It is observed that the sintered sorbent and the hydrated sorbents have the same peaks which are the characteristic values of CaO. However, the intensity and peak breadth of XRD spectra for CaO before and after the hydration are different, possibly leading to their distinct performance on the CO₂ carrying capacity. The intensity of each crystal plane of the sorbents obtained from different conditions is summarized in Table 4.5. It can be seen that the intensity of a CaO(111) plane and a CaO(200) plane increases and decreases for the rest, once hydration is applied. For example, in Table 4.5, hydrated_CaO sorbent calcined at 1100 °C for 16 hour has 19.9% of a CaO(111) plane and 49.1% of a CaO(200) plane, however, sintered_CaO sorbent only has 16.9% of a CaO(111) plane and 46.9% of a CaO(200) plane. The CO₂ capture capacities are 55.1 wt% and 3.1 wt%, respectively. This trend can be observed for
each sorbent at a given calcination temperature and/or calcination time before and after the hydration.

The crystallographic planes are the fictitious planes linking nodes. Each of them may have different atomic arrangements, resulting in a higher density of nodes and leading to different behavior of the crystal such as optical properties, surface tension, cleavage, microstructure defects, adsorption and reactivity. Once CO$_2$ molecules diffuse to the surface, they tend to adsorb on the site with a lower energy barrier. In addition, a charge transferred from the oxygen anion (O$^2-$) on CaO surface to the CO$_2$ molecule can lead to energetically favorable carbonate species (CO$_3^{2-}$). Depending on the geometric difference of each crystallographic plane, the coordinated number of surface oxygen would not be the same and thus it may affect the CO$_2$ adsorption on the CaO surface. Due to the nature of CaCO$_3$, the CO$_2$ would tend to interact more strongly with lower coordinated numbers of surface oxygen$^{137}$. The intensity of each plane on the CaO surface with respect to reactivity is plotted in Figure 4.17. It can be seen that more CaO(111) planes and CaO(200) planes on the
CaO surface leads to a better CO$_2$ capture capacity. Jensen et al. has shown that CO$_2$ would adsorb as monodentate on both edge and corner site on a regular CaO(100) plane but no stable CO$_2$ adsorption is found on the terrace site $^{137}$. That is, the energy barrier of CO$_2$ molecules on a given crystal plane may vary a lot and hence different preferred orientations on a CaO surface lead to different performance on the CO$_2$ capture capacity.

Once the hydration is applied to the deactivated sorbents, it not only improves the macroscopic properties such as surface area, pore volume and pore size distribution but also the microscopic structure, i.e. the concentrations of crystallographic planes on the CaO surface. The latter could play a very significant role in the CO$_2$ sorption capacity, leading to distinctly improved performance between deactivated sorbents and reactivated sorbents. More comprehensive study on the behavior of CO$_2$ adsorption on a given crystal surface of CaO will be investigated in the following chapter.
4.4. Conclusions

Calcium-based looping processes can be applied to a variety of energy and environmental systems. However, the decay of the reactivity of the sorbents under cyclic operations has posted challenges in their sustained usage in process applications. However, with the inclusion of the hydration step in the calcination-carbonation scheme, the sorbent decay during their multiple cycle operations can be practically avoided, as demonstrated in 2008 by the CCR process for CO$_2$ capture using calcium-based sorbents at a 120 KWth coal combustion sub-pilot facility at the Ohio State University. This study systematically examines the fundamental reactivity characteristics of CaO derived from various precursors along with the hydration effects. In the study, Graymont limestone is subjected to different calcination conditions, leading to different degrees of sintering properties. It is found that an increase in calcination temperatures and/or calcination times yields a negative effect on CO$_2$ sorption capacity, but the reactivity of sintered sorbents is effectively restored through hydration with water. The results indicates that hydrated sorbents have
improved morphological properties such as surface area, pore volume and pore size distribution, which enhance the CO$_2$ sorption capacity. Further, the CO$_2$ sorption capacity is also improved with the alteration of microstructural properties due to the hydration, such as the preferred orientation on a CaO surface. Specifically, it is shown that the first two planes on the CaO surface, i.e. a CaO(111) plane and a CaO(200) plane, are found to increase after the hydration. It is observed that the preferred crystallographic planes on a CaO surface have a significant effect on the CO$_2$ sorption capacity. That is, with more CaO(111) planes and CaO(200) planes in the CaO sorbents, the CO$_2$ capture capacity can be enhanced. This finding has been further substantiated using the density-functional theory (DFT) calculation. The detailed quantum calculation of the interaction between CO$_2$ and each plane on the CaO surface is to be presented in next chapter.
4.5. Notations

\( d: \) The spacing between the planes in the atomic lattice (cm)

\( n: \) An integer

\( t: \) Time (min)

\( W_0: \) Initial sample weight after fully calcination (mg)

\( W_t: \) Sample weight at any given time \( t \) (mg)

\( \lambda: \) The wavelength (cm)

\( \theta: \) The angle between the incident ray and the scattering planes
<table>
<thead>
<tr>
<th>Component (%)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>Total Sulfur</th>
<th>MgCO$_3$</th>
<th>Mg</th>
<th>CaCO$_3$</th>
<th>Ca</th>
<th>LOF$^a$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.8</td>
<td>0.3</td>
<td>0.1</td>
<td>0.05</td>
<td>1.2</td>
<td>0.3</td>
<td>97.8</td>
<td>39.1</td>
<td>43.2</td>
</tr>
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</table>

Table 4.1 Compositions of Graymont Limestone.

($^a$ Loss on Fusion)
<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>Ca(OH)$_2$</th>
<th>CaCO$_3$</th>
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<tbody>
<tr>
<td><strong>Molar Mass (g/mol)</strong></td>
<td>56</td>
<td>74</td>
<td>100</td>
</tr>
<tr>
<td><strong>Density (g/cm$^3$)</strong></td>
<td>3.29</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.71 (Calcite)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.947 (Aragonite)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.645 (Vaterite)</td>
</tr>
<tr>
<td><strong>Crystal Structure</strong></td>
<td>Cubic</td>
<td>Hexagonal</td>
<td>Aragonite (orthorhombic)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Vaterite (hexagonal)</td>
</tr>
</tbody>
</table>

Table 4.2 Physical parameters comparison of various calcium compounds.
<table>
<thead>
<tr>
<th></th>
<th>CaO&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CaCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Ca(OH)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>CaCO&lt;sub&gt;3&lt;/sub&gt;-CaO&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Ca(OH)&lt;sub&gt;2&lt;/sub&gt;-CaO&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface area (m&lt;sup&gt;2&lt;/sup&gt;/g)</strong></td>
<td>6.72</td>
<td>0.9</td>
<td>10.16</td>
<td>20.21</td>
<td>25.90</td>
</tr>
<tr>
<td><strong>Pore volume (cc/g)</strong></td>
<td>0.03</td>
<td>0.003</td>
<td>0.047</td>
<td>0.152</td>
<td>0.159</td>
</tr>
<tr>
<td><strong>Reactivity</strong></td>
<td></td>
<td></td>
<td></td>
<td>57.36</td>
<td>51.80</td>
</tr>
<tr>
<td>(wt capture %)</td>
<td>22.37</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
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</tbody>
</table>

Table 4.3 The surface area, pore volume and CO<sub>2</sub> sorption capacity.

<sup>a</sup> Graymont quick lime  
<sup>b</sup> Graymont limestone  
<sup>c</sup> Graymont calcium hydroxide  
<sup>d</sup> Obtained by calcining its precursor at 700 °C
Table 4.4 Effect of calcination temperature and time on the morphological properties of sintered_CaO and hydrated_CaO
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**1100 °C**

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Table 4.5 The intensity of each crystallographic plane for various calcium oxides.
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Table 4.5 Continued.

(Reactivity: carbonated at 650°C with 10% CO₂ stream for 20mins)

(S: sintered_CaO sorbent; H: hydrated_CaO sorbent)
Figure 4.1 Experimental Procedures.
Figure 4.2 Pore size distributions of different sorbents before and after calcination.
Figure 4.3 XRD spectra of calcium oxides from various precursors (a) lime (b) limestone_CaO (c) Ca(OH)$_2$_CaO (PDF number: 37-1497).
Figure 4.4 The reactivity of various CaO towards carbonation at 650 °C for different calcination temperatures:
(a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C (Total gas flow rate: 120 ml/min; [CO2]=10%) (H: hydrated_CaO sorbents).
Figure 4.4 Effect of calcination temperatures and times on the surface area of sintered_CaO and hydrated_CaO sorbents: (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C (S: sintered_CaO sorbents; H: hydrated_CaO sorbents).
Figure 4.5 Effect of calcination temperatures and times on the pore volume of sintered_CaO and hydrated_CaO sorbents: (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C (S. Sintered_CaO sorbents; H: hydrated_CaO sorbents).
Figure 4.0.6 Pore size distributions for sintered_CaO and hydrated_CaO Sorbents for different calcination temperatures: (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C (S: sintered, H: hydrated).
Figure 4.7 (a) Effect of surface area on the reactivity of various calcium-based sorbent; (b) Effect of pore volume on the reactivity of various calcium-based sorbents.
Figure 4.8 Illustration of hydrated CaO sorbents.
Figure 4.9 SEM images for limestone sintered at 800°C for an hour (a) sintered_CaO sorbents (b) hydrated_CaO sorbents.
Figure 4.10 Crystal structure of (a) CaO (b) Ca(OH)$_2$ (c) Calcite CaCO$_3$ (d) Aragonite CaCO$_3$ (e) Vaterite CaCO$_3$. 
Figure 4.11 XRD spectra of CaCO$_3$ from sintered_CaO sorbent (top) and hydrated_CaO sorbent (bottom) (*: calcite, PDF number: 47-1743; #: calcium oxide, PDF number: 37-1497).
Figure 4.12 XRD Spectra for limestone sintered at 800 °C of sintered_CaO sorbents (left) and hydrated_CaO sorbents (right).
Figure 4.13 XRD Spectra for limestone sintered at 900 °C of sintered_CaO sorbents (left) and hydrated_CaO sorbents (right).
Figure 4.14 XRD Spectra for limestone sintered at 1000 °C of sintered_CaO sorbents (left) and hydrated_CaO sorbents (right).
Figure 4.15 XRD Spectra for limestone sintered at 1100 °C of sintered_CaO sorbents (left) and hydrated_CaO sorbents (right).
Figure 4.16 The effect of relative intensity of each crystallographic plane on the CO$_2$ sorption reactivity.
CHAPTER 5

Interpretation of the Effects of Hydration on the CO₂ Capture Capacity in CaO Using the Density Functional Theory

5.1. Introduction

The calcium-based sorbents have been widely used for a variety of applications, including the removal of CO₂ and the enhanced hydrogen production via calcium-based looping processes. In principle, the CO₂ capacity of the calcium-based sorbents is governed by the equilibrium relationship between CO₂, CaO and CaCO₃. In practice, however, due to diffusion limitation, the calcium-based sorbents can only reach close to the equilibrium sorption capacity in the first cycle. Due to the sintering effect of the spent sorbents in the regeneration cycle, the sorbent reactivity deteriorates leading to the decline of the sorbent capture capacity in the pursing cycle. From the empirical correlation, the reactivity of the sorbents can quickly decay to less than 20% in sorbent capture capacity within the first 20 cycles. In order to circumvent the rapid
reactivity decay, several approaches have been investigated, including synthesis of a high-surface-area calcium oxide from precipitated calcium carbonate $^{22}$, using different organometallic precursors $^{40}$, calcium oxide doped with alkali metals $^{54}$ and steam/water reactivation $^{15,95,120}$. In the Carbonation-Calcination Reaction (CCR) process developed at the Ohio State University, it was demonstrated in 2008 in a 120 KWth coal fire sub-pilot plant that CaO undergoing the carbonation-calcination–hydration scheme can capture CO$_2$ in many cycles while maintaining non-deteriorating CO$_2$ sorption capacity $^{95,120}$. In subsequent studies, it was found that the hydration process results in favorable sorbent morphology properties, including both macrostructural and microstructural properties. That is, the sintered sorbents retain a high surface area, a high pore volume and a predominately mesoporous structure after the hydration. Further, the preferred orientations on the CaO surface and the grain size are altered after the hydration and thus a greater carrying capacity is obtained $^{91,94,120}$.

On the study of CaO-CO$_2$ reactions at the molecular level, it is shown in the work of Jensen et al. that a lower Madelung potential causes a more delocalized electron distribution of surface oxygen and a more efficient overlap with the orbitals of adsorbing molecules, leading to a higher reactivity of CaO $^{137}$. Doyle et al. found that accordingly CO$_2$ adsorbs on oxygen sites of the CaO(100) surface, producing the carbonate-like species involving lattice oxygen $^{138}$. Additionally, the adsorption kinetics and dynamics
of CO₂ on reduced CaO(100) was investigated in the work of Kadossov et al. However, the studies of the CO₂ adsorption on the CaO surface are rather rare and merely focus on a single crystal surface of CaO, i.e. CaO (100), the dominate plane on the CaO surface.

The objective of this chapter is to illustrate the behavior of CO₂ adsorption on the CaO surface from the molecular viewpoint based on quantum calculation techniques. The density functional theory (DFT) calculation is employed to interpret the different behavior of CO₂ adsorption on three dominating crystallographic planes on the CaO surface, i.e. (100), (110) and (111), with CO₂ molecules adsorbed via the C atom of CO₂ molecules on Ca sites or O sites of CaO with the O atom of CO₂ molecules pointed to the Ca atom or the O atom of CaO. That is, the possible sites on a given CaO single crystal for CO₂ adsorption with respect to the possible orientations of CO₂ molecules will be examined. This study will base on the calculation of the adsorption energy on a given plane with an effort to provide a rationale interpretation of molecular activity in light of the available experimental data. This study is of significant importance to understand the effects of surface structures of CaO on the carbonation reaction.
5.2. Materials and Methods

Graymont limestone, composed of a highly pure calcite (97.8 %) with about 0.8 % silica, 1.2 % magnesium carbonate and traces of iron oxide and aluminum oxide, is used in this study. The limestone is calcined at 800 to 1300°C for 16 hours to produce calcium oxide under various degree of sintering. Then, the sintered sorbents are hydrated by excess water at room temperature.

The performance of various samples on CO$_2$ adsorption before and after reactivation is conducted in a Perkin-Elmer Thermogravimetric Analyzer (Pyris TGA 1). The reactive gas flow rate is 120 ml/min with a CO$_2$ concentration of 10% (balanced with N$_2$). The total gas flow rate and a CO$_2$ concentration are kept unchanged in throughout the study, unless otherwise indicated. The temperature for the carbonation reaction is set at 650°C and the carbonation duration is 20 min. Examination of the TGA results shows that 20 min of carbonation is sufficient for the transition from a fast reaction condition to a slow reaction controlled by diffusion condition. The sample weight is continuously recorded for analysis and corresponding weight gain of the sorbents is used to determine the amount of carbonate in the sample. The sensitivity of the TGA balance weighing mechanism is in an order of 1 µg.
The morphologies of selected samples are examined by scanning electron microscopy (XL-ESEM) with 15 kV of accelerating voltage. The samples is placed on an aluminum specimen with a carbon adhesive tab and coated with gold before examination. Images obtained by secondary electrons are presented in this study. Identification/quantification of the sintered samples before/after reactivation is also done by X-ray diffraction (XRD), with data collected on a Scintag XDS2000 diffractometer over the angular range 25°-70° (2θ) in 0.03° and 1.8 s per step. The phases of samples are identified and quantitative analyses.

5.3. Theory and Calculations

In the computation study, the first-principles calculations are carried out based on density functional theory (DFT) using Vienna Ab-Initio Simulation Package (VASP)\textsuperscript{140},\textsuperscript{141} Projector Augmented Wave (PAW) approaches of Generalized Gradient Approximation in the Perdew-Burke-Ernzerhof (GGA-PBE) form is used for the calculation.

The CaO low-index surfaces, CaO(111), CaO(100) and CaO(110) are cleaved from bulk CaO structures (a=b=c=4.81050 Å, α=β=γ=90°), as shown in Figure 4. These
surfaces structures are represented as semi-infinite slab models. There are 32 O atoms and 32 Ca atoms in a CaO(100) surface and a CaO(110) surface, respectively. In both cases, the top four layers are relaxed but the bottom four layers are fixed, instead. Further, there are 24 O atoms and 24 Ca atoms in a CaO(111) surface with top 6 layers relaxed and bottom 6 layers fixed. A vacuum layer with a thickness of 10 Å is used to separate the surfaces and their images.

A kinetic energy cutoff of 350 eV is used. K-point mesh of 2×2×1 Monkhorst-Pack scheme is used for a CaO(100) surface, 2×4×1 Monkhorst-Pack scheme is used for a CaO(110) surface and 4×4×1 k-point grid determined by the Gamma centered method is employed for a CaO(111) surface. A conjugate-gradient algorithm is adopted to relax the ions until the forces on unconstrained atoms are less than 0.01eV/Å.

The physical adsorption energy of CO$_2$ on CaO surface for each configuration is calculated by the follows:

$$\Delta E_{ads} = E_{CO_2+surf} - (E_{CO_2} + E_{surf})$$ (5.1)
Where $E_{CO_{2+surf}}$ the overall energy of the surface with is physically adsorbed CO$_2$, and $E_{CO_2}$ denoted the energy of a free carbon dioxide molecule calculated by placing a single CO$_2$ molecule in a 10×10×10 Å$^3$ cube. $E_{surf}$ represents the surface energy of the calcium oxide. A negative value of $\Delta E_{ads}$ corresponds to the possible adsorption configurations on a CaO surface. From the energy standpoint of view, more negative the value of $\Delta E_{ads}$ is, more favorable the adsorption process will be. The carbonation reaction can be considered as several elementary steps, including adsorption/desorption and reaction steps. When the adsorption energy is too low, the following reaction cannot take place. Therefore, there should exist an optimal adsorption energy which allows the adsorption process proceed but do not impede the formation of calcium carbonate.

5.4. Results and Discussions

5.4.1. The CO$_2$ Sorption Capacity Before and After Reactivation

The limestone is calcined at a milder calcination temperature of 700˚C to represent a reference sample, indicated as an original sorbent in the study. First, the
limestone is calcined at 800°C to 1300°C for 16 hours. After that, reactivation of the
sintered samples is carried out with excess water at room temperature. In Figure 5.1, it
shows the decay of reactivity of the sorbents with an increasing calcination temperature
and also the effect of water hydration on CO₂ sorption capacity of the sorbents. As can be
seen, the reactivity of limestone is decreasing with increasing calcination temperatures
due to enhanced sintering. Further, Figure 5.1 illustrates that the hydration improves the
CO₂ carrying capacity of the spent sorbents obtained from a given condition. The
sorption capacity changes of each sample before and after the hydration are summarized
in Table 5.1. The current work also shows that water hydration at room temperature is a
rapid process and almost complete hydration can be achieved in about 5 min, even for
highly sintered samples.

Figure 5.2 shows the differences in morphological properties of the samples
before and after the hydration. The agglomeration phenomenon is illustrated in Figure 5.2
(a) and Figure 5.2 (b). As can be seen, the limestone calcined at an extremely high
temperature of 1300°C produces nearly nonporous structures in the particles. The
blockage and collapse of pores of the sintered sorbents can hamper to the passage of CO₂
when the carbonation proceeds. In Figure 5.2 (c) and Figure 5.2 (d), however, the SEM
analyses show a significant fracture of particles after the hydration. Further, it is found
that the hydrated samples contain large cracks on the surface caused by the sample
swelling during the hydration and also there are still a lot of pores to be observed in the sorbents after the hydration. This structure is found to be beneficial to the carbonation reaction.

During the hydration, massive microstructural changes occur simultaneously with macrostructural changes as a result of a complex interplay of the carbonation reaction. The changes in phase of the sintered sorbents before and after the hydration are examined by XRD analyses, as illustrated in Figure 5.3. It is observed that the sintered sorbent and the hydrated sorbents have the same peaks which are the characteristic values of CaO. That is, there is no difference in terms of the crystal structure between the sintered sorbents and the hydrated sorbents. However, the intensity and peak breadth of XRD spectra for CaO before and after the hydration are different, leading to their distinct performance on the CO$_2$ carrying capacity.

The mean grain size can be determined from Scherrer equation based on the XRD line breadth as follows:

\[
L = \frac{k\lambda}{\beta \cos \theta} \tag{5.2}
\]
As can be seen in the XRD spectra that the main peak of the CaO crystal appears at $2\theta = 37.3^\circ$. A larger value of the peak breadth leads to a smaller grain size of the crystal. The main peak breadth in XRD spectra of each sorbent before and after the hydration are summarized in Table 5.2. It is known that sintering attributes to the growth of the CaO grain and thus the main peak breadth of the sintered sorbents is smaller compared to that of the hydrated sorbents. That is, a larger grain size of CaO results in a smaller the space between two CaO grains, leading to a greater CO$_2$ diffusion resistance and yielding the poor performance on the CO$_2$ sorption capacity.

Further, the intensity of each single crystal on the CaO surface before and after the hydration are given in Table 5.3. The intensity is represented as the concentration of each plane on a CaO surface. In this study, only the first three planes are considered. It is clearly shown that the fractions of a CaO(111) surface and a CaO(100) surface increase but that of a CaO(110) decreases after the hydration. The increasing concentration of a CaO(111) surface and a CaO(100) surface on the hydrated sorbents may be relevant to their superior CO$_2$ sorption capacity. Further, the energy barrier of CO$_2$ adsorption on a given crystal surface is different due to the variance in the atom arrangement on the surface. The CO$_2$ adsorption has not been studied intensively before by theoretically methods, therefore, the detail investigation using DFT calculation will be performed in the following section to further verify the above finding.
5.4.2. Computation Results

Different positions on a CaO surface and various orientations of CO$_2$ molecules are tested to obtain the most stable adsorption configuration of CO$_2$ molecules on a given CaO surface. The three low-index surfaces, (110), (100) and (111) as shown in Figure 5.4, are investigated.

The CO$_2$ molecules can attach onto the CaO surface either via the C atom on the top of the O sites or the Ca sites of CaO. In Figure 5.5, four possible positions of CO$_2$ adsorption on a CaO(110) surface are conducted first. Besides the position on the CaO surface, the orientations of CO$_2$ molecules also have a notable impact on the adsorption energy. Two orientations are chosen, i.e. the O atom of CO$_2$ molecule pointed to the Ca atom of CaO (Figure 5.5 (a) (c)) and that to the O atom of CaO (Figure 5.5 (b) (d)).

The calculated adsorption energies are given in Table 5.4. It is shown that configurations (a) and (b), obtaining the negative adsorption energy, are favored in the adsorption process of CO$_2$. The configurations (c) and (d), however, cannot be adsorbed by CO$_2$ molecules. The site on the top of the O atom of CaO, as expected, is the most favorable position among all the possible sites on a CaO(110) surface to form the CO$_3^{2-}$ compound. Such a negative adsorption energy is resulted from the redistribution of
electrons between the Ca atom of the CaO and the O atom of a formed compound (CO$_3^{2-}$). That is, the adsorption energy drastically decreases when the CO$_2$ molecules adsorb on top of the O atom on a CaO(110) surface with the O atom in a CO$_2$ molecule pointed to the Ca atom on the surface.

The preferred orientation on the surface is capable of redistributing electrons between CO$_2$ and the surface by locating anions and cations close to each other. This is in good agreement with the work of Jensen et al. and Kadossov et al.$^{137,139}$ They found that on a CaO(100) surface, the most stable adsorption configuration of CO$_2$ molecules is to adsorb via the C atom on O sites of CaO surface. Even though our calculation result of the adsorption energy is based on the semi-infinite slab model, it is consistent with the cluster model.$^{137,139}$ The configuration of CO$_2$ adsorbed on a CaO(110) surface after energy optimization is shown in Figure 5.6.

There are two different structures of a CaO(111) surface, including an O-terminated surface and a Ca-terminated surface, which is different from a CaO(110) surface. An O-terminated surface is investigated in this study to represent a CaO(111) surface since the carbonation reaction usually occurs in an oxidative environment. In Figure 5.7, various adsorption sites are also tested, such as above the oxygen triangle center, above the oxygen line center, and vertically above one oxygen anion on the
surface, with the O atom of CO$_2$ molecules towards to the Ca atom of CaO. However, a negative adsorption energy is only obtained in configuration (c). The adsorption energies of these configurations are summarized in Table 5.5.

DFT calculations similar to those for the (110) and (111) surfaces are performed for the CaO(100) surface to identify the relevant CO$_2$ adsorption minima. The calculated adsorption energy of the most stable configuration of CO$_2$ molecules on the three low-Miller index surfaces are summarized in Table 5.6. The relaxed adsorption images of CO$_2$ molecules on a surface are illustrated in Figure 5.8.

Stable configurations for CO$_2$ molecules on all the three surfaces are obtained. The CO$_2$ adsorption on a CaO(110) surface is found to be extremely stable, as indicated by its adsorption energy shown in Table 5.6. This can be interpreted from the structures of the CaO(110) surface relative to the other two surfaces. There are no Ca atoms on a O-terminated CaO(111) surface. As a result, adsorption of CO$_2$, which involves redistribution of the electrons between CO$_2$ molecules and the surface, tends to be more difficult on the CaO(111) surface. Although CaO(100) and CaO(110) surfaces both contain Ca atoms, the O atom on the CaO(100) surface is more saturated with five adjacent Ca atoms as compared to four adjacent Ca atoms on the CaO(110) surface. Therefore, a stronger binding between CO$_2$ molecules and surface oxygen atoms on the
CaO(110) can be expected. The strong binding on the CaO(110) surface can cause an irreversible adsorption of CO$_2$ molecules. That is, CO$_2$ adsorption on the CaO(110) surface may result in a stable structure that is difficult to convert to other chemical configurations. This will hinder subsequent formation of CaCO$_3$ thus reducing the CO$_2$ capture capacity of oxide particles with predominant (110) facets.

Unlike a CaO(110) surface, the adsorption energies of a CaO(111) surface and a CaO(100) surface are within a reasonable range and thus both surfaces are more important in the carbonation reaction than a CaO(110) surface. This result coincides with the previous experimental results. After the hydration, the concentrations of a CaO(111) surface and a CaO(100) surface are found to increase but that of a CaO(110) surface decreases, yielding an enhanced CO$_2$ sorption capacity. Hence, higher concentrations of a CaO(100) surface and a CaO(111) surface lead to a superior performance of CaO on the carbonation reaction. The adsorption images of CO$_2$ on a given surface are illustrated in Figure 5.8.
5.5. Conclusions

The hydration is a promising step in recovery the CO$_2$ capture capacity of the sintered calcium-based sorbents. It is shown that the hydration improves not only the pore structure, the surface area and the pore volume but also the grain size and the preferred orientations on a CaO surface. In this study, quantum chemical investigation of CO$_2$ adsorption on a CaO surface is performed using the density functional theory (DFT) calculation. The theoretical and experimental results obtained in this study are used to interpret the carbonation mechanism in the context of CO$_2$ adsorption on different single crystal surfaces of CaO sorbents. It is shown that the CO$_2$ molecules tend to be adsorbed on the O site of CaO through the C atom with the O atom of CO$_2$ molecules towards to the Ca atom of CaO. Further, it is shown from the calculations that CO$_2$ adsorption is more favorable on a CaO(111) surface and a CaO(100) surface than a CaO(110) surface. Even though the adsorption energy of CO$_2$ molecules on a CaO(110) surface is the most negative among all three planes, an extremely stable configuration can prohibit a further transformation of the intermediate (CaO-CO$_2$) into the calcium carbonate. This finding is in good agreement with the XRD results which show that more CaO(100) surfaces and CaO(111) surfaces are presented in the hydrated-calcined calcium-based sorbents, leading to a better CO$_2$ carrying capacity for the sorbents.
5.6. Notations

\[ E_{CO_2} : \] The energy of a free carbon dioxide molecule (eV)

\[ E_{surf} : \] The surface energy of the calcium oxide (eV)

\[ E_{CO_2+surf} : \] The overall energy of the surface with physically adsorbed CO\(_2\) (eV)

\[ k : \] The Scherre constant (~0.9)

\[ L : \] The grain size of CaO derived from different conditions (nm)

\[ \beta : \] The main peak breadth in XRD spectra (FWHM: full width at half maximum)

\[ \lambda : \] The X-Ray wavelength (=0.15406 nm)

\[ \theta : \] Bragg angle (degree)

\[ \Delta E_{ads} : \] The adsorption energy (eV)
Table 5.1 Comparison of reactivity (wt capture %) before and after hydration.

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Table 5.2 The main peak breadth (FWHM) of the sorbents before/after hydration.
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<td>30.02</td>
<td>26.75</td>
<td>31.04</td>
<td>30.00</td>
<td>29.22</td>
<td>32.05</td>
</tr>
<tr>
<td><strong>After</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydration</td>
<td>(111)</td>
<td>20.87</td>
<td>19.84</td>
<td>19.87</td>
<td>22.16</td>
<td>20.36</td>
</tr>
<tr>
<td>(200)</td>
<td>51.19</td>
<td>55.87</td>
<td>53.84</td>
<td>55.40</td>
<td>56.18</td>
<td>55.17</td>
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<tr>
<td>(220)</td>
<td>27.94</td>
<td>24.29</td>
<td>26.29</td>
<td>22.44</td>
<td>23.46</td>
<td>24.38</td>
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</tbody>
</table>

Table 5.3 The intensity of the first three planes on the CaO surface of various sorbents before and after hydration.
<table>
<thead>
<tr>
<th>Configuration</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy (eV)</td>
<td>-2.12</td>
<td>-0.10</td>
<td>0.9</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Table 5.4 Comparison adsorption energy of various configuration of CO$_2$ adsorption on (110) surface.
<table>
<thead>
<tr>
<th>Configuration</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy (eV)</td>
<td>0.12</td>
<td>1.15</td>
<td>-0.71</td>
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</tbody>
</table>

Table 5.5 Adsorption energy of CO₂ molecules on various position of a CaO(111) surface.
<table>
<thead>
<tr>
<th>Surface</th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy (eV)</td>
<td>-0.9</td>
<td>-2.12</td>
<td>-0.71</td>
</tr>
</tbody>
</table>

Table 5.6 Adsorption energy of CO$_2$ molecules on various CaO surfaces.
Figure 5.1 Effects of calcination temperatures on CO$_2$ sorption capacity of Graymont limestone and effects of water hydration on the sintered samples. (Calcination temperature, 800°C to 1300°C, for 16 hour; carbonation temperature, 650°C, for 20 min; total gas flow rate, 120 ml/min; [CO$_2$]=10%).
Figure 5.2 SEM images of samples before and after hydration (a) (b) sintered sample; (c) (d) hydrated samples. (Calcination temperature: 1300 °C, for 16 hour).
Figure 5.3 XRD spectra of the sintered sorbents obtained from different temperatures (a) Sintered (b) hydrated.
Figure 5.4 The low-index CaO surface (a) (100) (b) (110) (c) (110). (top: top view; bottom: side view).
Figure 5.5 Various initial configurations of CO$_2$ adsorption on a CaO(110) surface (top view).
Figure 5.6 Relaxed adsorption configuration of CO$_2$ adsorption on a CaO(110) surface.
Figure 5.7 Different relaxed configurations of CO₂ adsorption on a CaO(111) surface.

Carbon above (a) oxygen triangle center (b) oxygen line center (c) oxygen anion.
Figure 5.8 Relaxed adsorption images of CO$_2$ molecule on CaO surfaces.
CHAPTER 6

Conclusions and Recommendations

6.1. Integration of Hydration into Calcium Looping Process (CLP)

The idea of incorporating an intermediate hydration reactor, hydrator, in the carbonation-calcination process was first put forward by OSU and since then several studies conducted at relevant scales have confirmed the merit of such scheme. As of now, the biggest demonstration of the cyclic carbonation-calcination-hydration has been performed in a 120 kWth unit at OSU\textsuperscript{95,120}. In this sub-pilot demonstration utilizing coal at 20 pounds per hour along with natural gas with Ca(OH)\textsubscript{2} as the sorbents for CO\textsubscript{2} capture, over 90\% CO\textsubscript{2} capture and near 100\% SO\textsubscript{2} capture was achieved on a once through basis at a Ca:C mole ratio of 1.3. At this molar ratio, the sorbent reactivity could be maintained over multiple carbonation-calcination-hydration cycles\textsuperscript{95,120}.

It is found that the hydration can not only recover the reactivity of CaO sorbents but also impede the sintering of sorbents at a given temperature. The effect of the hydration on the extent of sintering is shown in Figure 6.1. It is shown that original
sorbent calcined at 900 °C for 22 hour only maintained CO₂ capture capacity of 10 wt %; however, the reactivity is restored to ~ 60 wt % after the hydration. Further, as can be seen, the reactivity of hydrated sorbents decayed slower compared to that of original sorbent. That is, the required time to reduce the reactivity of hydrated sorbents to ~10 wt % is much longer (~ 336 hour) compared that for original sorbent (~ 22 hour) at a given temperature. Hence, it can conclude that the unique morphological properties of CaO sorbents after the hydration can retard the occurrence of sintering. Additionally, it also can be seen from Figure 6.1 that regardless of the extent of sintering, hydration can effectively recovery the CO₂ sorption capacity of CaO sorbents.

From a practical point of view, the durability of the sorbent is more important than the single cycle reactivity. It was found that the hydration can also improve the recyclability of CaO sorbents. As can be seen from Figure 6.2, the weight capture of original limestone reduced to ~32 % after 15 calcination-carbonation reaction cycles; however, the calcined sorbents can retained about 53 wt % CO₂ capture capacity over 15 calcination-carbonation reaction cycles while the hydration is applied. On the other hand, CaO sorbents derived from Ca(OH)₂ have a better durability compared to that of CaO sorbents derived from CaCO₃. This is in good agreement with the work of Materic et al.⁹¹ and Arias et al.⁹⁴. It is found that the rate of carbonation in the diffusion controlled region is accelerated due to the hydration and thus reducing the decay rate of sorbent reactivity.
6.2. Concluding Remarks

A novel chemical looping gasification processes, the calcium looping process (CLP), is developed for hydrogen and electricity co-production from carbonaceous fuels. Through the assistance of calcium-oxide sorbents, this process is highly efficient with zero carbon emissions.

The performance of the calcium-based sorbents is the key to the process. An effective reactivation strategy is developed. The physical and chemical properties of the sorbents before and after reactivation are investigated, including the alterations in microstructure and macrostructure properties, reactivity and recyclability. It is found that hydration can fully eliminate the effect of the sintering caused by the high regeneration temperature on the CaO sorbent and thus the reactivity of CaO sorbents is effectively recover after the hydration. It is observed that the hydration results in a higher surface area and pore volume, and produces a predominately pore structure, leading to better CO$_2$ capture capacity. Moreover, it is indicated that the changes in microscopic levels play an important role in the CO$_2$ sorption capacity as well. The changes at the molecule level are further investigated using the quantum mechanics technique. This reactivation method is deemed suitable for the calcium looping process with strong theoretical and experimental supports.
6.3. Recommendations

The development of the CLP evolved from a new idea to successful bench scale test over the last six years. A 25 KW\textsubscript{th} sub-pilot unit has been constructed and continuous tests are underway. Aspen Plus® process simulation and preliminary economic analysis show that the processes are highly attractive both technically and economically.

Even the water hydration can result in a superior performance on CO\textsubscript{2} capture capacity of CaO sorbents; however, it is believed that operation of the hydrator at high temperatures (400-600 °C) will provide high quality heat which will be useful for heat integration in the plant. The hydration through high pressure steam at high temperatures does not require the cooling and reheating of the sorbents, thereby significantly reducing the parasitic energy consumption of the process. It is believed that the hydrated sorbents would need to perform consistently for at least 12-15 cycles to have realistic solids purge and make-up rates of 6-8%. However, as temperatures above 500 °C will require pressurized vessels, the hydrator operating conditions will be ultimately dictated by the economics.

While the investigations conducted on a bench-scale fixed-bed reactor setup at OSU using different limestones indicate that this is possible, further studies are being
undertaken to look at parameters like steam to CaO ratio, steam residence time, types of reactors, and modes of operation etc. with the aim of designing an actual commercial-scale hydrator. The future work should focus on further validating the feasibility of the process with commercialization as the ultimate goal. To achieve such a goal, future R&D efforts should concentrate on both the process scale up and reactivation strategy.

Besides scale up demonstrations, studies on the reactivation mechanism, and sorbent reactivity, recyclability and physical stability improvements are of vital importance to the success of the looping process. Further study should be focus on examining the subsequent transformation of the CO$_2$ adsorbed intermediate to the calcium carbonate. This can be done by synthesizing well defined surface and characterizing the adsorption energy of CO$_2$ molecules using Temperature Programmed Desorption (TPD) and also by perfecting the VASP model to match the experimental data better. Comprehensive studies on effective reactivation strategy of calcium-based sorbents will provide strong supports to the demonstration and can significantly improve the looping process economics.
Figure 6.1 Effect of calcination time on the hydrated sorbent at 900 °C, (■: original sorbents; ♦: sintered sorbents; ▲: hydrated sorbents).
Figure 6.2 Effect of the hydration on the decay rate of CO$_2$ sorption capacity of CaO sorbent (both calcination and carbonation at 700 °C for 30 min in each cycle; hydration with water was performed after 15$^{th}$ cycles).
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