Steam Reactivation and Separation of Limestone Sorbents for High Temperature Post-combustion CO₂ Capture from Flue Gas

THESIS

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ABSTRACT

Increasing global population and demand for energy has raised concerns of excessive anthropogenic greenhouse gas emissions from consumption of fossil fuels. Coal, in particular, will continue to be the backbone energy source for the electricity generation. Coal-fired power plants are expected to contribute 33% of the domestic and 40% of the global CO₂ emissions (EIA, 2010). In response to this global problem, the Environment Protection Agency (EPA) on March 27 of this year proposed the nation’s first carbon pollution standard that would limit the amount of CO₂ emissions from new power plants.

The Clean Coal Research Group at The Ohio State University has developed an innovative high temperature technology –the Carbonation Calcination Reaction (CCR) process - that utilizes limestone sorbents to simultaneously remove the CO₂ and SO₂ from coal combustion flue gas. A 120 kWth sub-pilot scale CCR system has demonstrated the ability to capture greater than 90% CO₂ and almost 100% SO₂ from coal combustion flue gas. However, application of the CCR process on the industrial scale requires solid circulation rates on the order of thousands of tons per hour, in which case the gas-solid separation efficiency and sorbent recyclability become crucial issues that need to be addressed.

This thesis addresses two critical parts of the CCR process – the particulate capture device and the hydrator. Two cyclones were designed and tested for their separation efficiency of fine Ca(OH)₂ powder. The two cyclones in series design demonstrated
exceptional capture efficiency during our cold model tests. Testing for its capture efficiency as part of the sub-pilot scale CCR system yielded over 99% efficiency for Ca(OH)$_2$ powder with particle size distribution less than 10 µm. The current cyclone design provides a cost-effective way to control the gas-solid separation of the flue gas stream containing micro-size particles. In addition, a bench-scale high temperature hydrator was fabricated to investigate the reactivation of spent calcium sorbent via intermediate steam hydration. The results showed that over 80% hydration conversions were attainable with a mere 10-min residence time. A positive relationship was observed between the hydration rate and steam partial pressure. In addition, the hydration rate seemed to be inversely related to the reaction temperature and particle size. Steam flow rates had a negligible effect on the overall conversion. The hydrated sorbent was superior to CaO because of its improved surface morphology - reduced particle size, higher surface area and increased pore volume. An absolute 45% rise in the carbonation conversion of the hydrated sample was observed. Due to the inherent particle size reduction of Ca(OH)$_2$ formation, significant elutriation of the hydrate product was observed also during our tests. Such behavior may be advantageous to our process as it abates the entrainment of un-hydrated calcium sorbents.

Future investigation of the hydration process may focus on its kinetic behavior with respect to pressure and temperature at isothermal conditions. For scaling up, the installment of a heat-exchanging device is highly recommended. The heat of reaction can be extracted to preheat the combustion air, thus contributing to the overall process heat integration.
Dedication

This document is dedicated to my family - mother, father and sister,
whom I love.
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1.1 BACKGROUND

The conflicting issues of energy security and global climate change present a great dilemma for our generation. Increasing global energy demand, especially in advanced developing countries like China and India, in combination with the political instability of several energy producing countries has created chaos in the world energy market. Furthermore, excess fossil fuel consumption has led to unprecedented atmospheric greenhouse gas (GHG) levels. Despite the debate surrounding the correlation between GHG emissions and global warming, the overwhelming consensus is that global climate change is occurring. Faced with the aforementioned challenges, developing a clean and economic energy conversion process and implementing viable GHG mitigation measures become imperative.

In 2010, world energy consumption increased by over 5%, resulting in a 6% increase in CO₂ emissions – the highest level ever (Enerdata, 2011). According to the World Energy Outlook published by the U.S. Department of Energy (DOE), global fossil fuel-derived
energy demand will continue to increase until 2030 (U.S. EIA, 2011). As shown in Figure 1.1, liquid petroleum, coal and natural gas will remain as the backbone of our energy source, accounting for over 85% the world’s energy supply, for the next a few decades (U.S. EIA, 2007).

Liquid petroleum refers to crude oil-derived high-energy liquid fuels and chemicals, the majority of which is utilized for transportation. Despite rising oil prices and advancement in hybrid automobile technology, crude oil will remain as the leading energy supply for
next thirty years. As a result of our unrelenting dependence on crude oil, its global market price fluctuations retain significant influence on the consumption of other energy forms, especially natural gas and renewable energy. The volatile nature of crude oil price suggests that it is not solely dictated by the market supply and demand, but rather by a congregation of other factors, including inflation, geopolitics and future market speculations. In recent history, political tension in major oil producing countries – Egypt, Syria and Iran – has resulted in drastic hikes in oil prices. In January 2011, the political unrest in Egypt pushed the crude oil price to over $100 per barrel for the first time in two years (Brent, see folder). In addition, the 2008 British Petroleum (BP, 2008) energy review estimates that over 60% of petroleum reserves are located in the Middle East. The share of petroleum-derived energy supply is expected to decrease from 37% to 33% due to volatile oil prices and limited resources (EIA, 2008).

In the U.S., the amount of proven natural gas reserves account for 30% of the world’s total (BP, 2008). Domestically, natural gas is commonly utilized for heating, electricity generation, and hydrogen production. Price of natural gas fluctuates significantly depending on locations and sources. From the emissions perspective, natural gas is the cleanest among fossil fuels. Natural gas combustion produces 45% less carbon dioxide than coal combustion and 30% less than burning petroleum on an equal heat basis (NGO, 2012). Consumption of natural gas will rise in the near future with respect to the imported crude oil price.
The continued growth of renewable energy forms – solar, wind, hydro, geothermal and biomass – will alleviate our dependence on fossil fuels only to a small extent. Despite pro-renewable federal and state legislations, the intermittent nature and lack of economic competitiveness make these innovative energy sources less appealing. Energy experts predict it will be rather unlikely for renewable forms of energy to make any significant contribution to the overall energy demand in the near future (Jacobson, 2000; McVeigh, 2000).

Nuclear power generation remains a controversial subject in this modern age. Compared to fossil fuels, nuclear power emits minimal air pollution at a level comparable to renewable energy and mitigates dependence on foreign energy imports because it is essentially sustainable. Moreover, nuclear power plants can produce base-load power unlike the intermittent production generated from renewable sources. Currently, nuclear power accounts for only 13-14% of world’s electricity and 6% of world’s energy (WNN, 2010). Increasing demand for electricity will cause nuclear power generation to rise steadily during next 30 years. However, the potential nuclear power resurgence seems improbable after the recent disaster at the Fukushima nuclear plant in Japan. The major concern with nuclear power by the public rests on plant safety and radioactive waste disposal and containment. Combining that with the threats of unforeseen natural disasters
and potential terrorist attacks will limit the growth of nuclear power sector in the near future.

The outlook for coal usage in the U.S. remains the most desirable and practical because coal is a domestically available, abundant, and is a low-cost energy source. In the near future, the production cost of domestic coal is not expected to increase significantly (NRC, 1995). However, the environmental consequences of uncontrolled coal usage are well documented. Being the most carbon-intensive energy source, combustion of coal will produce CO$_2$ as well as SO$_2$, NOx, mercury, particulate matter and other hazardous pollutants. Unlike other fossil fuels, coal is primarily utilized as a stationary fuel source for power generation. Implementation of advanced pollution control technology will meet the need to comply with more stringent environmental protection requirements, thus allowing for increased coal usage and its continuance as a major energy contributor by 2030 (EIA, 2007).

1.2 COAL POWERED ELECTRICITY GENERATION

Coal is one of our most abundant domestic energy resources. According to a BP energy review (2008; Figure 1.2), China and India, two of the worlds fastest growing developing countries, also hold significant amounts of coal reserves that will likely be used to fuel their increasing electricity demand. As a result, world coal consumption is expected to
increase by 48% from 2006 to 2030 (EIA, 2008; EIA, 2009). The domestic coal reserves, at the current consumption rate, can last for another 250 years (NRC, 2007). Most of coal is combusted in pulverized coal (PC) power plants for electricity generation. In fact, PC power plants account for about 90% of the domestic coal consumption. Currently, over half of the electricity in the U.S. and about 40% of worldwide electricity is generated from coal.

![Coal, oil and natural gas reserves in major countries and regions](image)

**Figure 1.2** Coal, oil and natural gas reserves in major countries and regions

In a typical PC power plant, coal is first processed into a powder form with 70% of particles less than 74 μm (200 mesh). The combustion of coal powder produces high
quality heat required to drive the steam turbine cycle. Conventional PC fired power plants operate at subcritical conditions with steam pressure up to 22MPa and temperature around 550 °C. These power plants have relatively low overall energy conversion efficiencies ranging from 33% to 37% HHV (MIT, 2007). Increasing the steam temperature and pressure to supercritical or ultra-supercritical conditions can yield higher process efficiency. However, further research in higher quality superalloys for boiler construction is necessary for this technology to mature.

Besides fuel market prices and energy demand, coal’s continued growth as a major domestic energy resource will depend heavily on its environmental acceptability relative to competing fuels. As a carbon-intense solid fuel, the mining, processing and burning of coal all present severe environmental and health impacts. In addition to the obvious safety concerns of coal excavation, coalmines also release significant amount of methane, which is a known GHG with 21 times more global warming potential than carbon dioxide. Furthermore, the mining waste products, such as uranium, thorium and other radioactive heavy metals along with acid water, are all considered environmental hazards. Moreover, combustion of coal produces additional atmospheric pollutants, namely SO₂, NOx, CO₂, fly ash, mercury and other particulate matter.

The 1970 Clean Air Act and the 1990 Clean Air Act amendments together established a standard for particulate matter, SO₂, NOx and photochemical ozone emissions control.
Since then significant progress has been made in the capability to mitigate undesirable emissions from commercial PC power plants. Now most domestic coal combustion power plants are equipped with pollutant abatement measures to comply with federal emission regulations that are likely to become even more stringent. Generally, 90% SOx removal can be achieved via flue-gas desulfurization (FGD), where alkaline slurries – typically lime – are used to scrub flue gas from the boiler. Flue gas NOx is removed by selective catalytic reduction (SCR), which is driven by a simple catalytic reaction that converts NOx, ammonia and oxygen to nitrogen and steam. Commonly, electrostatic precipitators, cyclones or fabric filters can be used to remove the majority of particulate matter. Lastly, trace heavy metals – mercury, selenium, and arsenic – can be removed using activated carbon sorbent (Gupta, 2007; Taerakul, 2007).

Coal-fired power plants account for nearly a third of all anthropogenic CO₂ emissions (Armor, 2007). Carbon capture from coal combustion flue gas is heavily discussed but not yet regulated or implemented. Growing evidence to support the rising atmospheric GHG level and its effects on the negative shift in global climate further affirms the necessity for carbon management. Even though technologies exist to remove CO₂ from coal combustion flue gas, implementing the current technology is uneconomical at the commercial scale, and no proven technology exists to safely store the collected CO₂ (MIT, 1993). Development of a cost-effective carbon capture technology to retrofit the existing fleet of coal-fired power plants is the goal of our research.
1.3 CARBON CAPTURE AND STORAGE

Global warming was a concept first proposed in 1975 to explain the increase in global temperature caused by fossil fuel combustion derived CO₂ emission (Broecker, 1975). Since early 1900s, the average earth surface temperature has increased by about 0.8 C with most of it occurring in the last 40 years (Sheppard and Socolow, 2007). This rise in temperature has resulted in global climate change, widespread melting of ice cores and potential rising of global sea level according to the Intergovernmental Panel on Climate Change (IPCC). Studies have shown global warming is directly correlated with rising GHG concentrations ((Pachuri and Jallow, 2007; Figure 1.3). Current known greenhouse compounds include water vapor, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (NO), and chlorofluorocarbons (CFCs). These GHG compounds serve to trap solar radiation within the earth’s atmosphere – a function that is essential to the thermal regulation of our planet – however, too much solar radiation can lead to an undesired global temperature increase.

Based on the radioactive force index, carbon dioxide has the most significant contribution to global warming because of its relative abundance in the atmosphere (Forster et al, 2007; Hofmann, 2009). In 2006, worldwide CO₂ emissions were estimated to be a staggering 30 billion tons per year, 20% of which was from the United States (EPA, 2009). The majority of anthropogenic CO₂ is emitted by combustion of fossil fuels for
transportation and electricity generation. Reduction in transportation related CO₂ emissions can be more effectively achieved through advancements in hybrid or electric automobile engine technology. However, CO₂ emissions from coal-fired power plants for electricity generation are stationary sources that can be more readily targeted for capture and sequestration. In 2006, coal-combustion for electricity production accounted for 35% of domestic and 42% of worldwide CO₂ emissions (EIA, 2008).

Figure 1.3 History of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (NO) concentration change in the ice cores
Growing concern over global warming has led to speculation of future CO₂ emission regulations. As early as 2002, President Bush announced the U.S. Global Climate Change Initiative (GCCI) to reduce green house gas (GHG) intensity by 18% by 2012 (Granite, 2004). The following year, Senators John McCain and Joe Lieberman proposed the Climate Stewardship Act, which established an economic cap-and-trade system for U.S. GHG emission reductions (Turley, 2009). In recent years, President Obama further outlined the guidelines on a federal cap-and-trade program for CO₂. In December 2009, the Environmental Protection Agency (EPA) declared current GHG concentrations, including CO₂, as a threat to public health and welfare of current and future generations (Turley, 2009). Given this circumstance, significant research efforts have been invested in the development of novel CO₂ capture and storage (CCS) technologies for existing energy conversion processes.

The carbon management scheme involves three steps: CO₂ capture and compression, transportation and lastly sequestration - among which the capture process is the most energy intensive (MIT, 2007; Chatel-Pelage, 2006). Existing CO₂ capture research focuses on amine scrubbing, oxy-combustion, membrane separation, and solid sorbent reaction. There are several challenges in direct CO₂ capture from coal combustion flue gas. First, coal combustion flue exits the boiler at well over 1300 °C; thus a high temperature CO₂ capture method is preferred for better heat integration. Second, flue gas CO₂ concentration ranges from 10-15%. At this relatively low percentage, the mass
transfer coefficient and partial pressure are considered unfavorable for absorption or adsorption reactions. Lastly, larger size coal fired power plants, such as the Bowen plant in Cartersville, GA or the Miller plant in Quinton, AL, produce over 55,000 tons of CO₂ daily (ScienceDaily, 2007). Scaling up any CO₂ capture technology to that magnitude is a difficult task on its own. According to the specific target set forth by the DOE, advanced technologies must achieve 90% CO₂ capture at less than 20% increase in cost of electricity for post-combustion and oxy-combustion, and less than 10% increase for pre-combustion (Figueroa et al, 2008). In a report prepared by the National Energy Technology Laboratory (NETL), the timeline to commercialization for potential advanced CO₂ technologies is shown in Figure 1.4.

Figure 1.4 The potential advanced CO₂ technologies (NETL)
Solvent-based carbon dioxide capture technologies have been available for over half a century. Amine-based solvents, such as Monoethanolamine (MEA), Diethanolamine (DEA), and Methyl Diethanolamine (MDEA), are the most commonly used. In fact, such systems have been implemented at the commercial scale for natural gas combustion. In this process, fresh amine first absorbs the CO₂ from the cooled flue gas stream (~40 °C); then spent amine is regenerated in a stripper at slightly higher temperature (100 – 150 °C) followed by CO₂ recovery at 1 – 2 atm. Overall this is still a low temperature process that is expected to pose severe energy penalties. Studies have shown that amine scrubbing from coal-fired power plants can reduce the net power produced by as much as 42% (Ramezan et al, 2007), which will likely increase the cost of electricity by over 85% according to NETL estimations (DOE, 2007; DOE, 2008). Although amine scrubbing is the most mature technology available, absent a significant technical breakthrough, meeting the cost target established by the DOE will be difficult.

Cryogenic oxygen combustion provides another relatively mature approach for carbon management in coal-fired power plants. Here, pure oxygen is used for coal combustion instead of air. The flue gas will then consist primarily of CO₂; thus avoiding the need for CO₂ capture. The biggest drawback of this process is the cryogenic air separation unit’s (ASU) energy consumption, which can reduce the overall plant efficiency by 20 – 35% (Chatel-Pelage, 2005; MIT, 2007; Lu, 2005). Retrofitting the oxy-combustion process to an existing power plant requires significant boiler modifications because conventional
burners cannot withstand the oxy-combustion flame temperature. Flue gas recirculation can dilute the burner oxygen content to 30-35%; at this concentration, the heat transfer characteristics will be similar to that of air combustion (NETL, 2008). Babcock and Wilcox Company have successfully demonstrated this process on a 1.5 MWth pilot scale PC unit. However, the largest ASU available cannot supply enough oxygen for an average sized coal-fired power plant. There may be unforeseen scale-up consequences.

Selective membrane separation is another potential technology being developed. Currently slipstream application of membrane CO$_2$ capture is demonstrated at the APS Cholla power plant. Membrane durability is a major concern for large-scale operation. Furthermore, studies have shown that producing a compression-ready high-purity CO$_2$ stream requires membrane selectivity of at least 200; however current membrane selectivity is only around 60 (IPCC, 2005; Favre, 2007, Yang et al, 2008).

Solid sorbent reaction separation is one of the more promising CO$_2$ capture technologies. Unlike solvent scrubbing, oxy-combustion or membrane separation, solid sorbents – typically metal oxides - can perform at elevated temperatures with high efficiency. The Ohio State University (OSU) has successfully demonstrated one possible system, the Carbonation Calcination Reaction (CCR), that utilizes naturally occurring limestone to simultaneously capture CO$_2$ and SO$_2$ from the post-combustion flue gas stream. Simulations of the CCR process at the 500 MW$_{th}$ scale indicate that its energy penalty
ranges from 15 – 20%, which is significantly lower than that of amine scrubbing (Wang, 2011). Chapter 2 will focus on the calcium sorbent based clean coal technologies under development at OSU. Other than the aforementioned CCR process, it will also provide a brief description of the Calcium Looping Process (CLP), where we investigated hydrogen and electricity production from coal-derived syngas via improved water gas shift (WGS) reaction with in-situ CO₂ removal. Chapter 3 will cover the experimental results from cold-model testing of the redesigned cyclone setup for gas-solid separation on the 120kWₜh CCR system. Chapter 4 will unveil the conceptual design of a mechanically agitated bubbling bed high temperature hydration reactor, including both cold-model fluidization and hot-model reaction test results. Chapter 5 includes the results from preliminary high temperature hydration tests. Chapter 6 provides conclusions and recommendations.
2.1 INTRODUCTION

Calcium oxide based solid sorbent is an attractive option for CO₂ removal because of its relative abundance, low cost and high CO₂ absorption capacity. There are 1600 companies operating over 3,900 quarries and 93 underground mines in all 50 states, with Ohio being the sixth largest producer. In 2011, the limestone production in the U.S. exceeded 700 million tons, most of which was used in the construction, soil treatment and steel industry at a market price less than $15 per ton (USGS, 2011). If calcium sorbent were to be used for CO₂ capture from coal-fired power plants, the limestone industry would have to expand significantly. However, the price should remain relatively stable because of market competition. From an absorption perspective, 56 grams of CaO is capable of retaining 44 grams of CO₂ via carbonation reaction. That is the equivalent of 78.5% capture by weight. Compared to amines that can only perform at a 18% CO₂ capture capacity (Gray, 2002) and molecular sieves with 24% capture capacity, calcium sorbents can theoretically perform over 3-4 times better.
2.2 CARBONATION CALCINATION REACTION (CCR) PROCESS

2.2.1 Overview

The Carbonation Calcination Reaction (CCR) Process at The Ohio State University is a high temperature calcium-based reaction separation process. Shown in Figure 2.1 (Wang, 2010) is the general process flow scheme, which consists of three main reactors – carbonator, calciner and hydrator – and multiple particulate capture devices (PCD). The design and performance of the PCDs and the hydrator will be discussed in more detail in Chapters 3 and 4, respectively.

Figure 2.1 The general process flow scheme of Carbonation Calcination Reaction (CCR) at The Ohio State University
Initially, a mesoporous Precipitated Calcium Carbonate (PCC) exhibited promising reactivity for both SO2 and CO2 capture over multiple cycles (Gupta and Fan, 2002; Iyer et al., 2004). This finding subsequently led to successful pilot scale demonstrations, known as Ohio State Carbonation Ash Reactivation (OSCAR) Process and the Calcium-Based Reaction Separation for CO2 (CaRS-CO2) Process (Fan, 2002; Fan et al., 2008; Gupta et al., 2007). However, the operating cost associated with using PCC for flue gas cleaning is significantly higher than that of calcium hydroxide, which later emerged a promising and more economical alternative. The current CCR process is an extension of the previous two processes developed at OSU (Wong, 2007). At the 120 kWth subpilot facility, prior experiments using calcium hydroxide particles demonstrated over 90% CO2 and nearly 100% SO2 removal at low calcium to carbon ratios for five cycles (Wang, 2010; Fan, 2008). For the CCR process to be technically and economically feasible, this level of capture must be maintained for a longer duration. Previous research has confirmed that calcium sorbents tend to lose their CO2 capture capacity over multiple cycles (Wang, 2005). In order to understand the cause for sorbent reactivity decay during multicyclic operation, we must first study the fundamental reaction mechanisms involved in the CCR process.

2.2.2 Reversible Carbonation and Calcination Reactions

\[
CaO_{(s)} + CO_{2(g)} \xleftrightarrow{\text{Carbonation}} \rightarrow \xrightarrow{\text{Calcination}} CaCO_{3(s)} \quad (1)
\]

\[\Delta H = -178 \text{ kJ/mol}\]
The carbonation and calcination reactions are two reversible reactions that occur at different thermal conditions, shown in Equation (1) and Figure 2.2. The carbonation reaction is exothermic, and has favorable reaction kinetics at temperatures between 450°C and 750°C (Abanades and Alvarez, 2003; Lee, 2004). In contrast, the calcination reaction is highly endothermic, and the operating temperature can range from 450°C to 1550°C depending on the calcination environment (Glasson, 1958; Borgwardt, 1989; Wang and Thompson, 1995), which is dictated by the end product functionality. Heat generated from the carbonation reaction must be recovered; whereas additional heat is
required to drive the calcination reaction. An effective process integration scheme is crucial to minimizing the parasitic energy consumption of the CCR process.

Figure 2.3 Basic grain model of carbonation (Alvarez, 2005)

Carbonation is a selective chemical absorption reaction, during which CO₂ from the flue gas reacts with CaO sorbent to form CaCO₃. The carbonation reaction mechanism is studied extensively using thermal gravimetric analyzers (TGA). The general agreement is that carbonation is a surface reaction that follows the basic grain model, shown in Figure 2.3 (Alvarez, 2005). It was found that carbonation could be divided into two regimes: an initial fast phase followed by a slower approach to a conversion plateau (Baker, 1973).
The initial rapid regime is controlled by the chemical reaction rate. Once the CaCO₃ product layer reaches a critical thickness of roughly 49 nm, the reaction rate will be dominated by the slower diffusion rate (Alvarez, 2005). Product layer formation impedes CO₂ from reacting with the CaO core; therefore this CO₂ diffusion rate through the CaCO₃ layer will become the rate-limiting factor during the second phase.

The carbonation kinetics depends strongly on the reaction conditions, namely temperature and CO₂ partial pressure. However, for coal combustion flue gas, the CO₂ stream is relatively dilute – at such conditions, Bhatia and Perlmutter (1983) reported that partial pressure had little effect on reaction rate. Furthermore, particle properties, such as particle size, surface area, porosity and, pore size, can all impact the reaction conversion. Generally, larger surface area and pore volume and smaller particle size will yield increased carbonation rate (Agrinier et al., 2003). The presence of specific pore size and structure (mesopores and micropores) has been suggested to produce favorable results (Abanades and Alvarez, 2003). Reaction temperature is another interesting parameter – the optimal carbonation condition must strike a balance between high temperatures that will enhance the reaction rate, and low temperatures that will improve the equilibrium conversion. Under the DOE guideline that requires at least 90% CO₂ removal, a typical coal combustion flue gas stream containing 10 – 15 % CO₂ must to be purified to 1 – 1.5 % CO₂ concentration before it can be released (Ciferno et al., 2009). As shown in Figure 2.2, 1 and 1.5 % CO₂ concentrations correspond to equilibrium temperatures of 643°C
and 660°C respectively (HSC Chemistry, 2008). If the reaction temperature exceeds 660°C, then 90% CO₂ would not be possible under the aforementioned dilute conditions. A low reaction temperature will negatively impact the overall process heat integration. Therefore, the optimal carbonation temperature for the CCR process lies between 600°C and 660°C.

As mentioned before, in the CCR system, flue gas CO₂ and SO₂ removal will proceed simultaneously. This is a major advantage of CCR over amine scrubbing, where SO₂ concentration above 10 ppm will actually degrade the amine solvent (Rao and Rubin, 2002; Supap et al., 2009). The sulfation reaction between lime and SO₂ is a well-studied subject because of the interest in using limestone to control SO₂ emissions. At the same temperature, carbonation rate will far exceed the speed of sulfation (Anthony and Granatstein, 2001). Although these are two competing reactions, virtually all of the SO₂ can be removed even at low Ca:C molar ratios. The reason is that SO₂ concentration in coal combustion flue gas stream is at ppm level, which is significantly less than that of CO₂. A 1:1 calcium to carbon ratio is equivalent to about 80:1 Ca:S molar ratio. However, the problem with simultaneous SO₂ capture is that CaSO₄ does not decompose at the calcination temperature. Thus, a purge stream is required to prevent inert CaSO₄ build-up in process solid concentration.
The calcination reaction is the reverse of carbonation. As mentioned before, this is an energy intensive thermal decomposition reaction where the spent sorbents are regenerated. Similar to carbonation, this is also a surface reaction, but reaction mechanism follows the shrinking core model, shown below in Figure 2.4 (Boateng, 2008). First, sufficient heat must reach the reaction surface to decompose CaCO₃ into CaO and CO₂. Then, CO₂ molecules will diffuse through the ash layer (lime) on the particle surface until it reaches the exterior surface of the solid. The unreacted CaCO₃ core will shrink until the whole particle is fully reacted.

Figure 2.4 The calcination reaction model of calcium carbonate
The calcination of calcium carbonate depends on a number of factors including temperature, calcination environment and particle properties. On the commercial scale, limestone calcination to produce quicklime is often carried out in shaft furnaces or rotary kilns at around 900°C. This is consistent with the reaction thermo-equilibrium data. As shown in Figure 2.2, 1 atmosphere of CO₂ partial pressure corresponds to equilibrium temperature of 900°C (HSC Chemistry, 2008). Raising the calcination temperature can accelerate the calcination rate; however, it will also induce thermal sintering, which should be avoided because it produces unreactive lime (Glasson, 1958; Borgwardt, 1989). Kumar et al. (2007) reported that lime produced from limestone calcined at above 1550 °C was practically unreactive. For application in the CCR process, highly reactively lime is desired.

Sintering is favored by both high calcination temperature and extended time at temperature, and is accelerated by the presence of CO₂, H₂O and other impurities such as salt, calcium sulfate and chloride (Stanmore and Gilot, 2005; Glasson, 1967). During sintering, inter-particle bridges are formed, leading to adhesion between adjacent grains and pore closure on the grain surface. Decrease in both sorbent surface area and porosity, and change in pore structure, specifically growing of macropores at the expense of meso- and micropore shrinkage, are all results of sintering (German, 1996; Shimizu, 1999). Sorbent sintering is a major challenge for multi-cyclic CO₂ removal using limestone because it drastically deteriorates sorbent reactivity and consequently incurs additional
sorbent usage. For the commercial competitiveness of the CCR process, thermal sintering during calcination must be avoided.

As briefly mentioned in the previous paragraphs, calcination conditions, like CO$_2$ partial pressure and steam presence, directly affect calcination temperature and the lime quality. Lime produced in a concentrated CO$_2$ environment tends to exhibit reduced reactivity and surface area (Ewing et al., 1979; Glasson, 1961). In contrast, calcination under vacuum or in the presence of a sweep gas (N$_2$) at reduced temperatures can create the opposite effects, which are more favorable for producing high surface area lime (Baker, 1973; Glasson, 1961). Previous research has demonstrated a positive correlation between the calcium oxide surface area to its CO$_2$ capture capacity (Sakadjian et al., 2007). However, the effects from using steam as diluent gas are relatively inconclusive although steam is a more practical and economic choice than nitrogen or vacuum. Numerous studies have supported the benefits of adding steam during calcination to the reaction kinetics (Wang, 1995). However, other studies also cited that the presence of steam promotes sintering (Agnew, 2000; Borgwardt, 1989). While a faster calcination rate can reduce both the solid residence time in the calciner and the reactor volume, sintering will hinder the sorbent reactivity. In addition, feeding steam at the calcination reactor operating temperature of 900 °C is an energy intensive procedure.
Calcination, being a gas-solid reaction, will be affected by certain particle characteristics. The solid particle size distribution can dictate both mass and heat transfer kinetics (Borgwardt, 1985). Smaller particle size can abate the inhibitive effects from product layer formation, thus enhancing reaction rate (Criado and Ortega, 1992). However, fine grinding to sub 5 μm particles is not recommended for several reasons (Ye, 1995): excessive cost of grinding, a decrease below 5 μm only has a limited effect on conversion, and ultrafine particles can complicate system fluidization behavior. Studies have found particles < 90 μm will calcine uniformly throughout (Borgwardt, 1986).

2.2.3 Hydration Reaction

\[
CaO + H_2O \xrightleftharpoons{\text{Hydration}}^{\text{Dehydration}} Ca(OH)_2 \quad (Eqn 2.2)
\]

\[\Delta H = -105 \text{ kJ/mol}\]

Lime hydration is an exothermic reaction that occurs spontaneously at room temperature (Equation 2.2). The idea of utilizing this reaction for sorbent reactivation was first suggested by Argonne National Laboratories in 1980 for SO₂ removal using lime (Shearer et al., 1980). Their report proposed that formation of calcium hydrate, whose molar volume is greater than that of lime, follows the process of particle expansion, surface cracking and eventual flaking off of hydrate particles. Calcium hydrate (Ca(OH)₂) formed through both steam and water hydration has natural particle size less than 10 μm -
much smaller than the typical particle size of ground CaO. As aforementioned, reduced particle size will enhance both carbonation and calcination kinetics. Moreover, Ca(OH)$_2$ particles on average have significantly greater surface area than CaO particles, as illustrated in Table 2.1 (Boynton, 1980). Regardless of the calcination condition, the surface area of hydrate particles ranges from 10 to 20 times higher than that of lime (Boateng, 2008). Additional surface area allows for faster diffusion rate and higher carbonation conversion. Consequently, calcium hydrate is widely considered as a more superior sorbent than calcium oxide (Bruce, 1989).

Researchers have experimented with various sorbent reactivation techniques. Iyer (2004) and Sakadjian (2007) studied precipitated calcium carbonate (PCC) and claimed it to be more reactive than lime during the first five cycles. However; PCC production is complicated and more expensive than that of fresh limestone. Treating CaO with ethanol/water or acetic acid solution has also been found to increase sorbent carbonation conversion (Li, 2008, 2009). Unfortunately, these solvents are expensive, and the subsequent drying and distillation processes can result in significant energy penalties. The reagents required for hydration include only lime and water, both of which are abundantly available and low cost. Economic appeal and simple reaction mechanism led to its emergence as a viable sorbent reactivation path over for multi-cyclic CCR process.
Table 2.1 Comparison of surface area of CaO and Ca(OH)$_2$ particles

<table>
<thead>
<tr>
<th>Calcination Condition</th>
<th>High T</th>
<th>High T</th>
<th>Low T</th>
<th>Low T</th>
<th>Low T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area of Lime (m$^2$/g)</td>
<td>0.44</td>
<td>0.55</td>
<td>1.18</td>
<td>1.30</td>
<td>0.67</td>
</tr>
<tr>
<td>Surface Area of Hydrate (m$^2$/g)</td>
<td>26-32</td>
<td>14.6</td>
<td>17-24</td>
<td>13-22</td>
<td>17.6</td>
</tr>
</tbody>
</table>

Hydration of lime can proceed via two options: water or steam hydration. Commercially, lime hydration is achieved by slaking quicklime with water in stirred tanks. Temperature of the slurry is carefully controlled by adding excess water to absorb the exothermic heat of reaction. The optimal temperature for this liquid hydration should not exceed 82 °C (Whitman, 1926; Hassibi, 1999) - under this condition, the hydrate product is known to have high reactivity. In addition, the reaction proceeds rapidly in a slurry condition because its thermodynamics favor low temperature. However, integration of liquid hydration into a high temperature system, such as the CCR process, will impose severe energy penalties.

Considering overall system integration, hydration of lime using superheated steam is more suitable for the application of the CCR process. At elevated temperatures, high quality heat of hydration can be utilized for energy production in a steam turbine cycle. Zeman et al. (2008) investigated the steam hydration kinetics at 300 °C and atmospheric pressure. Hydrated lime retained 60% carbonation capacity after 10 cycles; however,
reagent grade calcium carbonate was tested instead of ground limestone (Zeman, 2008). Ground limestone and reagent grade CaCO₃ differ in particle size; and ground limestone contains other solid impurities that are known to accelerate sintering (Dobner, 1977). If Zeman’s methods were implemented in a practical system, the results will not be nearly as favorable. Furthermore, Hughes et al. (2004) have successfully demonstrated pretreating lime with steam at 150 °C and 4.7 atm for 2 hours can improve its carbonation conversion. After 20 cycles, they maintained the conversion above 52% (Hughes et al., 2004). Kuramoto et al. (2003) also studied superheated steam hydration at pressurized conditions for the application of the HyPr-RING Process in Japan. In their process, calcium sorbent showed stronger durability for repeated CO₂ sorption (Kuramoto et al., 2003). Unlike the CCR, HyPr-RING is a gasification-based process where pressurized steam is innately present in the system. Injection of calcium sorbent in such an environment will inevitably lead to hydration. Unfortunately pressurized hydration is not feasible for our design because the CCR process targets the current fleet of coal fired power plants that operate at atmospheric conditions. For maintaining the retrofit advantage of our process, we plan to study steam hydration of lime under atmospheric conditions.
The thermo-equilibrium data, shown in Figure 2.5, indicate that 1 atm partial pressure of steam corresponds to an equilibrium temperature of 518°C (HSC Chemistry, 2008). Without pressurizing the steam, calcium hydroxide will decompose if the reaction temperature exceeds 518 °C. In addition, considering the highly exothermic nature of the hydration reaction, the practical operating temperature range is limited to 350 – 450°C for
the CCR process. Theoretically, the excess reaction heat can be used for additional energy generation, but heat extraction from a gas-solid reaction can be a challenge.

2.2.4 120 kWth Sub-pilot Scale CCR Demonstration

We have developed a 120 kWth sub-pilot scale CCR process demonstration system (Figure 2.6 and 2.7) at the OSU west campus facilities. This system is designed based on a few important criteria:

1. Generation of coal combustion flue gas under realistic conditions. Instead of using syngas, real coal combustion flue gas contains other components, such as fly ash, SO2, mercury and other impurities, which may affect sorbent reactivity.

2. Installation of an indirectly heated electric rotary calciner that is capable of producing fresh CaO sorbent.

3. Other than the rotary calciner, the entire system is under negative pressure created by a downstream induced-draft (ID) fan. The ID fan should create sufficient suction to entrain all calcium sorbent at the desired solid loading level.

4. Particulate capture devices, such as metal cyclones or baghouse, must be present to separate spent solids from the clean flue gas stream.

5. System measurement equipment needs to overcome severe operating conditions – high temperature and possible solid clogging – to accurately measure the temperature, pressure drop and gas composition throughout the process.
6. Safety control measures, including gas alarms and temperature alarms, are installed on the calciner, the coal stoker, and around the system to prevent possible gas leak, pressure build-up and temperature overshoot.

Figure 2.6 The process flow diagram of a 120 kWth sub-pilot scale CCR process demonstration system (Wang, 2010)
Due to space limitations, an on-site sorbent reactivation reactor was not part of the original design. Consequently, the current CCR system is only capable of single cycle testing. Although continuous multi-cyclic testing is implausible at the moment, we have demonstrated the CCR process over five reaction cycles via a rather tedious approach - spent sorbent is captured by the baghouse, decomposed in the rotary calciner, and then shipped to an off-site facility for reactivation. Carus Lime & Stone (Pittsburgh, PA) converts our spent sorbent to hydrated lime by dry atmospheric hydration. Shown in the process flow diagram, Figure 2.6, the 120 kWth CCR process consists of five major components: an underfeed stoker that consumes about 20 pounds of coal per hour, an entrained bed carbonation reaction, an electrical rotary calciner, a baghouse that collects spent sorbent and a variable speed ID fan that controls the gas flow in the system.

![Figure 2.7 Image of 20 pound per hour coal combustion sub-pilot scale facility.](image)

1: Stoker. 2: Upstream gas analyzer. 3: Flyash/SO2 sorbent injection hopper. 4: Main sorbent injection hopper. 5: Rotary Calciner. 6: Entrained bed reactor. 7: Downstream gas analyzer. 8: Air dilution valve. 9: Baghouse. (Wang, 2010)
The underfeed stoker was obtained from Babcock & Wilcox in support of our project. Under normal operation conditions, the stoker co-combusts about 20 lbs of stoker grade coal and 3 actual cubic feet per minute (ACFM) of natural gas with 20% excess air. Two force induced (FD) fans supply the air for combustion. By design, the positive pressure from the FD fans is negated by the negative pressure from the ID fan to create a zero-pressure point in the stoker. The ID fan also ensures the entire CCR system is under negative pressure so that no flue gas or sorbent will be released into the surrounding environment. Flue gas exits the stoker at around 1000 °C containing 12 – 15 % CO₂ and 2000 ppm of SO₂. Two sets of California Analytical Instruments (CAI) analyzers are installed to monitor the flue gas composition, specially the percent CO₂, SO₂, NOx, CO and oxygen. One analyzer samples directly from the exit of the stoker upstream to sorbent injection to establish a baseline. The other analyzer measures the clean flue gas composition downstream to the carbonator. The difference between the two measurements represents the percent gas removal. Furthermore, over twenty thermocouples are installed throughout the system to monitor the temperature profile. All data are continuously recorded on a computer.

The indirectly heated electric rotary calciner was provided by FEECO. The calciner operates with a maximum shell temperature of 982 °C, and it is positioned with a 2 deg downward slope so that solids can flow down by gravity. The solid residence time in the calciner is controlled by varying the revolutions per minute. For the calcinations of both
limestone and calcium hydroxide, the average residence time is maintained at 35 minutes. In the calciner, calcium carbonate is decomposed into calcium oxide and CO$_2$. The calciner temperature of 980°C is however not high enough to decompose calcium sulfate. A Sunco double-dump valve is installed at the exit of the calciner to inject sorbent in the carbonator while providing a seal between the CO$_2$ rich calciner environment and flue gas from the stoker. Even though rotary calciners are capable of handling high solid loading, the extended residence time can induce sintering and deteriorate sorbent reactivity. A possible alternative is the more advanced flash calciner that can significantly reduce calcinations time and abate the effects of sintering.

The carbonation / sulfation reactor is essentially a riser operating in entrained bed mode within the temperature range of 450°C and 700°C. Past the sorbent injection point, the flue gas, accelerated by the ID fan suction, will fluidize and carry the solids through the reaction zone. Based on the volumetric flue gas flow rate, the gas residence time in the carbonation friendly temperature range is found to be less than one second. Vigorous gas solid mixing during entrained mode operation allows the reaction to proceed rapidly. As previously mentioned, the carbonation reaction contains two phases: the rapid reaction controlled phase and a slow diffusion dominated step. For the purpose of this system, conversion depends primarily on extent of reaction during the initial fast phase. From our sub-pilot scale testing, at calcium to carbon molar ratio of 0.75 to 1, we have demonstrated 50% CO$_2$ removal from a flue gas stream containing 10% CO$_2$ (Wang,
Combining that with our other results, the data extrapolate to 90% CO₂ removal at 1.3:1 calcium:carbon ratio, which translates to a reasonable amount of solid loading for an industrial chemical looping system. Since SO₂ is present in the flue gas at the ppm level, this amount of calcium sorbent corresponds a calcium:sulfur ratio of over 50:1. Under this condition, 99% sulfur removal can be achieved simultaneously.

The carbonation reactor leads to a Donaldson Torit baghouse that separates the calcium solids from flue gas. However, before the flue gas stream can enter the baghouse, it needs to be cooled to the baghouse operating temperature of 60°C. An air injection blastgate is installed between the carbonator and the baghouse to provide the dilution needed for cooling. The solids captured by the baghouse are collected in a 55-gallon drum for off-site reactivation while clean flue gas is vented by the ID fan.

2.3 CALCIUM LOOPING PROCESS

2.3.1 Overview

The Calcium Looping Process (CLP) is another novel clean coal technology built on the concept of producing H₂ from coal gasification fuel gas via the water gas shift (WGS) reaction. The major challenge, existing in the slow kinetics of the WGS reaction, can be overcome by the integration of a CO₂ absorbing reaction. The in-situ removal of CO₂
product through CaO carbonation can drive the equilibrium-limited WGS reaction forward, and simultaneously achieve removal of sulfur and halide contaminants. As shown in Figure 2.8, the integrated hydration reactor combines H₂ production along with CO₂, sulfur and chloride capture into a single step (Ramkumar, 2011).

Figure 2.8 The integrated hydration reactor combining H₂ production along with CO₂, sulfur and chloride capture into a single step
Calcium oxide is a promising sorbent for this application because of its higher tolerance toward sulfur than other commercial metal oxide catalysts (Haussinger, 2000). Studies have shown that improved equilibrium reaction conditions derived from in-situ CO₂ removal can significantly reduce the steam consumption required for the WGS reaction. Similar to the CCR process, sorbent reactivation is the key to the economic feasibility of this technology. A three-stage process that incorporates sorbent reactivation via steam hydration has been proposed (Ramkumar, 2010). Thus far, experimental and thermodynamic studies have demonstrated over 99% H₂ purity can be achieved at stoichiometric steam to carbon ratio at high pressure.

Furthermore, sorbent activation through hydration was found to be very effective. The economics of this process hinges on the efficacy of sorbent reactivation and its recyclability over multiple cycles. The unique advantages of this chemical looping process include:

- Overall process design can be vastly simplified through integration of multiple reactions into a single-stage reactor that encloses the WGS reaction, carbon capture, and removal of trace elements such as sulfur and halides. Reduction in reactor quantity not only directly alleviates the plant’s capital and operating cost, but also offers better heat integration via direct heat transfer within the reactor. Consequently, that also eliminates the need of additional heat exchangers.
• The addition of calcium sorbent can effectively improve the WGS reaction thermodynamics. The amount of steam required can be reduced to near stoichiometric level. Conventional catalyzed WGS reactions operate at steam to carbon ratio as high as 30:1.

• This CLP can accept flexible fuel sources, such as coal gasification syngas or methane reforming fuel gas - both feedstocks contain amounts of H₂ and CO at varying ratios. The overall conversion and product H₂:CO ratio is controlled by the WGS reaction. In the modern era, the fuel market economics can be highly volatile, having the option to produce either H₂ or various forms of hydrocarbons via Fischer-Tropsch Synthesis can be a distinct advantage.

• Simultaneous removal of multiple contaminant species can be achieved for this near-zero carbon emission chemical looping system, especially for coal gasification syngas. A sequester-ready CO₂ stream can be produced through spent sorbent regeneration in a calciner.

2.3.2 Water Gas Shift Reaction:

\[
CO (g) + H_2O (v) \xrightleftharpoons{Forward}^{Reverse} CO_2 (g) + H_2 (g) \quad (Eqn 2.3)
\]

\[
\Delta H = -41 \text{ kJ/mol}
\]
The WGS reaction provides a viable method for extracting clean energy from the toxic CO by converting into H₂ gas suitable for fuel cell applications. The reaction is slightly exothermic ($\Delta H = -41 \text{ kJ/mol}$), thus elevated reaction temperatures are detrimental to the reaction thermodynamics. However, as a catalytic reaction, the kinetics are definitely more favorable at higher temperatures. Ideally, this reaction should be operated within its thermodynamic limits while maintaining high reaction rates – at high temperature. In order to overcome this dilemma, the WGS reaction is typically conducted in multistage adiabatic reactors that include a high temperature shift (HTS) in the temperature range 350 °C – 600 °C and a low temperature shift (LTS) less than 300 °C. Conventionally, metal catalysts- iron and copper based- are utilized in the HTS and LTS reactors respectively to improve the reaction equilibrium. Three commonly used commercial shift catalysts are:

- **HTS Catalyst**:  
  - Fe₃O₄ with Cr₂O₃ as stabilizer  
  - Operating Conditions: 350 °C – 500°C, sulfur content < 100 ppm

- **LTS Catalyst**:  
  - Cu with ZnO and Al₂O₃ support  
  - Operating Conditions: 185 °C – 275°C, sulfur content < 0.1 ppm

- **Sour Shift Catalyst**:  
  - Sulphided Co and Mo  
  - Operating Conditions: 250°C – 500°C, sulfur content > 300 ppm
Even under catalytic conditions, additional steam is required to achieve a satisfactory reaction rate. Typically, a steam:carbon monoxide ratio of at least 2:1 is adopted to avoid catalyst deactivation from carbon deposition onto the particle surface, and to mitigate undesired hydrocarbon, specifically methane, formation (Callaghan, 2006). Table 2.2 lists the known side reactions under WGS conditions. Unwanted methane production is adverse to achieving high purity H₂ in the product stream. In addition, carbon formation can lead to increasing pressure drop across the reactor bed and possible plugging and fouling of equipment.

Thermodynamic studies have shown that carbon formation can be effectively abated if the steam:CO ratio is greater than 2 and the reaction temperature is higher than 230°C (Xue, 1996). In addition, simultaneous H₂ extraction from the product stream can prevent methane-favoring side reactions. However, implementing the minimum steam:CO ratio of 2 may result in high outlet temperature (560°C), which can lead to irreversible catalyst deactivation by sintering (Carbo et al., 2007). Utilization of calcium sorbents instead of traditional catalysts will avoid the catalyst sintering issue because calcium sorbents’ sintering temperature is greater than 1000°C. Furthermore, in-situ removal of CO₂ – the other product of WGS reaction- should also reduce unwanted side reactions.
Table 2.2 Possible side reactions under WGS conditions.

<table>
<thead>
<tr>
<th>Possible Side Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$</td>
</tr>
<tr>
<td>$\text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$2\text{CO} + 2\text{H}_2 \leftrightarrow \text{CO}_2 + \text{CH}_4$</td>
</tr>
<tr>
<td>$\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4$</td>
</tr>
<tr>
<td>$4\text{CO} + 2\text{H}_2\text{O} \leftrightarrow \text{CH}_4 + 3\text{CO}_2$</td>
</tr>
<tr>
<td>$\text{CH}_4 + 2\text{CO} \leftrightarrow 3\text{C} + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{C} + \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

2.3.3 In-situ Carbon Capture

$$\text{CO} \ (g) + \text{H}_2\text{O} \ (v) + \text{CaO} \ (s) \leftrightarrow \text{CaCO}_3 \ (s) + \text{H}_2 \ (g) \quad (Eqn \ 2.4)$$

$$\Delta H = -219 \ \text{kJ/mol}$$
\[
\text{CaO (s)} + \text{H}_2\text{O} (\nu) \xrightleftharpoons[^{\text{Hydration}}]_{^\text{Dehydration}} \text{Ca(OH)}_2 (s) \quad (\text{Eqn 2.5})
\]
\[
\Delta H = -105 \text{ kJ/mol}
\]

Figure 2.9 Comparison of reactions of WGS-Carbonation and hydration of CaO
Injection of calcium sorbents into the integrated hydrogen reactor will lead to either hydration or carbonation depending on the reactor temperature and partial pressures of reactant gas species. Thermodynamics of both reactions are shown in Figure 2.9 (Ramkumar, 2011). The equilibrium composition of the reactor system depends on the H$_2$O/CO/CO$_2$ composition in the feed stream and the reaction conditions. Typical air-fired gasifier syngas stream contains about 15% CO$_2$ while oxygen-fed syngas stream has a lower CO$_2$ content, ranging from 1.6 to 10.2 % (Ramkumar, 2010b). The amount of calcium sorbent needed to achieve effective CO$_2$ removal should be adjusted according to the feed stream composition. The aforementioned CCR process has already demonstrated over 90% CO$_2$ removal for flue gas stream containing 10% CO$_2$ (Wang, 2010). The presence of steam and CO in the syngas stream should not adversely affect the carbonation kinetics.
Table 2.3 The typical syngas composition from various gasifiers

<table>
<thead>
<tr>
<th>oxidant</th>
<th>moving bed, dry</th>
<th>moving bed, slagging</th>
<th>fluidized bed</th>
<th>entrained flow, slurry</th>
<th>entrained flow, dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>fuel</td>
<td>air</td>
<td>oxygen</td>
<td>oxygen</td>
<td>oxygen</td>
<td>oxygen</td>
</tr>
<tr>
<td>Pressure (atm)</td>
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<td>31.6</td>
<td>9.9</td>
<td>41.8</td>
<td>24.8</td>
</tr>
<tr>
<td>CO (mol %)</td>
<td>17.4</td>
<td>46</td>
<td>48.2</td>
<td>41</td>
<td>60.3</td>
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<td>H₂ (mol %)</td>
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<td>26.4</td>
<td>30.6</td>
<td>29.8</td>
<td>30</td>
</tr>
<tr>
<td>CO₂ (mol %)</td>
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<td>2.9</td>
<td>8.2</td>
<td>10.2</td>
<td>1.6</td>
</tr>
<tr>
<td>H₂O (mol %)</td>
<td>-</td>
<td>16.3</td>
<td>9.1</td>
<td>17.1</td>
<td>2</td>
</tr>
<tr>
<td>N₂ (mol %)</td>
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<td>2.8</td>
<td>0.7</td>
<td>0.8</td>
<td>4.7</td>
</tr>
<tr>
<td>CH₄ + HCs (mol %)</td>
<td>5.8</td>
<td>4.2</td>
<td>2.8</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>H₂S + COS (mol %)</td>
<td>0.2</td>
<td>1.1</td>
<td>0.4</td>
<td>1.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

As shown in Figure 2.9, combined WGS-Carbonation and hydration of CaO are competing reactions. Ideally, our reaction conditions should lie between the thermo-equilibrium curves for the two reactions to ensure that the carbonation is thermodynamically favored and to avoid sorbent hydration with steam, which is a reactant for the WGS reaction also. The typical syngas composition from various gasifiers is shown in Table 2.3 (Stulz, 1992). Based on the incoming syngas compositions and relevant reaction kinetics, the feasible operating temperature for the hydrogen reaction falls within 500 °C – 750 °C (Ramkumar, 2010b).
2.3.4 Sorbent Reactivation via Hydration

Sintering from the calcinations process deteriorates the sorbent reactivity, leading to reduced CO₂ capture capacity. The hydration reaction can effectively reverse this phenomenon by increasing the sorbent pore volume and surface area. High temperature hydration process (~500 °C) can reduce the extent of cooling and reheating of solids between the calciner and the hydrogen reactor. Addition of a steam hydration step can benefit the CLP process for several reasons:

1. Steam hydration can improve sorbent reactivity over multiple reaction cycles, thus providing a means of sorbent regeneration. Prolonged sorbent lifespan can reduce the plant operating cost and the parasitic energy associated with heating fresh sorbent feed.

2. Dehydration of Ca(OH)₂ in the hydrogen reactor is a highly endothermic reaction. The combined carbonation and WGS reaction is intensely exothermic, thus maintaining the reactor temperature within the optimal range of 500 – 750 °C may be a challenge. The endothermic nature of Ca(OH)₂ dehydration will help offset the excess energy generation.

3. Ca(OH)₂, upon decomposition, will act as an additional steam source for the WGS reaction. The steam produced from dehydration of Ca(OH)₂ will be consumed by the WGS reaction. In theory, part or all of the steam required for the WGS can be
supplied by the hydrated sorbent, thus avoiding the need for additional steam input.

2.3.5 Sub-pilot Calcium Looping Process (CLP) System

Based on the promising results from the bench-scale fixed bed reactor, a sub-pilot scale fluidized bed reactor has been constructed at OSU. This sub-pilot system includes only the hydrogen reactor, which is designed to operate in a once-through fluidized bed mode. As shown below in Figure 2.10 (Phalak et al., 2012), the riser section stands 11.5 ft tall and consists of four identical flanged sections with 4” I.D. Reaction temperature is attained by indirect electrical heating provided by a set of high temperature ceramic heaters (OMEGA Engineering, Inc.).
Graymont high calcium Ca(OH)₂ was utilized as the CO₂ acceptor for this process. A Schenck Accurate volumetric screw feeder / hopper was used to inject solid sorbent into the system. A downstream double-gate valve acts as double-dump valve to prevent reaction gas from escaping through the hopper. The solids fall through an inclined
standpipe to reach the fluidized bed region. Figure 2.11 shows an actual picture of the standpipe and solid feeding mechanism (Phalak et al., 2012).

Figure 2.11 An actual picture of the standpipe and solid feeding mechanism
The syngas mixture, comprised of CO, CO₂, H₂ and steam, was used as the fluidization medium. Prior to entering the fluidized bed, the gas mixture must be preheated to reaction temperature by a set of heating coils. The gas flow rate is controlled by a complex Swagelok constructed gas mixing panel consisting of multiple mass flow controllers. The extent of reaction is monitored through both solid and gas analyses. After each run, the solids in the baghouse were collected and tested for their composition and reactivity using a thermogravimetric analyzer (TGA). In addition, during each run, a slipstream of the gas passing through the top of the riser is fed to a micro-GC analyzer (Varian) for analysis. The micro-GC can accurately measure the gas composition intermittently every 5 minutes.

2.4 CONCLUDING REMARKS

As described in this chapter, at The Ohio State University we have developed two unique chemical looping processes – CCR and CLP - that are based on the employment of metal oxide sorbents for in-situ CO₂ removal. Flue gas or syngas CO₂ engage in the high temperature carbonation reaction with the sorbent to form metal carbonate. Screening test of possible metal oxides based on their reactivity toward carbonation presents calcium oxide as a feasible CO₂ acceptor. Naturally formed limestone and dolomite, both CaO precursors, provide an abundantly available and inexpensive supply of solid sorbent. Implementation of these novel technologies on a commercial scale requires thousands of
tons of sorbent per hour, thus sorbent reactivity over extended reaction cycles becomes a critical issue that will dictate the process economics. Prolonged exposure in a high temperature calcination environment can lead to sorbent morphological variations caused by sintering. Previous research has suggested that steam hydration is a viable method for reversing the sintering effect and maintaining constant reactivity over extended cycles. The cohesive nature of fine Ca(OH)₂ particles in a steam-rich moist environment poses a severe challenge in terms of reactor design. Such a hydration reactor has not been investigated or operated at a larger scale. Conceptual design of a hydrator is integral to the successful demonstration of a multi-pass reaction study in both the CCR and CLP processes.

The CCR process has demonstrated promising results as a viable option for post-combustion CO₂ removal. Currently the CCR process is one of the few high temperature CO₂ capture technologies that can be readily retrofitted to the existing fleet of coal combustion power plants. As a high temperature process, it allows for more efficient heat integration to the steam turbine cycle. ASPEN simulation of the process of the CCR process suggests the overall process energy penalty to be 15.1% with 10% arising from CO₂ compression alone (Wang, 2012) – this means the amount contributed by the CCR process is only about 5%. These numbers compare favorably to competitive processes such as amine scrubbing or oxy-combustion. Amine scrubbing using MEA can decrease the power plant efficiency by as much as 30% while raising the cost of electricity by at
least 80% (Ciferno et al., 2009). Similarly, oxy-combustion by cryogenic separation can increase the cost of electricity by almost 60% (McCauley et al., 2009).

The calcium sorbent and steam usage requirements were the two main parameters studied in the sub-pilot system. Through initial testing, we found that at calcium to carbon ratio of 1.5 and steam to carbon ratio of 3, a 50% pure hydrogen product steam can be achieved at 600 C and ambient pressure (Phalak et al., 2012). This result is promising for WGS reaction in the absence of any catalyst. The bench-scale scale results were more favorable. In the fixed bed reactor, 70% purity H₂ can be obtained with steam to carbon ratio of only 1 at similar reaction conditions. The performance disparity can be attributed to the scale-up factors.
CHAPTER 3
GAS-SOLID SEPARATION USING CYCLONES

3.1 INTRODUCTION:

3.1.1 Separation technology

Separation technology is an integral part of the chemical industry, especially for multi-phase flow systems, to resolve problems such as dust collection, particulate separation and particle recirculation. Typical approaches employed to achieve solid-gas separation involves centrifugation, filtration, sieving, jet impaction, gravitational settling or wet scrubbing. Cyclones are one of the most commonly utilized gas-solid separation devices in the industry (Figure 3.1). Typically, particulate carrying gas enters the cyclone tangentially near the top. The centrifugal and inertia force push the particles to collide with the outer cylindrical wall, and then particles slide downward to the bottom as they lose momentum due to wall friction. Near the bottom of cyclone, gas-solid separation occurs as the particles exit through the bottom through a sealed pipe and the gas reverses its direction by entering an upward inner vortex flow. Clean gas exits the cyclone through a vortex-finder tube. The cyclone separator is an attractive option for particulate removal
because of its simplicity of construction, low energy consumption, ease of maintenance, and ability of operate at high temperatures (Koch and Licht, 1980).

Figure 3.1 Cyclone separator
Conventional high efficiency cyclones often employ the Stairmand design, which composed of a cylindrical body coupled to a conical section. Even thought cyclone geometry is relatively simple, the three-dimensional swirling flow pattern within the cyclone has long been a complex subject of many experimental and theoretical works. The performance of a cyclone is determined by a combination of eight geometric parameters: the inlet height, \( h_i \), and width, \( w_i \), the vortex finder diameter, \( D_{vf} \), and height, \( h_{vf} \), cylinder height, \( h_1 \), and diameter, \( D_c \), cyclone total height \( H_c \) and cone-tip diameter \( D_a \) (Figure 3.1). Cyclone performance can be gauged by its collection efficiency, \( \eta_c \), pressure drop and cut-off diameter, \( X_{50} \), where

\[
\eta_c = \frac{\text{mass of solids captured}}{\text{total mass of solids in}} \quad \text{Eqn (3.1)}
\]

\( X_{50} \) = Mean particle size when \( \eta_c \) is equal to 50%

Sometimes, in order to achieve high particle capture efficiency, multi-stage gas-solid separators setup based on a combination of several components, such as cyclones in series, are also employed.

3.1.2 Cyclone implementation of the CCR Process

The CCR process developed at The Ohio State University is a solid-sorbent based chemical looping process. Calcium oxide particles react with post-combustion flue gas to simultaneously remove CO\(_2\) and SO\(_2\) gas. Based on pilot-scale experiment results, it can be assumed that a Calcium:Carbon mole ratio of 1.4 is necessary to achieve 90% CO\(_2\) and
100\% SO₂ removal from flue gas stream (Wang, 2010). For a typical 500 MWe coal-fired power plant, which consumes about 200 tons of coal per hour, implementation of the CCR process will circulate over 4800 tons of calcium sorbent per hour. This magnitude of solid loading exceeds that of the largest fluidic catalytic cracking (FCC) systems. At such a scale, it becomes imperative and challenging to control any undesired particulate emissions.

Prior research has indicated that calcium oxide sorbent reactivity will decrease over multiple cycles. Furthermore, SO₂ from flue gas will react to form calcium sulfate, which doesn’t decompose at the 900 °C operating temperature of a CCR calciner. Without a purge stream, the calcium sulfate particles will accumulate in the system as inert solids. Therefore, spent solids must be purged and replaced with fresh calcium oxide particles to maintain 90\% CO₂ capture at a Calcium:Carbon mole ratio of 1.4. Ideally, if the post-Carbonator/Sulfator Particulate Capture Device (PCD) can operate at an efficiency level such that the amount of un-captured solids equals the amount we intend to purge, then that eliminates the need for a separate purge stream.

Overall, considering the amount of solid circulation in the system; the efficiency of the PCDs will have a strong impact on the economics of the CCR process. Higher gas-solid separation will reduce the amount of undesired solid entrainment with clean flue gas that may cause equipment complications downstream, such as the fouling factor of heat
exchangers. Furthermore, efficient solid capture can reduce the solid make-up rate and thermal energy required to heat up fresh feed, thus lowering overall operating cost.

Table 3.1 (Wang, 2011) illustrates the effects of PCD capture efficiency and purge rate on the process solid loading. The calculation is based on installation of the CCR process into the same 500 MW coal-fired power plant described in the previous paragraphs. Other assumptions include 90% fly ash removal prior to the carbonator, complete calcinations, 99.5% calciner gas-solid separation, complete hydration and a CaO/CaCO₃ cycle. The simulation results suggest the solid circulation, fresh feed consumption and solid exiting with the flue gas all have strong dependence on the PCD efficiency. For instance, increasing the purge rate from 0% to 10% results in significantly higher fresh feed consumption. Fresh feed consumption of over 200 tons per hour has a detrimental impact on process economics. Clearly, the operating condition at 0% purge and 99.5% capture efficiency is not feasible. The augmented numbers account for the continuous accumulation of calcium sulfate inert and decay in calcium oxide reactivity. We also notice that solid circulation rates are comparable at 0% purge with 95% PCD and 5% purge with 99.5% PCD; and at 5% purge with 95% PCD and 10% purge with 99.5% PCD, respectively. This confirms the initial thinking of avoiding a dedicated purge stream if we can accurately control the PCD efficiency. The actual purge percentage will be determined by the amount of SO₂ in the flue gas stream and downstream equipment requirements.
Table 3.1 The process solid loading at varying PCD efficiencies and purge rates

<table>
<thead>
<tr>
<th>PCD Efficiency</th>
<th>95%</th>
<th>99.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids Circulation (tons per hour)</td>
<td>Solids Circulation (tons per hour)</td>
<td></td>
</tr>
<tr>
<td>Carbonator: 1586</td>
<td>Carbonator: 3244</td>
<td></td>
</tr>
<tr>
<td>Calciner: 1787</td>
<td>Calciner: 3441</td>
<td></td>
</tr>
<tr>
<td>Hydrator: 1286</td>
<td>Hydrator: 2942</td>
<td></td>
</tr>
<tr>
<td>Fresh Feed: 105</td>
<td>Fresh Feed: 31</td>
<td></td>
</tr>
<tr>
<td>Solids Exit: 88</td>
<td>Solids Exit: 17</td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids Circulation (tons per hour)</td>
<td>Solids Circulation (tons per hour)</td>
<td></td>
</tr>
<tr>
<td>Carbonator: 1415</td>
<td>Carbonator: 1557</td>
<td></td>
</tr>
<tr>
<td>Calciner: 1628</td>
<td>Calciner: 1759</td>
<td></td>
</tr>
<tr>
<td>Hydrator: 1115</td>
<td>Hydrator: 1256</td>
<td></td>
</tr>
<tr>
<td>Fresh Feed: 184</td>
<td>Fresh Feed: 113</td>
<td></td>
</tr>
<tr>
<td>Solids Exit: 80</td>
<td>Solids Exit: 9</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids Circulation (tons per hour)</td>
<td>Solids Circulation (tons per hour)</td>
<td></td>
</tr>
<tr>
<td>Carbonator: 1353</td>
<td>Carbonator: 1403</td>
<td></td>
</tr>
<tr>
<td>Calciner: 1577</td>
<td>Calciner: 1617</td>
<td></td>
</tr>
<tr>
<td>Hydrator: 1052</td>
<td>Hydrator: 1102</td>
<td></td>
</tr>
<tr>
<td>Fresh Feed: 263</td>
<td>Fresh Feed: 193</td>
<td></td>
</tr>
<tr>
<td>Solids Exit: 77</td>
<td>Solids Exit: 8</td>
<td></td>
</tr>
</tbody>
</table>
3.1.3 Previous and Current Cyclone Design

The 120kW\textsubscript{th} CCR facility previously included a metallic cyclone, which, however, was never properly tested due to the failure of a rotary valve that was intended to create a seal at the bottom of the cyclone and capture the solids. The picture of the cyclone and its physical dimensions are shown in Figure 3.2 (Wang, 2011). This metal cyclone was disconnected from the CCR process and tested independently under cold flow conditions for its efficiency.

![Image of previous CCR cyclone](image-url)

**Figure 3.2** Image (left) and physical dimensions (right) of the previous CCR cyclone
The metal cyclone, as specified by the manufacturer, has a capture efficiency over 97% for particles larger than 4 microns and 72% for particles larger than 1.5 micron under the right operating conditions.

Even though the specified operating conditions are consistent with CCR operating conditions, the metal cyclone failed to capture 5 micron calcium hydroxide particles at the specified efficiency. As aforementioned, one possible explanation is the failure of rotary valve. In addition, reaction conditions at high temperature are difficult to predict due to changes in gas flow rate, density and viscosity.

For the CCR process to perform as designed, the PCDs must be able to efficiently capture 5 micron calcium hydroxide particles. Two plexi-glass cyclones were designed by PSRI, Particulate Solids Research Inc., for cold flow testing of the CCR process. The dimensions of Cyclone 1 and 2 are shown in Figure 3.3 (Wang, 2011). According to the manufacturer specifications, Cyclone 1 was designed to remove particles 250 μm and above, and Cyclone 2 removes finer particles with mean diameter of about 5 μm. The two cyclones were connected in series to improve overall capture efficiency. Ideally, Cyclone 2 would capture the finer Ca(OH)₂ derived CaCO₃ particles and send them to the calciner for decomposition. Cyclone 1 would capture the coarse particles (>250 μm) back to the hydrator for sorbent reactivation.
Figure 3.3 Current Cyclone Design #1 (left) and #2 (right)
The goal of this experiment was to investigate whether the two cyclones can provide adequate gas-solid separation and particle elutriation by size without exerting an excessive amount of pressure drop to the CCR process.

3.2 MATERIALS AND METHODS

To simulate the flow conditions of the CCR process, the two cyclones were connected to the CCR ductwork just prior to the blastgate leading to the baghouse. A Dwyer Series 160S pitot tube was positioned upstream of the cyclones to measure, at three radial positions, the pressure drop profile, which determines the inlet gas velocity entering the cyclone setup. Even though a manometer was attached to the inlet and outlet pressure taps to measure the cyclone pressure drop, solid accumulation in the pressure ports significantly affected the reliability and accuracy of the pressure readings. External vibration was exerted to the cyclone during testing to reduce solid coating onto the inner cyclone wall. Excess solid deposition can increase wall friction, and reduce effective cyclone diameter, both of which have negative effects on the capture efficiency. Detailed experiment schematics are shown in Figure 3.4. The two cyclones were tested both in series and independently.

During operation, solids were manually fed into the setup through the solid injection port at a rate that is equivalent to 1:1 Calcium: Carbon mole ratio solid flow rate in the 120
kW_{th} systems. For each run, the positive pressure air blower and negative pressure ID fan were operated at the desired setting for a short duration until stable conditions were reached prior to any solid injection. Graymont high-calcium calcium hydroxide (D_{50} = 10 μm) and Graymont high-calcium calcium oxide (D_{50} = 300 μm) were tested in a 50:50 weight percent blend (total mixture weight 20 pounds (9.5kg)) and independently (10 pounds (4.5kg)). The physical properties of the solid sorbent are listed in Table 3.2.

Figure 3.4 Experiment schematics of current study
Table 3.2 Physical properties of the solid sorbent for this study (NLA, 2007; Boyton, 1980)

<table>
<thead>
<tr>
<th>Particle</th>
<th>Ground Lime</th>
<th>Ca(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>True Density (g/cm³)</td>
<td>3.34</td>
<td>2.21</td>
</tr>
<tr>
<td>Packing Density (g/cm³)</td>
<td>0.88-0.96</td>
<td>0.40-0.56</td>
</tr>
<tr>
<td>Particle Size (µm)</td>
<td>D₅₀ = 300</td>
<td>D₅₀ &lt; 10</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>.44</td>
<td>26-32</td>
</tr>
<tr>
<td>Heat Capacity (J/mol*K)</td>
<td>49.95</td>
<td>83.89</td>
</tr>
</tbody>
</table>

The combined effects of air blower, compressed air injection and negative pressure from the variable speed ID fan allowed us to test the cyclone efficiency at various conditions. The compressed air injection was putting out a steady 75 SCFM of air. The air blower from the stoker was capable of producing gas flow rates of 50 SCFM according to its manual. The negative pressure induced flow from the ID fan was gauged by pressure drop (in. H₂O) across the fan. The exact volumetric flow rate produced by the ID fan was unknown. Therefore, we relied on the pitot tube measurements for the inlet gas velocity to the cyclones. Based on the manufacturer, the Dwyer Series 160S pitot tube was governed by the following empirical equation (3.2).

\[
u = 1096.2 \times C_p \times \sqrt{\frac{\Delta P}{\rho_g}} \quad Eqn(3.2)
\]
where $u$ is the superficial velocity, $C_p$ is the pitot tube coefficient equaling 0.84, $\Delta P$ is the sensed pressure difference (in. H$_2$O) across the pitot tube and $\rho_g$ is the gas density in lbs./ft.$^3$. For each configuration, the pitot tube traverses radially at four different locations as shown below in Figure 3.5. We averaged the four readings to obtain the final $\Delta P$ value.

![Figure 3.5 Pitot tube measurements](image)

Initially, the two cyclones were tested in series as designed. A 20 lbs. mixture of 50/50 wt% calcium oxide and calcium hydroxide was fed into the system at 4 lbs/min. Table
3.3 shows the experimental conditions, where solid loading was defined as kg solids / kg air.

<table>
<thead>
<tr>
<th>Positive Pressure Air Injection (scfm)</th>
<th>Negative Pressure Suction (inches H2O)</th>
<th>Air Velocity (m/s)</th>
<th>Solid Loading (kg solids/kg air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 + 75</td>
<td>0</td>
<td>2.96</td>
<td>1.05</td>
</tr>
<tr>
<td>50 + 75</td>
<td>20</td>
<td>6.16</td>
<td>0.50</td>
</tr>
<tr>
<td>50 + 75</td>
<td>35</td>
<td>9.85</td>
<td>0.32</td>
</tr>
</tbody>
</table>

3.3 RESULTS AND DISCUSSION

3.3.1 Cyclone Separation Efficiency

The cyclone’s separation efficiency and pressure drop are two of the most important parameters with respect to process economics. Typically, increasing gas velocity will lead to better separation efficiency but also higher pressure drop. As shown in Figure 3.6, both cyclones demonstrated exceptional solid removal capability, particularly at higher gas flow rates. Under pure positive pressure, the air velocity of 2.96 m/s was significantly lower than the cyclone’s designed operating velocity. Without sufficient air flow, solids-settling between the feed injection and cyclone inlet was an issue, which also led to
uneven transport and non-uniform solids loading. Lastly, without negative suction, it was
difficult to establish a tight seal at the cyclone’s solid collection drum. Leakage into the
collection drum reduces the cyclone’s separation efficiency.

When operated at high velocities, cyclone 1 removed over 95% of the solids while
cyclone 2 captured all of the remaining particulates. Since cyclone 1 was designed with a
cut-size of 250 μm, it was surprising to observe over 95% capture of a solid mixture that
also contained 50% wt of 5 μm calcium hydroxide. With most of the solids separated,
gas-solid flow into the cyclone 2 became very dilute relative to normal operating
conditions – about 1/20 of the solid loading into the first cyclone. As a result, despite its
robust separation efficiency, there was still a need to test the cyclone 2 independently at a
more reasonable solid loading level.
For testing the second cyclone, we injected 10 \( \mu \text{m} \) Ca(OH)\(_2\) particles at a rate of 4 lbs./min for consistency. The inlet gas flow conditions were consistent with those listed in Table 3.4. Assuming the cyclone efficiency would not be altered when tested either independently or as the first cyclone of a series, cyclone 1 was not included in this test. Testing results are presented in Table 3.4.
Table 3.4 Separation efficiency of the cyclone 2 when tested independently

<table>
<thead>
<tr>
<th>Air Velocity (m/s)</th>
<th>Solid Loading (kg solids/kg air)</th>
<th>Separation Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.96</td>
<td>1.05</td>
<td>100</td>
</tr>
<tr>
<td>6.16</td>
<td>0.50</td>
<td>76</td>
</tr>
<tr>
<td>9.85</td>
<td>0.32</td>
<td>100</td>
</tr>
</tbody>
</table>

The aberration at air velocity of 6.16 m/s cannot be fully explained. One possible cause could be minor leakage into the drum below the cyclone leading to disruption of normal operating conditions. If we neglect this procedural error, cyclone 2 performed exceptionally well for removal of 10 µm Ca(OH)₂ particles, per its design specifications.

3.3.2 Cyclone Grade Efficiency

A composition analysis of the separated solids by each cyclone was performed using a TGA. This study was able to determine each cyclone’s capability to capture the ultra-fine calcium hydroxide particles and, in addition, indirectly reflect on the cyclone grade efficiency. Figure 3.7 shows that with increasing inlet gas velocity, the capture efficiency of Ca(OH)₂ particles by the first cyclone decreased gradually. Higher gas velocity could improve the collection efficiency (Wan, 2003); however the cyclone grade efficiency
may suffer because a stronger vortex can carry more fine-tailing particulates out of the cyclone. This is acceptable because cyclone 1 was designed to separate particles on the scale of 250 µm. In addition, since the solid feed rate of 4 lbs./min was kept constant during these tests, increasing gas flow rate translated to decreasing solid loading at the cyclone inlet. Muschelknautz et al. (1970) suggested the theory of “critical load”, above which the solids were removed independent of their particle size. Our operating condition ranging from 0.32 to 1.05 kg solids / kg gas is equivalent of 372 to 1,239 g solids / m³ gas, which was well above the solid loading range considered by Muschelknautz (1970). For this case, we assumed the given solid loading level had negligible effect on the cyclone’s separation efficiency. The increased gas velocity directly contributed to a higher percent of fine Ca(OH)₂ particles escaping from the first cyclone.
As previously mentioned, the second cyclone captured 100% of the entrained solids from cyclone #1. Due to the first cyclone’s inefficiencies, more Ca(OH)$_2$ fines were available for separation as the test progressed. Thus we observed an increasing hydrate content in the solids captured by the second cyclone. Additional particle size distribution analysis on the separated solids from both cyclones confirmed this trend. About 300 g of solid sorbents were extracted from the drums of cyclone 1 and 2, respectively. The solids were subjected to sonic-vibration sieving using sieves with mesh sizes ranging from 20 µm to 700 µm. Results are shown in Figure 3.8 and 3.9.

Figure 3.7 A composition analysis of the separated solids by the two cyclones
Per its design specifications, the sieving study showed cyclone 1 had a cut-size $x_{50}$ between 250 µm and 300 µm. The particle size distribution of cyclone 1 solids exhibited a bimodal trend with peaks at 100 µm and 500 µm (Figure 3.9). This finding is consistent with previous results from the cyclone separation performance tests. Since cyclone 1 was able to capture over 95% of the solid feed consisting of half coarse CaO and half fine Ca(OH)$_2$ particles, the mean particle size is expected to fall somewhere between the 200-
300 µm range. The bimodal peaks corresponded to the particle size of the two feed species (Figure 3.9).

![Particle size distribution](image)

**Figure 3.9 Particle size distributions of solids captured by the two cyclones**

Coarse ground lime has a known mean particle size $d_{50} = 300$ µm, which is accurately measured through sieving. Ca(OH)$_2$ particles are very fine and typically less than 10 µm in size. For granular materials finer than 150 µm, accuracy of dry sieving measurements
is significantly compromised – partly due to the surface effects between the particles themselves and between the particles and sieve apertures. Geldart Type C particles, such as Ca(OH)$_2$, can be very cohesive and easily form agglomerates, especially when induced by vibration. In fact, particle agglomeration was evident on the sieves with mesh size less than 150 µm. Therefore, it is safe to assume that the limitations of the sieving process prevented a true representation of Ca(OH)$_2$ particle size distribution. It was confirmed that the material from the 106 µm and 149 µm sieves was indeed Ca(OH)$_2$ via further TGA analysis.

Similarly, the results indicated the cut-off size for cyclone 2 was in the 100 µm range, which actually represented agglomerates of Ca(OH)$_2$ particles with true particle size less than 10 µm. Although the sieve measurements for fine particles were appreciably less accurate, it still provided a means of understanding which particle species was captured by each cyclone – whether coarse or fine. Furthermore, knowledge of the exact form of the grade efficiency is less important because the separation efficiency or total mass recovery of each cyclone, has more practical implications for industrial applications.
3.3.3 Scale up for High Temperature Operation

Thus far, the two cold model cyclones have demonstrated exceptional solid separation capacity at room temperature. Both cyclones operated according to their design grade efficiency. The first cyclone performed better than expected by capturing over 95% of the solid feed regardless of their particle size distribution (Figure 8.9). The second cyclone effectively removed all the remaining solids composed primarily of fine Ca(OH)$_2$ particles.

<table>
<thead>
<tr>
<th>Table 3.5 Denotations for dimensions of the two cyclones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclone Dimensions (in.)</td>
</tr>
<tr>
<td>Diameter cylinder, Dc</td>
</tr>
<tr>
<td>Length cylinder, H1</td>
</tr>
<tr>
<td>Length conical section, H2</td>
</tr>
<tr>
<td>Diameter apex, Da</td>
</tr>
<tr>
<td>Diameter vortex finder, Dvf</td>
</tr>
<tr>
<td>Height gas inlet, Hi</td>
</tr>
<tr>
<td>Width gas inlet, Wi</td>
</tr>
</tbody>
</table>

Considering the overall design of the CCR process, particulate capture devices (PCD) such as the cyclones will be installed post-carbonator where the operating temperature is
in the range of 650 °C – 700 °C. We must use our knowledge of empirical correlations to estimate the cyclone performance when scaled up to high temperature operations. Traditionally researchers have predicted cyclone performance using direct correlations based on the cyclone geometry and flow properties, such as the procedure by Leith and Licht (1980). More recent cyclone design methods utilize two important dimensionless groups: the resistance coefficient defined as the Euler number, Eu (Dewil, 2008) and the Stokes number Stk50, shown in Equations (3.3) and (3.4).

\[
Eu = 9.84 \times \frac{D_c^2}{h_{lw} D_{cf}^2} - 24.3 \quad \text{(Eqn 3.3)}
\]

where the denotations for cyclone dimensions are listed in Table 3.5.

The Stokes number is typically defined as:

\[
Stk_{50} = \frac{x_{0_{50}} \rho_s \cdot v}{18 \mu \cdot D_c} \quad \text{(Eqn 3.4)}
\]

as where \(\mu\) is the gas viscosity and \(\rho_s\) is the solid density and the characteristic velocity \(v\) is defined as:

\[
v = \frac{4Q}{\pi D_c^2}
\]

Where Q is the volumetric gas flow rate and \(D_c\) is the cyclone inside diameter.
For well-designed cyclones, the two dimensionless groups can be directly correlated by (Svarovski, 1986),

$$Stk_{50} = \frac{12}{E u^2}$$

Other researchers also provided alternative definitions of Stk50:

Davis (1952)

$$Stk_{50} = \frac{h_i \cdot w_i}{D_c^2} \cdot \frac{D_c}{H_c} \cdot \frac{1}{4\pi} \left[ 1 - \left( 1 - \frac{w_i}{D_c} \right)^4 \right]$$

Barth (1956)

$$Stk_{50} = \frac{8}{\pi} \cdot \alpha \cdot \left( \frac{w_i}{D_c} \right)^2 \cdot \left( \frac{h_i}{D_c} \right)^2 \cdot \left( \frac{D_{of}}{D_c} \right)^2,$$

$$\alpha = \frac{(Q/\pi) \cdot D_{of}^2/4}{Q/h_i w_i}$$

According to the correlations above, we can calculate the Stokes number based on the known cyclone dimensions, listed in Table 3.6.

For determining the cut-size, $x_{50}$, we can back-calculate using Equation (3.4) once we find the appropriate approximation for the Stokes number. None of the empirical correlations in Table 3.6 accurately approximates the cut-size of our cyclones. One possible reason is that Ca(OH)$_2$ powder’s cohesive property can lead to abnormal results,
i.e. coating on the cyclone inner wall and yielding higher wall friction coefficient or forming agglomerates due to the electrostatic interactions in the cyclone.
Table 3.6 Calculated Stokes number for the two cyclones based on the known cyclone dimensions

<table>
<thead>
<tr>
<th></th>
<th>Cyclone #1</th>
<th>Cyclone #2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T (°C)</strong></td>
<td>25</td>
<td>650</td>
</tr>
<tr>
<td><strong>P (atm)</strong></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>ρ (kg/m³)</strong></td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td><strong>ρ_s (kg/m³)</strong></td>
<td>2211</td>
<td>2211</td>
</tr>
<tr>
<td><strong>μ (Ns/m²)</strong></td>
<td>2.18E-05</td>
<td>3.96E-05</td>
</tr>
<tr>
<td><strong>Q (m³/s)</strong></td>
<td>0.08</td>
<td>0.188</td>
</tr>
<tr>
<td><strong>Feed (kg/s)</strong></td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td><strong>Cs (kg s/kg g)</strong></td>
<td>0.44</td>
<td>0.19</td>
</tr>
<tr>
<td><strong>v (m/s)</strong></td>
<td>2.47</td>
<td>5.80</td>
</tr>
<tr>
<td><strong>Svarovsky (1986)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Eu</strong></td>
<td>513.1</td>
<td>513.1</td>
</tr>
<tr>
<td><strong>Stk50</strong></td>
<td>4.6E-05</td>
<td>4.6E-05</td>
</tr>
<tr>
<td><strong>X50 (m)</strong></td>
<td>8.2E-07</td>
<td>7.2E-07</td>
</tr>
<tr>
<td><strong>Davies (1952)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Stk50</strong></td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td><strong>X50 (m)</strong></td>
<td>6.9E-06</td>
<td>6.1E-06</td>
</tr>
<tr>
<td><strong>Barth (1956)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>α</strong></td>
<td>5.971</td>
<td>5.971</td>
</tr>
<tr>
<td><strong>Stk50</strong></td>
<td>0.0166</td>
<td>0.0166</td>
</tr>
<tr>
<td><strong>X50 (m)</strong></td>
<td>1.56E-05</td>
<td>1.37E-05</td>
</tr>
<tr>
<td><strong>Experimental</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>X50 (m)</strong></td>
<td>2.60E-04</td>
<td>1.00E-05</td>
</tr>
</tbody>
</table>
In theory, the dimensionless number calculations of Eu and Stk_{50} should offer reasonable estimations for cyclone performance when scaling up to high temperature or high pressure operations. The effects of change in gas viscosity and density are both accounted for in the expression for X_{50}. In this case, the exact empirical prediction of the cyclone cut-size is not as critical as the overall mass recovery for our interests. Despite the inaccurate estimation, the calculations provided some useful information on the relative trend of cyclone performance when the operating temperature is increased. At the CCR operation temperature of 650°C, the gas viscosity almost double that at room temperature. According to Equation (3.4), this will lead to larger cyclone cut-size. However, at higher temperature, volumetric gas flow rate will also increase due to thermal expansion, thus the characteristic velocity will become higher. These two effects offset each other. At our operating conditions, all three empirical correlations predicted a slight decrease in cyclone cut-size for both cyclones if the operating temperature increased to 650°C.

Comparing the grade efficiency of the two cyclones, calculations indicated the cut-size was progressively lowered by 65-80% moving from the first cyclone to the second. This is consistent with the original design of this two-stage cyclone setup. Ca(OH)₂ particles are expected to agglomerate entering the cyclones. The first cyclone should have higher solid loading and lower inlet gas velocity and thus separate the coarse and agglomerated particles. As a result, the second cyclone will receive a much more dilute feed. Although
decreased solid loading can reduce the separation efficiency (Hoffman, 1992), the second cyclone captured 100% of the feed containing mostly fine Ca(OH)₂ particles during our experiments.

3.4 CONCLUSION

In this study, we conducted an extensive test on two prototypes of cyclone separators designed for the CCR process. The cyclones were installed onto the existing CCR framework so that we were able to simulate the flow conditions used for the actual experiment. A 50/50 weight % mixture of coarse ground lime and finer calcium hydroxide particles was used as the feed stock. Both the gas flow rate and solid feed rate were adjusted to emulate the CCR operating conditions. Because the prototypes were fabricated using plexi-glass, our operating temperature was limited to ambient conditions.

Both cyclones demonstrated exceptionally high solid separation efficiency under our testing conditions. The first cyclone achieved higher than expected separation efficiency – removing over 95% of both 300 µm and 10 µm particles. Its dimensions have been proven to be adequate for the CCR solid loading level as no sign of clogging was observed. Due to the first cyclone’s robust performance, only a very dilute stream of solids, consisting of mostly 10 µm Ca(OH)₂ particles, was fed to the second cyclone. Despite the reduced solid loading in the feed stream, the second cyclone still effectively
captured all the fine tailing particles. An independent test of the second cyclone under higher inlet solid concentration produced consistent results.

In general, the effects of increased temperature on cyclone performance can be broadly predicted using empirical correlations. Based on our calculations, the cyclone cut size should decrease with increasing temperature. However, for practical cyclone applications, the overall mass separation efficiency is often more important. Although the separation efficiency is known to be affected by temperature, most known predictions are not completely reliable. Part of the reason is that the effects of agglomeration or attrition have not been properly investigated, and high temperatures can be conducive to aggregation or even sintering of agglomerates. This may be a realistic concern for our application because Ca(OH)$_2$ particles are known to be cohesive. The dimensionless Stokes number, Stk$_{50}$, based calculations can provide some useful information as it accounts for the change in gas viscosity and density with respect to change in temperature. For the CCR process, in addition to thermal expansion of the gas stream, combustion of coal will also produce a significant amount of flue gas compared to our cold flow model testing conditions. Consequently, the actual solid loading during CCR operation may be appreciably lower, which can reduce the overall separation efficiency. However, that reduction in performance is not expected to be too large, and the cyclone cut-size should be within an order of magnitude of the measurements from ambient tests.
CHAPTER 4

DESIGN OF A BENCH-SCALE HYDRATION REACTOR

4.1 INTRODUCTION

As an extension of the calcium sorbent-based clean coal technologies developed at The Ohio State University, this study focused efforts on the design of a bench-scale mechanically-agitated-bubbling fluidized bed reactor that is capable of reactivating the spent lime sorbents via steam hydration. For simplicity, we will refer to this reactor as the hydrator.

Calcium sorbents provide an attractive route for high temperature CO$_2$ capture. Calcium oxide (CaO) captures carbon dioxide (CO$_2$) via the high temperature carbonation reaction. The spent sorbent (CaCO$_3$) is then regenerated via the calcination process at over 900 °C. However, thermal induced sintering can severely reduce the sorbents reactivity toward CO$_2$. Hydration can be a promising sorbent reactivation method for recovering some of the loss in reactivity toward CO$_2$. However, for a more efficient integration into the high temperature CCR process, the hydration stage also needs to be held at elevated temperature (300- 500 °C).
Thus far, at a reasonable calcium to carbon ratio of 1.4:1, the CCR process has demonstrated over 90% CO₂ and nearly 100% SO₂ removal from the coal combustion flue gas stream at our 120 kWₘₜ subpilot facility (Wang, 2010). ASPEN simulation of the CCR Process integrated into a typical 500 MWₑ pulverized-coal power plant further demonstrated its superior energy efficiency to competing technologies – amine scrubbing and oxy-combustion. Wang et al. (2012) showed that, with intermediate hydration, a mere 20-22% decrease in electricity generation efficiency would be incurred on the power plant; however, this is under the assumption that the exothermic heat of reaction can theoretically be extracted from the high temperature (>350 °C) steam hydration step, and then utilized in the Steam Turbine Cycle.

Steam hydration as a feasible means of reactivating spent limestone sorbent has been studied extensively (Yu et al., 2012). Furthermore, multi-cyclic steam hydration has been studied extensively in a small laboratory-scale fixed bed. Based on our investigation, steam hydration can maintain sorbent CO₂ capture capacity at nearly 50% for over 15 cycles. Although increased recyclability may be required for better economics on the industrial scale, the decay in sorbent reactivity during our study was not significant over the 15 cycles. These promising results encouraged us to design a larger bench-scale hydration reactor that can better represent realistic operating conditions and overcome several limitations of the fixed bed reactor:
• Fixed bed experimental results can differ significantly from that of fluidized bed reactors. A dense phase bubbling fluidized bed reactor can offer higher heat and mass transfer rates from gas to particle leading to uniform temperature and solid distributions in the bed. This is especially true for Ca(OH)\(_2\) particles – a Geldart Type C powder that is difficult to fluidize. Thus, it’s imperative for us to conduct a detailed study of the fluidization behavior of such particles.

• Significant pressure build-up was observed during fixed bed operation that may have skewed the overall hydration conversion. Our goal is to design a hydration reactor that operates at elevated temperature (>350 °C) and ambient pressure. A pressurized reactor would incur additional capital and operating cost, and create design complications for integrating into the CCR process, which operates at a slight negative pressure.

• The aforementioned series of fixed bed experiments were conducted using excess steam to achieve isothermal reaction conditions. The steam to calcium ratio reached as high as 30 to 1, which would be uneconomical for an industrial process. The current study will utilize realistic steam to calcium ratios for more practical results.
4.2 MATERIALS AND DESIGN

4.2.1 Reaction Chemistry and Particle Properties:
Lime hydration is an exothermic reaction (Eqn 4.1) that occurs spontaneously at room temperature. The idea of utilizing this reaction for sorbent reactivation was first suggested by Argonne National Laboratories in 1980 for SO₂ removal using lime (Shearer et al., 1980). Their report proposed that formation of calcium hydrate (Ca(OH)₂), whose molar volume is greater than that of lime, followed the process of particle expansion, surface cracking and eventual flaking off of hydrate particles.

\[
CaO + H_2O \xrightleftharpoons{\text{Hydration}} \xrightleftharpoons{\text{Dehydration}} Ca(OH)_2 \quad (\text{Eqn 4.1})
\]

\[\Delta H = -105 \text{ kJ/mol}\]

Calcium hydrate, formed through both steam and water hydration, has natural particle size less than 10 μm - much smaller than that of generic ground lime. In addition, Ca(OH)₂ particles exhibit greater surface area and pore volume (Boynton, 1980; Boateng, 2008), which allow for faster mass transfer kinetics and higher carbonation conversion (Yu., F.C. et al., 2012).

Hydration of lime can proceed via two options: water or steam hydration. Commercially, lime hydration is achieved by slaking quicklime with liquid water in stirred tanks.
Temperature of the slurry is carefully controlled by adding excess water to absorb the exothermic heat of reaction. Although low temperature hydration can produce highly reactive sorbent, its integration into a high temperature system, such as the CCR process, will impose severe energy penalties. In contrast, high temperature hydration using superheated steam produces high quality heat that can contribute to additional electricity generation in the Steam Turbine Cycle (Fan, 2008). The thermo-equilibrium data, shown in Figure 4.1, indicate that 1 atm partial pressure of steam corresponds to equilibrium temperature of 518 °C (HSC Chemistry, 2008). Due to the cohesiveness and fouling tendency of Ca(OH)₂ powder, we anticipate heat extraction from the hydration reactor to be a challenge. Considering the reaction’s high exothermicity, the practical hydration temperature in the CCR process was limited to the 350 – 450°C range.
Figure 4.1 Thermodynamic relationship between Ca(OH)$_2$ and H$_2$O partial pressure

Hydration of lime produces a very fine and cohesive particle that is difficult to fluidize. Table 4.1 below contains the physical properties of both the reactant (calcined pulverized limestone) and product (calcium hydroxide). The pulverized limestone from Graymont was decomposed in the rotary calciner from the 120 kW$_{th}$ CCR process to produce fresh CaO.
Table 4.1 Solid Sorbent Physical Properties (from NLA, 2007; and Boynton, 2008)

<table>
<thead>
<tr>
<th>Particle</th>
<th>Calcined Graymont Pulverized Limestone</th>
<th>Graymont High-Calcium Ca(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>True Density (g/cm$^3$)</td>
<td>3.34</td>
<td>2.21</td>
</tr>
<tr>
<td>Packing Density (g/cm$^3$)</td>
<td>0.88-0.96</td>
<td>0.40-0.56</td>
</tr>
<tr>
<td>Particle Size ($\mu$m)</td>
<td>D$_{50} = 20$</td>
<td>D$_{50} &lt; 10$</td>
</tr>
<tr>
<td>Surface Area (m$^2$/g)</td>
<td>.44</td>
<td>26-32</td>
</tr>
<tr>
<td>Heat Capacity (J/mol*K)</td>
<td>49.95</td>
<td>83.89</td>
</tr>
<tr>
<td>Min Fluidization Velocity (cm/s)</td>
<td>$4.08 \times 10^{-2}$</td>
<td>$1.68 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The theoretical minimum fluidization velocity was calculated based on the Wen and Yu equations (Eqn 4.2 & 4.3; Wen, 2003):

$$u_{mf} = \frac{\mu_g}{\rho_g d_p} \left[ \sqrt{33.7^2 + 0.0408 \times Ar} - 33.7 \right] \quad (Eqn \ 4.2)$$

and

$$Ar = \frac{\rho_g (\rho_p - \rho_g) g d_p^3}{\mu_g^2} \quad (Eqn \ 4.3)$$
where $\mu_g$ is the dynamic gas viscosity (kg m$^{-1}$ sec), $\rho_g$ is the density of carrier gas (kg/m$^3$), $d_p$ is the solid particle size (m) and $Ar$ is the Archimedes number defined in Eqn 4.3.

4.2.2 Design Considerations:

From the solid particle size and density listed in Table 4.1, we point out both calcined pulverized limestone and calcium hydroxide particles belong to Geldart Group C (Figure 4.2). Fluidization of such particles poses a realistic challenge because of the presence of strong inter-particle interactions, such as van der Waals, capillary and electrostatic forces, all of which apply for Ca(OH)$_2$ particles. Usage of steam as the fluidization medium and elevated reaction temperature both are expected to complicate the fluidization behavior. Increased moisture content can induce stronger capillary and van der Waals forces. Elevated temperature will decrease gas density and viscosity – leading to reduced motive force and higher bed voidage.
In fact, Geldart stated that Group C particles could not be subjected to normal fluidization (Geldart, 1973). Fluidization of such particles under typical settings would commonly result in slugging or channeling flow (Fan, 1998), which likely occurred during our previous hydration study using a 2” ID fluidized bed reactor. One possible solution was the addition of a fluidization aid. In the past, operation of the CCR process relied on the assistance of coarse CaO particles as a fluidization aid. However, in an industrial process, addition of a fluidization aid will increase the solid loading, which can lead to other
detrimental effects to overall process efficiency – amount of solid circulation directly affects reactor size, process operating cost and parasitic energy consumption.

Refer to Figure 4.3 for the relationship between increasing gas velocity and various fluidization regimes; we have already discussed the adverse effects of the fixed bed operation; however, operating in the accelerated lean-phase regime may not be suitable either. High temperature steam hydration proceeds at a slower rate than water hydration. In fact, the reported residence time required for steam hydration to achieve sufficient sorbent reactivation is in the range of 15-20 minutes (Laursen, 2003; Zeman, 2008).
Turbulent and fast fluidization regimes are better suited for rapid reactions with residence time in the order of seconds, such as the carbonation reactor of the CCR process. If we were to design a hydration reactor that operates in the turbulent regime, it would be difficult to control the elutriation of fine calcium powder. In addition, the necessary reactor size allowing for sufficient residence time and the amount of steam required to achieve the operating gas velocity would be considered uneconomical for industrial implementation. Therefore, bubbling fluidization is the most feasible operating regime for this high temperature steam hydration reactor. Formation of bubbles will induce vigorous particle motions and improved solid-gas contact. Under this approach, a bench scale plexi-glass hydrator prototype was fabricated for preliminary hydrodynamic study.

4.3 COLD-MODEL HYDRATOR PROTOTYPE

Figure 4.4 illustrates the design and dimensions of the cold model hydrator setup. Figure 4.5 shows the actual pictures of (a) the plexi-glass hydrator, (b) the mixer, and (c) the central air nozzle. Cold model experiments in the hydrator were carried out using compressed air. The hydrator consists of a porous polymeric perforated plate that sits between the plenum and reactor body, an internal mixer and a secondary air injection nozzle. The main bed stands 12 inches tall with inner diameter (ID) of 5 inches. An inclined standpipe is positioned at 5 inches above the perforated plate for gas and solid discharge. A separate gas exhaust is located on the top flange for additional gas relief. An
optional hopper / screwfeeder, identical in size to the reactor, can be attached for solid feeding during continuous operation.

Figure 4.4 Schematic diagram of cold model hydrator

This hydrator can operate in either batch or continuous mode, depending on the experiment type, by sealing the downpipe and screw feed inlet. Batch mode operation is
better suited for study of reactor hydrodynamics with respect to various gas flow rates, gas distribution between bottom and central inlets, and mixer rotation rate. Continuous operation was primarily set up to study the average solid residence time with respective to bed height, standpipe location, gas flow rate and solid feed rate.

Figure 4.5 Photographs of (a) the reactor body, (b) double-helical mixer, and (c) central jet injection nozzle

Graymont high-calcium calcium hydroxide (Table 4.1) was the primary sorbent used for hydrodynamic testing. Mixtures of calcium hydroxide and calcined pulverized limestone
were also tested to investigate potential solid segregation. Hydration of calcium oxide will alter the particle morphology and grain size (Laursen, 2001). The extent of this effect also depends on the type of calcium sorbent feed. For our study, the calcined pulverized limestone \((d_p \approx 20\mu m)\) has similar fluidization behavior as calcium hydroxide. However, if we were to use 300\(\mu m\) Graymont ground lime, this effect of solid segregation may be more significant.

4.3.1 Key Design Features:

Double Helical Mixer

Geldart C type particles, such as \(\text{Ca(OH)}_2\), have the tendency to agglomerate while fluidized. Formation of larger and denser agglomerates can compromise the gas-solid mixing because these aggregates are impermeable to the gas flow (Valverde, 2011). We expect severe agglomeration in the hydration reactor for two reason: (1) the cohesive nature of \(\text{Ca(OH)}_2\) powder, and (2) the use of steam as the fluidization medium. For calcium sorbents, fluidization without assistance tends to behave as “agglomerate bubbling fluidization” (ABF) with very little bed expansion and higher than normal gas bypassing through either channeling or large bubble formation (Wang et al. 2002). Generally, “agglomerate particulate fluidization” (APF) is preferred because it represents a more uniform liquid-like flow. It has been suggested that agglomerates larger than 500
μm should be removed or broken apart for better fluidization quality (Ruud van Ommen et al., 2012). Therefore, the double helical mixer was installed to provide external assistance through mechanical stirring motion. The mixer was positioned at the bottom of the reactor, where it scraped closely to both the perforated plate and the reactor wall. King’s study (2008) has shown that radial stirring can prevent channel formation, and complement the axial flow of fluidizing gas. In addition, the wall scraping motion can help break up larger agglomerates, which tend to accumulate at the reactor base near the wall.

**Central Jet Injection Nozzle**

Secondary flow in the form of microjets can also improve the fluidization by promoting more turbulent mixing. Microjet assistance in some cases can convert ABF type behavior to APF type behavior. Quevedo et al. (2010) have shown that, at sufficient velocity (up to 100 m/s), microjet injection can significantly increase the bed expansion during fluidization, and produce a smoother and more homogeneous flow with very little elutriation. For our hydration reactor, the jet injection nozzle is positioned in the center of the reactor to complement the stirring effect from the mixer. As shown in Figure 4.5(c), 1mm injection holes pointing horizontally outward at every 45 deg are located at varying heights on the nozzle. Others (Pfeffer and Quevedo, 2011) have suggested secondary microjet flow should be at a higher pressure than the primary flow through the air.
distributor to: (1) prevent gas/solid backflow into the nozzle, and (2) create sufficient jet velocity. The horizontal jet penetration should be strong enough to create a coupling effect between the nozzle and the mixer blade scraping the wall. Jet penetration length is a complicated parameter that varies with gas flow rate, orifice size and the fluidization regime in the bed (Wang, 2010; Chyang, 1997).

4.3.2 Observations and Discussion:

This plexi-glass cold model study provided some very important information on the fluidization behavior of Ca(OH)\textsubscript{2} powder in this prototype hydrator. The inherent challenges from fluidizing a Geldart Group C particle, specifically fouling of pressure ports, did not allow us to perform a more quantitative study. Fluidization information was gathered via visual observations that were noted and recorded using a video camera. We have relied on these in designing the high temperature hydration reactor:

- For pure Ca(OH)\textsubscript{2} powder, the actual minimum fluidization velocity (without agitation or central air injection) of 4 cm/s far exceeds the calculated value of \(1.68 \times 10^{-3} \text{ cm/s}\) from Wen and Yu (Eqn 2 & 3). Although we understood the Wen and Yu Equation was not well-suited for predicting the minimum fluidization velocity of fine materials (Gupta, 2009; Xu, 2009), we didn’t expect the estimation to be off by a factor of 1000. Particle agglomeration was the likely
reason for this miscalculation. As others have suggested, agglomeration has a strong effect on the minimum fluidization voidage - an important parameter in the Ergun Equation. Uniform fluidization under this condition was more closely correlated to the agglomerate properties instead of their original particle size (Valverde, 2007).

- For pure Ca(OH)$_2$ powder, the optimal fluidization condition was found at the air flow rate of 4.8 SCFM, corresponding to superficial velocity $U = 18 \text{ cm/s}$, with the assistance of both mechanical agitation and central jet injection ($\approx 1.5 \text{ SCFM}$). At this setting, the fluidization was “smooth” meaning no large bubble or channel was observed.

- For a 50/50 weight mixture of calcined pulverized limestone and Ca(OH)$_2$, satisfactory fluidization was achieved at air flow rate of 2.0 SCFM ($U = 7.5 \text{ cm/s}$), and with the assistance of both agitation and central jet injection at $\approx 1 \text{ SCFM}$. Less gas was required to fluidize this mixture - a trend that was consistent with the Wen and Yu calculations, as the $U_{mf}$ for calcined pulverized limestone is significantly lower than that of Ca(OH)$_2$.

- The addition of mechanical mixing and central jet injection significantly enhanced the fluidization pattern. As designed, the mixer’s rotary motion exerted sufficient shear and radial grinding force on the neighboring solids to reduce agglomerate growth and prevent channeling and large bubble formation. Furthermore, secondary microjet injection at the center introduced more turbulent mixing.
Collectively, the microjets would push the solids outward to the mixer so they will be exposed to the stirring effect. If the mixer was abruptly stopped while operating at the aforementioned favorable conditions, the bed would immediately develop permanent channels through which the majority of gas flow would bypass.

- Even with agitation assistance, noticeable amounts agglomerates were formed during fluidization. These aggregates had average particle size of 1-3 mm, and they tended to accumulate in the low gas velocity regions of the reactor bed, such as the base of the reactor especially near the wall. Improved mixer design or increased gas flow should mitigate this problem.

4.4 BENCH-SCALE HIGH TEMPERATURE HYDRATOR:

A bench-scale stainless steel reactor was constructed based on the cold model design (Figure 4.6). Minor modifications were made to the mixer so that it swept more closely to the reactor wall, and bottom blades could cover the entire gas distributor plate (Figure 4.7).
Figure 4.6 Schematic diagram of high temperature hydrator.
4.4.1 Key Design Modifications:

**Vertical Baffles**

Two thermocouples were inserted from the top reactor flange to: (a) accurately monitor the solid temperature profile during reaction, as hydration is highly exothermic, (b) act as
internal baffles to promote better mixing. Vertical rods, such as the rigid ¼” thermocouples in this case, are desirable for fluidized bed applications due to their design simplicity, ease of installation and removal, and no interference with reactor loading or emptying (Davidson, Harrison and Grace, 1971). Insertion of vertical baffles could reduce bubble coalescences (Grace, 1968); in our case, we expected the combined effect with the radial stirring motion of the mixer could prevent large bubble formation. For future scale-up considerations, these vertical baffles can also be in the forms of heating/cooling tubes. However, these vertical baffles cannot be placed too close together as they are also capable of inducing gas channeling through the gaps (Grace and Harrison, 1968a).

4.4.2 Observations and Discussion:

From the cold model study, we found the optimal gas flow for fluidizing pulverized calcined limestone was 2 SCFM. This total flow rate was used as a basis for the following fluidization tests. Clip 1 below compares the high temperature (250°C) fluidization pattern using pure steam, 50/50 mixture of steam and air, and just preheated air as the fluidization medium. Clip 2 shows the effects from the baffle and mechanical mixer. Clip 3 demonstrates the effect of a side secondary air injection port.
Preheated air (250°C) produced a satisfactory fluidization pattern that was similar to if not more vigorous than using ambient compressed air. This was expected as heated air had higher viscosity and larger volumetric flow rate. Fluidization using pure steam (250°C) was unsuccessful. The solid bed was virtually defluidized, and the sole agitation pattern was derived from the mixer’s stirring motion. Instead of forming round agglomerates, the particles solidified into large chunks – a phenomenon likely induced by the hydration reaction. The encouraging discovery was that diluting superheated steam with air significantly improved the fluidization behavior. As shown in the last part of the clip, the mixture of 50/50 steam and air yielded sufficiently vigorous mixing. According to HSC chemistry (2008), at 50% steam partial pressure, the hydration thermodynamics should still favor the forward reaction as long as the temperature does not exceed 450°C, which is within our operating range.

Clip 2: High temperature fluidization with external assistance

Presence of the vertical baffle and mechanical agitation significantly improved the fluidization pattern in the reactor. In particular, the mixer’s radial stirring motion was the key to mitigating gas channeling. However, this stirring motion alone was insufficient because spots of defluidization were still observed without the baffle assistance. Part of
the reason may be attributed to the rotation rate of the mixer. As limited by the motor capacity, the highest possible mixing speed was set at 21 rpm. With a more powerful motor, the mixing motion alone may provide sufficient agitation for the proper operation of the hydrator. The addition of the vertical baffle effectively broke up the defluidized chunks to create a uniform fluidization regime, shown in the first segment of the video. Granted, 33% air dilution was necessary to achieve this smooth fluidization behavior, we need to further investigate the reaction kinetics at this steam partial pressure to conclude whether this configuration is feasible. Ideally, we want to minimize the amount of air dilution because, by maximizing the steam pressure, we can achieve faster hydration kinetics and better overall conversion. Unfortunately, fluidizing with pure steam with both vertical baffle and mixer was less effective. In the last segment of the video, as soon as the mixer was stopped, multiple gas jets immediately penetrated through the bed of solids to form stable channels. This confirms that operating the lime hydration in a traditional fluidized bed reactor is not feasible. Without any external assistance, fluidization of fine Ca(OH)₂ particles will lead to severe channeling.

Clip 3: High temperature fluidization with dual gas injection

The original design of the central air injection nozzle proved to be rather ineffective in the high temperature hydrator. Part of the reason could be attributed to the limited capacity and pressure threshold of the steam generator. Consequently, the saturated steam
feed could not generate as much motive force as compressed air. In addition, steam-
sorbent contact would lead to immediate hydration reaction and consumption of the
injected steam. Combination of these effects drastically reduced the penetration distance
of central gas injection, thus mitigating its effectiveness. From my observation, in our
operating range, the central gas injection as originally designed could only penetrate 1/3
to half of the reactor radius, which translates to just 1/9 or 1/4 of the reactor volume
(Figure 4.8).

One solution to that problem is to relocate the gas injection nozzle to an off-set position,
such as at the midpoint between reactor center and wall, shown in Figure 4.9. The stirring
mechanism from the mixer will move the solids in a circular motion. Over one entire
revolution, a higher portion of solids will affect the jet penetration of the gas injection nozzle. This design modification should yield better solid-gas contact in the reactor.

![Diagram](image)

**Figure 4.9 Relocation of Secondary Air Injection**

This [link](#) can be clicked for a video of the fluidization pattern observed with pure steam feed under the dual injection mode at the offset position. As shown, with this configuration, the fluidization behavior was smooth and uniform without any dilution or fluidization aid.
4.5 CONCLUSION

With this reactor hydrodynamic study, we have established a range of feasible conditions and configurations for the hydrator operation. Diluting the inlet steam stream with compressed air had a positive effect on fluidization pattern in the reactor. In addition, the installation of external assistance, such as the vertical baffle, mixer and off-set gas injection nozzle, provided a means of establishing particulate-like fluidization behavior with a Geldart Type C particle. More importantly, we avoided the need for any additional fluidization aid, which would exert excess stress on the overall solid circulation. From that point on, the research focus was shifted to the reaction kinetics, including studying the effects of steam to calcium ratio, reactor temperature, and steam partial pressure on sorbent reactivation. The configuration of steam dilution with mixer agitation and one baffle assistance was used for the ensuing high temperature hydration tests in the next chapter.
CHAPTER 5

BENCH SCALE HIGH TEMPERATURE HYDRATION TEST

5.1 INTRODUCTION

In the previous chapter, we have described the design and hydrodynamic testing of the bench scale hydrator. Upon establishing the single-baffle configuration, we proceeded with preliminary high temperature hydration tests. The goal was to investigate the effects on sorbent hydration and carbonation conversion from the following set of parameters:

- Steam flow rate
- Reactor temperature
- Steam partial pressure
- Steam to calcium ratio
- Sorbent characteristics

The idea of utilizing the exothermic hydration reaction for sorbent reactivation was first suggested by Argonne National Laboratories in 1980 for SO$_2$ removal (Shearer et al., 1980). High temperature hydration produces high quality heat that can contribute to additional electricity generation in the Steam Turbine Cycle (Fan, 2008). The
thermodynamic equilibrium plot (Figure 4.1) indicates that 1 atm steam partial pressure corresponds to an equilibrium temperature of 518 °C (HSC Chemistry, 2008). Ideally, higher hydration temperature is preferred because it minimizes the process temperature swing. Moreover, reaction heat extracted at 500 °C can be passed through the high/medium/low pressure steam turbines for additional electricity generation. For intermediate hydration to be feasible, the additional thermal load from the temperature swing must not outweigh the benefits of higher sorbent recyclability.

Previous studies on steam reactivation of spent calcium sorbent have indicated that hydration can enhance the sorbent surface morphology – formation of cracks on the particle, channels extending to the inner core and surface mesopores (Kuramoto, 2003; Han, 2010; Zeman, 2008; Hughes 2004; Wu, 2010). Shearer et al. (1980) studied steam hydration kinetics in the range of 100 – 300°C and partial steam pressure from 0.07-0.5 atm (Figure 5.1). As expected, reaction temperature and partial steam pressure both had appreciable effects on the hydration rate. Higher hydration rate was achieved with reduced temperature and rising partial steam pressure. The fastest hydration rate was found at 200°C and 50% steam. In addition, we could deduce from Shearer’s results that steam hydration of lime was a relatively slow reaction with residence time in the order of tens of minutes.
Laursen et al. (2003) investigated steam hydration kinetics under slightly higher temperature and steam partial pressure of 0.8 bar in a TGA. The highest hydration conversion achieved in his experiment was 80% after about 8 minutes of reaction time at 300°C. Again, reaction temperature seemed to have a sizable effect on the hydration conversion as the 500°C sample never hydrated after 30 minutes (Figure 5.2).
Figure 5.2 Hydration conversions with respect to temperatures.

For steam hydration kinetics at elevated pressures ($P_{H2O}=0.67 – 3.8$ Mpa), we referred to the study done by Lin and Harada (2006) for applications in the HyPr-Ring process. As expected, increasing the partial pressure of steam could substantially accelerate the reaction rate. As shown in Figure 5.3, at $500^\circ$C and $P_{H2O}$ of 2 MPa, the hydration reaction proceeded to completion in less than 3 minutes. However, their reaction conditions are not suitable for the CCR process, which operates at close to atmospheric pressure.
The CCR process hydration reactor operates close to the reaction thermodynamic equilibrium boundary, at which conditions the reaction rate is expected to be relatively slow. Additional work is required to evaluate the precise reaction rate at the proposed conditions. Another challenge exists in designing a reactor that represents realistic operating conditions. The aforementioned experiments were all conducted using different variations of TGA apparatus that operate at ideal heat and mass transfer conditions. Due to the cohesive nature of Ca(OH)$_2$ (Geldart Group C), establishing a smooth fluidization pattern for this gas-solid reaction will be challenging. Thus far, no prior research has proposed a possible design for this hydration reactor. To address these issues, this research project seeks to explore a novel reactor design that allows for smooth...
fluidization of Ca(OH)$_2$ particles, and also to investigate the high-temperature steam hydration rate at the proposed reaction conditions.

5.2 MATERIALS AND METHODS

5.2.1 Calcium Sorbent

The sorbent was derived from Graymont high calcium pulverized limestone ($d_{50} = 20 \mu m$). The limestone was calcined in the sub-pilot scale rotary calciner (FEEO) at 900°C for over 2 hours until over 90% of solids were decomposed. Graymont high calcium ground lime ($d_{50} = 300 \mu m$) was also tested in the hydrator for comparison. The characterization of sorbent properties can be found in a separate publication (Wong, 2006).

5.2.2 Hydrator Apparatus

A bench-scale stainless steel (SS 304) reactor is fabricated based on the cold-model design (Figure 4.5). The reactor column stands 13.5” tall with inner diameter (ID) of 5”. A horizontal outlet pipe (1” ID) is positioned 2” from the upper flange for steam and solid discharge. The plenum section, that is 3.5” in height, includes two symmetrically-aligned inlets (1” ID) for better gas distribution. In addition, two ports are located on the top flange: one for the aforementioned thermocouple insertion and another solid sampling
port for the real-time extraction of reactor solids. A pair of high temperature ceramic heaters (Watlow Inc.) provides the external heating required to reach the initial reactor setpoint temperature. The reactor body and heaters are surrounded by sufficient ceramic wool insulation to minimize heat loss. Multiple Type K thermocouples were installed to measure the solid bed, steam inlet, steam outlet, steam generator outlet temperatures respectively. The temperature data was recorded by a data-acquisition box (Measurement Computing), which then relays the information to the DAQ-Factory program on a local computer. The mixer was powered by a D/C motor (Leeson) that operated at the speed of 28 rpm. The hydrator standpipe discharged the excess steam and entrained solids to a large water drum. The photograph (Figure 5.4) and schematic diagram (Figure 5.5) of the hydrator setup can be found in the following page.

The steam generator consists of a 2 ft. tall stainless steel heating coil surrounded by two high temperature ceramic heaters (OMEGA Engineering Inc.). The superheated steam (200-300 °C) produced from this generator was used as the primary fluidization medium for the hydrator. Water feed to the steam generator was controlled with a high precision Optos 3HM liquid metering pump (Eldex Laboratories) that could accurately deliver water flow up to 60.00 ml/min. The heaters on hydrator body and the main steam generator are controlled by two OMEGA i-series PID temperature controllers.
**Figure 5.4 Bench-scale hydrator setup:** 1-Hydrator body, 2-Steam Exhaust Pipe, 3-Secondary Steam Generator, 4-Main Steam Generator, 5-Mixer Motor, 6-Temperature and solid sampling ports, 7-Mixer Motor Speed Controller, 8-Waste collection drum.
5.2.3 Hydration Procedure

The hydrator was operated as a semi-batch bubbling fluidized bed reactor. For each test, a pre-determined amount of solid sorbent was fed into the reactor. The moles of solids were calculated based on active CaO only, meaning the small portion of CaCO₃ present in the sample was disregarded. The reactor was then heated to its set point temperature and maintained at that temperature until steam injection. Steam feed was preheated to at
least 200°C prior to injection. The reaction time of each test was fixated at 30 min. Solids were extracted from the reactor at every 5 minute or 10 minute intervals. In addition, initial feed sorbent and bulk solids from the reactor after each test were sampled.

The steam flow rates were extrapolated from the previous cold-flow results. The density and viscosity difference between steam and air at various temperatures were accounted for. Hydration reaction is expected consume a portion of the steam feed; however thermal expansion due to the temperature rise in the reactor will increase the volumetric flow rate. Without knowledge of the reaction rate, it is difficult to estimate the real time change in gas velocity during reaction. The steam flow rates (1, 2, and 3 CFM) are chosen because they are within the critical transition velocity between bubbling and turbulent fluidization regime. For simplicity, the steam flow rates were calculated at the initial set point temperature.

5.2.4 TGA Analysis for Sorbent Reactivity

Solid samples were tested in a thermogravimetric analyzer (Perkin Elmer Pyris 1 TGA) for their composition and reactivity toward CO₂. The sample was heated to 700 °C at a rate of 25 °C per minute in pure nitrogen. Calcination at 700 °C for 5 minutes effectively decomposed the hydrate and carbonate in the sample. Subsequently, the sample was exposed to 10% CO₂ with balance N₂ at 650 °C for 30 minutes of carbonation (Figure
The percent hydrate in the sample and the 30-min carbonation conversion were calculated using the following formulae:

\[
X_{hyd} = \frac{\Delta m_{hyd}/18}{m_0 - \Delta m_{cal}/44} \quad (5.1)
\]

\[
X_{carb} = \frac{\Delta m_{carb}/44}{m_0/56} \quad (5.2)
\]

Figure 5.6 TGA solid analysis results
5.3 RESULTS AND DISCUSSION

5.3.1 Reactor Hydrodynamics

The performance of this fine-particle vigorously bubbling reactor where \( u_o \gg u_{mf} \) can be modeled by the Kunii and Levenspiel (K-L) model. (Levenspiel, 1968). However, without the precise reaction kinetics in our operating range, the reactor performance cannot be quantified. The goal here is to outline an applicable model that can be used once the reaction kinetic information is available. Moreover, it is apparent that the overall conversion rate depends not only on the reaction kinetics but also the hydrodynamic constraints. On the basis of this model, the hydrodynamic constraints are functions of the gas velocity and particle properties. For instance, the fraction of bubbles is directly correlated with the gas velocity, and the minimum fluidization velocity and voidage are both related to particle size and density. High concentration (80-100%) superheated steam is used as the fluidization medium. Steam consumption by the hydration reaction is expected to significantly reduce the gas velocity. In addition, formation of Ca(OH)_2 will inherently reduce the particle size distribution and particle density. This change in the bed composition will affect the hydrodynamic constraints, such as the gas interchange coefficients and solid distribution in the bubble, cloud and emulsion phases. Interestingly, the hydrodynamic behavior and the reaction conversion are coupled in this complicated interfering relationship.
5.3.2 Effect of Steam Partial Pressure

To investigate the effect of steam partial pressure on the hydration reaction, samples were hydrated for 30 minutes at 300°C and at steam partial pressures 0.6, 0.8 and 1 atm. Total pressure (1 atm) and gas flow rate (2 CFM) were held constant. The advantage of using higher steam partial pressure was clearly demonstrated (Figure 5.7). With pure steam, 65% of the CaO was hydrated after 30 min, which was significantly higher than the 50% conversion achieved at 0.8 atm steam partial pressure. At 0.6 atm, the conversion was further reduced to 43%. Increased steam concentration promoted the forward reaction that was the formation of Ca(OH)$_2$. These results are consistent with the previous findings (Lin, 2006 and Shearer, 1980) that have shown that hydration rate is about 1.5 – 2 order of the steam partial pressure. In its simplest terms, the relationship can be expressed as:

$$R = k_0 \cdot e^{(-\frac{E}{RT})} \cdot (P_{H_2O} - P_{H_2O}^*)^2$$

(5.3)

Interestingly, the hydration rate ($dX_A/dt$) was markedly different during the first 10 min of reaction. The initial hydration rate with pure steam was almost 3 times as fast as that at steam pressure of 0.6 atm, about 50% faster than the rate at 0.8 atm $P_{H_2O}$. This finding suggests that the initial reaction rate shortly after steam induction is controlled by the chemical kinetic constraints, thus heavily dependent on the steam partial pressure. After the induction phase, the conversion rates of the three runs became comparable possibly
because the diffusion resistance and other hydrodynamic constraints began to have stronger effects.

Limited by the active volume in the 5” ID bench scale hydrator, no heat exchanging mechanism was installed. The hydration reaction is highly exothermic, thus we expected the heat of reaction to raise the reactor temperature appreciably. The exothermic reactor temperature profile provided a good indication for the hydration rate (Figure 5.8). The initial temperature rise was much more rapid with pure steam, and reached a peak temperature of 500°C – more than 100°C higher than max temperatures at reduced steam pressures. In fact, at $P_{\text{H}_2\text{O}}=0.6$ atm, the reactor temperature was practically isothermal in the range of 300-330°C. The fluctuation in reactor temperature in a way was positively correlated with the steam pressure and hydration rate. To maintain isothermal operation conditions, a heat removal mechanism must be designed to overcome the rapid temperature spike associated with various steam feeds.
Figure 5.7 Hydration at varying steam partial pressures, 300°C, 2CFM

Figure 5.8 Temperature profiles of hydration at varying steam partial pressures
5.3.3 Effect of Temperature

Although the hydrator operates at non-isothermal conditions, varying the initial reaction temperature can still offer an insight on the hydration rate with respect to a certain temperature range. The steam pressure (1 atm) and flow rate were kept constant while the starting temperatures were chosen at 200°C, 300°C and 400°C. Due to the exothermic heat of reaction, the average reactor temperature during each test was at least 100°C higher than the initial setpoint temperature (Figure 5.9). The results, shown in Figure 10, indicate that initial temperature has a strong influence on the conversion rate. The highest conversion (82%) was achieved with the initial temperature of 200°C in just 10 minutes (Figure 5.9). With the initial temperature of 400°C, the reaction was essentially maintained isothermally around the thermo-equilibrium limit of 506°C for majority of the experiment (Figure 5.10). At such conditions, the hydration rate was relatively slow – increasing linearly for 30 minutes to around 46%. Operating at the thermo-equilibrium boundary means the product Ca(OH)₂ may not be thermodynamically stable. Such a rate is most likely too slow to achieve effective sorbent reactivation for the CCR process.

Being a highly exothermic reaction, the forward reaction is more favorable at lower temperatures on the basis of thermodynamics. The conventional interpretation of the Arrhenius equation states that the reaction rate should increase with respect to temperature. However, such a generalization is not consistent with the findings of this
research. Our results clearly indicate that lower reaction temperature yields higher hydration conversion. This result may be explained by the equation for reaction rate constant (Eqn 5.3). Increasing the reactor temperature from 300°C to 506°C raises the equilibrium steam pressure $P_{\text{H}_2\text{O}}^*$ exponentially from 0.01 to 1 atm (Figure 4.1). Without pressurizing the reactor, the maximum steam pressure obtainable is 1 atm. The rise of reactor temperature therefore shrinks the steam pressure gradient necessary for the hydration reaction to proceed rapidly. Ideally, a cooling mechanism should be installed so that the hydrator can operate at slightly below the thermo-equilibrium temperature to ensure faster reaction.

In addition, even at the relatively favorable reaction condition of 200°C, full conversion to Ca(OH)$_2$ was not achieved. The hydration reaction halted upon reaching 81% conversion after 10 min. A similar pattern was observed for the 300°C experiment where hydration rate was noticeably reduced during the final 10 min. The extent of reaction approached a plateau around 70%. One possible explanation for this might be that the sorbent pore volume was reduced due to thermal sintering experienced during sorbent preparation, thus the inner parts of CaO core are not available for hydration. Considering the CaO sorbet was produced from calcination at 900°C for over 2 hours, the extent of sorbent sintering may be significant. This finding is in agreement with Serris’ (2011) suggestion that such a “blocking effect” could be observed for sintered CaO particles.
Figure 5.9 Hydration conversions with varying starting reactor temperatures at steam pressure of 1 atm

Figure 5.10 Temperature profiles of hydration at varying reactor temperatures
5.3.4 Effects of Steam Flow Rate and Steam: Ca Ratio

Application of the CCR process to the commercial scale requires circulation of thousands of tons of calcium sorbent per hour. Hydration of the spent sorbent is expected to consume a significant amount of steam. Excess steam usage leads to additional operating cost and energy penalty. For this reason, the effects of steam flow rate and steam to calcium mole ratio on the hydration rate were examined at 300°C and 1 atm P_{H2O}. As previously mentioned, we were able to established smooth fluidization at gas flow rate of 1 CFM, which was selected as the baseline. Increased steam flow should theoretically improve the reaction hydrodynamics and provide better solid-gas contact. Another possible benefit of feeding excess steam may be its inherent cooling effect because the inlet steam temperature was appreciably lower than the peak reactor temperature. Lastly, since fluidization medium consisted of mostly steam, consumption of which via hydration will reduce the gas flow rates. To account for these factors, higher flow rates (2 and 3 CFM) were also investigated.

Contrary to expectations, this study did not find a strong correlation between the hydration rate and steam flow rate (Figure 5.11). In comparison to the effects of pressure and temperature, the steam flow rate only had slight impacts on the hydration rate. In fact, the final hydration conversions (30min) are within ±5% statistically, such a variation
can very well be attributed to experimental noise. It is difficult to explain this result but it may be related to the fluidization pattern in the reactor.

![Graph showing hydration conversions with varying steam flow rates.](image)

**Figure 5.11 Hydration conversions with varying steam flow rates**

5.3.5 Effect of Particle Characteristics

Previous studies on the TGA scale have reported the sample particle size to only have slight effects on the hydration rate (Wang and Lin, 2008). However, in this bench-scale reactor, the solid particle size distribution directly affects the hydrodynamic constraints of the heterogeneous hydration reaction. To assess its effect, the hydration rate of Graymont high calcium ground lime ($d_{50} = 300$ µm) and calcined Graymont pulverized limestone


(d_{50} = 20 \, \mu m) \text{ are compared in Figure 5.12. Under the same reaction conditions, 
hydration rate of the finer 20 \, \mu m particles was noticeably faster, especially during the 
first 20 min. This result supports the idea that the initial hydration rate is related to the 
particle surface morphology, and finer particles have more surface area available for 
reaction. However, the final extent of hydration at 30 min was comparable for both 
sorbents. This data can be explained by the fact the molar volume of Ca(OH)\textsubscript{2} is 
significantly higher than that of CaO. Conversion from CaO to Ca(OH)\textsubscript{2} leads to volume 
expansion and formation of cracks and channels on the particle surface. Such a “popcorn”
effect allows for continuous gas diffusion into the un-reacted core until it reaches a 
barrier. For instance, if the particles are severely sintered, there may exist a “blocking 
effect” that prevents complete conversion.

Interestingly, although the ground lime sample reached higher hydration conversion, the 
extent of sorbent reactivation quantified by its carbonation conversion was lower than the 
other samples (Figure 5.13). For instance, the 30 min ground lime sample contained over 
15\% more hydrate than the pulverize lime hydrated at 400\,\textdegree C. However, at the same 
carbonation conditions, the hydrated pulverized lime demonstrated a higher CO\textsubscript{2} capture 
capacity (Figure 5.13). This discrepancy can be attributed to the fact that the carbonation 
reaction is more sensitive to particle size. It has been suggested that the carbonation 
reaction follows the shrinking core model (Stanmore, 2005). Formation of CaCO\textsubscript{3} is 
expected to develop a layer of carbonate on the particle surface; and once a critical
thickness is reach, the gas diffusion resistance becomes the rate limiting factor. This pattern clearly deviates from the mechanism of the hydration reaction.

In addition, a compilation of the hydrated 20 µm samples exhibited a strong linear correlation between the hydration conversion and sorbent reactivity toward CO₂ (Figure 5.14). This trend confirms that Ca(OH)₂ is a better sorbent due to its smaller particle size distribution and superior surface morphology – higher surface area and porosity. This exact mathematical correlation must be interpreted with caution. As it has been shown, this equation will be different for the same Graymont limestone with larger particle size. The same can be said about other limestone sources with different CaO content.

Figure 5.12 Hydration conversions with respect to solid particle size
Figure 5.13 Carbonation conversions with respect to particle size

Figure 5.14 Correlation between carbonation and hydration conversions
The following series of plots showed the sorbent carbonation conversion with respect to its hydration conditions (Figure 5.15, 5.16, 5.17).

Figure 5.15 Carbonation conversions at varying steam partial pressures
Figure 5.16 Carbonation conversions at varying initial reaction temperatures

Figure 5.17 Carbonation conversions at varying steam flow rates

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5.4 CONCLUSION

Based on the high temperature hydration experiments carried out in the bench scale hydrator, steam hydration of spent sorbent appeared to be a very promising technique for restoring the calcium utilization. Spent sorbent was obtained by thermal decomposition of pulverized limestone (dp$_{50} = 20$ µm) in a rotary calciner at 950°C for over 2 hours. The initial calcined sorbent only showed 20-25% extent of carbonation, which could be subsequently improved to over 60% after reactivation. The rate of hydration was tested with respect to the reactor temperature, steam partial pressure, steam flow rate, steam to calcium ratio, and sorbent particle size. The following results were obtained:

- Steam partial pressure and reaction temperature both have strong influence on the rate of hydration. The hydration conversion increases with higher steam pressure and reduced reaction temperature.

- Solids with smaller particle size distribution yielded higher hydration conversion. The effect of particle size on carbonation rate was more evident. Sorbents larger in particles size could not reach the same level of CO$_2$ capture capacity even when they were better hydrated. This finding can be attributed to the fact that gas diffusion resistance is more relevant for the carbonation reaction due to the formation of a dense CaCO$_3$ product layer.

- The effect of steam flow rate on the CaO hydration rate was not significant. Theoretically, higher steam flow rate should lead to more vigorous mixing and
lower reactor temperature; however these potential effects did not correlate to higher hydration conversion under the current design.

- Complete conversion of CaO to Ca(OH)$_2$ was not achieved at our reaction conditions. A maximal extent of hydration, or a “blocking effect”, was observed. One possible explanation was the morphological condition of the calcined sorbent. If the calcined sorbent was severely sintered, hydration reaction could only proceed to a certain extent.

- A direct and linear correlation was found between the hydration conversion and sorbent carbonation capacity. This correlation is expected to change with respect to the sorbent particle size distribution, CaO content and carbonation conditions.

The increased calcium utilization from steam hydration reactivation is integral to the CCR process. The reusability of the spent calcium sorbent directly extends to an appreciable reduction in the limestone consumption rate, the quantity of solid waste produced and the process operating costs, including both the raw material cost and energy penalty from preheating the fresh limestone feed. Currently, from an economic perspective, the CCR process has a decided advantage over its competing technologies because of the low cost of limestone. However, based on preliminary analysis of the process energy penalty, at least 70% hydration conversion at 500°C and 1 atm partial pressure of steam is desired for the CCR process with intermediate hydration to be competitive in its efficiency. Thus far, at target operating conditions, we could only
demonstrate 46% hydration conversion. Future work is required to improve the hydrate rate, and my recommendations include:

- The weak correlation between steam flow rate and hydration conversion implied the reactor hydrodynamics was not yet optimal, especially when pure steam was used as the fluidization medium. Further reactor modifications, such changing the baffle or mixer design, can improve the hydrodynamic constraints.

- For the hydration reaction to proceed in the forward direction at 500°C, the steam partial pressure must be at least 1 atm, which is also the maximum reactor pressure under the current design. Hydrodynamic testing in the bench-scale reactor revealed that a mixture of steam and preheated air can yield smoother fluidization. If the reactor can operate under a slight pressure (<1.5 atm) while maintaining the steam partial pressure at 1 atm, the fluidization pattern may be significantly improved.

- The current study was limited by the uncontrolled temperature fluctuation during reaction. Because reaction temperature has a major influence on the hydration rate, the addition of an effective cooling mechanism is highly recommended. Assuming perfect mixing, the energy balance in the hydrator can expressed as,

\[
\Delta H_{\text{accumulation}} = \Delta H_{\text{rxn}} + (H_{\text{steam,in}} - H_{\text{steam,out}}) + Q_{\text{loss}} \tag{5.4}
\]

where,
The other terms, $\Delta H_{\text{accumulation}}, \Delta H_{\text{rxn}}, H_{\text{steam,out}}$, are all functions of the hydration conversion $X_A$, which can be determined with more information on the reaction kinetics. Ideally, if the reactor temperature can be maintained between 480-500 °C, it will provide a 20°C buffer to the thermo-equilibrium temperature at $P_{\text{H}_2\text{O}}=1$ atm. Under such conditions, the hydration rate should be improved.
CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

The Carbonation-Calcination Reaction (CCR) Process is a very promising high temperature post-combustion CO₂ capture technology. This process operates on the principle of cycling a metal oxide that acts as a CO₂ acceptor in an absorption – desorption chemical looping system. Limestone was chosen as the solid sorbent because of its abundant availability and low cost. Industrial application of this process requires continuous circulation of thousands of tons of sorbent per hour. On such a scale, gas-solid transport along with the mass and heat transfer rates will dictate the process efficiencies.

The work outlined in this thesis addressed two critical parts of the CCR process – the particulate capture device and the hydrator. Two cyclones were designed and tested for their separation efficiency of fine Ca(OH)₂ powder. The two cyclones in series demonstrated exceptional capture efficiency during cold model tests. Efficiency is expected to decrease slightly at higher temperature, but not significantly enough to be a concern. The current cyclone design provides a cost-effective way to control the gas-solid separation of the flue gas stream containing micro-size particle size distribution. In addition, the operation of a bench-scale high temperature hydrator was investigated under
conditions suitable for the CCR process. Preliminary results were very encouraging – 80% hydration conversion and higher than 70% carbonation capacity were achieved. Hydration rate was found to be more favorable at lower reaction temperature and higher steam partial pressure. Sorbents with a smaller particle size distribution also showed slightly enhanced hydration conversion.

However, the hydrator, as it is, is not yet a finished product. Integration of a scaled-up unit into the CCR process requires additional modifications to test for its operation in continuous mode and with a heat extraction mechanism. Heat removal from a high concentration gas-solid fluidized bed is a challenge that requires special attention. The presence of fine calcium powder can lead to pipe fouling complications, in which case the heat transfer rate will be drastically reduced. Installment of some methods of cooling will allow for operation of the bench-scale hydrator at close to isothermal conditions. Because reaction temperature has demonstrated strong influence on the hydration rate, only when it is held constant, will we be able to deduce an accurate calculation of the reaction kinetics from the bench scale experiments. Currently, a hydration kinetics study is underway using a high pressure and high temperature steam TGA apparatus. The conversion vs. time data can be modeled by the following equations, depending on the rate controlling step:
Gas film diffusion control: \[ X = k_1 t \]

Shrinking core of unreacted CaO: \[ 1 - (1 - X)^{1/n} = k_2 t \quad n = 1, 2, 3 \]

Homogeneous first-order reaction: \[ -\ln(1 - X) = k_3 t \]

Power law reaction: \[ (1 - X)^{-n} = k_4 t \quad n > 0 \]

Product nucleation and growth on grain surface: \[ [\ln(1 - X)]^{1/n} = k_5 t \quad n = 1, 2, 3 \]

Product layer diffusion: \[ 1 - 3(1 - X)^{2/3} + 2(1 - X) = k_6 t \]

In the bench scale hydrator, reaction rate depends on both the kinetics and mass/heat transfer rates, which are coupled with the reactor hydrodynamics. Comparison of the TGA and bench reactor results provides an indication of the hydrodynamic efficiency in the hydrator. In depth understanding of the hydration kinetics at our operating conditions will allow for an accurate estimation of the hydrator residence time, which dictates the location of the standpipe and screw feeder inlet as well as the solid bed height.

Furthermore, the calciner must be redesigned to produce highly reactive calcium oxide and a compression-ready CO₂ stream. An oxygen or natural gas fired flash calciner design has been proposed. Initial tests performed at an off-site facility indicated that complications derived from particle agglomeration could hinder the calcination conversion. Therefore, once again, this becomes a gas-solid transport problem that may require external fluidization assistance.
Completion of the aforementioned tasks will provide a basis, at least from a design perspective, for a continuously circulating CCR cycle. The overall process efficiency will be governed by the performance of the redesigned calciner and hydrator. ASPEN simulations need to be updated with realistic inputs for more accurate results that can be used for a detailed economic analysis on the integration of the CCR process into a power plant. All in all, the future of the calcium looping process for CO₂ capture is bright. The research efforts at The Ohio State University and all over the world will continue to push this process forward toward commercialization.
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