CALCIUM LOOPING PROCESSES FOR PRE- AND POST-COMBUSTION
CARBON DIOXIDE CAPTURE APPLICATIONS

DISSERTATION

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ABSTRACT

Growing scientific consensus about the occurrence of global warming due to the anthropogenic emission of greenhouse gases, in particular carbon dioxide (CO₂), has led to a surge in research efforts to develop carbon capture and sequestration (CCS) technologies. CCS is perceived to be very important since it will allow the continued use of fossil fuels without causing significant harm to our environment. Majority of the CCS work is targeted towards coal, since it is the most abundant, widely-used and carbon-intensive fossil fuel. Though on a decline recently, coal still maintains the highest share in the electricity generation in the U.S. and consequently accounts for nearly a third of the CO₂ emission.

CO₂ control using the calcium looping process has received significant attention in the past two decades and is considered to be a viable CCS technology. Calcium looping employs a calcium sorbent – typically in the form of calcium oxide (CaO) – which can react with CO₂ present in flue or fuel gases to form calcium carbonate (CaCO₃). This reaction is reversible and the CaO can be regenerated to release a pure CO₂ stream for sequestration. When used in the post-combustion scenario, the process can be used for CO₂ removal only; however, in the pre-combustion case, production of H₂ from coal-derived syngas, natural gas, etc. can be achieved in addition to carbon capture.
The sorbent regeneration step in calcium looping requires high temperatures and leads to a decrease in reactivity toward CO₂ due to sintering. While the process has been rapidly scaled up to pilot plant demonstrations, the sintering challenge has persisted and has been the focus of the majority of the recent studies in this area. To overcome this problem, Prof. L.-S. Fan’s research group at The Ohio State University (OSU) has led the development of a unique three-step calcium looping process. The third step is the reactivation of the sorbent using steam hydration. The hydration occurs after regeneration (calcination) and prior to the reaction with CO₂ (carbonation), in every cycle. The integration of this sorbent reactivation step reverses the effect of sintering and maintains the reactivity of the sorbent toward CO₂ over many cycles.

This work advances the development of the calcium looping processes at OSU and builds on the foundation laid by previous researchers. The construction and operation of the sub-pilot scale reactor for hydrogen (H₂) production with in-situ CO₂ capture is the highlight of this work. The design of the sub-pilot reactor was based on the data obtained at bench-scale in prior work. Parametric tests quantifying the effect of sorbent loading and steam requirement were performed and it was found that syngas could be converted to a product gas containing 70% H₂ at a calcium to carbon mol ratio (Ca:C) of 1.5 and steam to carbon mol ratio (S:C) of 3.

To demonstrate the viability of the sorbent reactivation via hydration, CaO derived from several commercially-available limestones was subjected to multiple cycles of carbonation-calcination-hydration. More importantly, the hydration conditions employed
in this work were selected such that they are relevant to a commercially viable process. It was found that steam hydration could successfully maintain reactivity of CaO toward CO\textsubscript{2} over many cycles. It was also observed that the extent of hydration of CaO is a function of the CaO-precursor.

A detailed kinetic study of steam hydration of CaO was also undertaken to identify the optimum operating parameters for the calcium looping hydrator. The parametric tests included the study of the effect of steam partial pressure (0.4 – 0.8 atm), temperature (300 – 400 °C), and different calcination conditions. Steam-solid reaction kinetic data is usually rare and hence, the data obtained from this investigation makes a useful contribution to the scientific literature.

The non-isothermal direct carbonation of Ca(OH)\textsubscript{2} was also explored and the findings have important implications for OSU’s three-step calcium looping process. It was found that the sorbent achieved complete conversion to CaCO\textsubscript{3} when it was exposed to CO\textsubscript{2} under non-isothermal conditions. The direct carbonation did not exhibit the distinct two-regime reaction (kinetically-controlled and diffusion-limited) which is a characteristic of the calcium-CO\textsubscript{2} reaction.

The calcium looping process was also investigated for application to energy conversion systems that use natural gas as the feed. From the tests conducted using a bench-scale fixed-bed reactor, high-purity H\textsubscript{2} production and CO\textsubscript{2} capture was achieved via enhanced reforming of higher hydrocarbons like ethane and propane. The effects of S:C,
temperature, catalyst type, and different combinations of the feed gas mixtures were also studied. Post-combustion CO\textsubscript{2} capture from natural gas combined cycle (NGCC) plants was evaluated using Aspen Plus process simulations. The results indicated that calcium looping may not be the best technology for this scenario in terms of efficiency; however, it does present a unique advantage of maintaining the electric output of the plant unlike any other process.
Dedicated to my parents and sister.
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PUBLICATIONS


**FIELDS OF STUDY**

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CHAPTER 1
BACKGROUND AND MOTIVATION

The advancement of renewable energy sources notwithstanding, fossil fuels are expected to continue their domination as major energy providers in the near future. The predictions of the U.S. Energy Information Administration (EIA) – as outlined in the biennial study, International Energy Outlook – indicate that liquid fuels (i.e. crude oil) will remain the mainstay of world energy supply even in 2035, followed by coal and natural gas (U.S. EIA, 2011). From the EIA forecast, renewable energy appears to be the fastest growing mainly owing to the smaller baseline; its contribution in the energy mix still falls short of being momentous. From Figure 1.1, it is also interesting to note that most of the 53% rise predicted in the total energy consumption is principally driven by countries not part of the Organization for Economic Cooperation and Development (OECD). The OECD includes U.S., U.K., European Union, etc. and excludes emerging economies like China, India, Brazil, etc.

Future trends specific to coal are shown in Figure 1.2. While the popular impression may be that coal will eventually lose out to cleaner energy sources (e.g. natural gas and renewables), the EIA has predicted a robust growth rate of 1.5% (annual) in coal consumption, again galvanized by non-OECD nations. Heavy carbonaceous fuel
utilization will lead to substantial rise in carbon dioxide (CO$_2$) emission and there seems to be a growing consensus that this will alter climatic patterns (Broecker, 1975; Oreskes, 2004). In general, it can be envisaged that all the energy conversion technologies will become more efficient; however, a mere 2% improvement in energy-related CO$_2$ intensities does not seem sufficient if the goal is to combat global climate change (U.S. EIA, 2011). With this background, the development of carbon capture and sequestration (CCS) technologies has become necessary.

Figure 1.3 shows the three ways in which large-scale CO$_2$ removal can be performed – post-combustion, oxy-combustion and pre-combustion. In post-combustion, CO$_2$ is removed from a gas mixture (flue gas) produced from combusting the fuel. Oxy-combustion entails the combustion of the fuel in high-purity oxygen (O$_2$) so that the resulting flue gas is CO$_2$-rich. The advantage of oxy-combustion is that a CO$_2$ separation step is not necessary. In pre-combustion, the fuel is gasified (not combusted) to produce synthesis gas (syngas), which is a mixture of carbon monoxide (CO) and hydrogen (H$_2$). The syngas is then passed through several gas clean-up units, water gas shift (WGS) reactors and a CO$_2$ capture system. The fuel is mainly in the form of high-purity H$_2$ before it is used for any downstream applications like electricity production, chemical manufacturing or liquid fuel synthesis. The U.S. Department of Energy (DOE) has been promoting several CCS technologies which fall under the aforesaid categories (see Figure 1.4) (Figueroa et al., 2008). As per DOE, it is imperative that CCS technologies meet the target of ‘90% CO$_2$ capture at less than 35% increase in cost of electricity’ (Ciferno et al., 2009). It is believed that these technologies will allow prolonged use of
fossil fuels with minimum CO₂ emission to the atmosphere. The majority of the technology development is targeted towards coal, since it is the most abundant, widely-used and carbon-intensive fossil fuel.

The Ohio State University (OSU), led by Prof. L.-S. Fan’s research group, has been a pioneer in clean coal technology development in general, and chemical looping in particular. Calcium looping has been under development at OSU since early 2000 and several aspects have been scrutinized by erstwhile researchers (Iyer, 2006; Ramkumar, 2010; Wang, 2009). This study furthers the process development by providing relevant experimental data from reactor scale-up, addressing key issues related to sorbent recyclability and broadening the scope of process applicability.

Chapter 2 gives an introduction to calcium looping and provides a critical review of the recent work. It also highlights the important differences in the approach adopted by Prof. Fan’s group, when compared to competing efforts in this area.

Chapter 3 describes the scale-up of the Calcium Looping Process (CLP) and is the highlight of this study. Based on laboratory-scale data obtained by previous researchers, a sub-pilot scale reactor was designed, constructed and successfully operated. These details are discussed here; challenges faced during reactor operation are also briefly highlighted.

Chapter 4 discusses the results obtained from the investigation of calcium sorbents for CO₂ capture over several cycles, employing intermediate steam hydration. An important
aspect of this study is that realistic process conditions were used to evaluate the potential of OSU’s novel approach. In addition, several limestone samples from commercial vendors were obtained and examined to draw conclusions with greater confidence.

Chapters 5 and 6 focus on calcium looping for pre- and post-combustion CO₂ capture, respectively, when using natural gas as the fuel. Bench-scale experiments and process simulation using ASPEN Plus software were performed as a part of this investigation. The work assumes greater importance given the recent progress in the hydraulic fracturing technology for shale gas extraction which has made natural gas abundant and inexpensive.

Chapter 7 brings out an interesting aspect of CO₂ capture by calcium sorbents, which is specific to OSU’s calcium looping. The direct carbonation of calcium hydroxide (Ca(OH)₂) was studied and the results shed light on additional operational advantages, which were till now unidentified. The results also provide more insights into selection of operating parameters for key reactors.

Chapter 8 describes the construction and operation of a thermogravimetric analyzer (TGA) capable of handling high-temperature steam. The successful operation of this system marks a prominent step since it enables the kinetic investigation of high-temperature gas-solid reactions involving steam – a capability that was absent prior to the development of this steam TGA. Calcium oxide (CaO) hydration kinetics has been
studied using this TGA and the results are presented in this chapter. Chapter 9 provides recommendations for future work.

This study will also subtly elucidate the role of ‘external factors’ when conducting research in CCS and related fields. At the inception of this study, the ‘H\textsubscript{2} economy’ was considered to be an attractive proposition. The vision of the H\textsubscript{2} economy, proposed by the National Research Council (NRC) and National Academy of Engineering (NAE), was based on the presumption that H\textsubscript{2} production could be achieved from domestic energy sources like coal ‘in a manner that is affordable and environmentally benign’ and that H\textsubscript{2} could be used for applications like electricity production via fuel cells, powering vehicles, etc. (NRC and NAE, 2004). Consequently plentiful research funding was directed towards technologies capable of large-scale H\textsubscript{2} production and it was during this time that the idea of coal-to-H\textsubscript{2} (with CCS) became popular. This set the stage for the evolution of the CLP coal-to-H\textsubscript{2} process (discussed in Chapter 3). However, in early 2009, the repercussions of the progress in hydraulic fracturing for shale gas extraction could be clearly seen. Natural gas became abundant and inexpensive, and switching from coal to natural gas became an important strategy to decarbonize the energy industry. Since then stricter regulations for existing coal plants have further precipitated coal’s decline in the U.S. energy mix and has made concepts like coal-to-H\textsubscript{2} less appealing. On the other hand, natural gas-based electricity generation is set to grow rapidly. It is, therefore, logical to foresee a need for CCS technologies that suit natural gas plants and this became the main driving force for the study reported in Chapter 5. Considering past events, it is difficult to predict with reasonable accuracy the direction which the energy industry will take in the
long run. Nonetheless, the work conducted here proves that calcium looping is a dynamic and versatile concept that can adapt to any situation.
Figure 1.1. (a) World energy consumption (quadrillion BTU). (b) World energy consumption by fuel (quadrillion BTU) (U.S. EIA, 2011).
Figure 1.2. World coal consumption (quadrillion BTU) (U.S. EIA, 2011).
Figure 1.3. Large-scale CO$_2$ control strategies.
Figure 1.4. CO₂ capture technologies currently under development – cost reduction benefit versus time to commercialization (*can also be used for pre-combustion). Adapted from Figueora et al., 2009.
CHAPTER 2
INTRODUCTION AND CRITICAL REVIEW

Solid sorbents have attracted significant attention as a means of capturing CO₂ from gases emanating from fuel combustion and gasification. These sorbents can be broadly classified as physisorbents (e.g. zeolites, activated carbons, silica, etc.) and chemisorbents (e.g. hydrotalcites, metal oxides, etc.) (Lee et al., 2008). Among the metal oxides, extensive work has been reported on the metal oxide-carbonate (e.g. calcium, magnesium) and metal carbonate-bicarbonate (e.g. sodium, potassium) cycles. The former are more suitable for high-temperature applications (300 – 600 °C) while the latter operate at low temperatures (60 – 80 °C). The prodigious variety in solid sorbents has led to the development of numerous processes for pre- and post-combustion CO₂ removal. Since several comprehensive and authoritative reviews of this subject already exist in literature (Lee et al., 2008; Samanta et al., 2012; Sircar and Lee, 2010), a congruent one is not presented here.

1Parts of this chapter will appear in a paper in the journal Chemical Engineering & Technology. The material is reproduced here with permission from “Ca(OH)₂-based calcium looping technology development at The Ohio State University; N. Phalak, W. Wang, L.-S. Fan; Chemical Engineering & Technology – Chemical Looping Special Issue, in press. Copyright © 2013 Wiley-VCH.”
In the past two decades, the calcium oxide (CaO) – calcium carbonate (CaCO₃) cycle has been the most widely studied cycle with the prospect of developing into a large-scale CO₂ control technology (Blamey et al., 2010a; Fan, 2010). The reversible reaction between CaO and CO₂ forms the crux of this technology –

\[
\text{CaO(s)} + \text{CO}_2(g) \leftrightarrow \text{CaCO}_3(s)
\]

In a quintessential calcium-based CO₂ capture process, the carbonation of CaO by reaction with CO₂ from flue/fuel gas results in the formation of CaCO₃ and the reverse reaction (calcination) regenerates the CaO, releasing a pure CO₂ stream which can be sequestered. The sorbent is used repeatedly and cycled between the two reactors – carbonator and calciner – thus the name, calcium looping. Technically, calcium looping can be typecast under two CCS technology categories – solid sorbents and chemical looping (see Figure 1.4).

The large CO₂ carrying capacity (theoretically, 785 g CO₂/kg CaO) of CaO is an important advantage over other solid sorbents. CO₂ capture by CaO occurs at high temperatures (>500 °C), which offers good flexibility for integration in different energy systems. The naturally-occurring CaO precursors (limestone, dolomite, etc.) are abundant and inexpensive, adding to the economic attractiveness of the process. Extensive research on different aspects of calcium looping has led to rapid development; several projects have advanced to pilot-scale demonstrations indicating a strong commercialization potential in a carbon-constrained scenario (Dean et al., 2011; Fan et al., 2012). However, the decreasing CO₂ carrying capacity of CaO when used over multiple cycles is an important challenge that needs to be addressed.
It is now well-known that the reactivity of CaO toward CO$_2$ reduces with each successive cycle and this decay is mainly attributed to sintering (Wang and Anthony, 2005). A study by Iyer et al. showed that this phenomenon is true for all calcium sorbents – naturally-occurring and synthetic (Iyer et al., 2004). In calcium looping, sintering occurs during calcination because of the high temperatures (900 °C or greater) necessary to drive the reverse reaction. Sintering leads to a decrease in surface area and voidage of the sorbent due to grain growth and coalescence (Barker, 1973; Stanmore and Gilot, 2005). Since these physical properties directly correlate to the CO$_2$ capture capacity, the multicyclic sorbent performance is negatively affected (Sun et al., 2007). It has been reported that the extent of sintering is higher at greater times (calcination residence times) and elevated temperatures (Fuertes et al., 1991). Similarly, the presence of CO$_2$ and H$_2$O in the gas phase also accelerates sintering (Borgwardt, 1989; Fuertes et al., 1991).

Consequently, much of the recent research efforts have been directed toward overcoming the aforementioned problem. Researchers have suggested different techniques to improve multicyclic sorbent performance. These include pretreatment methods such as thermal activation, synthesis of novel sorbents by physical and chemical modifications, and reactivation using water/steam hydration (Liu et al., 2012; Yu et al., 2012).

The Ohio State University (OSU) has spearheaded the development of a unique three-step calcium looping process, which incorporates an intermediate sorbent reactivation step (Fan, 2010; Fan et al., 2011; Ramkumar and Fan, 2009). The inclusion of the additional step provides a highly reactive sorbent every cycle and new avenues for
process integration. The remainder of this chapter provides an overview of OSU’s research and discusses the development of two processes – the Carbonation-Calcination Reaction (CCR) process and the Calcium Looping Process (CLP) for post- and pre-combustion CO$_2$ removal, respectively. Important differences in the approach adopted by OSU, when compared to competing efforts in this area, have also been highlighted.

2.1. OSU Process versus Traditional Process

Figures 2.1 and 2.2 depict the comparison between the traditional calcium looping process and OSU’s version of the same. The traditional process cycles the sorbent between two reactors – carbonator and calciner. As discussed earlier, high-temperature sorbent regeneration in the calciner also leads to sintering; this diminishes the CO$_2$ absorption capacity. The consequence is that higher solid inventories, and sorbent make-up rates and purge rates become necessary to maintain desired level of CO$_2$ removal. In the OSU process, the sorbent is cycled between three reactors. The third reactor – hydrator – is placed between the calciner and carbonator such that it accepts the CaO generated in the calciner and converts it to Ca(OH)$_2$ which is then sent to the carbonator.

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In this document, the terms ‘calcium looping’ and ‘calcium looping process’ are used to generically describe the field and the process embodiment, respectively. However, the term ‘Calcium Looping Process (CLP)’ is the name given to the OSU-patented pre-combustion CO$_2$ capture/H$_2$ production process and is exclusively used to refer to the same. The term ‘Carbonation-Calcination Reaction (CCR) Process’ refers to a similar process developed by OSU for post-combustion CO$_2$ removal. It is important that the reader note this terminology while reading through this document.
Hydration successfully reverses the sintering effect and produces a highly reactive sorbent every cycle. The result is that the solid inventories and tonnages are lower and comparable to existing commercial gas-solid processes, and additional options for reactor operation become available.

Experimental investigations conducted by OSU and several other researchers have confirmed the merit of intermediate hydration (Liu et al., 2012; Yu et al., 2012). The CaO derived from the hydrated sorbent has superior morphological properties (surface area and pore volume) and hence, high CO₂ carrying capacity. However, many researchers have essentially looked at hydration as yet another reactivation technique, employing experimental conditions which do not seem feasible for process scale-up. For example, hydration has been reported using saturated water vapor at ambient or low temperatures (~100 °C), atmospheric moisture, etc. over time intervals ranging from a few hours to days (Fennell et al., 2007; Hughes et al., 2004; Materic et al., 2010). On the contrary, OSU has consistently championed the use of hydration as an indispensable part of the process and has reported relevant results that will suit a commercial process. For example, the results of using high-temperature (500 °C) steam hydration show excellent multicyclic sorbent performance (a detailed description of this study is included in Chapter 4). Further, these results have been used to determine parameters that have been incorporated in the technical evaluation of the process (Wang et al., 2012; Wang et al., 2013).
2.2. Comment on Current Strategies for Sorbent Enhancement

Various approaches have been adopted to overcome the sorbent decay during calcium looping. While hydration has received significant attention, other notable efforts include synthesis of novel calcium sorbents by using physical and chemical modification, thermal pretreatment/activation and addition of inert materials as binders or supports to improve strength, mechanical stability and sintering-resistance (Liu et al., 2012; Yu et al., 2012). More recently, researchers have also focused on calcium nano-sorbents and integration of mesoporous silicates (Yu et al., 2012). All the aforementioned techniques have resulted in a superior sorbent as compared to commercially available limestone-derived CaO. However, it is important to consider other aspects when evaluating these techniques/sorbents –

- The majority of the sorbent enhancement studies lack an economic perspective when the results are presented. Synthesis of novel sorbents at laboratory-scale may not present challenges; however, replicating the same at larger scales is unlikely to be feasible. This is confirmed by the recent trends in this field – successful laboratory-scale efforts are rarely followed-up with larger-scale implementation. Commercial limestone is a very inexpensive sorbent (~$20/ton) and represents one of the biggest advantages of calcium looping. Without a strong economic case, continuing efforts to develop more expensive synthetic sorbents does not seem appropriate.

- Occasionally, the experimental conditions used for testing novel/modified sorbents do not mimic realistic conditions. Many studies employ milder calcination environments (e.g. pure N₂ atmosphere, lower temperatures, etc.) which limit sorbent sintering and fail to exhibit the real potential of the sorbent enhancement technique. Other
contaminants like fly ash, acid gases, etc. which may be present in reality, are absent when synthetic sorbents are tested. A combination of these factors can lead to an overestimation of the potential of such techniques.

- Modified sorbents containing binders/supports will also lead to higher solid circulation rates (on a mass basis) and inventories. These additional materials will act as inerts and increase the sensible heat demand in the process, especially during calcination.

In the early 2000s, OSU also developed and patented a technique to synthesize a highly reactive sorbent – precipitated calcium carbonate (PCC) (Gupta and Fan, 2002; Fan and Gupta, 2006). Though PCC exhibited excellent multicyclic reactivity and outperformed all other available sorbents (Iyer et al., 2004), similar performance was difficult to replicate in a pilot-scale system using actual coal-combustion flue gas. Moreover, OSU’s three-step process involving intermediate hydration has proven to be highly effective irrespective of the CaO-precursor. Combined with the cost differential between PCC and commercial limestone (approximately 5 times), further research efforts were discontinued in this area.

2.3. Intermediate Hydration – Challenges and Opportunities

Though very promising, calcium looping with intermediate hydration also presents significant challenges. Principal among them is the poor mechanical strength of the hydrated sorbent (Blamey et al., 2010b). Irrespective of the particle size of the starting CaO, the resulting Ca(OH)$_2$ due to hydration will be in 2-10 μ size range (Boynton, 1980). Such small particles would require highly efficient particle capture devices
(cyclones, etc.) to prevent sorbent losses during circulation. Additional complications may be encountered during the operation of the reactors. However, OSU’s work in this area has led to interesting findings which will be useful in overcoming these issues –

- When a dual-stage cyclone system to capture fine Ca(OH)$_2$ particles was tested, it was found to be extremely efficient in collecting the solids. In fact, this testing revealed that cyclones, which were designed to capture much higher particle sizes (>100 µ), were also very efficient when used with fine Ca(OH)$_2$ particles. This is likely due to *clustering*. The term ‘cluster’ is used to denote a group of particles that are brought together by external forces, most commonly hydrodynamic and are mainly encountered in fast-fluidized beds (Horio and Clift, 1992). Clusters are different from agglomerates, which are group of particles that are held together by interparticle forces like van der Waals effects, etc. It is believed that the cyclones ‘see’ particles which are larger in size (due to the formation of clusters) and thus successfully capture particles which are otherwise smaller than the cut size they are designed for.

- Attrition is often pointed out as an obstacle when using hydration. This is true when hydration is used as an intermittent reactivation technique with the majority of the particles in the process being of significantly larger size. However, when hydration is integrated in the process (like in Figure 2.2), all reactors and peripherals will be designed to handle fine particles. It is also interesting to note that once the sorbent passes through the hydrator, it will be reduced to a fine particle size (2 -10 µ); further particle size reduction is unlikely, making attrition a non-issue.
Supplementary to the stable multicyclic sorbent reactivity, intermediate hydration offers several other advantages –

(a) The hydration reaction is extremely exothermic and the heat can be utilized for additional electricity generation in the plant. This can help offset the energy penalty imposed due to calcium looping. For example, a study found that the net output of the power plant (to the grid) could be maintained or even increased when using the three-step process for CO₂ control (Wang et al., 2012).

(b) Ca(OH)₂ is traditionally known to be a highly reactive sorbent than CaO. The use of Ca(OH)₂ as the sorbent in the carbonator allows use of extremely small reaction times for achieving the desired CO₂ removal. For example, it was established that the carbonator can operate with a residence time of a few seconds (Wang et al., 2010). Such a carbonator can be operated in the fast fluidization regime (e.g. entrained flow mode). The carbonator in the two-step process is expected to be a bubbling or circulating fluidized-bed reactor to provide sufficient time for the CaO to undergo carbonation (Dean et al., 2011; Shimizu et al., 1999).

(c) Using Ca(OH)₂, a calcium to carbon mol ratio (Ca:C) of ~1.3 was found sufficient to remove 90% CO₂ from flue gas (Wang et al., 2010). Higher Ca:C is required for the same in the traditional two-step process (Charitos et al., 2011). Lower calcium loading and residence times will result in cost savings because of smaller process equipment.

(d) When Ca(OH)₂ is used in the carbonator, the carbonator operation tends to be mildly exothermic rather than highly exothermic. This is because the exothermic carbonation reaction is balanced by the endothermic dehydration reaction. This potentially
reduces the load on the heat transfer surfaces inside the carbonator. In fact, if the carbonator inlet gas is injected at an appropriate temperature, heat-neutral operation can be achieved (Wang et al., 2012).

(e) The formation of CaSO$_4$ during calcium looping has been found to hamper the fast kinetically-controlled stage of the CaO-CO$_2$ reaction (Symonds et al. 2012) and overall sorbent utilization. Such effects can be minimized or eliminated by using intermediate hydration. In fact, reactivation by hydration was first proposed in 1980 to improve sorbent utilization for SO$_2$ capture in fluidized-bed combustion (FBC) systems (Fee et al., 1980; Shearer et al., 1980). It was suggested that hydration converted the unreacted CaO to Ca(OH)$_2$ and the resultant expansion cracked the CaSO$_4$ surface layer, which otherwise prevented further reaction with SO$_2$. The same phenomenon will help here for improved CO$_2$ uptake by the sorbent.

(f) Recent findings on the ‘direct carbonation’ of Ca(OH)$_2$ suggest that the sorbent can undergo complete conversion. A comparison between the carbonation of Ca(OH)$_2$-derived CaO and Ca(OH)$_2$ is shown in Figure 2.3 and a more detailed examination is reported in Chapter 7. It should be noted that the comparison is performed between isothermal carbonation of CaO and non-isothermal carbonation of Ca(OH)$_2$ (where the conversion of Ca(OH)$_2$ to CaO does not occur prior to the reaction with CO$_2$). While the former can occur in both the two- and three-step calcium looping process, the latter is a possibility only in the three-step process and more so, if a significant difference exists between the operating temperatures of the carbonator and the hydrator. From Figure 2.3 it is clear that when Ca(OH)$_2$ undergoes non-isothermal direct carbonation, the reaction does not enter a slow diffusion-controlled regime.
which is a characteristic of the CaO-CO$_2$ reaction (Bhatia and Perlmutter, 1983). This allows the sorbent to reach 100% conversion, and it will offer excellent sorbent utilization if it occurs in the process. Further, higher degree of carbonation has been reported to favor higher residual CO$_2$ carrying capacity over successive cycles (Arias et al., 2012); however, this aspect does not have an important bearing if the process has hydration as a reactivation step. The direct carbonation finding has been confirmed by other researchers (Materic and Smedley, 2011; Montes-Hernandez et al., 2012).

2.4. Strategies for Process Integration – Post-combustion CO$_2$ Removal

From the design of the recently constructed pilot plants (Kremer et al., 2012; Sanchez-Biezma et al., 2012), it is interesting to note that calcium looping is being viewed as a back-end scrubbing technology giving rise to two possible scenarios – one, where the carbonator is placed after the existing flue gas desulfurization (FGD) unit and designed solely for CO$_2$ control and second, where the carbonator replaces the FGD unit and is designed for co-capture of CO$_2$ and SO$_2$. The main argument in favor of designing the process solely for CO$_2$ capture can be that existing pulverized coal (PC) power plants have FGD units which remove the SO$_2$ from the flue gas. Moreover, this strategy will allow easy process integration with minimum modification to the existing plant setup (see Figure 2.4). However, this argument implicitly assumes that utility operators will be averse to the idea of discontinuing the use of FGD even if the economics are favorable for co-capture of CO$_2$ and SO$_2$ using calcium looping. Discussions between OSU and
major American utility companies have indicated that the co-capture scenario is realistic and the current FGDs may be decommissioned or simply bypassed.

Instead of viewing it as a back-end scrubbing technology, it may be more advantageous to integrate the calcium looping process upstream (near the boiler) as shown in Figure 2.5. The flue gas exiting the convective section of the boiler is available at the carbonator operating temperature (~650 °C) and can be used directly. Since the CO$_2$-lean gas exiting the carbonator will also be available at a similar temperature, it can be returned to the boiler for further heat exchange. Such a process design will require minor boiler modifications so that the flue gas can be extracted from the appropriate location and then returned. These modifications may necessitate moving/removing heat transfer coils, adding/moving piping, or adjusting/altering measurement devices. Similar exercises are routinely undertaken in the industry during boiler maintenance and thus, may not represent a major obstacle. More importantly the upstream process integration provides superior heat integration options since the gas entering the carbonator will not require additional pre-heating prior to entering the carbonator. It is, however, vital to consider the effect of alteration in gas properties (e.g. volumetric flowrate, composition, etc.) with respect to the boiler, in this scenario.

One disadvantage of the co-capture scenario is that CaSO$_4$ will be formed in the carbonator. Since CaSO$_4$ cannot be decomposed, this results in permanent loss of active calcium sorbent and consequently, higher purge and make rates. Interestingly, formation of CaSO$_4$ is inevitable during calcium looping even when it used for CO$_2$ removal only.
This is because the calciner is expected to be oxy-coal fired and the coal sulfur will exit the calciner as CaSO₄. Thus it may be a good idea to have CO₂-SO₂ co-capture with CaSO₄ circulating in the loop. Using spent sorbent material from calcium looping for upstream SO₂ removal in the boiler is another attractive alternative (Manovic and Anthony, 2007).

Several studies have confirmed the ability of calcium looping to produce additional electricity (Romeo et al., 2009, Wang et al., 2012). This is mainly due to the additional fuel used for conducting calcination as well as several high-temperature gas and solid streams available in the process that can be used for heat integration. However, current PC power plants may not be able to expand their existing steam turbine cycles to accommodate more steam. Since most plants have multiple boilers, one alternative could be to retire one or more boiler(s) in the plant and use the associated steam turbine capacity to accept steam produced from the calcium looping heat integration. In this case, the calciner and/or hydrator serve(s) as the boiler and the plant net output remains unaffected even when 90% or greater CO₂ is captured.

2.5. OSU’s Process for Pre-combustion CO₂ capture

Though the majority of the recent calcium looping research has been dedicated to post-combustion CO₂ reduction, much of the earlier work has also addressed the pre-combustion application. Using a CO₂ acceptor during coal gasification, steam methane reforming (SMR) or water-gas shift (WGS) reaction, it is possible to maximize the production of CH₄- or H₂-rich product gas (Fan, 2010; Harrison, 2008; Sircar and Lee,
Based on this concept, several processes have been developed – the CONSOL CO₂ Acceptor Process and the HyPr-RING (hydrogen production by reaction-integrated novel gasification) process are the more notable ones. The CO₂ Acceptor Process, represented using a simplified block flow diagram in Figure 2.6, was designed to produce synthetic pipeline gas (CH₄-rich gas) from lignite or sub-bituminous coal (Curran et al., 1966; Curran et al., 1967). The system consisted of a gasifier containing a calcium-based CO₂ acceptor (dolomite) and operating at about 800 °C and 10 atm. The H₂-rich product from the gasifier was further sent to a methanator to produce synthetic natural gas (90+% CH₄). The CO₂ acceptor was regenerated in another reactor – regenerator – operating at about 1000 °C. The char produced in the gasifier was transferred to the regenerator along with the acceptor and the char combustion provided the heat for the endothermic regeneration reaction. In principle, the HyPr-RING process (Figure 2.7) is very similar to the CO₂ Acceptor Process, except that the former was aimed at the production of high-purity (~80%) H₂ (Lin et al., 2002, 2005). Consequently, HyPr-RING does not have a downstream methanation system. Also, the gasifier operates at a lower temperature (~650 °C) and significantly higher pressure (30 – 60 atm), which thermodynamically favors the CaO-CO₂ reaction, thereby enhancing H₂ production. Both processes advanced to pilot-scale demonstrations – the CO₂ Acceptor Process was demonstrated at a 40 ton/day (coal feed to gasifier) pilot plant at Rapid City, South Dakota and the HyPr-RING process was operated in a unit with 3.5 kg/h coal process rate in Japan (Fan, 2010).

The Calcium Looping Process (CLP), which is currently under development at OSU, produces H₂ and/or electricity from coal-gasified syngas (Ramkumar and Fan, 2009;
Ramkumar, 2010). It is depicted in Figure 2.8. Like the post-combustion CO$_2$ control process developed by OSU, the CLP consists of three reactors. The carbonator accepts the syngas produced from a coal gasifier which is then converted to H$_2$ via the WGS reaction assisted by in-situ CO$_2$ removal. The steam necessary for the WGS reaction is supplied by the decomposition of Ca(OH)$_2$. Other acid gases present in syngas – hydrogen chloride (HCl), hydrogen sulfide (H$_2$S) and carbonyl sulfide (COS) – also react with CaO to form CaCl$_2$ and CaS, respectively. Thus, the exit gas from the carbonator is rich in H$_2$ and the solid product mainly contains CaCO$_3$ and small quantities of CaCl$_2$ and CaS. The operation of the calciner and hydrator is similar to the post-combustion case, except that the calciner operation is complicated by the presence of sulfur in the solids coming in from the carbonator (Connell et al., 2013). Extensive bench-scale studies performed using fixed-bed reactor showed that the H$_2$ purity produced in the carbonator was dependent on the operating pressure – ~70% H$_2$ could be produced at 1 atm and the purity exceeded 99% at higher pressures (21 atm) (Ramkumar and Fan, 2010a, 2010b). The optimum operating temperature for the carbonator was found to be 600 °C. One of the most important advantages of the CLP is that the carbonator does not require a WGS catalyst which results in cost savings. Based on these results, a sub-pilot scale fluidized-bed carbonator was designed, constructed and successfully operated. Chapter 3 describes this scale-up effort.

While the underlying concept is the same, the CLP is different from and offers significant improvement over earlier processes like CO$_2$ Acceptor and HyPr-RING –
(a) In particular, the main difference lies in the way the acceptor is introduced in the system. In the CLP, the gasification and the CaO-CO$_2$ reactions occur in two independent reactors (gasifier and carbonator, respectively). This offers an important advantage because the calcium sorbent does not directly interact with coal under harsh (gasification) conditions. It has been reported that direct interaction of Ca-based sorbents with coal minerals causes deactivation of the sorbents (Kuramoto et al., 2004). Though common to both CO$_2$ Acceptor and HyPr-RING processes, this problem is likely to be more aggravated in the latter due to higher operating pressures in the gasifier. This deactivation will further decrease the CO$_2$ sorption capacity of the sorbent. It should be noted that this decrease is in addition to the characteristic reactivity decay that all calcium sorbents exhibit when cycled continuously. It was suggested that a shortened holding time of the feedstock could avoid such deactivation (Kuramoto et al., 2004).

(b) To overcome the multicyclic reactivity decay that calcium sorbents exhibit, the HyPr-RING process relied on the in-situ hydration of CaO in the gasifier (Lin et al., 2006). Steam, which primarily served to gasify carbonaceous fuel, also reacted with CaO to form Ca(OH)$_2$ prior to reacting with CO$_2$. Hydration restored the reactivity of the recycled CaO and provided exothermic heat to support the endothermic gasification. In contrast, the CLP has a dedicated hydrator to hydrate CaO every cycle. Using the CLP configuration, complete and controlled hydration can be achieved by regulating the reaction parameters. The same may not be true for the HyPr-RING configuration – some CaO may react directly with CO$_2$ without undergoing hydration in the gasifier.
(c) The CO$_2$ Acceptor process used dolomite as the acceptor in the Rapid City pilot plant (Fan, 2010) based on the results obtained from laboratory-scale experiments – dolomite performed better than limestone over several cycles (Curran et al., 1967). This can be attributed to the presence of magnesium oxide (MgO) in dolomite, which resists sintering (Silaban et al., 1996). This strategy does have one drawback – since dolomite contains about 50% (by wt.) MgO, approximately half the sorbent is inert and is simply circulated between the reactors without participating in the process reactions. Substitution of limestone by dolomite will roughly increase circulation rates by a factor of two, which will present bigger challenges for scale-up. Moreover the sensible heat demand of the inerts will consume significant process heat in all reactors. To avoid these issues, using limestone seems a better option. As discussed earlier, an independent sorbent hydration step (as in the CLP) will help even further.

(d) The CLP calciner is fueled by coal and operated in an oxy-combustion mode while the unreacted coal char from the gasifier is used to fuel the regenerator in the other processes. As a result, the total coal requirement of the CLP plant is larger but heat integration allows production of additional electricity. This means that a CLP plant would necessarily co-generate electricity in order to be economically viable (Connell et al., 2013).

It is interesting to note that the drivers for technology development have evolved with time even though the concept has remained more or less the same. The CO$_2$ Acceptor process was developed with the aim of utilizing the abundant U.S. coal and converting it into synthetic natural gas. On the contrary, greenhouse gas reduction has been the underlying theme of the recent processes like HyPr-RING and CLP.
Connell et al. recently published the most comprehensive technical and economic analysis of a calcium looping system to date (Connell et al., 2013). This study analyzed OSU’s CLP in different pre-combustion scenarios – coal-to-H₂, integrated gasification combined cycle (IGCC) and SMR. Figures 2.9 and 2.10 show block flow diagrams of a typical coal-to-H₂ plant with CO₂ capture and the CLP coal-to-H₂ plant, respectively. Since the CLP-carbonator is designed to accomplish several key process steps, a number of unit operations – water quench, syngas scrubber, shift reactors, syngas coolers, two-stage Selexol unit, Claus plant, etc. – are not required in the CLP plant. For a plant producing 26,000 kg/h H₂ from coal, it was found that the CLP would result in a significant co-production of electricity (~300 MWe), which can be sold to the grid, while potentially reducing the costs of H₂ and electricity by about 10%. Similar savings were observed for the IGCC and SMR plants as well. In the SMR plant, the CLP carbonator can become a common reactor to conduct both methane reforming and CO₂ capture (Ramkumar et al., 2012). This concept can be further extended to a coal-to-liquid fuels plant by using CLP with a Fischer-Tropsch reactor (Ramkumar et al., 2010).

Few researchers are still pursuing calcium looping for pre-combustion CO₂ control and a majority of the recent studies have reported laboratory-scale experiments with special emphasis on the development of ‘fancy’ sorbents. No large-scale demonstrations have been planned or are currently in operation. This decline can be attributed to several factors, but principal among them is the development of shale gas hydraulic fracturing technology which has resulted in an abundance of natural gas. SMR is the most efficient and economical process that exists today for H₂ production and the recent developments
have only helped it to become even more cost-competitive. Coupled with rising opposition to coal utilization (especially in U.S.) and lack of a robust CO$_2$ legislation, it is difficult to envisage serious consideration of such technologies for large-scale implementation in the near term.

2.6. Concluding Remarks

Rapid development in the field of calcium looping has occurred in the past two decades, leading to serious consideration of this promising technology for large-scale deployment. Several current and planned demonstration plants indicate the feasibility of scaling up this process. However, the problem of degrading multicyclic sorbent performance has persisted and needs to be convincingly addressed. As discussed here, OSU has been leading the development of a novel three-step calcium looping process incorporating an intermediate hydration step. Such a configuration provides additional advantages and work is currently underway to refine it further and overcome certain challenges. It is also important to consider some non-conventional approaches of process integration, some of which have been highlighted in this chapter.
Figure 2.1. Traditional calcium looping process.
Figure 2.2. OSU’s three-step calcium looping process.
Figure 2.3. Comparison of direct and indirect carbonation of Ca(OH)$_2$. Direct carbonation conducted non-isothermally by heating Ca(OH)$_2$ in 10% CO$_2$ (balance N$_2$) from 25 °C to 700 °C at 25 °C/min. Indirect carbonation conducted isothermally at 700 °C by treating Ca(OH)$_2$-derived CaO with 10% CO$_2$. 

- **Direct Carbonation**
- **Indirect Carbonation**
Figure 2.4. Downstream integration of the calcium looping process in a PC power plant.
Figure 2.5. Upstream integration of the calcium looping process in a PC power plant.
Figure 2.6. CO\textsubscript{2} Acceptor Process (Curran et al., 1966).
Figure 2.7. HyPr-RING process (Lin et al., 2002).
Figure 2.8. OSU’s Calcium Looping Process (CLP). *Operating pressure of the carbonator is dictated by the \( \text{H}_2 \) purity desired in the product gas (Ramkumar and Fan, 2010a). Only major reactions have been shown. For more details, see Figure 3.1.
Figure 2.9. Traditional coal-to-H₂ plant with CO₂ capture. Adapted from Connell et al., 2013.
Figure 2.10. Coal-to-H₂ plant integrated with CLP. Adapted from Connell et al., 2013.
CHAPTER 3

CALCIUM LOOPING PROCESS (CLP): DESIGN, CONSTRUCTION AND OPERATION OF THE SUB-PILOT SCALE CARBONATOR

The Calcium Looping Process (CLP) employs a calcium-based CO$_2$ acceptor to enhance H$_2$ production via the water gas shift (WGS) or reforming reaction. Though applicable in any pre-combustion scenario, the discussion in this chapter is more relevant to H$_2$ production from coal-derived syngas. The first part of this chapter briefly describes the CLP and the major reactions occurring in the three reactors. The most important results obtained from the extensive bench-scale testing conducted by prior OSU researchers are also concisely summarized. These results became the basis for the design of the sub-pilot scale reactor system. The remainder of the chapter details the construction and operation of the sub-pilot system. The challenges encountered during reactor operation are also highlighted.

---

3.1. Introduction

The CLP consists of three reactors – carbonator, calciner and hydrator. The CO₂ capture occurs in the carbonator. However, the CLP carbonator may be referred to as an ‘integrated reactor’ because several other reactions also occur here –

\[
\text{Ca(OH)}_2(s) \rightarrow \text{CaO}(s) + \text{H}_2\text{O}(g) \quad (\Delta H = 109 \text{ kJ/mol})
\]

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \quad (\Delta H = -41 \text{ kJ/mol})
\]

\[
\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) \quad (\Delta H = -178 \text{ kJ/mol})
\]

\[
\text{CaO}(s) + \text{H}_2\text{S}(g) \rightarrow \text{CaS}(s) + \text{H}_2\text{O}(g) \quad (\Delta H = -62 \text{ kJ/mol})
\]

\[
\text{CaO}(s) + \text{COS}(g) \rightarrow \text{CaS}(s) + \text{CO}_2(g) \quad (\Delta H = -92 \text{ kJ/mol})
\]

\[
\text{CaO}(s) + 2\text{HCl}(g) \rightarrow \text{CaCl}_2(s) + \text{H}_2\text{O}(g) \quad (\Delta H = -218 \text{ kJ/mol})
\]

The carbonation of CaO drives the equilibrium-limited WGS reaction forward and enhances H₂ production. The steam required for the WGS reaction is obtained from the decomposition of Ca(OH)₂. Since CaO is highly reactive to several acidic gases, it also removes sulfur and halide impurities which are typically present in syngas obtained from coal gasification. The gas-solid mixture at the exit of the carbonator is separated and the gas is sent for further downstream processing/application, and the solids are sent to the calciner.

In the calciner, the CaCO₃ formed in the carbonator is decomposed to regenerate CaO –

\[
\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad (\Delta H = 178 \text{ kJ/mol})
\]

The CaO becomes available for the reaction in the next cycle and the CO₂ can be sent for sequestration after appropriate conditioning. The other calcium compounds entering the calciner cannot be converted back to CaO. Consequently, a purge stream and a make-up
stream (consisting of fresh limestone) are needed in the process. In reality, it is expected that the calciner operation will be more complicated due to the likelihood of several side reactions (Connell et al., 2013).

The CaO from the calciner is reacted with steam to form Ca(OH)$_2$ in the hydrator –

\[
\text{CaO}_{(s)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Ca(OH)}_{2(s)} \quad (\Delta H = -109 \text{ kJ/mol})
\]

This step ensures robust multicyclic sorbent reactivity. In the CLP, hydration also becomes the pathway for steam injection in the process which is ultimately used for the WGS reaction in the carbonator. The CLP is schematically represented in Figure 3.1.

### 3.2. Prior Work on CLP

The CLP has been studied extensively at laboratory- and bench-scale and the experimental results have been reported in literature (Ramkumar and Fan, 2010a, 2010b; Ramkumar et al. 2011). The experimental work initially focused on using the calcium sorbent in conjunction with a WGS catalyst in the carbonator (Ramkumar et al, 2011). Excellent CO conversions and H$_2$ purities could be achieved in the carbonator at temperatures (600 – 650 °C) greater than conventional WGS reactors. The H$_2$ purity increased with increase in steam to carbon mol ratio (S:C) and pressure. However, further testing revealed that similar carbonator operation could be achieved even in the absence of the WGS catalyst, which meant that the presence of the calcium sorbent alone was sufficient to drive the WGS reaction (Ramkumar and Fan, 2010a, 2010b). This finding presents a significant advantage because the elimination of the traditional two-stage
(high- and low-temperature) catalytic WGS system will lead to lower operational and material costs.

Figures 3.2 – 3.4 summarize the important results obtained from the non-catalytic investigation of the CLP reactions that occur in the carbonator, which were used as the bases to design the sub-pilot scale system. All experiments were conducted using OSU-patented precipitated calcium carbonate (PCC) as the CaO-precursor. It was found that the operating pressure of the carbonator is an important variable – H₂ purity was 70% at 1 atm and >99% at 21 atm at 600 °C and S:C of 1. The H₂ purity increased with an increase in the S:C. However, this effect was absent at higher pressures. 600 – 650 °C was found to be an optimum temperature range for the carbonator. It should be noted that this temperature favors fast kinetics of the CaO-CO₂ reaction and thermodynamically favors near-complete CO₂ removal from any gas atmosphere. Calcination and hydration were also investigated in the bench-scale fixed-bed reactor. Since only the carbonator scale-up was accomplished in the current work, the results related to the calciner and hydrator were deemed irrelevant for a discussion here.

3.3. Design and Construction of the Sub-Pilot Scale System

Of the three CLP reactors, only the carbonator was scaled-up to the sub-pilot scale as a part of the current work. Consequently, the system was designed for short-duration once-through testing only.
3.3.1. Reactor support structure

The reactor is supported using a metal frame as shown in Figure 3.5. The frame occupies an area of 10’x 8’ and is 13.5’ tall. The entire structure is made using I-beams. Metal stairs have been provided to access the upper area of the frame which is at a height of 10.5’. The stairs have a hand railing for the safety of the operators. Railings are also provided on the upper level along the circumference. The different flanged sections of the reactor are supported on the structure in such a way that each section can be removed independently, which allows easy maintenance. The top level has a metal mesh floor.

3.3.2. Reactor design

The sub-pilot scale CLP carbonator is a fluidized-bed reactor designed for once-through testing. Figure 3.6 provides the detailed design of this reactor. The riser section of the reactor is 11.5’ in height and 4” I.D. It is mainly composed of four identical flanged sections. A three-dimensional view of one such section has also been provided in Figure 3.6. Each section has ports for measuring temperature and pressure, and for drawing product gas for analyses. The entire assembly has been constructed using SS 304. To achieve the desired operating temperature, high-temperature ceramic heaters (3200 W, 220 V, OMEGA Engineering, Inc.) are used along the length of the riser. The heaters are mounted using easily removable metal support frames. Appropriate ceramic wool insulation is provided to minimize heat losses. Multiple Type K thermocouples monitor the temperature of the riser. These thermocouples also provide feedback to the ceramic heaters so that the desired operating temperature is achieved and maintained throughout
the experiment. The feedback process control loop is programmed in LabVIEW (National Instruments, Inc.). Figure 3.7 provides a snapshot of the reactor.

The calcium sorbent is continuously delivered to the reactor using a Schenck-Accurate mid-range volumetric hopper and screw feeder. The revolutions per minute (rpm) of the motor-driven screw decides the solids feed rate and it is kept constant throughout the experiment. The solids feeding section also consists of two pneumatically-operated gate valves, which open and close alternately and thus, imitate a double-dump valve. This action prevents the gas entering the reactor from escaping through the solids feeding section (out of the hopper). The opening and closing sequence of the valves has also been programmed in LabVIEW and the time intervals in the sequence can be specified by the operator. The screw feeder feeds the sorbent in the stand pipe containing these valves. An inclined section then carries the solids into the reactor.

A gas mixing panel (shown in Figure 3.8), designed and constructed by Swagelok Company, is used to deliver the reactant gases to the reactor. The gas mixing panel consists of independent mass flow controllers (MFCs) (Brooks Instruments) for CO, H₂, CO₂ and N₂. The MFCs are controlled using a dedicated digital read-out controller. The mixing panel has been provided with a manual ball valve and pneumatically-operated diaphragm valve for each gas. Gas cylinders are used to supply the gases to the gas mixing panel. For the flammable gases – H₂ and CO – the gas cylinders are stored in gas cabinets (Air Liquide) provided with independent ventilation. Automatic switch-over valves (Scott Specialty Gases) have been installed for each gas to enable cylinder
changeover during an experiment. Figure 3.9 shows the gas cabinets and the cylinder switch-over valves inside each of them. For the safety of the operators, flash arrestors, check valves and maximum flow limit shut-off valves have been installed in the gas lines.

The gaseous mixture delivered by the gas mixing panel is preheated to a suitable temperature before its injection into the reactor. The gas preheater (Figure 3.10) is a stainless steel helical coil (~25’ length, ~0.6” I.D.) surrounded by a high-temperature ceramic heater. The diameter of coiling is 3” and the final coiled length is approximately 2’. The coil is supported on a stand, which also provides a support-base to the heater. Two such preheaters are used in series. The preheated gas is then mixed with steam, produced using a combination of high precision Optos 3HM water pump (Eldex Laboratories) and HGA-S steam generator (Micropyretics Heaters International). The steam generator is capable of producing steam up to a maximum temperature of 500 °C. The steam-gas mixture then enters the reactor through a sintered haste alloy plate. The sintered plate is porous enough to allow minimum pressure drop across it; however, it has suitable strength to support the weight of the solids in the reactor.

A slipstream of the gas exiting the reactor is drawn through one of the gas sampling ports provided on the riser. The gas sampling port contains a 2 µ Swagelok in-line filter to prevent the solids from entering the gas analyses equipment – micro-GC (Varian). The gas analyses setup is shown in Figure 3.11. An independent diaphragm micro-pump (KNF Neuberger) has been installed to extract the sample gas from the port. The pump allows sample gas in excess of 1 L/min to be delivered to the micro-GC. Prior to entering
the micro-GC, the product gas is passed through a desiccant bed (anhydrous calcium sulfate) to remove the moisture. The gas-solid mixture from the reactor is diluted with air before it enters the Donaldson Torit downflow baghouse (Figure 3.12). The air dilution cools the exit gas to a suitable temperature for the baghouse and also maintains the gas composition outside the explosion limits. The solid-free gas from the exit of the baghouse is vented out of the facility. The reacted solids are recovered from the baghouse for analysis.

The reactor heaters and the preheaters are connected to transformers placed in an electrical panel (shown in Figure 3.13) designed by IWI, Inc. The panel also provides electricity for several other devices. It is provided with an emergency shut-off and can be controlled using a programmable logic controller or a personal computer.

Figure 3.14 is the diagram of the entire sub-pilot facility showing important components.

3.4. Experimental Section

3.4.1. Chemicals

Pure gases – CO (99.5%), CO₂ (99.9%) and H₂ (>99.9%) – supplied by Praxair were used to simulate a syngas mixture for all the tests. Nitrogen (N₂) was used as the carrier gas. Since large volumetric flowrates of N₂ were required, liquid N₂ dewars were used as the source of gaseous N₂. Ultra-high purity (99.999%) helium and argon were used as the carrier gases in the micro-GC. The calibration of the micro-GC was conducted using
certified standard gases – 9.5% CO, 3% CO$_2$ and 5% H$_2$. Compressed air, available at the facility, was used to dilute the vent gas.

The sorbent used in all the tests was commercial-grade, high-calcium Ca(OH)$_2$, obtained from Graymont Inc. The manufacturer-specified composition of the sorbent and other sorbent characteristics have been provided in Table 3.1. As discussed in Section 3.2, all the fixed-bed tests were carried out using PCC. Though PCC was identified to be a superior sorbent when compared commercial limestone and dolomite (Iyer et al., 2004), the cost of PCC is almost five times the cost of limestone. Also, since the CLP includes intermediate sorbent reactivation by hydration, the CaO-precursor ceases to have any effect on the sorbent performance. Hence, the use of PCC was discontinued in the sub-pilot work taking into account the favorable economics afforded by commercial lime products.

3.4.2. Operating procedure

The reactor was heated to the operating temperature and maintained at that temperature. The feed gas to the reactor was also preheated to the same temperature. During preheating, only N$_2$ was flowed through the reactor. Once the desired temperatures were attained, the reactive component (CO$_2$ or CO or a mixture of CO, CO$_2$ and H$_2$) was introduced in the feed gas and the sorbent was injected using the screw feeder. The product gas was analyzed using the micro-GC. Prior to each experimental run, the micro-GC was calibrated using certified standard gases. Based on the results obtained from the
bench-scale tests (Ramkumar and Fan, 2010a, 2010b), all the experiments in the current work were conducted at 600 °C and 1 atm.

The solids feeder was also calibrated before each experimental run. To calibrate the feeder, the hopper was filled with solids and the feeder was operated at a given setpoint for different time intervals (5, 10, 15, 30 min) and the average value (kg/min) was selected as the feedrate at that setpoint. This value was used to calculate the Ca:C in the experiment (discussed in Section 3.4.5).

After the completion of every experimental run, solids from the baghouse were collected and analyzed for their CO₂ content using a thermogravimetric analyzer (TGA). The data obtained from the micro-GC were also analyzed. The data obtained from gas analyses were in good agreement with the data obtained from the solids analyses.

After each experiment, the bottom-most part of the reactor – T-section (see Figure 3.15) – was disconnected, inspected and cleaned. For convenience, the T-section is supported on a trolley-jack. This section also provides access to the sintered plate, which was also cleaned.

3.4.3 Leak testing

Since the gases used in the tests included H₂ and CO, a two-pronged leak testing procedure was adopted to ensure operator safety and reliability of results. This procedure is detailed below.
**Pressurized testing**

The reactor was “blanked-out” at an easily accessible location, which means that the reactor had an inlet for gas but no outlet. It was then pressurized using air and tested for leaks using SNOOP solution. The position of the blank was chosen such that a major portion of the reactor was included in the leak test. An exact leak rate was established using the following procedure –

- The reactor was pressurized to the same amount of pressure that it will experience during operation.
- The air was delivered using a high-precision digital flowmeter. The air flow rate was set to the minimum flow rate necessary to maintain the desirable pressure in the reactor.
- The flowrate measured by the flowmeter then equals the rate (volume of air or gas/time) of the leak from the system.

It was found that the hopper of the solids feeder was the major source of the leak. To mitigate the leaks through the hopper, it was almost completely filled with solids and then sealed using impermeable tape.

Occasionally, the entire reactor setup was dismantled for a thorough servicing of different parts. Servicing included cleaning the ceramic gaskets and replacing worn-out gaskets, cleaning and applying anti-seizing material on the nuts and bolts, etc. When re-assembled, better sealing was obtained between the flanges and other joints.
*Testing using micro-GC*

The pressurized testing was followed by leak testing using the micro-GC at cold conditions. For these tests, the reactor was setup in exactly the same way as it would be in an actual experiment and subjected to negative pressure using a downstream induced draft (ID) fan. N₂ was flowed through the reactor and gas samples were drawn from the reactor sampling ports to test in the micro-GC. The micro-GC results showed negligible O₂ leaking in to the system.

**3.4.4. Cold-flow testing**

Prior to operating the reactor using reactive gases (CO, CO₂, etc.), it was necessary to conduct cold-flow tests to ensure smooth functioning of the unit. These tests were conducted at room temperature using air and satisfactory results were obtained. During these tests, an air compressor was used as the source of air and connected to the reactor through a variable area flowmeter. Gas velocities that would be employed during actual operation were maintained and the sorbent feeder was operated at different feed rates. Each cold-flow run lasted for 1-2 h. The sorbent used in these tests was hydrated lime (Ca(OH)₂) obtained from Graymont Inc.

No major issues like plugging, etc. were observed. The sorbent flow into the reactor was satisfactory and approximately 70-80% of the sorbent was entrained out of the reactor at the operating velocities. The sorbent left in the reactor formed a bed of turbulently fluidizing particles. At end of the test, a thin coating of the hydrated lime could be seen at various parts (internally) of the reactor.
3.4.5. Hot-flow testing

Following the successful completion of the cold flow tests, as discussed in 3.4.4, the reactor was operated at hot conditions. Prior to testing reactions in the unit, all the cold flow tests were replicated at high temperatures. The following procedure was adopted –

- Air was sent in to the reactor using the variable area flowmeter. The actual air flowrate through the flowmeter was reduced to account for volumetric expansion at higher temperatures. Thus, the flowrate of air was maintained such that the operating velocities (and hence gas residence times) were identical to the ones used in cold flow tests.
- The reactor was heated to 600 °C. Preheaters were used to preheat the air entering the reactor.
- Once the desired temperatures were achieved, solids were fed from the screw feeder continuously for 1 h.

Following were the observations/results –

- The main reactor (riser) achieved the desired temperature in 2.5-3 h. However, the heating time was also a function of the surrounding temperature and quality of insulation.
- The heating of the gas (air) entering the reactor proved to be the ‘rate-limiting’ step. About 4.5-5 h were required for the gas to reach the desired temperatures (>550 °C).
- No issues like clogging were observed during solids feeding. It was found that the extent of entrainment of the solids was in agreement with the cold flow tests.
3.4.6. Reaction testing

Initially, only the calcium-CO\textsubscript{2} reaction was investigated. The purpose of was two-fold. First, this testing provided one more opportunity to identify any possible issues that might come up during syngas/CO testing. And second, since CO\textsubscript{2} capture by CaO is the crux of the CLP, positive results would confirm that the WGS reaction could be carried out non-catalytically in the future tests. For the syngas/CO testing, important parameters like S:C and Ca:C were investigated. It should be noted that this reactor presented the first opportunity to test Ca:C, since both gas and solids were in continuous mode unlike the fixed-bed tests (where the gas was continuous and the solids were in batch mode). The description of the experiments, results and complete analyses are presented in Section 3.5.

3.5. Results and Discussion

3.5.1. CO\textsubscript{2} capture tests

In these tests, air was used as the carrier/diluent gas to minimize expenses of using pure N\textsubscript{2}. Two tests were performed at 650 °C with different CO\textsubscript{2} concentrations in the inlet gas and Ca:C –

Test 1 – 4\% CO\textsubscript{2}, Ca:C = 1, and
Test 2 – 8.4\% CO\textsubscript{2}, Ca:C = 0.74.

In both tests, satisfactory CO\textsubscript{2} removal was observed. The results are shown in Figure 3.16 and compared with previously obtained results at OSU (Wang et al., 2010). The previous results have been obtained from experiments conducted in the 120 kWth CCR
unit. Good agreement was found to exist between the two data sets. An average CO$_2$ removal of 50% and 70% occurred in Tests 1 and 2, respectively.

Figures 3.17 and 3.18 show the actual data obtained during the two tests. It is important to note the large fluctuations in the outlet CO$_2$ concentration. This is mainly due to the variability introduced in the solids feeding. As described in Section 3.3.2, the feeder used in this setup was a volumetric feeder, which is based on the bulk density of the solids. Thus, any variation in the bulk density, which is inevitable, will alter the mass feed rate. Therefore, at times when more solids were delivered to the reactor, sudden drop in CO$_2$ concentration occurred (e.g. at 10 min in Test 1, Figure 3.17) and the CO$_2$ concentration spiked when lesser solids entered the reactor (e.g. at 20 min in Test 2, Figure 3.18). The Ca:C reported here is the average Ca:C during the experiment.

3.5.2. Parametric investigation$^4$

Effect of Ca:C

The Ca:C, which quantifies the calcium loading in the carbonator, was investigated and Figure 3.19 shows the results. Two Ca:C – 1.5 and 2.3 – were used. The Ca:C is calculated based on the carbon entering in the feed gas. For Ca:C investigation, the experiments were performed using CO, and hence the ratio of moles of Ca(OH)$_2$ to moles of CO is the Ca:C. Since both the molar feedrates were kept constant throughout the experiment, the Ca:C at the reactor inlet was constant.

$^4$The parametric tests were performed with only CO as the reactant in the feed gas.
Similarly, in the experiments in which the feed gas contained both CO and CO$_2$ (Section 3.5.3), the Ca:C equaled the ratio of moles of Ca(OH)$_2$ to the combined moles of CO and CO$_2$.

The selection of the Ca:C was based on the results obtained in prior work conducted at OSU (Wang et al., 2010). In that work, the effect of Ca:C was investigated on the extent of CO$_2$ removal from coal-combustion flue gas and it was found that CO$_2$ removal is a strong function of Ca:C. These results are shown in Figure 3.16. E.g. it was found that for 90% and 100% CO$_2$ removal, the Ca:C required is ~1.3 and ~1.6, respectively. In the present work, to begin with, a Ca:C of 1.3 was chosen, which meant that if all the CO sent to the carbonator got converted via the WGS reaction, then 90% of the CO$_2$ produced would be captured. However, from the fixed-bed tests, it was known that a CO conversion of 70% could be achieved at 600 °C and 1 atm (Ramkumar and Fan, 2010a, 2010b). Moreover, this conversion was recorded during the initial period of the fixed-bed experiment, when the Ca:C is practically infinite, making it the maximum conversion possible (For a fixed-bed experiment, where breakthrough curves are obtained for gas concentration, a parameter like Ca:C cannot be calculated; nonetheless, since all the sorbent is fresh when the experiment begins, the Ca:C can be said to be infinite). Hence it was expected that CO conversion would never exceed 70%. Assuming 70% CO conversion is achieved, the effective operating Ca:C in the reactor would exceed 1.6, which is sufficient to achieve 100% CO$_2$ capture.
Although the Ca:C desired was 1.3, the calculation of the actual Ca:C ‘delivered’ to the reactor was performed post-experiment. This is because of the variability introduced during the operation of the solids feeder. The screw feeder is a volumetric-based feeder and prior to each experiment, it was calibrated for mass-based solids feedrate. However, during the course of the experiment, this feedrate (being a function of the bulk density of the solids) fluctuated (see related discussion in Section 3.5.1 and Figures 3.17 and 3.18) due to the way the solids ‘packed themselves’ in the storage hopper. Hence, at the end of each experiment, the mass of the sorbent left in the hopper was measured and subtracted from the initial amount of sorbent fed to the hopper. The difference equaled the mass of the sorbent delivered to the reactor over the duration of the experiment. Knowing the duration of the experiment, the actual (average) sorbent feedrate was calculated which led to a marginally different value of Ca:C. When Ca:C was set at 1.3 and 2, post-experiment calculations indicated that the actual inlet Ca:C during the experiment was 1.5 and 2.3, respectively.

From Figure 3.19, it can be seen that a change in Ca:C did not significantly alter the CO conversion. In both cases, approximately 45-50% CO conversion was achieved. However, results from the tests conducted previously at OSU indicate that CO$_2$ removal is a strong function of the Ca:C (Wang et al., 2010). Since CO$_2$ capture drives the equilibrium-limited WGS reaction in the CLP carbonator (Ramkumar and Fan, 2010a, 2010b), it is reasonable to expect a similar trend here – higher the Ca:C, higher the CO conversion. Since such a trend was not observed, it is hypothesized that for the given scale of operation, the difference between the two Ca:C that were selected for the
investigation, is not large enough to significantly affect CO conversion. 100% CO$_2$ capture was, however, observed in all the experiments that were conducted. Figure 3.19 also shows that the CO conversion is low initially and then increases as the experiment progresses, ultimately reaching a steady value. The initial low conversion is mainly due to the large response-time of the micro-GC toward CO. The start-up of the experiment, where the system is essentially in an unsteady-state, also contributes to this profile. A similar profile was observed in all the experiments. For the case where Ca:C of 2.3 was used, sudden drop in conversion can be observed at 20 and 40 minutes. This was due to the clogging of the gas sampling line by the sorbent. The sample gas flow to the micro-GC was momentarily suspended for cleaning of the line which affected the concentration of CO.

Another phenomenon which is believed to have hampered the CO conversion in the experiments was the contact of ‘cold’ solids with hot gas. As stated earlier, the current design of this system allows for once-through testing only. Thus, the solids fed to the reactor were at room temperature while the preheated gas was fed at operating temperature (600 °C). At the point of contact of the gas and the solid sorbent, a temperature drop is inevitable. Lower temperatures will lead to poor kinetics, especially for the carbonation reaction. Since the carbonation reaction is expected to drive the WGS reaction, this ultimately affects the final conversion of CO. If this phenomenon is significantly more important, then the Ca:C will cease to have a bearing on the final CO conversion.
A significantly higher Ca:C (5 to 10 or higher) may have resulted in higher CO conversions. However, these experiments were not performed because from the point of view of the overall process, a higher Ca:C will increase the solids circulation among the different units of the CLP, leading to less attractive process economics and other solids handling and waste disposal issues (Connell et al., 2013). As a result, there exists a trade-off between superior performance in the carbonator and the overall feasibility of the CLP.

**Effect of S:C**

‘Excess steam’ could be added to the reactor using a water pump-steam generator combination. Hence, to investigate the effect of S:C, experimental results from two runs – with and without excess steam – were compared. The calculation of the S:C was based on the total steam available for the reaction including the steam obtained from the dehydration of Ca(OH)₂. E.g. when the Ca:C was maintained at 1.5 and 1.5 moles of excess steam were supplied per mole of C fed to the reactor, the overall S:C was 3. In absence of the excess steam, the overall S:C was the same as Ca:C (=1.5).

The effect of S:C on H₂ purity is shown in Figure 3.20. When no excess steam was supplied and dehydration of Ca(OH)₂ was the only source of steam for the WGS reaction, a H₂ purity of 37% was obtained. The H₂ purity increased to 49% when excess steam was supplied to the carbonator. This result is expected as per Le Chatelier’s principle – increase in the concentration of one of more reactants drives the reaction in the forward direction. Replicate runs were conducted which confirmed the reproducibility of these results (see Figure 3.21).
Figure 3.19, which shows the effect of Ca:C on CO conversion also inherently represents the effect of S:C on CO conversion and hence, H₂ purity. In Figure 3.19, the S:C is equal to the Ca:C in each case. But unlike Figure 3.20, no significant difference in CO conversion (and hence H₂ purity) is observed. Comparing results from Figures 3.19 and 3.20, it can be hypothesized that the enhancement provided by externally supplied steam is superior to the one provided by increasing the supply of steam via increment in the moles of Ca(OH)₂. The externally supplied excess steam is readily available for the WGS reaction while in the other scenario, Ca(OH)₂ has to decompose to provide the steam in-situ. When the steam is readily available, it is likely to be well distributed throughout the reactor and cause a more pronounced effect on the forward reaction.

**Carbon formation via Boudouard reaction**

In addition to enhancing the H₂ purity, the presence of excess steam also aided in suppressing the Boudouard reaction. In the Boudouard reaction, CO cracks to form CO₂ and carbon, as follows –

\[ 2\text{CO}_\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{C}_\text{(s)} \]

This reaction is thermodynamically feasible at the operating conditions used in the CLP carbonator in this work (HSC Chemistry, 2008). Occurrence of the above reaction is undesirable for the CLP because it results in loss of the reactant CO. In the absence of the Boudouard reaction, a one-to-one ratio exists between the moles of CO reacted and the moles of H₂ produced.
It was difficult to accurately quantify the extent of the Boudouard reaction because the product CO$_2$ gets captured by the calcium sorbent and the C is left behind in the reactor, mainly as a deposition on the reactor walls. The difference in total CO conversion and CO converted to H$_2$, as obtained from the micro-GC data, provided an indication of the extent of the Boudouard reaction. In the case where excess steam was supplied to the reactor, the difference between the two conversions was found to be negligible. However, approximately 15% of the CO that was converted did not result in the production of H$_2$, when no excess steam was supplied. Figure 3.22 presents the comparison between the sorbent that was fed in the reactor and the sorbent that was recovered from the walls of the reactor after the experiment. The difference is clearly visible – the sorbent in Figure 3.22(b) is discolored due to the C formed during the experiment. It is believed that the presence of more steam favors the occurrence of the WGS reaction over the Boudouard reaction.

### 3.5.3. Testing with syngas-like mixture

For the parametric investigations discussed in the preceding sections, the experiments were conducted with only CO as the reactive component in the feed gas. Experiments using the major syngas constituents – CO, CO$_2$ and H$_2$ – in the feed gas were also performed. The result from one such experiment is shown in Figure 3.23. The composition of the feed gas used in this experiment is provided in Table 3.2. This composition is based on the syngas composition derived from a GE entrained-flow gasifier (U.S. DOE, 2010). The S:CO was maintained at 3, due to which the overall S:C
was reduced to ~2.2. The overall S:C is lower because the C contributed by CO\(_2\) is also considered in the calculation.

As can be seen from Figure 3.23, the final product contained only H\(_2\) and CO. All the CO\(_2\) – the one supplied in the feed and the one generated in-situ – was captured. On a N\(_2\)- and steam-free basis, the product was found to contain ~70% H\(_2\) and balance CO. Based on the data obtained from the micro-GC, it was found that the CO conversion was 50%, which is similar to the conversion observed in the tests conducted using CO only. Theoretically, all other conditions remaining the same, presence of H\(_2\) and CO\(_2\) in the feed should lower the CO conversion by Le Chatelier’s principle. However, since such an effect was not observed, it can be concluded that the presence of the CO\(_2\) acceptor helps to overcome this limitation.

3.6. Challenges during Reactor Operation

Several challenges were encountered during operation. Important ones are described below.

3.6.1. Temperature drop in the reactor

Out of the three CLP reactors, only the carbonator was scaled-up and consequently the system had to be operated as once-through since the solids were not being regenerated and recycled back from the calciner/hydrator. Due to such a design, it was found that there was a substantial temperature drop due to the contact of the cold solids with the preheated gas (see Figure 3.24). The solids entering the reactor were at ambient temperature and the specific heat of the solids combined with the endothermic
dehydration of Ca(OH)$_2$ caused the temperatures to drop significantly in the zone where the solids entered the reactor. The lower temperatures are likely to have led to inferior kinetics for CaO carbonation, affecting the overall WGS reaction conversion. To overcome this problem, electrical heating tapes were used on the inclined section feeding the solids so that the solids could be pre-heated. However, significant improvement in the reaction conversion was not observed. The situation in the sub-pilot system is very different from the one expected in an actual process where solids entering the carbonator will be hot (and at the hydrator exit temperature). Also, it should be noted that the temperature drop was experienced only in the bottom-most part of the reactor; majority of the riser was at the desired operating temperature (600 °C) throughout the experiment.

3.6.2. Limitation of the gas pre-heater

The gas preheater was designed in-house at OSU (see Figure 3.10). It was found that the maximum achievable temperature of the preheated gas was highly dependent on the gas flowrate itself. As a result, conducting tests using lower gas flowrates/velocities (higher gas residence times) became difficult since suitable temperatures could not be attained by the pre-heated gas. It was also found that the preheater required ~5-6 hours to pre-heat the gas from room temperature to 600 °C. Since pre-heating was done using N$_2$, each experiment consumed large amounts of pure N$_2$.

3.6.3. Operating regime of the reactor

Though the majority of Ca(OH)$_2$, which is a fine powder (D50 = 3 µ), was expected to entrain at the operating conditions, it was found that there was agglomeration of the fines
which led to a solids build up in the reactor over time. These solids, if unreacted, can be expected to marginally alter the operating Ca:C in the reactor even though the inlet Ca:C is controlled by the operator.

3.7. Hardware Issues

There were numerous hardware issues which were addressed during the test campaign. Few of these could not be anticipated in-advance; however, attempts were made to solve all problems within the constraints of the available resources. Some of the issues are highlighted in this section.

3.7.1. Rotary valve

In the original design, a rotary valve was included in the solids feeding line. This valve was placed between the screw feeder and the first (top) gate valve, as shown in Figure 3.25. The rotary valve proved to be the biggest bottleneck in the solids feeding section as the solids clogged in its vanes. The clogging progressively became worse till absolutely no solids were discharged into the reactor. Therefore, in the subsequent design modification, the rotary valve was removed and replaced with a vertical straight pipe section. No clogging was observed after this modification and uninterrupted solids feeding could be achieved. The clogging of the rotary valve can be attributed to the very small particle size and cohesive nature of the sorbent. Moreover, the material is also hygroscopic and all efforts of sealed-storage notwithstanding, some moisture retention inevitably occurred which accelerated the clogging.
3.7.2. Standpipe

The standpipes in the solids feeding line also had a tendency to accumulate solids. Generally the solids accumulation began on the walls (in the form of a coating) followed by bridging and eventually, clogging. To avoid this, pneumatic vibrators were installed on the standpipes. Some vibrators were not effective due to dampened vibrations. In such an event, operators had to resort to physical/manual agitation to help solids flow.

3.7.3. Addition of a new flanged section to the reactor

A small section (11” in length) was added to the reactor between the perforated plate and the first flanged riser section, as shown in Figure 3.26. This was done because in the original setup the inclined section intersected the vertical section exactly at the location of the perforated plate. Thus, when a solids bed was formed on the plate, it provided a resistance to the flow of fresh solid feed, leading to solid accumulation inside the inclined section. The new section provided more volume for bed solids and allowed the fresh feed to enter easily.

3.7.4. Gas sampling port

Unlike the issues discussed above, problems with gas sampling ports were anticipated and hence, provisions were made (during the design stage) to overcome them. During the test campaign, it was found that the severity of the problems was underestimated and the port design went through many iterations before a suitable one was identified. The original gas sampling port design is shown in Figure 3.27a. It consisted of a 0.25” tube with an in-line Swagelok particulate filter. Collection of the fine solid particles near the
filter element was obviously expected; however, the filters clogged quickly and completely during the experiments which did not allow the product gas to reach the micro-GC. Hence, alternate designs were evaluated, two of which are also shown in Figure 3.27. In the first modification (3.27b), two filters were used in parallel. At any time, only one filter was used for sampling the gas and the other was cleaned by the operator. Though this arrangement worked better, it was not satisfactory due to two reasons. One, many more fittings and bends were introduced which encouraged solid accumulation. And two, the length of the line from the filter exit to the micro-GC was very long (approximately 20 m); consequently, a time lag was introduced when the filters were switched. Moreover, the time needed to achieve steady-state gas analysis by the micro-GC almost equaled the time the filter could operate without clogging; this defeated the purpose of parallel filters. A completely new design, shown in Figure 3.27c, was then adopted. In the new design, sufficient length of S.S. tubing was provided between the reactor opening and the filter. The idea was to help the solids deposit (or coat internally) in this tubing due to collision with the tube walls so that the gas is almost solids-free when it reaches the filter. Also, instead of having the entire arrangement horizontal, the gas-solid mixture was made to travel through a vertical U-shape to gain gravity-assistance to further aid solids settling. Moreover, a significantly bigger tubing (1” O.D.) was used followed by a larger filter (0.5” tube inlet instead of 0.25”). The larger filter took longer time to get completely clogged. The combined effect was that uninterrupted gas supply for longer time durations to the micro-GC became possible.
3.8. Concluding Remarks

Simultaneous CO$_2$ capture and enhanced H$_2$ production was investigated in the presence of a calcium-based CO$_2$ acceptor in the sub-pilot scale CLP carbonator. Parametric investigation revealed that at Ca:C = 1.5 and S:C = 3, H$_2$ purity of 50% could be achieved via the WGS reaction at 600 $^\circ$C and 1 atm in the absence of a catalyst. Results from the experiments conducted using a syngas-like mixture showed that the equilibrium limitation imposed by the presence of H$_2$ and CO$_2$ in the feed gas was not significant and CO conversions were similar to the ones observed in tests performed with CO only. In all the experiments conducted, no CO$_2$ was detected in the product gas. Previously conducted tests on the bench-scale fixed-bed reactor resulted in ~70% purity H$_2$ at 600 $^\circ$C and 1 atm at S:C = 1. The superior performance in the fixed-bed reactor is likely due to better gas-solid contact and very high Ca:C. The scale up factor is also believed to have affected the performance. The operation of the sub-pilot reactor could not be tested at certain conditions due to hardware/design and safety limitations; thus, future work must focus on overcoming these limitations.
Figure 3.1. Schematic representation of the CLP.
Figure 3.2. Bench-scale fixed-bed reactor testing – effect of temperature on the H₂ purity achieved in the carbonator in the presence of PCC-CaO and no WGS catalyst. S:C = 1, P = 1 atm (Ramkumar and Fan, 2010a, 2010b).
Figure 3.3. Bench-scale fixed-bed reactor testing – effect of pressure on the H₂ purity achieved in the carbonator in the presence of PCC-CaO and no WGS catalyst. S:C = 1, T = 600 °C (Ramkumar and Fan, 2010a, 2010b).
Figure 3.4. Bench-scale fixed-bed reactor testing – effect of S:C on the H₂ purity achieved in the carbonator in the presence of PCC-CaO and no WGS catalyst. T = 600 °C, P = 1 atm (Ramkumar and Fan, 2010a, 2010b).
Figure 3.5. Reactor support structure (a) Left-hand side view. (b) Right-hand side view.
Figure 3.6. Design of the sub-pilot scale CLP carbonator.
Figure 3.7. Snapshot of the sub-pilot scale CLP carbonator.
Figure 3.8. Gas mixing panel (a) Mounted at the test-facility. (b) Detailed three-dimensional drawing. Reproduced with permission from Swagelok Company.
Figure 3.9. (a) Gas cabinets for storing H$_2$ and CO gas cylinders. (b) Automatic switch-over valves installed inside each gas cabinet.
Figure 3.10. Gas preheater.
Figure 3.11. Gas-analyses set-up for sub-pilot CLP carbonator.
Figure 3.12. (a) Baghouse. (b) Baghouse integrated with the CLP carbonator.
Figure 3.13. Electrical control panel.
Figure 3.14. Sub-pilot scale CLP carbonator testing facility. Adapted from Ramkumar, 2010.
Figure 3.15. Trolley jack to support the bottom-most section (T-section) of the reactor.
Figure 3.16. Results from the CO₂ capture tests conducted in the CLP carbonator.
Figure 3.17. CO$_2$ capture – Test 1 (650 °C, Ca:C = 1).
Figure 3.18. CO₂ capture – Test 2 (650 °C, Ca:C = 0.74).
Figure 3.19. Effect of the Ca:C on CO conversion.
Figure 3.20. Effect of the S:C on H$_2$ purity in the product gas (Ca:C = 1.5).
Figure 3.21. Replicate runs (Ca:C = 1.5, S:C = 3).
Figure 3.22. (a) Sorbent fed to the reactor – Ca(OH)$_2$. (b) Solids recovered from the reactor wall post-experiment.
Figure 3.23. Product gas composition for the test conducted with a syngas-like mixture in the feed (S:C = 3, Ca:C = 1.5).
Figure 3.24. Temperature drop during reactor operation. Temperature recorded by the thermocouple located approximately 6” from the perforated plate. Initial temperature (600 °C) drops instantly on solids injection (time = 0 min).
Figure 3.25. Rotary valve placed between the screw feeder and gate valve as per original design. Reproduced with permission from IWI, Inc.
Figure 3.26. Sub-pilot CLP carbonator (a) Original design. (b) Modified Design.
Figure 3.27. Gas sampling port (a) Original design. (b) Modified design. (c) Final design.
Table 3.1. Composition and properties of Graymont high-calcium Ca(OH)$_2$.

<table>
<thead>
<tr>
<th>Composition</th>
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<tbody>
<tr>
<td>CaO</td>
<td>Minimum 72%</td>
</tr>
<tr>
<td>MgO</td>
<td>Minimum 0.4%</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>Maximum 1.1%</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D50</td>
<td>3 µ</td>
</tr>
<tr>
<td>Bulk density</td>
<td>480 kg/m$^3$</td>
</tr>
<tr>
<td>Surface area</td>
<td>22.8 m$^2$/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.074 cm$^3$/g</td>
</tr>
</tbody>
</table>
Table 3.2. Composition of the feed gas used in the experiment with syngas-like mixture.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Volume %</th>
<th>N\textsubscript{2}-free volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>6.5</td>
<td>42.8</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>6.17</td>
<td>40.7</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>2.5</td>
<td>16.5</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>balance</td>
<td>-</td>
</tr>
</tbody>
</table>
CHAPTER 4
INVESTIGATION OF HIGH-TEMPERATURE STEAM HYDRATION OF CALCIUM OXIDE FOR IMPROVED MULTICYCLIC CARBON DIOXIDE CAPTURE\textsuperscript{5,6}

This chapter details the study of high-temperature (500 °C) steam hydration of CaO for sustained CO\textsubscript{2} capture capacity over several carbonation-calcination-hydration cycles. Though similar studies exist in literature, this work is the first to investigate hydration as an inherent part of the calcium looping process and thus, the experimental conditions used here are most relevant to the three-step process (as shown in Figure 2.2). Also, unlike many other studies, commercially-available calcium precursors (limestones) were used here. It should be noted that the limestones tested here include the ones that have been successfully tested in the 120 kWth sub-pilot unit at OSU.

\textsuperscript{5}Parts of this chapter have appeared in a paper in the journal Energy & Fuels. The material is reproduced here with permission from “Phalak, N.; Deshpande, N.; Fan, L.-S. Investigation of High-Temperature Steam Hydration of Naturally Derived Calcium Oxide for Improved Carbon Dioxide Capture Capacity over Multiple Cycles. Energy Fuels 2012, 26, 3903-3909. Available at - http://pubs.acs.org/doi/abs/10.1021/ef3003735. Copyright 2012 American Chemical Society.”

\textsuperscript{6}The work detailed in this chapter has been performed with equal contribution from Ms. Niranjani Deshpande.
4.1. Introduction

Hydration of CaO results in the formation of Ca(OH)$_2$ according to the reaction –

$$\text{CaO}_{(s)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Ca(OH)}_{2(s)} \quad (\Delta H = -109 \text{ kJ/mol})$$

The reactivation of CaO using steam hydration has been widely reported and there is a general agreement that the positive effect of hydration is due to the improved morphology of the sorbent (Han et al., 2010; Hughes et al., 2004; Kuramoto et al., 2003; Wu et al., 2010; Zeman, 2008). It is suggested that hydration causes cracks to be formed in the CaO particles, creating channels extending to the interior of the particles and thus improving CO$_2$ capture (Wu et al., 2010). Formation of larger pores due to hydration also improves performance of the sorbents as they become less susceptible to pore pluggage (Yu et al., 2012).

One of the shortcomings of the studies reported so far is that the hydration has been investigated at low temperatures (100 – 300 °C). For the effective integration of this reactivation method in the CO$_2$ capture process, operating conditions need to be suitable for utilizing the heat released during hydration. More recently, process analysis of the OSU CCR Process with intermediate hydration has been reported (Wang et al., 2012). In this work, computer simulations for integrating the CCR Process into a coal-fired power plant were conducted using Aspen Plus software. It was found that if the hydrator was operated at high temperatures (>350 °C), the exothermic heat of reaction could be utilized in the steam turbine cycle of the power plant. Commercially, hydration of lime is performed using excess water at ambient conditions and this technique is known to produce a highly reactive sorbent for CO$_2$ capture (Wang et al., 2010). However, the
integration of low-temperature hydration in a calcium-based CO\textsubscript{2} capture process will not generate useful heat and impose greater energy penalty on the process (Wang et al., 2012). Using a hydrator operated at 500 °C, Wang et al. report that 90% CO\textsubscript{2} removal and complete SO\textsubscript{2} removal can be achieved with a 28% increase in the thermal energy necessary to maintain a constant electrical output from the power plant (Wang et al., 2012).

The advantages notwithstanding, hydration at the aforementioned conditions has not been reported in literature and thus, there is a lack of experimental evidence that it will maintain the reactivity of CaO toward CO\textsubscript{2}, over many cycles. Hence, the purpose of this study is to investigate such hydration of CaO for multicyclic CO\textsubscript{2} capture. For the first time, the CO\textsubscript{2} capture capacity of the sorbent has been determined after every calcination and hydration in a cyclic study. This further elucidates the effect of hydration as the sorbent undergoes several cycles of carbonation-calcination-hydration.

4.2. Experimental Methods

4.2.1. Limestones

The limestones investigated in this study were obtained from Graymont Inc. and Carmeuse Lime and Stone. Two limestone samples were obtained from each supplier. The Graymont samples came from the quarries at Pleasant Gap - Pennsylvania (PG) and Townsend – Montana (TS); the Carmeuse samples came from the quarries at Maysville – Kentucky (MV) and Blackriver – Kentucky (BR). The limestone compositions, as provided by the suppliers, are given in Table 4.1. As can be noticed, three out of the four
limestones were obtained from regions in proximity to Ohio. The selected limestones do not form a representative sample for all limestone rocks; however, it is believed that the results obtained by testing more than one stone will help in drawing conclusions with greater confidence. The limestones were crushed and sieved to separate the particles in the size range of 250-300 µ, which were selected for further testing. The phenomenon of particle breakage/attrition due to hydration of CaO has been reported by several researchers (Blamey et al., 2010b; Hughes et al., 2004; Manovic et al., 2008). Therefore, the starting particle size ceases to have any bearing in experiments where hydration is performed in every cycle. As expected, in this work, it was found that after the first hydration, the particle size was reduced to <20 µ. Subsequent hydrations may result in still finer particles; this effect was however not studied in this work. No attempts were made to control the particle size in the multicyclic experiments.

4.2.2. Experimental setup

Calcination

The limestone samples were calcined in an oven (Fisher Scientific – Isotemp Muffle Furnace) capable of operating at a maximum temperature of 1100 °C. Samples were placed in an alumina crucible for calcination.

Carbonation and Hydration

The hydration and carbonation of the samples were conducted in a bench-scale fixed-bed reactor. A diagrammatic representation of this setup is shown in Figure 4.1. The reactor is an inconel tube having an internal diameter and length of 0.006 m and 0.254 m,
respectively. A perforated metal plate was welded inside the reactor and the solid samples were supported on this plate using quartz wool, forming a packed bed. During the experiment, the reactor was placed in a heated zone provided by a tube furnace (ThermoLyne 79300). Since the reactor was detachable from the heated zone, it enabled easy removal and loading of the solids. The heated zone consisted of two concentric cylindrical sections. The outer section served to preheat the gases entering the reactor and was maintained at the reactor temperature. The inner section housed the detachable reactor. A thermocouple and a pressure gauge were provided to monitor the temperature and pressure, respectively. The gases exiting the reactor passed through a back-pressure regulator. This was followed by a chilled water heat exchanger to condense the unreacted steam and the cooled gas was vented. The steam generating unit consisted of a high-precision water pump (ISCO 100DM) which delivered water into a preheated zone. The preheated zone consisted of S.S. tubing surrounded by heating tapes and appropriate insulation. This tubing was filled with quartz wool to increase the heat transfer area available for the formation of steam. The temperature of this zone was maintained at 230-250 °C, due to which the water that entered was immediately converted into steam. MFCs were used for delivering gases (N₂ and CO₂) to the reactor.

**Thermogravimetric analysis**

A thermogravimetric analyzer (Perkin Elmer Pyris1 TGA) was used to determine the extent of calcination and hydration, and the CO₂ capture capacity of the sorbent. A detailed description of this equipment is available elsewhere (Iyer et al., 2004).
4.2.3. Experimental procedure

*Preliminary screening of the limestone samples*

All the limestones were tested in the TGA for their CO$_2$ capture capacity. A small sample of the limestone (15-20 mg) was used for these tests. The samples were subjected to the following three steps in the TGA:

- The sample was heated from 25 °C to 700 °C in N$_2$ and held isothermally at 700 °C for 30 min (calcination).
- The temperature was reduced from 700 °C to 650 °C and then the sample was held isothermally in 10% CO$_2$ (balance N$_2$) for 30 min (carbonation).
- The sample was cooled down to 25 °C.

All heating and cooling steps were performed at a rate of 25 °C/min. The instrument recorded the sample weight and temperature with respect to time.

The aim of the preliminary screening was to determine the CO$_2$ capture capacity of the sorbent when it is subjected to minimum sintering. In the TGA, in pure N$_2$ atmosphere, CaCO$_3$ starts calcining at ~600 °C. 700 °C was used to ensure complete and quicker calcination within the time duration selected (30 min). For carbonation, 10% CO$_2$ was used because it represents a typical flue gas from a coal-fired boiler (Ciferno et al., 2011). Although the carbonation did not go to completion in 30 min, the selected duration is believed to be more than sufficient because the carbonators in calcium-based CO$_2$ capture systems are expected to have residence time of the order of seconds to a few minutes (Martinez et al., 2011; Wang et al., 2010). 650 °C was chosen for carbonation since...
thermodynamically, the maximum allowable CO$_2$ concentration is ~1%, which represents 90% CO$_2$ capture from a coal-fired flue gas stream (Wang et al., 2012). It also represents the temperature that has been used in several recent large scale demonstrations (Charitos et al., 2011; Fang et al., 2009; Kremer et al., 2012; Lu et al., 2008; Wang et al., 2010).

**Multicyclic tests**

Following the initial screening, multicyclic tests were conducted for each limestone. Each cycle consisted of the following steps:

- Calcination was performed at 950 °C in the muffle furnace for 120 min (including the time for ramping up the temperature). The furnace reached the said temperature in ~60 min.

- Hydration was performed using 90% steam and balance N$_2$ for 30 min in the fixed-bed reactor at 500 °C. The 10% N$_2$ acted as a carrier gas to convey the steam to the reactor.

- Carbonation was performed at 650 °C in the fixed-bed reactor for 120 min using 10-12% CO$_2$ (balance N$_2$) stream.

A set of 5 cycles (calcination-hydration-carbonation) was performed for each stone. After every step, a small amount of sample was tested in the TGA. The TGA testing consisted of the same steps as outlined earlier in Section 4.2.3.

The objective of the multicyclic tests was to demonstrate the low CO$_2$ capture capacity due to enhanced sintering at the higher calcination temperature and improved CO$_2$
capture capacity post-hydration. The calcination temperature (950 °C) used in the multicyclic tests is representative of the one employed in recent large scale demonstrations (Charitos et al., 2011; Fang et al., 2009; Kremer et al., 2012; Lu et al., 2008; Wang et al., 2010). While hydration using 100% steam at 500 °C would have been desirable, the fixed-bed reactor required a carrier gas to convey the steam into the reaction chamber; hence 10% N₂ was used during hydration. As a result, the partial pressure of steam was 0.9 atm at 500 °C, which is thermodynamically favorable for hydration to occur (Wang et al., 2012). While the carbonation temperature was the same as that used in the preliminary screening, longer carbonation times were used. This was done to account for the greater mass transfer diffusion resistance in the fixed-bed reactor as compared to the TGA. In the multicyclic tests, the carbonation serves only to complete the cycle – calcination-hydration-carbonation – and is the least important step among the three, for the purpose of this investigation. The focus of these tests is the CO₂ capture capacity of the sorbent post-calcination and post-hydration in each cycle. The evaluation of both the capacities was performed using the TGA as discussed earlier.

**Extended multicyclic testing of PG**

Based on the initial screening and the 5-cycle experiments, the best performing limestone – PG – was selected for long-term multicyclic testing. This testing extended the experiment to 15 cycles and the results were used to validate the assumptions made in the CCR Process Aspen study (Wang et al., 2012).
**Comparisons of limestones**

BET (Brunauer-Emmett-Teller) pore size distribution measurements were used to compare BR and MV. Samples obtained from the multicyclic tests were used in this study. The measurements were performed using N₂ adsorption and desorption isotherms at −196 °C on a Quantachrome NOVA 4200e series volumetric adsorption analyzer. Prior to testing, the hydrated samples were dehydrated to form CaO. The samples were degassed at 300 °C for 6 h. After degassing, the samples were weighed again and this weight was used for all calculations. The BJH method was used to obtain the pore size distribution measurements.

**4.3. Results and Discussion**

**4.3.1. Preliminary screening of the limestone samples**

The CO₂ capture capacity of the sorbent, calculated as ‘weight % CO₂ capture capacity’ and hereafter simply referred to as ‘capture capacity’, is defined as follows

\[
\text{Capture capacity} = \frac{W_t - W_o}{W_o} \times 100 \%
\]

where \( W_o \) is the sample weight after complete calcination (gm), \( W_t \) is the sample weight at a given time \( t \) (gm), and \( t \) is the carbonation time (min).

The values listed in Table 4.2 correspond to the carbonation time of 30 min in the TGA. Quite clearly, PG is the best performer followed by TS and BR. Although the theoretical maximum capture capacity of pure CaO is 78.5, it is not achieved in actual testing. This phenomenon has been widely reported in literature and is attributed to the product
(CaCO\(_3\)) layer which hampers the carbonation (Bhatia and Perlmutter, 1983). The increase in molar volume during conversion of CaO to CaCO\(_3\) also leads to diffusion resistance due to pore pluggage, limiting the conversion (Gupta and Fan, 2002). Since the limestones have been obtained from quarries, they do not consist of 100% CaCO\(_3\) and contain appreciable amount of inert matter. The presence of inerts reduces the CaO available, further limiting CO\(_2\) capture per unit mass of the calcined sample. The estimated amount of inerts present in each limestone is also provided in Table 4.2. The fraction (by weight) of inerts in the limestone was calculated using data obtained from the TGA according to the following formula:

\[
\text{Inerts \%} = (1 - f_{\text{CaCO}_3}) \times 100
\]

where \( f_{\text{CaCO}_3} = \frac{W_{\text{CO}_2} \times M_{\text{CaCO}_3}}{M_{\text{CO}_2} \times W_o} \)

\( f_{\text{CaCO}_3} \) = fraction (by weight) of limestone present as CaCO\(_3\)

\( W_{\text{CO}_2} \) = CO\(_2\) evolved from sample (gm)

\( M_k \) = Molecular weight of species ‘k’(gm/gmol)

\( W_o \) = weight of original sample (gm)

Small differences were found to exist between the limestone supplier data (Table 4.1) and calculated values (Table 4.2). Limestone compositions from the same quarry are likely to vary with time and the compositions reported in Table 4.1 may not accurately represent the samples that were procured for the tests carried out in this work. Nonetheless, Table 4.1 offers a good comparison between the compositions even though the absolute values cannot be used for any analyses with a high degree of confidence. Hence, for all further calculations, the calculated values from Table 4.2 have been used.
4.3.2. Multicyclic tests

A multicyclic test consisting of 5 cycles was performed using each limestone according to the procedure detailed in Section 4.2.3 and the results are shown in Figure 4.2. It can be seen that the capture capacity, post-calcination, is lower as compared to the values listed in Table 4.2. The higher temperature of calcination used in the multicyclic tests compared to the TGA (950 °C vs. 700 °C) results in greater sintering of the sorbent, which has a negative impact on the gas-solid reaction conversion (Fuertes et al., 1991). During these tests, the calcined samples were removed immediately from the muffle furnace after the furnace cooled down to room temperature. However, cycle 3 sample of BR was accidently left overnight in the furnace at room temperature. The longer time allowed this sample to atmospherically hydrate in the furnace due to which it exhibited higher post-calcination capture capacity in that cycle.

The post-hydration capture capacity is also shown in Figure 4.2. For each stone, it can be seen that for a given cycle, the capture capacity post-hydration is higher than post-calcination. Hydration helps to reverse the effect of sintering and this helps in restoring the capture capacity. Based on the findings reported earlier (Han et al., 2010; Hughes et al., 2004; Kuramoto et al., 2003; Zeman, 2008), this result was expected; however, it was found that when hydration is performed every cycle, it also has an impact on the capture capacity post-calcination. To illustrate that the capture capacity of CaO in a CaCO₃-CaO-Ca(OH)₂ cycle exhibits a different trend from CaO in a CaCO₃-CaO cycle, PG was subjected to the CaCO₃-CaO cycle. Figure 4.3 shows the comparison between the capture capacity of CaO in CaCO₃-CaO and CaCO₃-CaO-Ca(OH)₂ cycles. It should be noted that
for both the cycles – CaCO\textsubscript{3}-CaO and CaCO\textsubscript{3}-CaO-Ca(OH)\textsubscript{2} – calcination is a common step and the two curves in Figure 4.3 shown post-calcination capture capacity. Figure 4.3 leads to a hypothesis that hydration in every cycle halts the increasing sintering caused by successive calcinations, which prevents a decrease in the capture capacity even after high temperature calcination. From Figures 4.2 and 4.3, it can be observed that the data for post-calcination capacity of PG do not exactly match; this is because the data are obtained from two replicate runs and thus, provide an indication of the reproducibility of the results.

Barring TS, the capture capacity in Figure 4.2 does not exhibit any trend in particular. The minor increase/decrease observed in the capture capacity for MV, BR and PG is believed to be too insignificant to suggest any trend and can be regarded as constant over the 5 cycles investigated. However, the capture capacity of TS decreases significantly over the 5 cycles, and the fall is more pronounced post-calcination. It is unclear as to why the post-calcination capture capacity of TS dropped gradually as compared to the other stones. However, a similar trend resulting in the post-hydration capture capacity is consistent with prior findings reported by other researchers – capture capacity post-hydration is directly proportional to the capture capacity post-calcination (Blamey et al., 2011).

The different capture capacity observed for CaO obtained from different limestones could be likely due to certain stone characteristics. In particular, the capture capacity is affected by two factors – the calcium content of the limestone and the extent of hydration of the
derived CaO in the fixed hydration time (30 min) employed during these investigations. Hence it is important to consider these parameters in the calculations. Thus, the post-hydration capture capacities were re-evaluated taking these two factors into consideration.

The weight of the inerts in the original stone (obtained from the TGA data) is defined as weight of all species excluding CaCO₃. This weight is assumed to be constant, i.e. unreactive and inert with respect to temperature. This assumption is an approximation, since the limestone contains other species which, though being non-reactive toward CO₂, may undergo chemical transformation in the TGA at the said temperature. However, this assumption is believed to be reasonable because the fraction of the inerts present in the original stone is very low. It was found that unexpected changes in sample weight were insignificant in the TGA testing.

\[
\text{Capture capacity (calcium basis)} = \frac{\text{CO}_2 \text{ captured (gm)}}{\text{weight of active sorbent (gm)}} \times 100
\]

Active sorbent is defined as the fraction of the sample present in the form of CaO, free of inerts and therefore capable of capturing CO₂. It is calculated as follows:

\[
W_{\text{active}} = W_{\text{calcined}} \times (1 - f_i)
\]

where,

\[
f_i = \frac{w_i}{w_{\text{CaO}} + w_i} \times 100
\]

\[
w_{\text{CaO}} = \frac{f_{\text{CaCO}_3} \times W_o \times M_{\text{CaO}}}{M_{\text{CaCO}_3}} \quad \text{and} \quad w_i = (1 - f_{\text{CaCO}_3}) \times W_o
\]
\( W_{active} = \) active sorbent in the sample (gm)

\( W_{calcined} = \) sample weight after calcination and before carbonation (gm)

\( f_i = \) weight fraction of inerts in the calcined sample

\( w_i = \) inerts in the original sample (gm)

\( w_{CaO} = \) CaO in the calcined sample (gm)

The 5-cycle average capture capacity on the basis of the calcium content is shown in Figure 4.4. The numbers are in fair agreement with the data in Table 4.1, represented by the solid triangles in Figure 4.4. PG, which has the highest CaCO\(_3\) (calcium) content shows the greatest capture capacity and MV shows the lowest capacity.

For the second calculation, the estimation of the extent of hydration was required. It was assumed that the amount of water evolved during dehydration/calcination (prior to carbonation) in the TGA is indicative of the extent of hydration of the sorbent.

\[
\text{Capture capacity (hydrate basis)} = \frac{W_{CO_2,hydrated\ sorbent}}{W_{hydrated}} \times 100
\]

Where, \( W_{CO_2,hydrated\ sorbent} = W_{CO_2,total} - W_{CO_2,unhydrated\ sorbent} \)

\[
W_{hydrated} = \frac{W_{H_2O}}{18} \times 56
\]

\[
W_{unhydrated} = W_{active} - W_{hydrated}
\]

\[
W_{CO_2,unhydrated\ sorbent} = \frac{x_{calcined}}{100} \times W_{unhydrated}
\]

\( W_{CO_2,total} = \) total CO\(_2\) captured by the sorbent (gm)

\( W_{CO_2,hydrated\ sorbent} = \) CO\(_2\) captured by hydrated sorbent (gm)

\( W_{CO_2,unhydrated\ sorbent} = \) CO\(_2\) captured by unhydrated sorbent (gm)
\[ W_{\text{hydrated}} = \text{hydrated sorbent, in the form of CaO (gm)} \]
\[ W_{\text{unhydrated}} = \text{unhydrated sorbent, in the form of CaO (gm)} \]
\[ x_{\text{calcined}} = \text{capture capacity (%) of the calcined sorbent in the corresponding cycle} \]

As can be seen from Figure 4.4, the difference among the limestones is not very significant on ‘hydrate basis’ as compared to ‘calcium basis’. Thus, it can be concluded that the extent of hydration of CaO is a strong function of the precursor. A fixed hydration time (30 min) was used in this work and the results show that this time is not sufficient to hydrate CaO obtained from different precursors, to the same extent. While designing calcium-based CO$_2$ capture systems, this factor will assume greater importance to ensure flexibility of using different precursors to achieve the same performance.

### 4.3.3. Extended multicyclic testing of PG

On the basis of the results obtained in 4.3.1 and 4.3.2, PG was selected for multicyclic testing for more cycles because it showed the best performance over 5 cycles. The same experimental conditions that were used in 4.3.2 were employed here. However, the series of calcination-hydration-carbonation was extended to 15 cycles. The results are presented in Figure 4.5. The capture capacity of the sorbent post-hydration drops by approximately 5 percentage points from cycle 1 to cycle 15; this sorbent performance is superior to the performance reported in literature (Zeman, 2008). However, an even better performance of the sorbent may be expected in an actual process because of the sorbent purge that will occur every cycle. Since some of the circulating sorbent will get purged every cycle accompanied by fresh sorbent make-up, all the sorbent that enters the system in cycle 1 will not be present in cycle 15, unlike in the experiments performed in this work.
From the process simulations, it was found that the 15-cycle sorbent performance (as shown in Figure 4.5) represents a Ca:C equivalent to 1.44 (Wang et al., 2012). Prior work performed at OSU has experimentally confirmed this Ca:C to be suitable for 90% CO₂ removal from flue gas produced from coal combustion (Wang et al., 2010) and hence, the test was limited to 15 cycles only.

4.3.4. Comparison between BR and MV

The preliminary screening of limestones revealed that the amount of inerts present in BR and MV (as given in Table 4.2) was almost the same. When subjected to the CaCO₃-CaO-Ca(OH)₂ cycles, it was found that they exhibited significantly different capture capacities post-hydration. This difference is likely due to different extents of hydration, which is illustrated in Figures 4.4 – when the basis of calculation was changed to account for the extent of hydration, the capture capacities were found to be almost identical. However, to gain more insight, BR and MV were selected for BET analyses. BET was performed on cycle 5 samples to determine pore volume distribution. The pore volume distributions are provided in Figures 4.6 and 4.7. It was found that the total pore volume increased by 10% for MV and 47% for BR, post-hydration. From Figures 4.6 and 4.7, a shift in the pore size distribution to larger diameter pores can be observed after hydration. For the hydrated samples, comparatively bigger pores are likely to result in higher capture capacity (Yu et al., 2012). Since the increase in total pore volume for BR is higher as compared to MV, the capture capacity of BR post-calcination and post-hydration is higher than that of MV.
4.4. Other Strategies with Steam as a Reactivating Agent

For realizing the complete potential of steam as a reactivating agent, conducting hydration post-calcination (or pre-carbonation) seems to be the obvious and most effective strategy. Nonetheless, researchers have investigated alternative ways of introducing steam in the calcium loop to enhance sorbent performance e.g. conducting carbonation or calcination in the presence of steam, etc. Though some studies indicate that the presence of steam during either of the two steps can be advantageous, the results are debatable. Moreover, since steam already exists in combustion- and gasification-derived flue/fuel gases, it may be difficult to regulate these effects. Nevertheless, a study of this aspect may be helpful in reactor design. Liu et al. have performed a detailed review of all reactivation strategies using steam; hence a similar one is not included here (Liu et al., 2012). The author’s perspective about these strategies is summarized in Table 4.3.

4.5. Concluding Remarks

This work demonstrates that high-temperature steam hydration successfully maintains the reactivity of CaO toward CO₂ over several carbonation-calcination-hydration cycles. The ability to sustain high CO₂ capture capacity will further enhance the economic viability of the calcium-based CO₂ capture processes. CaO obtained from commercially available precursors was tested and it was found that the extent of hydration of CaO is a function of the precursor. Characterization studies conducted using BET indicate a shift in the pore size distribution between calcination and hydration.
Figure 4.1. Fixed-bed reactor setup.
Figure 4.2. CaCO$_3$-CaO-Ca(OH)$_2$ cycle (solid symbols – post-calcination capture capacity, hollow symbols – post-hydration capture capacity).
Figure 4.3. Comparison of the post-calcination capture capacity of PG in CaCO$_3$-CaO-Ca(OH)$_2$ and CaCO$_3$-CaO cycles.
Figure 4.4. $\text{CaCO}_3$-$\text{CaO}$-$\text{Ca(OH)}_2$ cycle – 5-cycle average post-hydration capture capacity.
Figure 4.5. CaCO₃-CaO-Ca(OH)₂ cycle – 15-cycle investigation conducted for PG.
Figure 4.6. Pore size distribution for BR (cycle 5).
Figure 4.7. Pore size distribution for MV (cycle 5).
Table 4.1. Characteristics and composition of the limestones investigated.

<table>
<thead>
<tr>
<th>Property / Composition</th>
<th>Unit</th>
<th>Limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carmeuse</td>
</tr>
<tr>
<td>Loss on Ignition (LOI)</td>
<td>%</td>
<td>43.3</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>%</td>
<td>0.03</td>
</tr>
<tr>
<td>Silica (SiO₂)</td>
<td>%</td>
<td>1.13</td>
</tr>
<tr>
<td>Ferric Oxide (Fe₂O₃)</td>
<td>%</td>
<td>0.14</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>%</td>
<td>0.28</td>
</tr>
<tr>
<td>Calcium Carbonate (CaCO₃)</td>
<td>%</td>
<td>94.6</td>
</tr>
<tr>
<td>Magnesium Carbonate (MgCO₃)</td>
<td>%</td>
<td>2.97</td>
</tr>
<tr>
<td>Free moisture</td>
<td>%</td>
<td>2.3</td>
</tr>
<tr>
<td>Loose Bulk Density</td>
<td>kg/m³</td>
<td>1377</td>
</tr>
<tr>
<td>Packed Bulk Density</td>
<td>kg/m³</td>
<td>*</td>
</tr>
</tbody>
</table>

*data not available.
Table 4.2. Results of the preliminary screening of the limestones.

<table>
<thead>
<tr>
<th>Limestone</th>
<th>Wt % CO$_2$ capture capacity</th>
<th>Inerts (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MV</td>
<td>47.98</td>
<td>4.07</td>
</tr>
<tr>
<td>BR</td>
<td>52.63</td>
<td>4.26</td>
</tr>
<tr>
<td>TS</td>
<td>54.08</td>
<td>5.28</td>
</tr>
<tr>
<td>PG</td>
<td>56.46</td>
<td>3.44</td>
</tr>
<tr>
<td>No.</td>
<td>Strategy</td>
<td>Comments</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Hydration after carbonation</td>
<td>Minimum or no effect. The outer carbonate layer prevents the reaction with the inner unreacted CaO core. Reaction may be possible if CaCO$_3$ layer is thin. Trade-off between reactivation and sorbent utilization.</td>
</tr>
<tr>
<td>2</td>
<td>Hydration after calcination</td>
<td>Most effective and proven. Complete restoration of CO$_2$ capture capacity possible. Requires additional reactor – hydrator – which uses significant amount of steam.</td>
</tr>
<tr>
<td>3</td>
<td>Carbonation in presence of steam</td>
<td>CaO hydration may or may not occur prior to carbonation. Some positive effect on carbonation rate is observed, but uncertainty related to the exact mechanism. Reversibility of the sorbent is not significantly improved.</td>
</tr>
<tr>
<td>4</td>
<td>Calcination in presence of steam</td>
<td>Results are debatable. Presence of steam (thermodynamically) reduces calcination temperature, but experimentally is found to accelerate sintering.</td>
</tr>
<tr>
<td>5</td>
<td>Periodic hydration</td>
<td>Can be effective. Advantages include use of lesser steam as compared to strategy 2. Likely to be difficult to incorporate in a continuous process.</td>
</tr>
<tr>
<td>6</td>
<td>Partial hydration</td>
<td>Can be effective. Advantages and disadvantages similar to strategy 5. Another drawback is that full potential of hydration as a reactivation technique is not realized.</td>
</tr>
</tbody>
</table>
CHAPTER 5
CALCIUM LOOPING PROCESS (CLP) FOR ENHANCED HYDROCARBON REFORMING

The application of the CLP for the production of H₂ from coal-derived syngas was discussed in Chapter 3. Another pathway in which the CLP can be used to produce H₂ is enhanced hydrocarbon reforming. In this case, the reforming reaction is carried out in the CLP carbonator along with the WGS, CO₂ capture, etc. The proof-of-concept for this scheme has been experimentally verified in prior work (Ramkumar, 2010; Ramkumar et al., 2012). In that work, experiments were performed in a fixed-bed reactor to produce high-purity H₂ by conducting steam methane reforming (SMR) in the presence of a calcium-based CO₂ acceptor and a conventional reforming catalyst. The work described here extends the concept to higher hydrocarbons including the effect of catalyst type. Based on the results obtained from the fixed-bed reactor, experiments were performed in the sub-pilot scale reactor and are also discussed here.

5.1. Introduction

As briefly mentioned in Chapter 1, recent research efforts have focused on the large-scale production of H\textsubscript{2} for generating electricity, powering automobiles, etc. (NRC and NAE, 2004). While the advantages of using H\textsubscript{2} as a fuel – zero CO\textsubscript{2} emission and excellent calorific value – are undisputable, the source of large quantities of H\textsubscript{2} that would be required to achieve a global switchover will most likely be fossil fuels, especially natural gas. In such a scenario, improving the efficiency of H\textsubscript{2} production from fossil fuels with the integration of CO\textsubscript{2} capture becomes vital. In this context, the work described in this chapter assumes importance.

Natural gas is a cost-effective feed for making H\textsubscript{2} due to wide availability, ease of handling and high hydrogen-to-carbon ratio as compared to coal. Although historically, U.S. has relied on imports to satisfy the natural gas requirement, the recent progress in the shale gas hydraulic fracturing technology has increased U.S. production, lowered prices and cut imports. As per the available data, 30% growth in domestic gas production will outpace the 16% growth in consumption (Newell, 2010). This indicates that natural gas will remain the leading source of H\textsubscript{2} even as technologies based on new sources are being developed.

SMR is the most efficient and economical process that exists today to convert natural gas to H\textsubscript{2} (Meyers, 2007). In a SMR plant, natural gas or CH\textsubscript{4} is first passed through a zinc oxide (ZnO) bed to remove the sulfur and is then reacted with steam in a reformer at 800 – 900 °C and 20 – 30 atm in the presence of a nickel-based catalyst to convert it into CO
and H₂. This reaction is highly endothermic and requires substantial quantity of supplemental fuel. The product gas from the reformer is then sent to a single-stage or dual-stage WGS reactor in which bulk of the CO is catalytically converted to H₂. The H₂-rich gas is further purified in a pressure swing adsorber (PSA) and the PSA-tail gas is combusted in the reformer. When CO₂ capture is desired, processes like amine scrubbing, etc. may be employed downstream of the WGS reactor(s). A simplified block flow diagram is depicted in Figure 5.1. Some drawbacks of SMR are high steam requirement in the reformer and WGS reactors, and high energy requirement in the endothermic reformer. With CO₂ capture, the tolerance level for several contaminants in the product gas is even lower to protect the solvents that are employed in the capture process; this negatively impacts the overall efficiency (Balasubramaniam et al., 1999).

To improve the efficiency of this process, process intensification by combining two or more reactions in a single reactor has been suggested. Specifically, H₂ production by the equilibrium-limited reforming and WGS reactions can be enhanced by in-situ removal of CO₂ using different sorbents (Fan, 2010; Harrsion, 2008; Sircar and Lee, 2010). Previous studies have shown that presence of a CO₂ acceptor along with a reforming catalyst can result in the production of 97% H₂ (dry basis) from CH₄ in a single step without using any shift catalysts (Han and Harrison, 1994; Harrison, 2008). Hydrotalcites, lithium zirconate (Li₂ZrO₃), lithium silicate (Li₄SiO₄), sodium zirconate (Na₂ZrO₃), calcium oxide (CaO), etc. and their synthetically modified versions are potential candidates for such applications (Lee et al., 2008; Ochoa-Fernandez et al., 2007). However, the abundance of naturally-occurring CaO precursors – limestone and dolomite – and the
very high CO₂ sorption capacity of CaO as compared to other natural or synthetic sorbents, make CaO an ideal candidate for such a process (Abanades et al., 2004).

Several studies have been reported in which different calcium sorbents have been used to enhance H₂ production via hydrocarbon reforming. Brun-Tsekhovoi et al. have investigated the steam-reforming of hydrocarbons in a fluidized-bed of catalyst, also containing CaO and have reported a H₂ purity of about 94-98% (mole) on a dry basis with trace amounts of CO and CO₂ in the product gas (Brun-Tsekhovoi et al., 1988). A similar, but more comprehensive study was reported by Harrison and coworkers where the effects of different parameters like temperature, steam-to-CH₄ ratio, acceptor-to-catalyst ratio, etc. were investigated (Balasubramaniam et al., 1999). Johnsen et al. conducted the sorption-enhanced SMR using dolomite over multiple cycles and found that even though the overall reaction rate remained unaffected, the CO₂ uptake capacity of the sorbent reduced with increasing number of cycles (Johnsen et al., 2006a). Reactor design and integration of this concept in a natural gas-to-H₂ plant have also been discussed in other studies (Johnsen et al., 2006b; Molburg and Doctor, 2003; Solieman et al., 2009). The CaO-assisted reforming of alcohols has also been reported (Okunev et al., 2005).

In the CLP, the reforming reaction can be performed in the carbonator in addition to the other gas clean-up reactions, as shown in Figure 5.2. As such, the CLP carbonator shown in Figure 5.2 can accept any hydrocarbon feed, most commonly natural gas. Though primarily CH₄, natural gas contains other higher hydrocarbons like ethane (C₂H₆),
propane (C₃H₈), etc. These hydrocarbons will also undergo the reforming reaction; however, this had not been experimentally verified. Similarly, in addition to H₂ production, the concept can be extended to a CTL plant and in this configuration, a mixture of hydrocarbons and syngas will enter the CLP carbonator (Ramkumar, 2010; Ramkumar et al., 2010). Hence, the work described in this chapter is aimed at experimentally validating the feasibility of such scenarios. Additionally, tests using CH₄ have been conducted in the sub-pilot scale reactor.

5.2. Prior Work

The process overview and the thermodynamic analyses for the CLP-enhanced SMR have been described in prior work and are therefore not presented here (Ramkumar, 2010). Extensive fixed-bed tests were also performed to investigate SMR in the presence of CaO. A typical breakthrough curve obtained in the fixed-bed reactor is shown in Figure 5.3. High-purity H₂ was obtained in the prebreakthrough region when the CaO was active and captured CO₂. It was also found that CH₄ was almost completely converted and the concentration of CH₄, CO and CO₂ in the product stream is only a few ppm. The removal of CO₂ by CaO enhances the WGS reaction and the reforming reaction resulting in the production of very pure H₂. As CaO gets consumed in the fixed-bed, the concentration of CO₂, CH₄ and CO begin to increase in the product gas. This region of the curve is the breakthrough period. At the end of the breakthrough period, CaO is completely converted to CaCO₃ and no further CO₂ capture is possible. The conversion of CH₄ to H₂ occurs only due to the catalytic reforming in the postbreakthrough period.
The effect of S:C and temperature was investigated on the above system and is shown in Figure 5.4. Purity of H\textsubscript{2} increased from <80\% in the presence of the catalyst alone to >95\% in the presence of the catalyst and sorbent. Higher H\textsubscript{2} purity was obtained at 650 °C than at 700 °C due to the favorable thermodynamics of the CO\textsubscript{2} removal and the WGS reactions at lower temperatures. In the presence of the catalyst and sorbent, the H\textsubscript{2} purity increased with S:C. The effect of pressure was also studied on the combined reaction at 650 °C and S:C = 3. A decrease in CH\textsubscript{4} conversion with the increase in pressure is expected, in the presence of only catalyst, according to the Le Chatelier’s principle. On the contrary, good conversions were achieved even at higher pressures when both CaO and catalyst were used (see Figure 5.5). Multicyclic experiments, where the CaO underwent successive cycles of carbonation/reforming, calcination and hydration were also conducted and hydration was found to be effective in arresting the decline in sorbent reactivity (Ramkumar et al., 2012).

It should be noted that when the CLP is used to enhance hydrocarbon reforming, the reforming catalyst is necessary. This is unlike the scenario where CLP is used to enhance the WGS reaction (as discussed in Chapter 3), where the WGS reaction is driven solely by the presence of the calcium sorbent.

5.3. Experimental Methods

5.3.1. Chemicals, sorbents and gases

The conventional reforming and pre-reforming catalysts were obtained from commercial vendors. CaO was obtained from precipitated calcium carbonate (PCC). Detailed
procedure of the synthesis of PCC is provided elsewhere (Gupta and Fan, 2002). High-purity (>99%) hydrocarbons – CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8} – were supplied by Praxair. A syngas mixture was also procured from Praxair for testing. The conventional reforming catalyst was used to test C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, and a mixture of syngas and CH\textsubscript{4}. The pre-reforming catalyst was tested with CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8} only.

5.3.2. Experimental setup

The fixed-bed reactor, described in Section 4.2.2, was used for these experiments after making minor modifications to the setup. These modifications included the addition of MFCs for the hydrocarbons and other gases, and gas analyzers (California Analytical Instruments – Model 200 and 600 FID). Figure 5.6 shows the modified experimental setup.

5.3.3. Experimental procedure

The combined reforming, WGS and carbonation reaction was investigated using a mixture of finely powdered PCC-CaO (<180 μ) and reforming catalyst. 2.5 g catalyst and 2.5 g PCC were fed into the reactor. The sorbent was calcined at 700 °C in 1 L/min N\textsubscript{2} for 4 h. Following this, the mixture was treated with pure H\textsubscript{2} for 1 h for reactivating the catalyst. The combined reaction was then conducted using different hydrocarbons (or hydrocarbon and syngas mixture) and steam, and the effect of temperature and S:C was investigated. From the outlet of the reactor, the product gas was cooled using the heat-exchanger, dehydrated further using the desiccant bed and then sent through the gas analyzers for monitoring the concentration of the species of interest.
The limitation of the gas delivery and analysis system did not allow the injection of additional components (H₂S, COS, HCl, etc) in the feed. Since the reaction of these species with CaO has already been proven independently at the operating conditions of interest (Ramkumar and Fan, 2010a; Sun et al., 2011), it is reasonable to expect that the desired CLP carbonator operation (as shown in Figure 5.2) can be achieved.

5.4. Results and Discussion

5.4.1. Tests using conventional reforming catalyst and calcium sorbent

Tests using C₂H₆

Figure 5.7a illustrates the effect of using different S:C on the purity of H₂ in the product gas. Higher S:C led to higher H₂ purity. The excess steam favors hydrocarbon conversion by reforming and WGS. Similar conclusion can be drawn from Figure 5.7b, where the C₂H₆ concentration is the lowest (in the pre-breakthrough region) when S:C is the highest. The use of more steam also results in better C₂H₆ conversion in the post-breakthrough region.

Tests using C₃H₈

The tests conducted using C₂H₆, as described above, were repeated using C₃H₈. The results are presented in Figures 5.8a and 5.8b. It can be seen that at higher S:C, the calcium sorbent is used up faster and thus the time for which high-purity H₂ can be produced is shorter. These results are similar to those obtained for C₂H₆.
**Tests using a mixture of syngas and CH₄**

The combined reaction was also investigated for a feed gas mixture consisting of syngas and CH₄. The composition of the feed gas is provided in Table 5.1. This composition is based on the Aspen simulation performed on a coal-to-liquids (CTL) plant integrated with the CLP (Ramkumar, 2010). The plant configuration in which the CLP block is placed after the F-T reactor was used in this model (Ramkumar, 2010). In all the prior tests, CO, CO₂ and H₂ were not present in the feed gas to the fixed-bed reactor. These gases were the products of hydrocarbon reforming and WGS reaction. However, in this case, the feed gas contained these components and hence this feed more realistically represents the actual scenario.

Figure 5.9a illustrates the effect of using different S:C on the purity of H₂ in the product gas. It can be observed that as the S:C increases, the duration of the pre-breakthrough region becomes shorter. At higher S:C, the presence of excess steam resulted in better conversion of the hydrocarbon by reforming and CO (in the syngas) by WGS reaction. Therefore, the rate of CO₂ formation at larger S:C was higher and the duration of the pre-breakthrough period was shorter. Figure 5.9b depicts the effect of S:C on the CO₂ concentration in the product. The higher rate of CO₂ production at larger S:C ratio is clearly visible. The calcium sorbent was able to capture CO₂ for 200, 310 and 380 sec at S:C of 4, 3 and 2, respectively. In Figure 5.10, the CH₄ concentration in the product stream is presented. Almost all the CH₄ was converted in the pre-breakthrough region when the calcium sorbent was active and captured CO₂.
5.4.2. Tests using pre-reforming catalyst

In all the experiments described so far, the conventional reforming catalyst was used. In this work, for the first time, another catalyst – pre-reforming catalyst – was also investigated. The pre-reforming catalyst is typically used in a temperature range of 300–600 °C and low S:C. Pre-reforming catalysts are employed in dedicated reactors – pre-reformers – placed upstream of the main steam methane reformer. The main purpose of the pre-reformer is to help in the conversion of higher hydrocarbons like C₃-C₄, naphtha, liquefied petroleum gas (LPG), etc. The use of a pre-reformer in a natural gas-to-H₂ plant not only ensures stable operation of the downstream reformer but also increases the lifetime of the reforming and shift catalysts as the sulfur in the hydrocarbon feed stream is absorbed by these catalysts.

Tests using CH₄(no calcium sorbent)

To start with, the catalyst performance was evaluated for SMR in the absence of the calcium sorbent. The temperature range selected for this investigation was based on the activity of the pre-reforming catalyst and the kinetics of the CaO-CO₂ reaction. As per the specification sheet provided by the vendor, the pre-reforming catalyst is typically active at 300 – 600 °C, temperatures which are lower than those expected for the CLP carbonator. 600 – 650 °C will allow excellent kinetics for the CaO-CO₂ reaction; however, this temperature may not be optimum with respect to the catalyst activity. Nonetheless, 500 – 700 °C was chosen because of the expectation that when the reforming and CaO-CO₂ reactions are combined in a single reactor, good hydrocarbon conversion will be obtained due to the rapid CO₂ uptake by CaO.
Figure 5.11a illustrates the H₂ purity at the outlet of the reactor. It can be seen that for both S:Cs the H₂ purity increases with the increase in temperature. This is because reforming reaction is endothermic. With the increase in S:C from 1:1 to 3:1, it was found that the H₂ purity increased at each temperature. Figure 5.11b depicts CH₄ concentration at the reactor outlet, which decreased with temperature. As expected, at a lower S:C, the amount of unconverted CH₄ in the product gas was higher.

**Tests using CH₄ (in the presence of calcium sorbent)**

To test the effectiveness of CaO in improving reaction conversion, calcium sorbent was added and the reaction was conducted in the presence of both sorbent and catalyst. Figure 5.12 depicts the concentration of H₂, CO, CO₂ and CH₄ in the product gas. It was found that H₂ purity in the pre-breakthrough region exceeded 99%, with complete conversion of CH₄ and trace amounts of CO and CO₂. This result is similar to the one obtained for the conventional reforming catalyst in prior work, as shown in Figure 5.3.

**Tests using C₃H₈ (no calcium sorbent)**

The reforming of C₃H₈ was also investigated. Figure 5.13a depicts the C₃H₈ concentration in the product gas. The amount of C₃H₈ in the product gas decreased with an increase in temperature due to the endothermicity of the reforming reaction. Like for CH₄ testing, the amount of unconverted C₃H₈ in the product gas was higher at lower S:C. Figure 5.13b shows the concentration of CO in the product gas. The amount of CO increased with temperature because higher temperatures helped to achieve better C₃H₈ conversion. No significant difference was observed between the CO content at the two
S:Cs that were investigated. More steam will enhance the conversion of CO to CO\textsubscript{2} through the WGS reaction and consequently, lesser CO should be observed. This was clearly seen at 700 °C, but the difference was insignificant at lower temperatures.

**Tests using C\textsubscript{3}H\textsubscript{8} (in the presence of calcium sorbent)**

The reforming of C\textsubscript{3}H\textsubscript{8} was also investigated in the presence of CaO at 600 °C using S:C of 3 and 1. Figures 5.14a and 5.14b show the results. >99% H\textsubscript{2} was obtained at S:C = 3. For S:C =1, the H\textsubscript{2} purity was marginally lower. In the pre-breakthrough region, at S:C = 1, outlet concentration of C\textsubscript{3}H\textsubscript{8} was ~4% while it was ~1% at S:C = 3.

**5.5. Tests Conducted in the Sub-Pilot Unit**

As detailed in Chapter 3, a sub-pilot scale CLP carbonator was designed, constructed and operated to study non-catalytic H\textsubscript{2} production from coal-derived syngas using a calcium sorbent. The same reactor was also used here to test hydrocarbon reforming after making minor modifications to the existing setup. The experiments and results are described below.

**5.5.1. Experimental methods**

*Modifications made to the existing system*

Since the gas mixing panel did not contain a MFC for CH\textsubscript{4}, additional calibration for a second gas was added on the CO\textsubscript{2} MFC so that CH\textsubscript{4} could be delivered to the reactor.

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8Only additional information relevant to the work described in this chapter is included here. Other details are provided in Sections 3.3 and 3.4.
This was possible because CO₂ and CH₄ are very similar in flow properties with respect to a MFC. The cost of adding a calibration was found to be substantially lower as compared to the cost of a new MFC dedicated to CH₄.

**Chemicals**

Pure CH₄ (99%) was used for testing. Nitrogen (N₂) was used as the carrier gas. The calibration of the micro-GC was conducted using certified standard gases – 9.5% CO, 3% CO₂, 5% H₂ and 3.01% CH₄. The conventional reforming catalyst used in the fixed-bed tests was also used here.

**Operating procedure**

The reactor was loaded with the catalyst and heated to the operating temperature (650 °C) and maintained at that temperature. The feed gas (CH₄ + N₂ mixture) was also preheated to the same temperature. For preheating, only N₂ was flowed through the reactor. CH₄ (5% by vol.) was introduced in the feed gas after the desired temperature was attained. Steam was injected 10 min prior to injecting CH₄. To activate the reforming catalyst, the catalyst was reduced using H₂ for 1 h, prior to injecting steam and CH₄. The product gas was analyzed using the micro-GC. In the tests where calcium sorbent was used, the injection of CH₄ to the reactor was followed by the injection of the sorbent.

The catalyst used in the sub-pilot testing was not finely powdered like in the fixed-bed tests. Big catalyst pellets (as supplied by the vendor) were used to form a bed of 6” in the reactor. Big pellets were used to ensure that the catalyst is permanently maintained in the
reactor; at the operating gas velocities, only the calcium sorbent could be entrained out of the reactor. Such an operating mode was necessary because the fixed-bed tests revealed that the catalyst is necessary when using CLP for hydrocarbon reforming; if the catalyst left the reactor, desired hydrocarbon conversion cannot be achieved.

5.5.2. Results and discussion

Investigation of SMR (no calcium sorbent)

Figure 5.15a shows the conversion of CH$_4$ achieved in the sub-pilot reactor. The duration of the run was about 30 min. Approximately 49% CH$_4$ was converted to CO, CO$_2$ and H$_2$ via the reforming and WGS reactions. This is substantially lower than the conversion achieved in the conventional reformers of a natural gas-to-H$_2$ plant. This is because even though the sub-pilot reactor (riser) is ~11’ tall, it is not completely packed with the catalyst, as in the conventional reformer tubes. The catalyst bed was only 6” in height, which reduced the time available for the reacting gas mixture for interaction with the catalyst. The complete composition of the product gas is depicted in Figure 5.15b. Over the duration of the run, the product gas contained ~65% H$_2$ and 23% CH$_4$. Another reason for the low conversion is the temperature drop during the run.

Figure 5.16 shows the temperature profile during the experiment. This temperature was recorded by the thermocouple placed inside the catalyst bed, near the perforated plate (bottom) of the reactor. A very rapid fall in temperature was observed as soon as CH$_4$ was injected into the reactor (t = 0 min) which can be attributed to the highly endothermic
reforming reaction. As the experiment progressed, the fall in temperature moderated and only a 2 °C drop was observed in the second half of the run.

**Investigation of SMR (in the presence of calcium sorbent)**

In this experiment, CH$_4$ + steam injection was followed by one additional step – using the screw feeder to supply calcium sorbent (Ca(OH)$_2$) to the reactor.

The overall S:C for the experiment was 5.41. For each mole of CH$_4$ injected in the system, 3 moles of steam were injected directly from an external source (water pump and steam generator setup) and the balance 2.41 moles were supplied by the decomposition of Ca(OH)$_2$. Like the previous experiment, the catalyst bed was only 6” in height. As seen from Figure 5.17a, (on an average) 39% CH$_4$ conversion was achieved throughout the run. However, a steady drop in the conversion was observed as the run progressed. The final product contained ~60% H$_2$, 30-35% CH$_4$ and balance CO (Figure 5.17b). Due to the addition of the calcium sorbent, all the CO$_2$ generated in the reactor was captured and hence no CO$_2$ was detected in the product gas.

Based on the results obtained from the fixed-bed reactor tests (Ramkumar et al., 2012), a higher CH$_4$ conversion was expected in the presence of the calcium sorbent as compared to the experiment where only catalyst was used. However, it was found that in the presence of the sorbent, the amount of H$_2$ present in the product gas (~60-65%) was not significantly different from the previous non-sorbent run (65%). Similarly, the amount of unconverted CH$_4$ in the product gas was higher (25-35%) as compared to the non-sorbent
run (23%). Typically, the in-situ CO₂ capture is expected to produce more H₂ due to enhancement of CH₄ conversion. However, this was not observed and again, can be mainly attributed to the temperature drop occurring in the reactor.

Figure 5.18 shows the temperature near the catalyst bed in the reactor. On comparing the temperature profiles of the two runs, it was found that the temperature dropped faster and to a value lower by ~40 °C within the same time, in the presence of the sorbent. While the endothermic (reforming) reaction is the common heat sink in both the experiments, the presence of the sorbent decreases the temperature further due to its heat capacity. Since this system has been designed for once-through testing, the solids entering the system are not heated to the operating temperature, leading to parasitic heat utilization. The fall in temperature reduced the extent of the endothermic reforming reaction and led to poor kinetics of the CaO-CO₂ reaction, ultimately resulting in poor CH₄ conversion.

5.6. Concluding Remarks

The investigation of enhanced hydrocarbon reforming was performed in the presence of a calcium-based CO₂ acceptor. Fixed-bed experiments showed that high-purity H₂ can be produced at 650 °C, 1 atm and a comparatively low S:C of 3. The effect of catalyst type was also studied and it was found that the carbonator can be combined with either the reformer or the pre-reformer in a natural gas-to-H₂ plant. Experiments were also conducted in the sub-pilot scale reactor; however, expected results were not obtained due to the limitation imposed by the once-through design of the system.
Figure 5.1. Conventional SMR process with CO₂ capture.
Carbonation: \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \)

Carbonator (Reformer)
Calciner (Regenerator)
CaCO\(_3\)
CaO
Pure CO\(_2\) gas
Calcination: \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \)
\( \Delta H = 178 \text{ kJ/mol} \)

Dehydration: \( \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \)
Reforming: \( \text{C}_x\text{H}_y + \text{xH}_2\text{O} \rightarrow \text{xCO} + \text{(x+y/2)H}_2\)
WGSR: \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\)
Carbonation: \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \)
Sulfidation: \( \text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} \)
Sulfidation: \( \text{CaO} + \text{COS} \rightarrow \text{CaS} + \text{CO}_2 \)
Chloridation: \( \text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \)

Hydrator (Reactivator)
Hydration: \( \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \)
\( \Delta H = -110 \text{ kJ/mol} \)

Figure 5.2. CLP for enhanced hydrocarbon reforming.
Figure 5.3. CLP-enhanced SMR in the fixed-bed reactor – typical breakthrough curve at 650 °C, 1 atm and S:C = 3. Adapted from Ramkumar et al., 2012.
Figure 5.4. CLP-enhanced SMR in the fixed-bed reactor – effect of temperature and S:C on H$_2$ purity at 1 atm. Adapted from Ramkumar et al., 2012.
Figure 5.5. CLP-enhanced SMR in the fixed-bed reactor — effect of pressure on CH$_4$ conversion at 650 °C and S:C = 3 Adapted from Ramkumar et al., 2012.
Figure 5.6. Modified fixed-bed reactor setup for investigation of CLP-enhanced steam reforming of hydrocarbons.
Figure 5.7. Enhanced \( \text{C}_2\text{H}_6 \) reforming at 650 °C and 1 atm – effect of S:C on (a) \( \text{H}_2 \) purity and (b) \( \text{C}_2\text{H}_6 \) concentration, in the product gas.
Figure 5.8. Enhanced C$_3$H$_8$ reforming at 650 °C and 1 atm – effect of S:C on (a) H$_2$ purity and (b) CO$_2$ concentration, in the product gas.
Figure 5.9. Combined reforming, WGS and CO$_2$ capture using syngas and CH$_4$ mixture in the feed at 650 °C and 1 atm – effect of S:C on (a) H$_2$ purity and (b) CO$_2$ concentration, in the product gas.
Figure 5.10. Combined reforming, WGS and CO₂ capture using syngas and CH₄ mixture in the feed – effect of S:C on the CH₄ concentration at 650 °C and 1 atm.
Figure 5.11. SMR using pre-reforming catalyst (no calcium sorbent) at 1 atm – effect of temperature and S:C on (a) H₂ purity and (b) CH₄ concentration, in the product gas.
Figure 5.1. Breakthrough curve for the composition of the product gases obtained during the simultaneous CH₄ reforming, WGS and carbonation reaction using pre-reforming catalyst at 600 °C, S:C = 3 and 1 atm.
Figure 5.13. Steam-C$_3$H$_8$ reforming using pre-reforming catalyst (no calcium sorbent) at 1 atm – effect of temperature and S:C on (a) H$_2$ purity and (b) CO concentration, in the product gas.
Figure 5.14. Breakthrough curve for the composition of the product gases obtained during the simultaneous C$_3$H$_8$ reforming, WGS and carbonation reaction using pre-reforming catalyst at 600 °C and 1 atm. (a) S:C = 3. (b) S:C = 1.
Figure 5.15. SMR in the sub-pilot reactor at 650 °C, S:C = 3 and 1 atm (no calcium sorbent) – (a) CH$_4$ conversion and (b) Product gas composition.
Figure 5.16. Temperature profile near the perforated plate (reactor bottom) during SMR conducted in the sub-pilot reactor at 650 °C, S:C = 3 and 1 atm (no calcium sorbent).
Figure 5.17. SMR in the sub-pilot reactor at 650 °C, S:C = 5.41 and 1 atm (in the presence of calcium sorbent) – (a) CH$_4$ conversion and (b) Product gas composition.
Figure 5.18. Temperature profile near the perforated plate (reactor bottom) for SMR in the sub-pilot reactor at 650 °C, S:C = 5.41 and 1 atm (in the presence of calcium sorbent).
Table 5.1. Composition of the feed gas for the test with syngas and CH₄ mixture.

<table>
<thead>
<tr>
<th>Component gas</th>
<th>Composition (%)</th>
</tr>
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<tbody>
<tr>
<td>CO</td>
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</tr>
<tr>
<td>CO₂</td>
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<tr>
<td>H₂</td>
<td>14</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.77</td>
</tr>
</tbody>
</table>
CHAPTER 6
POST-COMBUSTION CO₂ CAPTURE FROM NATURAL GAS COMBINED CYCLE (NGCC) PLANTS

The application of CLP in a pre-combustion scenario with natural gas as a feedstock was discussed in Chapter 5. It is also possible to use calcium looping to capture CO₂ from the flue gas generated from the natural gas combined cycle (NGCC) plants. In this scheme, the calcium sorbent performs its function after the fuel (natural gas) has been combusted. This process design, which is discussed in the current chapter, further highlights the flexibility of the calcium looping process and is important because it can be readily applied to several existing NGCC plants in the U.S. The work described here is not experimental; only process simulation using Aspen Plus software has been performed to conduct a preliminary evaluation of the feasibility of such a scheme. Nonetheless, the extensive experimental work conducted at OSU and elsewhere lends credence to its workability.

6.1. Introduction

Currently, natural gas accounts for approximately 24% of the total electricity in the U.S. and approximately 20% worldwide (U.S. EIA, 2011, 2013). It is a cleaner fossil fuel as compared to coal due to lower carbon intensity per unit of electricity generated. The
application of the hydraulic fracturing technique has ensured an abundant supply of natural gas and lowered prices. Moreover, plants using natural gas incur lower capital costs, shorter construction times and operate at higher efficiencies as compared to coal-fired power plants (U.S. EIA, 2011). A combination of these factors is expected to increase the new generating capacity additions – it is predicted that by 2040, 30% of the electricity in the U.S. will be obtained from natural gas (U.S. EIA, 2013). Other factors which will help natural gas capture a greater share of the electricity generation include the increasing aversion to new nuclear plants in the wake of recent accidents (The New York Times, 2011) and the retirements of coal plants outpacing new additions (U.S. EIA, 2013).

Recent CCS efforts have mainly focused on coal because of the omnipresence of coal plants and their heavy CO₂ emissions. Studies specific to natural gas are scarce. In fact, displacing coal by natural gas is in itself viewed as a promising short-term carbon mitigation option. While the use of natural gas instead of coal will significantly reduce (approximately 50%) carbon emissions from power generation, it cannot become a universal solution. This is especially true for countries where natural gas currently supplies majority of the electricity, e.g. U.K. – 40%, Netherlands – 60%, Singapore – 78%, Qatar – 100%, etc. (IEA, 2011). For these countries, two options exist in a futuristic carbon constrained scenario. First, purchasing carbon credits under a cap-and-trade system and second, implementation of CCS. Hence, it is important to develop CCS technologies that can cater to the existing and upcoming natural gas-based plants.
As discussed in Chapter 2, CO₂ capture using the calcium looping technology has attracted considerable attention worldwide. Pilot-scale demonstration projects in U.S., Europe and Canada and numerous techno-economic evaluations have established the feasibility and economic viability of this technology. However, majority of the work has been performed on post-combustion CO₂ capture from coal-fired power plants. Pre-combustion CO₂ capture for H₂/electricity generation from CH₄ (discussed in Chapter 5) has been studied at OSU and elsewhere; however, it is less relevant to existing NGCC plants because it will involve major gas turbine modifications. Therefore, it is important to assess the addition of post-combustion CO₂ capture to a NGCC power plant.

This study makes use of ASPEN process simulation software to evaluate the performance of a NGCC plant with post-combustion CO₂ capture using the CCR Process developed at OSU. Two process configurations have been investigated and comparisons have been drawn with competitive CO₂ capture technologies with respect to net electric output, overall plant efficiency and additional utilization of resources. A discussion on the possible modifications and modes of operation for a NGCC retrofit is also presented.

6.2. Methodology

Process simulation results for the baseline NGCC plant were adopted from the cases discussed in the U.S. Department of Energy’s (DOE) report titled “Carbon Capture Approaches for Natural Gas Combined Cycle Systems” (U.S. DOE, 2011). Using the same design basis, process models were developed using Aspen PLUS Version 2004.1 to assess the performance of the CCR Process.
6.2.1. Baseline NGCC plant

The baseline NGCC plant has been adopted from Case Ref1 from the aforementioned DOE Report. This case models a 555 MWe (net) NGCC power plant without CO₂ capture. Figure 6.1 is a block flow diagram of the baseline plant. The plant consists of two Advanced F-class combustion turbine generators, two heat recovery steam generators (HRSGs) and one steam turbine generator in a multi-shaft 2x2x1 configuration. A single reheat steam cycle of 16.5 MPa/566 °C/566 °C is employed in the plant. 75,901 kg/h of natural gas is combusted in the gas turbine which provides a gross power output of 362 MWe. The hot flue gas from the outlet of the gas turbine is used to raise steam in the HRSG and this steam is used in the steam turbine to obtain an additional gross power of 203 MWe. The auxiliary load (pumps, fans, etc.) consumes about 10 MWe, giving a net plant output of 555 MWe. The total thermal input to the plant is 1106 MWth (HHV) resulting in a net plant efficiency of 50.2%. Table 6.1 provides the characteristics of the natural gas, and Table 6.2 provides the composition of the flue gas emitted from the stack. The flue gas temperature drops successively as it passes from the gas turbine to the steam turbine and finally to the stack; its composition however, remains the same.

6.2.2. Process design

Two configurations were investigated for using the CCR process as a retrofit to the NGCC plant. The difference in the two configurations lies in the location of flue gas extraction point from the NGCC plant for the CCR process. In Configuration 1, the flue gas is taken from the exit of the gas turbine and in Configuration 2, it is taken from the exit of the steam turbine (see Figures 6.2 and 6.3).
Figure 6.4 presents the process flow diagram for Configuration 1 of the NGCC plant with post-combustion CO$_2$ capture using the CCR process, henceforth referred to as “NGCC+CCR plant”. In this configuration, the flue gas from the gas turbine is fed to the carbonator (CARB), which operates at 590 °C and 1 atm. Flue gas at the exit of the gas turbine is available at 629 °C and 1 atm (the flue gas composition is provided in Table 6.2). A flue gas cooler – GTCOOLER – is used to cool the gas to 567 °C prior to entering CARB. The heat recovered from GTCOOLER is used to raise steam. The flue gas contacts the Ca(OH)$_2$ in CARB and >90% CO$_2$ capture is achieved. A Ca:C of 1.3 is assumed to be sufficient for the required CO$_2$ removal (Wang et al., 2010). The RGibbs model in Aspen is used to model CARB. No exothermic heat is recovered from CARB.

The gas-solid mixture exiting CARB enters a particle capture device (cyclone) PCD-1 which also operates at 590 °C. PCD-1 is assumed to operate with 100% efficiency. The CO$_2$-lean flue gas is separated from the solids in PCD-1 and is then heated to 629 °C via heat-exchange with the CO$_2$-rich gas from the calciner. The CO$_2$-lean flue gas is then returned to the HRSG for steam generation for use in the steam turbine cycle.

The solids produced in CARB include CaO and CaCO$_3$. This is because of the greater than stoichiometric Ca:C and the operating conditions in CARB which favor the dehydration of Ca(OH)$_2$. This solid mixture is sent to the calciner for regeneration. A purge stream of 1% (by mass) is maintained ahead of the calciner. An equivalent (molar) amount of fresh limestone is added to compensate for the solids that are purged. The purge and the makeup streams are heat-exchanged using a cyclic dual gas-solid heat
exchanger. In the first heat exchanger, HEATX-1, the purge stream heats the air from 25 °C to 585 °C, while the purge cools from 590 °C to 50 °C. In the second heat exchanger, HEATX-2, the heated air cools to 25 °C and preheats the fresh feed. The preheated fresh feed is then mixed with the recycled stream prior to injection in the calciner. This heat exchange reduces the thermal energy required in the calciner. The cooled purge stream is the waste generated from the CCR process and is disposed appropriately.

The calciner – CALC – is designed to operate at 1000 °C and 1 atm, and is modeled as RGibbs. Natural gas is combusted using 95% (by vol.) O_2 to achieve the high operating temperature. The amount of O_2 sent to the calciner is 10% excess than the stoichiometric requirement. Combustion in high-purity O_2 is necessary to produce combustion products consisting mainly of CO_2 and H_2O. It should be noted that the natural gas used in CALC is in addition to the natural gas that is fed to the gas turbine. The additional natural gas is assumed to be available at 38 °C and 31 bar, same as that entering the gas turbine (U.S. DOE, 2011). The O_2 is supplied by a cryogenic air separation unit (ASU) and is available at 13 °C and 2 bar (U.S. DOE, 2008). It is preheated using HEATX-4. In CALC, CaCO_3 decomposes to form CaO and CO_2. The gas exiting the calciner contains CO_2 from two sources – sorbent regeneration and natural gas combustion.

The solids from the calciner exit are recovered using PCD-2 and delivered to the hydrator - HYD. PCD-2 is assumed to operate at 100% efficiency. HYD is designed to operate at 500 °C and 1 atm, and is modeled as RGibbs. The steam supplied to HYD is low pressure (LP) steam (281 °C, 5 bar) extracted from the steam turbine cycle of the plant. The
amount of steam supplied to the hydrator is in excess, 30% greater than the stoichiometric requirement. The heat from the exothermic hydration reaction is utilized in the steam turbine cycle. Ca(OH)$_2$ is produced in the hydrator which is fed to the carbonator, along with the excess steam.

HEATX-4 is a condensing heat exchanger for cooling the gas from the calciner to 60 °C, resulting in a CO$_2$ concentration of >95% (by vol.). The CO$_2$-rich stream is then sent for further drying and compression to 15 MPa.

The second configuration of the NGCC+CCR plant is shown in Figure 6.5. The major difference between the two configurations is the location of the flue gas draw-off point from the NGCC plant and the resulting heat integration. Here, the flue gas is obtained from the exit of the HRSG and is at a significantly lower temperature (106 °C) than in Configuration 1. Hence it is preheated in two stages to the required temperature before entering CARB. The CO$_2$-lean flue gas from CARB and CO$_2$-rich gas from CALC are used to preheat the gas in the first and second stage, respectively. CGCOOLER is used to further recover heat from the CO$_2$-lean flue gas before venting it out of the facility.

6.2.3. Electricity generation from the NGCC+CCR plant

In both the configurations, it is assumed that the location of the flue gas draw-off point does not affect the performance/output of the NGCC plant. Therefore, the same gross power is obtained from the gas turbine as in the original NGCC plant without CO$_2$ capture. A deduction in gross power produced from the steam turbine is however
necessary, to account for the LP steam extracted for the hydrator. For this calculation, the electric power equivalence of LP steam is taken to be 0.0911 kWh/lb (U.S. DOE, 2011a). For all the heat entering the steam turbine cycle from the CCR Process, a 90% thermal efficiency and 37.9% steam turbine efficiency is assumed. A 5% energy penalty is imposed on the total gross electric generation to account for in-house electric consumption. Finally, a 200 kWh/(tonne O₂) and 119 kWh/(tonne CO₂) electricity consumption is deducted from the net electricity output to account for the ASU and CO₂ compression, respectively (Darde et al., 2009; Wong, 2005). The calculations are shown in Table 6.3.

6.3. Results and Discussion

6.3.1. Performance of the NGCC+CCR plant

Calcium looping processes in general and the CCR Process in particular, offer a unique advantage over other CO₂ capture processes – additional electricity generation by integration of high-quality heat available from different sources. From the calculations in Table 6.3, it can be noted that the NGCC+CCR plant has the potential to match the net electric output of the baseline NGCC plant. This is unlike any other post-combustion CO₂ capture process which typically results in a significantly lower net electric output. This additional electricity is mainly due to the additional natural gas used in the calciner, and needs to be considered in the evaluation of the overall process efficiency. It was found that the NGCC+CCR plant has an efficiency of 38% (HHV) for either configuration. While this is 3-4 percentage points lower than a NGCC plant with MEA scrubbing (“NGCC+MEA”), the net output of the NGCC+CCR plant exceeds that of the
NGCC+MEA plant by 90 MWe (U.S. DOE, 2011). The comparison is shown in Figure 6.6.

Since the concentration of CO$_2$ in NGCC flue gas is low as compared to a PC power plant (10-15%), there is poor driving force for CO$_2$ absorption using MEA. On the other hand, the CCR process can achieve the same performance for any CO$_2$ concentration in the flue gas and does not require an increase in calcium loading. However, the operating temperature of the carbonator needs to be lowered to 590 °C, to thermodynamically enable 90% or greater CO$_2$ removal. The CCR carbonator for a PC plant is expected to operate at 650-700 °C.

Another advantage of the CCR Process is its tolerance toward other flue gas components like O$_2$. The O$_2$ concentration in NGCC flue gas is expected to be approximately 12%, which is higher than PC flue gas (2-4%). High O$_2$ concentration can prove to be a challenge to some solvents, but has no affect on the calcium-CO$_2$ reaction. Though it is unlikely that NGCC flue gas will contain sulfur, any trace amounts of H$_2$S or SO$_2$ will not be an issue either since calcium sorbents have been traditionally known to be very effective sulfur absorbents (Borgwardt and Roache, 1984; Srivastava, 2000).

Since the NGCC+CCR plant uses additional natural gas, the amount of CO$_2$ generated and captured is more than that in a NGCC+MEA plant. The oxy-fuel calciner increases the total natural gas use in the plant by a third and the total CO$_2$ captured by approximately 41%. The ASU also represents additional necessary investment for the
CCR process. The O₂ requirement of the NGCC+CCR plant is, however, significantly lower than that for an oxy-combustion NGCC plant (U.S. DOE, 2011).

Like in a NGCC+MEA plant, there will be an increase in water consumption in the NGCC+CCR plant. The MEA plant requires about 350 tons/h steam for solvent regeneration. The CCR plant requires about 150 tons/h steam for the hydrator, if the 30% excess steam is assumed to be sufficient for satisfactory hydration, as in this work. The hydrator is a unique feature of the CCR process and is critical to its success because it restores sorbent reactivity every cycle and provides high quality heat which helps to offset the penalty on the net electric output. Though hydration is expected to restore sorbent reactivity every cycle, a purge stream is maintained to account for some sorbent deactivation. The 1% purge rate used in this work is lower than that reported for PC plants retrofitted with the CCR process (Wang et al., 2012). This purge rate is still believed to be a conservative estimate since inert materials like flyash and deactivating agents like sulfur compounds are absent in the NGCC flue gas.

A 100% efficiency of PCDs, though unrealistic, is assumed for the sake of simplicity. In an actual CCR plant, a high-temperature filter may be necessary downstream of the PCDs for further particulate removal. However, these filters are not expected to majorly affect the performance of the NGCC+CCR plant as presented here; but their impact on the economics of the process will be important to consider.
6.3.2. Other considerations

For existing NGCC plants, certain modifications to the steam turbine section will be necessary so that steam can be extracted for the CCR hydrator. Lucquiaud et al. have presented different options for a NGCC+MEA plant, which requires steam for solvent regeneration and similar options are available for a NGCC+CCR plant as well – throttled LP turbine, replacement of existing LP turbine with a new low-capacity LP turbine designed to accept reduced steam flow, resetting of IP/LP crossover pressure to compensate for the drop due to steam extraction, etc. (Lucquiaud et al., 2009).

6.4. Concluding Remarks

Though the analysis conducted here has made some simplifying assumptions, the results provide important insights into the option of using calcium looping for post-combustion CO₂ control from NGCC plants. Using the CCR process, the overall plant efficiency is lower as compared to a NGCC+MEA plant. Similar conclusions have been drawn from a recently published study where the traditional two-step calcium looping process was used for analysis (Berstad et al., 2012). However, the NGCC+CCR plant does have the capability to match or exceed the net electric output of the original base plant – an advantage which no other retrofit CO₂ control technology can offer. Hence, in the future, an economic analysis must be performed to determine capital and operating costs for the NGCC+CCR plant. If the economics look attractive, the lower efficiency (as compared to MEA) may not prove to be a major obstacle.
Figure 6.1. Baseline NGCC power plant adopted from the DOE study (U.S. DOE, 2011).
Figure 6.2. NGCC plant with post-combustion CO₂ capture using CCR process – Configuration 1.
Carbonator Calciner
\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \\
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

Hydrator
\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2
\]

\[
\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}
\]

500 °C
1000 °C
590 °C

**Figure 6.3.** NGCC plant with post-combustion CO$_2$ capture using CCR process – Configuration 2.
Figure 6.4. Process flow diagram of NGCC+CCR plant – Configuration 1.
Figure 6.5. Process flow diagram of NGCC+CCR plant – Configuration 2.
Figure 6.6. Comparison between different cases based on (a) net electric output (MWe) and (b) net efficiency (%).

<table>
<thead>
<tr>
<th>Component</th>
<th>Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>93.1</td>
</tr>
<tr>
<td>Ethane</td>
<td>3.2</td>
</tr>
<tr>
<td>Propane</td>
<td>0.7</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.4</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Table 6.2. Composition of the flue gas emitted from the baseline NGCC power plant (U.S. DOE, 2011).

<table>
<thead>
<tr>
<th>Component</th>
<th>Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.89</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.04</td>
</tr>
<tr>
<td>H₂O</td>
<td>8.67</td>
</tr>
<tr>
<td>N₂</td>
<td>74.32</td>
</tr>
<tr>
<td>O₂</td>
<td>12.09</td>
</tr>
</tbody>
</table>
Table 6.3. Calculation of the electricity generated from the NGCC+CCR plant.

<table>
<thead>
<tr>
<th></th>
<th>Configuration 1</th>
<th>Configuration 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross output of the gas turbine</td>
<td>MWe</td>
<td>362.2</td>
</tr>
<tr>
<td>Gross output of the steam turbine</td>
<td>MWe</td>
<td>202.5</td>
</tr>
<tr>
<td>Deduction due to LP steam extraction</td>
<td>MWe</td>
<td>27.8</td>
</tr>
<tr>
<td>Thermal energy available from the CCR Process</td>
<td>MWth</td>
<td>319</td>
</tr>
<tr>
<td>Gross electricity produced due to CCR Process</td>
<td>MWe</td>
<td>108.8</td>
</tr>
<tr>
<td>Gross electricity produced from NGCC+CCR plant</td>
<td>MWe</td>
<td>645.7</td>
</tr>
<tr>
<td>In-house consumption</td>
<td>MWe</td>
<td>32.3</td>
</tr>
<tr>
<td>Net electricity produced from NGCC+CCR plant</td>
<td>MWe</td>
<td>613.4</td>
</tr>
<tr>
<td>CO₂ compression penalty</td>
<td>MWe</td>
<td>30.5</td>
</tr>
<tr>
<td>ASU penalty</td>
<td>MWe</td>
<td>19.8</td>
</tr>
<tr>
<td>Net electricity to grid from NGCC+CCR plant</td>
<td>MWe</td>
<td>562.9</td>
</tr>
</tbody>
</table>
CHAPTER 7

DIRECT CARBONATION OF CALCIUM HYDROXIDE

Ca(OH)$_2$ can react with CO$_2$ after losing the water and forming CaO (indirect carbonation) or ‘directly’ at temperatures lower than its dehydration temperature. The non-isothermal direct carbonation of Ca(OH)$_2$ was investigated and the effects of CO$_2$ concentration and heating rate were studied, for applications in calcium looping. Though the net chemical reaction is the same in both the modes of carbonation, different results with respect to sorbent conversion and multicyclic sorbent behavior were obtained. These findings and their implications on OSU’s three-step calcium looping process are discussed in this chapter.

7.1. Introduction

As discussed in Chapter 4, hydration offers a promising route to improve the multicyclic performance of calcium sorbents. With that background, the work discussed in this chapter explores the carbonation of Ca(OH)$_2$ via two pathways – indirect and direct carbonation. In indirect carbonation, the Ca(OH)$_2$ first dehydrates to yield CaO, which then reacts with CO$_2$ to form CaCO$_3$. Indirect carbonation is represented by reactions 1 and 2. In direct carbonation, the Ca(OH)$_2$ directly reacts with CO$_2$ in a single step, as shown by reaction 3.
\[
\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \quad (1)
\]
\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad (2)
\]
\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (3)
\]

The direct carbonation of Ca(OH)$_2$ has been investigated previously at lower temperatures (<100 °C) to study reaction mechanism and kinetics (Beruto et al., 2000; Shih et al., 1999). There has been a renewed interest in this area after recent findings reported by Materic and Smedley, and Blamey et al. (Blamey et al., 2011a; Materic and Smedley, 2011). These studies have been conducted at higher temperatures (>400 °C) and have suggested a novel mechanism – superheated dehydration – for improved sorbent carrying capacity.

The current work presents a study of direct carbonation of Ca(OH)$_2$ and explores two phenomena that have not been reported previously – enhanced product layer diffusion and mitigation of sintering. In particular, Ca(OH)$_2$ has been exposed to CO$_2$ isothermally and non-isothermally in a thermogravimetric analyzer (TGA). The effect of parameters like heating rate and CO$_2$ concentration on the reaction conversion has been studied. Sorbent characterization using BET analyses and calculations using the shrinking core model (SCM) have been used to support the experimental findings. Finally, the implications of the results for the three-step calcium looping process are discussed.
7.2. Experimental Section

7.2.1. Sorbent and gases

The sorbent used in all the experiments was 98% reagent grade Ca(OH)$_2$, procured from Acros Organics, NJ, USA. Gases – N$_2$ (99%) and CO$_2$ (99.9%) – for TGA testing and liquid N$_2$ required for BET analyses were supplied by Praxair, Inc.

7.2.2. Experimental setup

*TGA testing*

The reaction between Ca(OH)$_2$ and CO$_2$ was investigated in a Perkin Elmer Pyris1 TGA. A detailed description of this equipment is available elsewhere (Iyer et al., 2004). N$_2$ was used for calcination and a mixture of N$_2$ and CO$_2$ was used for carbonation. For each TGA run, ~18 mg of Ca(OH)$_2$ was loaded in the sample container. The outlet of the TGA was connected to a MAC125 moisture analyzer (MAC Instruments, OH, USA) to monitor the moisture content in the exhaust gas. This analyzer was calibrated (by the vendor) for measuring the moisture content in the range of 0-10% (v/v).

*Evolution of surface area and pore volume*

The evolution of surface area and pore volume during reactions 1 and 3 was studied using BET. Since the BET required significantly more amount (0.2 – 0.5 g) of sample for testing, these samples were generated using the fixed-bed reactor. A diagram (Figure 4.1) and a description (Section 4.2.2) of the reactor setup are provided in Chapter 4.
7.3. Results and Discussion

7.3.1. Comparison of direct and indirect carbonation of Ca(OH)$_2$

In the first set of experiments, the direct and indirect carbonation of Ca(OH)$_2$ were compared with respect to kinetics and conversion. For direct carbonation, the Ca(OH)$_2$ was heated in 10% CO$_2$ (balance N$_2$) from room temperature to 700 °C in the TGA. For indirect carbonation, Ca(OH)$_2$ was first calcined to form CaO by heating in pure N$_2$ to a temperature of 700 °C followed by isothermal carbonation in 10% CO$_2$. Throughout this work, all calcinations and carbonations have been performed at 700 °C, unless otherwise mentioned and the carbonation conversions have been noted at 60 min. All the heating and cooling steps have been performed at the rate of 25 °C/min, unless otherwise mentioned.

The TGA runs are shown in Figures 7.1 and 7.2. In direct carbonation (Figure 7.1), the weight of the sample starts increasing while the temperature is ramped to 700 °C. Figure 7.2 depicts the TGA run for indirect carbonation. As the sample is heated to 700 °C in pure N$_2$, a weight loss is observed at around 350 °C due to the dehydration of Ca(OH)$_2$. The second weight loss, which begins at about 520 °C, is due to the decomposition of CaCO$_3$ present in the sample. The presence of CaCO$_3$ in the sample can be attributed to the slow atmospheric carbonation of Ca(OH)$_2$ during storage (air contains approximately 390 ppm CO$_2$). Though the Ca(OH)$_2$ used in this work was carefully stored in sealed containers, some carbonation inevitably occurred. When the sample was fully calcined and the weight stabilized, the carbonation step was begun at t = 70 min, which is indicated by the weight gain in the sample.
For comparison, the carbonation conversions in the TGA runs depicted in Figures 7.1 and 7.2 are shown in Figure 7.3. Three important observations can be made from Figure 7.3. One, the rate of indirect carbonation is higher as compared to the rate of direct carbonation in the initial period. Two, the final conversions are 100% and 73% for direct and indirect carbonation, respectively. And three, direct carbonation does not exhibit the two regimes which are characteristic of the CaO-CO₂ reaction (Bhatia and Perlmutter, 1983) – kinetically-controlled (fast) regime followed by diffusion-limited (slow) regime – as seen in indirect carbonation. The first observation can be easily explained by the fact that direct carbonation occurred while the sample was being heated to 700 °C while indirect carbonation occurred isothermally at 700 °C. Hence the kinetics, a function of temperature, will be superior for indirect carbonation. For explaining the other observations, a hypothesis is proposed – it is believed that during direct carbonation, the H₂O which is being continuously evolved (as per reaction 3) maintains sufficient porosity in the CaCO₃ product layer. This outward diffusion of H₂O creates channels in the product layer which allow the inward diffusion of CO₂ through the product layer to the unreacted core. The enhanced product layer diffusion leads to complete calcium utilization via reaction 3 resulting in higher conversion. However, the CO₂ diffusing through the product layer during indirect carbonation encounters a resistance due to the less porous product layer. As a result, this carbonation enters a diffusion-controlled regime which is characterized by the slow rise in conversion (t = 10 to 60 min). Since the conversion achieved at the end of 60 min is only 73%, it can be concluded that the sample contains unreacted CaO.
Similar conversions have also been reported by Materic and Smedley (Materic and Smedley, 2011). They suggest a presence of water adsorbed on the surfaces of Ca(OH)$_2$ which has a catalytic effect on the conversion of Ca(OH)$_2$ to CaCO$_3$, when subjected to direct carbonation. From the results obtained in this work, it is believed that this mechanism is likely to be valid for low temperature-direct carbonation. At higher temperatures (>100 °C), the enhanced product layer diffusion mechanism will be applicable.

Figure 7.4 shows the data obtained using the moisture analyzer for the runs depicted in Figures 7.1 and 7.2. The evolution of the moisture begins earlier (at a lower temperature) in direct carbonation. This can be attributed to the presence of CO$_2$ in the gas stream, which helps to drive out the H$_2$O earlier. This seems reasonable considering Ca(OH)$_2$ and CO$_2$ react even at room temperature. In indirect carbonation, the evolution of H$_2$O is represented by the sharper peak, which occurs at a higher temperature (~350 °C). This corresponds to the simple dehydration of Ca(OH)$_2$ in N$_2$ as per reaction 1. The gradual release of H$_2$O during direct carbonation lends credence to the enhanced product layer diffusion hypothesis. The areas under the curves were found to be the same indicating that equal amount of moisture evolved in both the runs. This was expected since the starting amount of Ca(OH)$_2$ was also the same. However, the agreement between the data from the TGA and the moisture analyzer was not satisfactory with respect to the mass balance. This was likely due to the broader-than-required range (0-10 %) of the analyzer. Nonetheless, the data obtained from the moisture analyzer is considered good for qualitative analyses.
7.3.2. Effect of the type of carbonation on succeeding carbonation(s)

The runs shown in Figures 7.1 and 7.2 were extended to include one more calcination-carbonation (CC) cycle at 700 °C. For this particular cycle, the conditions were exactly identical for both cases unlike the first carbonation. The results are shown in Figure 7.5. These are henceforth referred to as ‘second carbonations’.

Figure 7.5 shows a significant difference in the second carbonation conversions – 83% versus 73% - a result that was unexpected because the second CC cycle occurred isothermally at 700 °C in both the cases. This result was confirmed by performing multiple replicate runs. The difference can be explained by the sintering phenomenon. It is hypothesized that the extent of sintering that occurred during/before the first carbonation was significantly different and this was manifested in the next cycle. This is because during the indirect (first) carbonation, the Ca(OH)₂ first decomposed to form CaO followed by reaction with CO₂. When the sorbent existed in the form of CaO, the sorbent pores were exposed to high temperature (in this case, 700 °C) which led to sintering. Ultimately these pores were occupied due to the formation of CaCO₃. This is different from direct (first) carbonation, where as soon as the pores were formed due to the evolution of H₂O (reaction 1) they were filled with the product CaCO₃. As a result, the sorbent pores were not exposed to harsher temperatures, thus protecting them from sintering. On account of this sintering history, the second carbonation conversions differed even though identical conditions were employed for the second CC cycle. This hypothesis is supported by the BET analyses presented in Section 7.3.5.
To investigate how long the effect of the sintering history persists, 10 CC cycles were conducted. In all, each set consisted of 11 carbonations – direct/indirect carbonation followed by 10 carbonations. The conversions obtained in each cycle are shown in Figure 7.6. It can be seen that the carbonation conversions decrease in both cases as expected. However, in each cycle (till cycle 3), the conversion was higher for the case where Ca(OH)$_2$ originally underwent direct carbonation. Cycle 4 onwards, both conversions were almost the same and seemed to be independent of the first-carbonation history. This result suggests that the pores which were protected (from sintering) by direct carbonation of Ca(OH)$_2$, eventually get sintered.

7.3.3. Effect of CO$_2$ concentration on the direct carbonation of Ca(OH)$_2$

CO$_2$ concentration in the reacting gas was varied and its effect was investigated on the direct carbonation of Ca(OH)$_2$. It was found that the CO$_2$ partial pressure has no effect either on the kinetics or on the final conversions achieved. This can be seen from Figure 7.7, where the data points for all the cases – 10%, 15%, 20% and 40% CO$_2$ (balance N$_2$) – overlap.

7.3.4. Effect of heating rate on the direct carbonation of Ca(OH)$_2$

The effect of heating rate was also investigated. Four heating rates – 5 to 25 °C/min – were used while exposing the Ca(OH)$_2$ sample to a constant CO$_2$ concentration of 10%. The results of this investigation are presented in Figure 7.8. It was found that unlike CO$_2$ concentration, heating rate strongly affected the rate of direct carbonation. For a heating rate of 10 °C/min, it required 56 min to achieve full conversion compared to only 20 min
when the heating rate was 25 °C/min. The results can be simply explained by the fact that at higher heating rates, higher temperatures are attained earlier leading to better kinetics and quicker conversion. However, it is interesting to note that when the heating rate of 5 °C/min was used, complete conversion was not achieved even after 120 min. This carbonation (5 °C/min) also exhibited the typical two regimes – kinetically-controlled and diffusion-limited. From this observation, one may surmise that a smaller heating rate slows down carbonation more than it slows than dehydration; since the H₂O escapes faster, there is no H₂O left for outward diffusion to enhance the inward diffusion of CO₂, limiting the final conversion.

7.3.5. Surface area and pore volume evolution

The evolution of the surface area and pore volume when Ca(OH)₂ is heated in pure N₂ and N₂-CO₂ mixture was studied using BET to further support the hypothesis put forward in Section 7.3.2. For generating the samples for BET analyses, 1 g of Ca(OH)₂ was loaded in the fixed-bed reactor and heated to the desired temperature and maintained at that temperature for 30 min. During the heating and isothermal steps, the Ca(OH)₂ was simultaneously exposed to N₂ or 10% CO₂ (balance N₂). The gas flowrate was maintained at 100 ml/min for all the runs and the heating was performed at an average heating rate of 25 °C/min. At the end of the isothermal step, the reactor was quenched in atmospheric air to minimize further changes in the physical properties of the sorbent due to sintering, as would be the case during passive cooling (Mai and Edgar, 1989).

The BET analyses of the samples was performed by Ms. Niranjani Desphande.
For the BET analyses, the measurements were performed using N\textsubscript{2} adsorption and desorption isotherms at -196 °C on a Quantachrome NOVA 4200e series volumetric adsorption analyzer. The samples were degassed at 300 °C for 6 h. After degassing, the samples were weighed again and this weight was used for all the calculations. The BJH method was used for the measurements.

Figure 7.9 shows the wt% Ca(OH)\textsubscript{2} left in the sample. In N\textsubscript{2}, no dehydration is observed at 200 or 300 °C, since Ca(OH)\textsubscript{2} begins to dehydrate only beyond 300 °C (as seen in Figure 7.2). For higher temperatures, the rate of dehydration is greater thus lowering the Ca(OH)\textsubscript{2} content in the sample. In 10% CO\textsubscript{2}, loss of Ca(OH)\textsubscript{2} was observed even at 200 °C, which is due to the direct carbonation of Ca(OH)\textsubscript{2} to form CaCO\textsubscript{3}. At higher temperatures, the rate of carbonation increases leading to complete conversion of Ca(OH)\textsubscript{2} at 600 °C and above. The data points in Figure 7.9 can be considered to closely represent the chemical changes that Ca(OH)\textsubscript{2} undergoes (from 40 to 60 min) during the TGA runs shown in Figures 7.1 and 7.2. Therefore, a BET analyses on these samples will indicate the changes in physical properties of the sorbent that occur in the TGA experiment in the aforementioned time interval.

BET results are shown in Figures 7.10 and 7.11. Figure 7.10 depicts the evolution of surface area with temperature. When the Ca(OH)\textsubscript{2} was dehydrated in the presence of N\textsubscript{2}, the surface area increased from 23 m\textsuperscript{2}/g and reached a peak of 44 m\textsuperscript{2}/g at 500 °C before decreasing to 25 m\textsuperscript{2}/g at 700 °C. This data is in good agreement with that reported by Irabien et al. (Irabien et al., 1990). However, when 10% CO\textsubscript{2} was used, the surface area
was lower than that obtained under pure N₂. A steady decrease from 9 m²/g to 3 m²/g is clearly visible. Similar profiles were obtained for pore volume, which are shown in Figure 7.11.

The BET results support the hypothesis presented Section 7.3.2. During indirect carbonation, the Ca(OH)₂ is heated in N₂ and pores are formed due to the release of H₂O. Up to 500 °C, the sintering is minimum resulting in increasing surface area and pore volume with temperature. However, for higher temperatures, the existing pores start to sinter leading to a decrease in the surface area and pore volume. When 10% CO₂ is used and the Ca(OH)₂ is directly carbonated, the pores formed due to the release of H₂O are immediately filled due to the formation of CaCO₃. This leads to a continuous decrease in the surface area and pore volume as the carbonation progresses. However, the CaCO₃ occupying the pores also protects them from sintering and this leads to higher carbonation conversion in the next (second) cycle, as observed from Figure 7.5.

7.4. Analysis using Shrinking Core Model (SCM)

The non-isothermal direct carbonation of Ca(OH)₂ (Figure 7.1) can be assumed to be to reaction-controlled since a diffusion-limited regime cannot be observed. Assuming spherical solid particles, following relationship is obtained for a gas-solid reaction (Levenspiel, 1999) –

\[
\frac{dX}{dt} = \frac{3}{\tau}(1 - t/\tau)^2 \quad \text{Equation 1}
\]

For isothermal conditions, Equation 1 can be integrated to obtain –

\[
X = 1 - (1 - t/\tau)^3
\]
where $\tau = (\rho_s d_p)/(2bkC)$ \hspace{1cm} \text{Equation 2}

The reaction rate constant $k$ is assumed to follow Arrhenius-type behavior and hence can be written as –

$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

For transient thermal conditions, $k$ and $\tau$ are not constant. Sarofim and coworkers (Snow et al., 1988) have shown that Equation 1 can be integrated considering $\tau = \tau(T)$ and $T = T(t)$ to yield conversion as a function of temperature –

$$X(T) = 1 - \left[1 - (k_o C/\rho_s R)(T/\lambda) \exp\left\{-\frac{E_a}{RT}\right\}/(2 + E_a/RT)\right]^3 \hspace{1cm} \text{Equation 3}$$

Knowing $T$ vs $t$ and using the $X$ vs $t$ data from the TGA (Figure 7.1), the value of $k$ was calculated using Equations 1 and 2. A plot of $\ln(k)$ vs $1/T$ gave the values of the constants $k_o$ and $E_a$.

Equation 3 was then used to calculate $X$ as a function of $T$. The result from the non-isothermal model is compared with the experimental data in Figure 7.12. The agreement between the experimental data and model-predicted values can only be termed as ‘fair’. While the reason for the larger disagreement at lower temperatures (<400 °C) could not be ascertained, one of the causes of the difference at $T>400$ °C could be the exothermicity of reaction 3. For a fast reaction, the rate of heat release can cause temperature gradients within the particle or between the particle and the solid. This heat can cause temperatures to be higher at the reaction interface as compared to the ‘bulk gas’ temperature recorded by the TGA thermocouple. Since higher heating rates have
found to enhance direct carbonation conversion (Section 7.3.4), the experimental conversions exceeded the model-predicted values.

7.5. Concluding Remarks

The results discussed here have some important implications for the calcium looping processes that use intermediate hydration to reactivate the sorbent. E.g. it is recommended that the hydration be carried out at or above 300 °C to reduce the temperature swing between the hydrator and the carbonator (Wang et al., 2012; Zeman, 2008). When the Ca(OH)\(_2\) formed in the hydrator (at 300 °C) is injected into the carbonator (expected to operate at 600 °C or higher), then it is likely to undergo direct carbonation and not the two-step reaction consisting of dehydration followed by carbonation. This will help in attaining higher conversions. In fact, if the temperature difference between the hydrator and carbonator is higher, then it would prove even more advantageous. This is because the Ca(OH)\(_2\) will experience a higher heating rate in the presence of CO\(_2\). However, final operating temperatures of both the hydrator and carbonator will be dictated by economics.

The physical and chemical properties of Ca(OH)\(_2\) limit the investigation of different parameters with respect to direct carbonation. It is well known that Ca(OH)\(_2\) has very small particle size (<10μ) and hence it was difficult to test the effect of particle size in this work. Secondly, Ca(OH)\(_2\) starts dehydrating at ~300 °C and hence the temperature window for testing the direct carbonation of Ca(OH)\(_2\) isothermally at different
temperatures is relatively smaller. Though such tests can be performed up to 300 °C, the results may not be very relevant for a high-temperature CO$_2$ capture process.

The results obtained in this work are similar to the ones reported by Sarofim and coworkers for SO$_2$ capture using limestone (CaCO$_3$) versus precalcined limestone (CaO) (Hajaligol et al., 1988; Snow et al., 1988), where the evolution of CO$_2$ during the direct sulfation of CaCO$_3$ helped in achieving higher conversion in contrast to sulfation of precalcined limestone.

**Nomenclature**

- $b =$ molar ratio of solid reactant to gas reactant
- $C =$ CO$_2$ bulk concentration, mol/cm$^3$
- $d_p =$ particle diameter, cm
- $E_a =$ activation energy, cal/mol
- $k =$ reaction rate constant, cm/sec
- $k_o =$ pre-exponential constant, cm/sec
- $R =$ universal gas constant = 1.987 cal/mol.K
- $t =$ time, sec
- $T =$ temperature, K
- $X =$ conversion

**Greek symbols**

- $\lambda =$ heating rate, K/sec
\( \rho_s = \) molar density of solid, \( \text{mol/cm}^3 \)

\( \tau = \) time required for full conversion, sec
Figure 7.1. Direct carbonation of Ca(OH)$_2$ in the TGA.
Figure 7.2. Indirect carbonation of Ca(OH)$_2$ in the TGA.
Figure 7.3. Carbonation conversion for direct and indirect carbonation of Ca(OH)$_2$ performed in the TGA.
Figure 7.4. Evolution of moisture during direct and indirect carbonation.
Figure 7.5. Carbonation conversion obtained in the second CC cycle conducted after direct/indirect carbonation of Ca(OH)$_2$. 
Figure 7.6. Carbonation conversions obtained in 10 CC cycles conducted after direct/indirect carbonation of Ca(OH)$_2$. 

![Diagram showing conversion vs cycle with data points for direct and indirect carbonation.]
Figure 7.7. Effect of CO$_2$ concentration on the direct carbonation of Ca(OH)$_2$. 
Figure 7.8. Effect of heating rate on the direct carbonation of Ca(OH)$_2$. 

[Graph showing conversion percentage over time for different heating rates (5 C/min, 10 C/min, 15 C/min, 25 C/min).]
Figure 7.9. Ca(OH)$_2$ left in the sample after exposure to N$_2$ and 10% CO$_2$ at different temperatures.
Figure 7.10. Evolution of surface area as a function of temperature for Ca(OH)$_2$ heated in pure N$_2$ and 10% CO$_2$. 

**Surface area (m$^2$/g)**

**Temperature (C)**

- **N$_2$**
- **10% CO$_2$**
Figure 7.11. Evolution of pore volume as a function of temperature for Ca(OH)$_2$ heated in pure N$_2$ and 10% CO$_2$. 
Figure 7.12. Comparison of the experimental data and model predictions for the non-isothermal direct carbonation of Ca(OH)$_2$. Heating rate = 25 °C/min.
CHAPTER 8
KINETICS OF STEAM HYDRATION OF CALCIUM OXIDE

The kinetic investigation of the hydration of CaO using steam was performed to aid the design of a high-temperature steam hydrator specifically suitable for the three-step calcium looping process developed at OSU. An existing instrument was modified to convert it into a steam TGA so that experiments using steam could be performed at conditions relevant to the process. The setting-up of this unique steam TGA proved to be a significant task and is therefore, described in detail in this chapter. The study of steam-solid reaction kinetics presents unique challenges; these are also discussed along with the methods used to overcome them. Finally, data for CaO hydration are presented.

8.1. Introduction and Literature Review
Steam hydration of CaO for enhanced multicyclic CO$_2$ capture has been discussed in detail in Chapter 4. In that study, the goal was to demonstrate that high-temperature steam hydration can be effective in restoring the CO$_2$ capture capacity of the sorbent over several cycles. As a result, CaO was hydrated using excess steam to ensure good extent of reactivation (hydration). However, for the successful integration in the three-step process, it is vital to consider the kinetics of such a reactivation mechanism. Therefore, this topic is the focus of the work discussed here.
The CaO-H$_2$O reaction has been of significant interest for a long time; hence, it is surprising to note the scarcity of relevant kinetic data, especially for steam hydration. The majority of the steam hydration literature (relevant to calcium looping) contains experiments aimed at studying sorbent morphology and CO$_2$ capture capacity post-hydration. Steam conditions, temperature and pressure, CaO-precursors, precursor pretreatment prior to hydration, etc. are some of the parameters/effects that have been investigated in these works (a detailed account of these studies is provided in Chapter 4 and therefore, not presented here). The paucity of data can be attributed to – first, the approach adopted by researchers in the field of calcium looping. Unlike OSU, other researchers have considered intermediate hydration as a sorbent reactivation technique with little or no emphasis on process integration. This has led to the use of unrealistic (but successful) operating conditions, as discussed in Chapter 2. Since hydration is not essentially conceived as an integral part of the calcium looping process, the lack of interest in aspects like reactor (hydrator) design, kinetics, etc. does not seem unreasonable. Second, performing steam-solid experiments for obtaining kinetic data is more challenging than studying other gas-solid reactions. Besides the need for special instruments that can handle steam, the ability to control the properties (flowrate, temperature, etc.) of the reactant gas (steam) greatly affects the accuracy of the results. A more detailed discussion of this aspect is provided in Section 8.2. A thorough review of the existing literature was conducted to establish the experimental design and procedure for this study.
In one of the earliest studies, Glasson reported the sorption of water vapor on CaO where CaO samples differing widely in surface area were hydrated by exposure to water vapor at room temperature (Glasson, 1958). Different surface areas were achieved by varying the calcination conditions. It was found that the rate of hydration was dependent on the CaO surface area (and hence, the calcination conditions) – samples having lower surface area hydrated slowly and did not achieve complete conversion within ‘reasonable time’. More recently, a CaO-hydration study using water vapor was conducted for applications in steelmaking (Maciel-Camacho et al., 1997). In this study, the CaCO$_3$ was pelletized and then calcined, followed by an exposure to air-water vapor mixture at 50 – 100 °C (water vapor partial pressures in the range of 0.014 – 0.035 atm). An increase in the hydration rate with partial pressure was seen. Higher hydration temperatures resulted in greater rates; however, the reverse effect was observed with respect to the calcination temperature. Hydration was confirmed by the cracking and disintegration of the pellets post-experiment. Serris et al. performed a similar study, albeit at higher temperatures (upto 150 °C) and partial pressures (upto 0.158 atm), leading to similar conclusions (Serris et al., 2011).

Researchers from Japan have investigated steam hydration of CaO extensively. Matsuda et al. reported a study for applications like chemical heat pump, etc. (Matsuda et al., 1985). Their experimental design and results are however, difficult to interpret since their publication is in Japanese. Lin and coworkers have looked at high-temperature and high-pressure steam hydration during the HyPr-RING process development. In their first study, they conducted hydration at 500 – 750 °C and 6.7 – 23 atm steam pressure (Lin et
al., 2006). Their results showed a strong correlation between hydration conversion and hydration temperature and pressure, but a very weak one with respect to particle size. In a follow-up study, they investigated the effect of CaO content in the sample using four limestones and concluded that higher CaO content led to slower rate of hydration (Wang et al., 2008). These findings were explained on the basis of sorbent porosity – the limestone with the lowest CaO had the highest porosity which aided the steam-CaO reaction. In their last study published on this topic, they reported kinetic data over many CaO/Ca(OH)$_2$ cycles at similar conditions. It was found that the hydration rate decreased with increasing number of cycles. However, ultimate conversions were unaffected – complete conversion to Ca(OH)$_2$ was observed in each cycle.

In a very recent study published by Schaube et al., kinetics of dehydration and rehydration of Ca(OH)$_2$ has been investigated for thermo-chemical heat storage application (Schaube et al., 2012). Among all available studies (as discussed in this section so far), this study has employed conditions (250 – 450 °C, 0.2 – 0.95 steam partial pressure) that are very relevant for the intermediate hydration in calcium looping. However, since a full factorial experimental design has not been used in this study, data at some important conditions are missing or must be predicted using the models suggested by the authors.

In this work, steam hydration has been investigated at 300 – 400 °C and atmospheric pressure, and steam partial pressures of 0.4 – 0.8 atm. From several process simulation
studies performed at OSU, it is expected that the operating conditions of the calcium looping hydrator are likely to lie in this range.

8.2. Design and Operation of the Steam TGA

In this section, the design and special features of the steam TGA are discussed in detail. Operational issues are also highlighted.

8.2.1. Limitation of conventional TGAs

Most TGAs cannot handle steam due to the potential of water condensation on the electronic components inside the instrument, which can permanently damage the instrument. Since these instruments have several inaccessible parts, the condensed water cannot be removed by simple drying. Some TGAs can handle moist gas – gas saturated with water vapor – to simulate steam-like conditions. However, such experiments do not mimic actual steam-solid (gas-solid) reaction conditions. Moreover, since the vapor carrying capacity of the gas is a function of the temperature, there are additional limitations on the conditions at which experiments can be performed.

8.2.2. Magnetic suspension balance

A magnetic suspension balance (MSB) allows sample weights to be monitored such that there is no ‘actual contact’ between the sample/sample holder and the balance (the balance is that part of the instrument which records and transmits weight of the sample). Unlike traditional balances (TGAs) that rely on samples ‘hanging’ directly from the balance, MSBs employ magnets – electromagnet and permanent magnet – to create a
contactless ‘link’ between the sample and the balance. The sample holder is physically connected to a permanent magnet (suspension magnet) and the balance contains an electromagnet (attached at the weighing hook). The interaction between the electromagnet and suspension magnet is referred to as ‘magnetic suspension coupling’. The magnetic suspension coupling makes it possible to have a contactless transmission of weight from the experimental chamber (location of the sample holder) to the balance located outside the chamber (under ambient conditions). The advantage of such a setup is that it overcomes limitations of conventional TGAs – harsh conditions (high temperatures and pressures) and toxic/corrosive gases can be used for experiments without any concern for damage to the instrument. The measuring method (using magnetic suspension coupling) has been found to be extremely accurate further enhancing the utility of such an instrument.

One such MSB was procured from Rubotherm GmbH (Germany) for investigating gas-solid reactions for chemical looping applications.

8.2.3. Rubotherm MSB at OSU

Figure 8.1 shows the Rubotherm MSB and the peripheral setup. The MSB setup was modified so that high-temperature experiments using steam could be performed.

Functional description of the MSB

As discussed in Section 8.2.2, the MSB consists of an electromagnet and a permanent magnet. The permanent magnet together with a sensor core and measuring load decoupling cage forms the suspension magnet. Figure 8.2 shows the schematic of the
MSB internals. The electromagnet is located at the bottom of the balance and interacts (lifts) the suspension magnet depending on the position specified by the user. Two positions are possible – zero-point and measuring-point. At zero-point, the suspension magnet suspends alone (i.e. not coupled with the permanent magnet) and thus represents an unburdened balance. At measuring-point, the suspension magnet couples the sample to the balance and thus transmits the weight of the sample to the balance. These positions are illustrated in Figure 8.2.

**Design of the MSB**

The design of the Rubotherm MSB is shown Figures 8.3 (front view) and 8.4 (sectional view). As can be seen from Figure 8.3, the top enclosure houses the balance and the suspension coupling. The suspension coupling is provided with a thermostat. The thermostat helps to maintain a constant temperature which is lower than the sample temperature (measuring cell temperature). This thermostat, made of copper and color-painted in black, is a simple jacket which uses a heat transfer fluid for temperature control. A flanged connection is provided below the thermostat using which the measuring cell is attached to the balance. The top and the bottom flanges are constructed using steel grades 1.4439 and 1.4571, respectively. The flanged connection also allows the user to access different parts in the vicinity for regular maintenance. Two gas connectors are provided near the flanged connection, which can act as gas inlets or outlets depending on the preference of the user.
The measuring cell, made of inconel, is the actual experimental zone of the MSB where the gas-solid reaction occurs. It is 2.5’ long and 1” in I.D. A tube fitting (union) is provided between the flanged connection and measuring cell (during regular usage, this fitting is frequently used to remove the measuring cell and access the sample holder; the flanged connection is used only for cleaning and maintenance purposes). A separate thermostat has also been provided for the measuring cell. It can be seen that it is quite small and does not cover the length of the measuring cell. This thermostat can serve as the sole heating mechanism if the sample is located in that region. However, the use of thermostat limits the operating temperatures, depending on the type of heat transfer fluid being used. For 80 °C or lower, water can be used and for higher temperatures, oils (silicone oil, mineral oil, etc.) can be used. Since most experiments for chemical looping applications employ significantly higher temperatures (500 – 1000 °C), the MSB was modified to provide a longer measuring cell surrounded by external electric heaters as shown in Figure 8.1. The wire holding the sample holder is made of Inconel (Tmax = 800 °C) and is 420 mm long (for higher temperatures – upto 1100 °C – a platinum wire is used). The length of the wire is such that the location of the sample is at the center of the measuring cell. A tee-connection is provided at the bottom – one end of the tee acts as gas inlet/outlet and the other allows a thermocouple to be inserted in the measuring cell to record sample temperature. The thermocouple is placed such that its measuring tip comes as close to the sample holder as possible. The sample holder is a cylindrical container (diameter – 0.9 cm, length – 2 cm) made of stainless steel (SS 316).
As per the vendor specifications, the suspension coupling can withstand a maximum of 250 °C and 150 bar. The measuring cell can withstand 150 bar for <750 °C and upto 50 bar for temperatures between 750 to 1000 °C.

**Modification of the setup to test steam-solid reactions**

For conducting experiments using steam, modifications were made to the original gas mixing panel that was provided with the MSB. No modifications were made to the MSB itself. The modifications included the provision of a steam generating section between the existing N₂ MFC and the MSB. The steam generating section consisted of a heated tube containing quartz packing. Water was pumped into the heated tube using a high-precision water pump. The steam was carried over to the MSB using an inert carrier gas (N₂). For all the experiments the top gas connector was used as the inlet and the product gas containing unreacted steam/condensed water exited from the bottom. The arrangement is shown in Figure 8.5.

**8.2.4. Steam TGA – operational issues**

The TGA/MSB does not have a minimum or maximum operational gas flowrate specified by the vendor. The maximum gas flowrate that can be used is dictated by the capacity of the MFC. Since the steam supplied to the TGA is created using water from a pump, the maximum allowable water flowrate from the pump (~20 ml/min) determines the maximum steam flowrate that can be used. It was found that a very broad range of gas flowrates could be used and hence the first exercise was to determine the optimum gas flowrate for conducting the experiments.
Two challenges exist when varying flowrates –

1. The amount of water that can be pumped to create steam is limited by the capacity of the heated section. Use of excess water will result in only partial conversion to steam (or wet steam) and such a steam will not represent true gaseous reactant nature in chemical looping reactions.

2. When experimenting with different steam partial pressures, the nature of the gas is different depending on the steam content (even though total flowrate is the same). For example, when using N\textsubscript{2} as the diluent, a gas containing 20% steam will flow better through the TGA since 80% of it is N\textsubscript{2}; whereas a gas containing 80% steam and 20% N\textsubscript{2} can be expected to reach the sample slowly due to the low self-driving (motive) force of steam; this phenomenon is also referred to as the ‘induction effect’ and has been reported by other researchers (Schaube et al., 2012). Besides diluting the steam, the N\textsubscript{2} served an important purpose of carrying the steam to the reaction chamber; it was therefore, difficult to perform any experiment with 100% steam since steam lacked the motive force to reach the reaction chamber by itself.

Due to the above challenges, it was important to identify an optimum gas flowrate where secondary effects (e.g. mass transfer limitations, etc.) do not influence the experimental results. To achieve this goal, a full factorial screening was performed using different flowrates and steam partial pressures. The description and results are provided in Section 8.4.1.
8.3. Experimental Section

8.3.1. Solids and gases

Commercially-available high-calcium limestone was used in this study. This limestone was procured from Graymont (Pleasant Gap quarry in Pennsylvania). The characteristics and composition of this stone have been provided earlier in Chapter 4 (Table 4.1). The D50 particle size of the limestone as-received was approximately 20 µ. High-purity N₂ (>99.99%) supplied by Praxair, Inc. was used for the experiments. Deionized water was used to generate steam for hydrating CaO. Dow Corning 550 oil was used in the MSB thermostats.

8.3.2. Experimental setup

The detailed description of the TGA is provided in Section 8.2.

8.3.3. Procedure

Experimental run

Each experiment consisted of two steps – limestone calcination to produce CaO and steam hydration of CaO. Approximately 0.23 g of the limestone sample was loaded in the sample holder. The sample was then heated to the desired calcination temperature (700 °C or higher) and maintained isothermally for 2 h. Only N₂ was used for calcination. Following calcination, the temperature was lowered to the desired hydration temperature (300 – 500 °C) while keeping the N₂ flowing. Once the hydration temperature was reached, the sample was held isothermally and exposed to steam-N₂ mixture. On
complete hydration (indicated by the mass balance), the steam was discontinued and the TGA was cooled to room temperature. N\textsubscript{2} was kept flowing during the TGA cooling.

**Estimation of flowrates**

A 100 °C reference point was chosen and all flowrates were estimated with respect to this point. Using the value of the desired flowrate (at 100 °C), the amount of N\textsubscript{2} and water to be supplied were back-calculated. For example, if 200 ml/min total flowrate and steam partial pressure of 0.5 atm were desired at 100 °C, then the N\textsubscript{2} flowrate (from the MFC) was set at 80 ml/min and the water flowrate to the water pump was set at 0.05988 ml/min. Ideal gas law was used for N\textsubscript{2} to account for the thermal-volume expansion and the specific volume of steam was taken to be 1.670 m\textsuperscript{3}/kg (from steam table). It is obvious that the actual gas flowrate experienced by the solid sample will be greater and temperature-dependent. Therefore, a full factorial screening of flowrates was performed to ensure that the flowrate selected for all the experiments was such mass transfer limitations were minimum in the temperature range of interest.

Published literature on kinetics of steam hydration of CaO seldom contains the details of flowrate estimation, like the one stated above. The estimation can be done in several ways and while all may be technically correct, it is important to know the exact calculation procedure to compare data.
8.4. Results and Discussion

8.4.1. Screening of operating flowrates

The aim of these experiments was to identify and minimize mass transfer limitations during operation. In other words, the goal was to determine appropriate gas flowrate for conducting the experiments. As stated earlier, a full factorial experimental design was chosen. The variables were steam partial pressure and total gas flowrate, while the temperature was held constant at 400 °C. Three partial pressures and flowrates were selected, and the rate of CaO hydration was investigated at each combination of the two parameters, in replicate runs.

The results are shown in Figures 8.6 and 8.7; same data are depicted using different bases – partial pressure and flowrate. Based on published literature, it was expected that the rate of CaO hydration will increase with steam partial pressure. This was clearly observed when using relative flowrate = 3 (Figure 8.6a). However, the difference in the rates was marginal at relative flowrate = 1 (Figure 8.6c). At relative flowrate = 2 (Figure 8.6b), there was essentially no difference between the cases where steam partial pressure increased from 0.6 to 0.8 atm. When the same data were plotted using partial pressure as the basis, important observations could be made which helped in finalizing the flowrate for the experiments. At all partial pressures, the rate of hydration increased with relative flowrate (relative flowrate = 2 at steam partial pressure = 0.4 was an anomaly). This highlights the importance of this screening study. For example, if all experiments were performed using relative flowrate = 1, then the data obtained would represent ‘apparent kinetics’ (due to mass transfer diffusion limitations) and not true kinetics. Comparing all
data, it can be seen that the fastest hydration occurred when relative flowrate of 3 was used at steam partial pressure of 0.8 atm. However, to ensure that further increase in flowrate did not result in further increase in the hydration rate, additional flowrate (relative flowrate = 4) was also investigated at this condition and is shown in Figure 8.7c. A satisfactory explanation for the nature of this curve – gradual rise initially and then sudden increase – could not be found; nonetheless, the nature of the curve seemed to be inconsistent with the data reported by other researchers. Also, the very large error bars indicated lack of good reproducibility. Hence, relative flowrate = 3 was chosen for all experiments.

Since most TGAs have an inherent mass transfer diffusion limitation (due to the resistance encountered by the gas during contact with the solid sample in the sample container), an additional experiment using smaller sample size was performed at the chosen flowrate (relative flowrate = 3). The results are shown in Figure 8.8. Again, the nature of the curve could not be explained reasonably. Secondly, the reproducibility of the data seemed poor. Hence the sample size of 0.23 g (corresponding to relative solid sample size = 1) was deemed appropriate for all experiments.

To the author’s knowledge, only one prior study (Maciel-Camacho et al., 1997) has made similar considerations when determining operating parameters. Moreover, prior studies do not clearly disclose the method of steam partial pressure and flowrate estimation, which makes it difficult to draw direct comparisons with data obtained in this work.
8.4.2. Effect of temperature and steam partial pressure

A full factorial set of experiments using single replicate experimental design were performed for $T = 300$, $350$ and $400 \, ^\circ\text{C}$ and steam partial pressures $= 0.4$, $0.6$ and $0.8$ atm. The results are shown in Figures 8.9 and 8.10. Again, same data are represented using different bases so that insightful observations can be made.

From Figure 8.9, it can be seen that the rate of hydration increases with steam partial pressure at all temperatures, as expected. However, the partial pressure effect becomes stronger as temperature increases, i.e. a clear difference when using different partial pressures is visible at $400 \, ^\circ\text{C}$ and the difference seems insignificant at lower temperatures due to overlapping error bars. When the same data is compared using steam partial pressure as the basis, the effect of temperature is found to be stronger at lower partial pressure.

The data obtained here also offers important information which can be used when finalizing operating parameters for the calcium looping hydrator. For example, at $400 \, ^\circ\text{C}$ (Figure 8.9a), when the steam partial pressure is increased from $0.6$ to $0.8$ atm, the time required to achieve complete conversion is reduced by approximately 2 min. This juxtaposes the fixed (capital) costs versus the operating costs with respect to performance improvement. Using lower partial pressure will translate to lower operating cost due to lesser steam requirement. However, a reactor that provides larger solids residence time will be necessary. This is likely to lead to larger reactors and inventories. Another interesting observation can be made from Figure 8.10b which shows that when partial
pressure of 0.6 atm is used, the kinetics of CaO hydration are not greatly affected in the temperature range of 300 – 400 °C. This ‘flexibility’ can prove advantageous to ‘shield’ the reaction from unforeseen variations in the hydrator temperature in the process.

8.4.3. Effect of calcination temperature

The effect of calcination temperature was investigated on the rate of CaO hydration at 350 °C and 0.6 atm steam partial pressure. The said conditions were chosen because the experimental data at the said conditions showed the best reproducibility. Three calcination temperatures – 700, 800 and 900 °C – were investigated and the results are shown in Figure 8.11. It was found that the rate of CaO hydration decreased with increasing calcination temperature. However, significant difference between 800 °C and 900 °C was not observed. Greater calcination temperatures lead to enhanced sintering of the CaO which affected the reactivity of the sample toward steam.

8.4.4. Multicyclic testing

Multiple cycles of calcination-hydration-carbonation were performed to test the effect of repeated cycling on the rate of CaO hydration. The calcination was performed at 700 °C and the carbonation was performed at 650 °C using 10% CO₂ (balance N₂). Again, hydration was conducted at 350 °C and 0.6 atm steam partial pressure. The results from the multicyclic testing are shown in Figure 8.12. No reduction in the rate of CaO hydration was observed with successive cycles. However, the incremental loss in sample due to frequent loading and unloading of the sample container between cycles prevented further testing for more cycles.
8.5. Concluding Remarks

The steam hydration of CaO was investigated at 300 – 400 °C and 0.4 – 0.8 atm steam partial pressure because the calcium looping hydrator is likely to operate at such conditions. It was found that the rate of hydration increased with an increase in steam partial pressure and this effect was more pronounced at higher temperatures. At lower partial pressures, the rate of hydration had an inverse relation with temperature. The hydration rate decreased with increasing calcination temperature. Multicyclic testing over five cycles showed that the kinetics of CaO hydration was not affected by the repeated calcination-hydration-carbonation cycling.
Figure 8.1. Rubotherm MSB at OSU.
Figure 8.2. MSB principle. Reproduced with permission from Rubotherm GmbH.
Figure 8.3. Overview of the assembled measuring cell and coupling housing. Reproduced with permission from Rubotherm GmbH.
Figure 8.4. Sectional view of the assembled measuring cell and coupling housing. Reproduced with permission from Rubotherm GmbH.
Figure 8.5. Steam TGA (MSB) setup.
Figure 8.6. Steam hydration of CaO at 400 °C and (a) relative flowrate = 1, (b) relative flowrate = 2, and (c) relative flowrate = 3 (continued).
Figure 8.6: Continued

![Conversion vs Time Graph](image)

- Steam PP = 0.8 atm
- Steam PP = 0.6 atm
- Steam PP = 0.4 atm

Conversion (%) vs Time (min)
Figure 8.7. Steam hydration of CaO at 400 °C and (a) steam partial pressure = 0.4 atm, (b) steam partial pressure = 0.6 atm, and (c) steam partial pressure = 0.8 atm (continued).
Figure 8.7: Continued

(c)
Figure 8.8. Effect of sample size – steam hydration of CaO at 400 °C, steam partial pressure = 0.8 atm and relative flowrate = 3.
Figure 8.9. Effect of steam partial pressure on CaO hydration at (a) 400 °C, (b) 350 °C, and (c) 300 °C.
Figure 8.9: Continued

![Graph showing conversion vs time for different steam PP values]

- Steam PP = 0.8
- Steam PP = 0.6
- Steam PP = 0.4
Figure 8.10. Effect of temperature on CaO hydration at (a) steam partial pressure = 0.8 atm, (b) steam partial pressure = 0.6 atm, and (c) steam partial pressure = 0.4 atm.
Figure 8.11. Steam hydration of CaO at 350 °C and 0.6 atm steam partial pressure – effect of calcination temperature. Calcination conducted in N₂.
Figure 8.12. Steam hydration of CaO at 350 °C and 0.6 atm steam partial pressure – effect of multicyclic testing. Calcination conducted at 700 °C in N₂ and carbonation at 650 °C in 10% CO₂ (balance N₂).
CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

The calcium looping technology evaluated in this work holds great promise for pre- and post-combustion CO₂ capture. Since several research groups, including OSU, have been working in this area for many years, the technology is well-understood and recent works such as this one have, therefore, focused on process improvements while also evaluating new scenarios.

The highlight of this work is the successful scale-up of the Calcium Looping Process for H₂ production from coal-derived syngas – non-catalytic H₂ production was achieved in a sub-pilot scale fluidized-bed reactor. The steam hydration of CaO at relevant process conditions was also investigated as a part of the multiple carbonation-calcination-hydration cycles. This testing showed that the reactivity of CaO toward CO₂ could be successfully maintained in the three-step process unlike the traditional two-step process. The kinetic data for steam hydration was also obtained which can be used for optimizing future hydrator designs. The investigation of direct carbonation of Ca(OH)₂ helped to uncover the phenomenon of very high sorbent utilization when operating with a substantial temperature gradient between the hydrator and the carbonator. This has important implications when choosing the hydrator operating temperature.
The process was also tested for application in natural gas-based energy systems. Fixed-bed tests using C$_1$-C$_3$ hydrocarbons showed that high-purity H$_2$ production could be achieved in the presence of a reforming catalyst and calcium sorbent. The evaluation of post-combustion CO$_2$ capture from NGCC plants using Aspen process simulations showed encouraging results. However, the advantage offered by calcium looping over MEA was not found to be as important as the one seen in coal-based systems.

Recent research work at OSU has resulted in the development of a novel steam hydrator (Wang et al., 2013). This hydrator is a fluidized-bed reactor with additional internals (mechanical agitation). Experimental results obtained from testing this hydrator showed that a hydration conversion of approximately 70% could be achieved in 30 min when operating at S:Ca of ~2.5. From the kinetic investigation of CaO hydration in the steam TGA, it was found that complete hydration was possible in 10-15 minutes (depending on the temperature and steam partial pressure). Thus, there is scope for further improvement in the hydrator design and this should be the focus of future work. Once an optimized design is achieved, the next step should be the integration of this hydrator in a continuous three-step calcium looping process.

For the CCR process, comprehensive economic analyses will be needed in the future to obtain important metrics like levelized cost of electricity and capital cost estimates for retrofitting the process to a coal-fired or NGCC power plant. Such a cost analyses will also determine the areas on which further work would be necessary to further improve commercial viability.
In the techno-economic study of the CLP conducted by CONSOL Energy, Inc., it was found the CLP has the potential to reduce the cost of producing H₂ from coal when compared with the use of conventional CO₂ capture and WGS technologies (Connell et al., 2013). However, the study also highlighted the possible complication due to sulfur chemistry in the loop which can have important effects on the performance of the process. For example, sulfur enters the calciner in the form of CaS from the carbonator and SO₂ from the oxy-fired coal burner. This sulfur can remain unreacted, or it can react with O₂, CO₂, H₂O or other calcium compounds in the calciner. The products of these interactions (like CaSO₄) can then react with CO and H₂ in the carbonator, thus affecting the final product (H₂) yield. While numerous reactions are possible between sulfur and calcium compounds, the ones which have maximum impact at the operating conditions need to be identified. This work needs to be conducted so that the validity of assumptions in the existing techno-economic study can be confirmed.
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