Steam Enhanced Calcination for CO_2 Capture with CaO

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Statement of Contribution of Collaborators

I am the sole author of all the chapters of this thesis. My supervisors, Dr. Arturo Macchi of the Department of Chemical and Biological Engineering and Dr. Edward John Anthony of CanmetENERGY and Cranfield University provided editorial comments and supervised my work.

Chapter 3 is an article which was published in Industrial and Engineering Chemistry Research in 2013. This article was written by me. The work was a collaboration with CanmetENERGY, Natural Resources Canada. Dr. Dennis Lu and Robert Symonds provided editorial corrections and supervised my work at CanmetENERGY's facilities.

Signature: ______________________ Date: ______________

Abstract

Carbon capture and storage technologies are necessary to start lowering greenhouse gas emissions while continuing to utilize existing thermal power generation infrastructure. Calcium looping is a promising technology based on cyclic calcination/carbonation reactions which utilizes limestone as a sorbent. Steam is present in combustion flue gas and in the calciner used for sorbent regeneration. The effect of steam during calcination on sorbent performance has not been extensively studied in the literature. Here, experiments were conducted using a thermogravimetric analyzer (TGA) and subsequently a dual-fluidized bed pilot plant to determine the effect of steam injection during calcination on sorbent reactivity during carbonation.

In a TGA, various levels of steam (0-40% vol.) were injected during sorbent regeneration throughout 15 calcination/carbonation cycles. All concentrations of steam were found to increase sorbent reactivity during carbonation. A level of 15% steam during calcination had the largest impact. Steam changes the morphology of the sorbent during calcination, likely by shifting the pore volume to larger pores, resulting in a structure which has an increased carrying capacity. This effect was then examined at the pilot scale to determine if the phase contacting patterns and solids heat-up rates in a fluidized bed were factors. Three levels of steam (0%, 15%, 65%) were injected during sorbent regeneration throughout 5 hours of steady state operation. Again, all levels of steam were found to increase sorbent reactivity and reduce the required sorbent make-up rate with the best performance seen at 65% steam.

Sommaire

Les technologies de capture et séquestration du carbone sont nécessaires pour réduire les émissions de gaz à effet de serre tout en continuant à utiliser les infrastructures de production d'énergie thermique existante. Une technologie prometteuse est basée sur les réactions cycliques de calcination/carbonatation du calcaire comme sorbant. La vapeur d'eau est naturellement présente dans les gaz de combustion et, dans le réacteur de calcination, est utilisée pour la régénération du sorbant. L'effet de la vapeur d'eau lors de la calcination sur la performance du sorbant n'a pas été largement étudié dans la littérature. Ici, des expériences ont été réalisées en utilisant un analyseur thermogravimétrique (TGA) et par la suite un lit fluidisé double, échelle-pilote, pour déterminer l'effet de l'injection de vapeur d’eau pendant la calcination sur la réactivité du sorbant lors de la carbonatation.

Dans le TGA, différents niveaux de vapeur d’eau (0-40 % vol.) ont été injectés lors de la régénération de l’adsorbant au cours de 15 cycles de calcination/carbonatation. Toutes les concentrations de vapeur ont augmenté la réactivité du sorbant pendant la carbonatation. Un niveau de 15 % de vapeur lors de la calcination avait le plus grand impact. La vapeur d’eau change la morphologie du sorbant au cours de la calcination, probablement en décalant le volume de pores vers les plus grands pores; ce qui entraîne une structure qui a une capacité d’adsorption accrue. Cet effet a ensuite été examiné dans un lit fluidisé à l'échelle pilote afin de déterminer si le taux de chauffe et le mode de contact des phases ont été des facteurs. Trois niveaux de vapeur (0%, 15%, 65%) ont été injectés pendant la régénération du sorbant sur une période de 5 heures d’opération en régime permanent. Encore une fois, tous les niveaux de vapeur d’eau ont augmenté la réactivité et réduit le taux d’appoint du sorbant, avec la meilleure performance obtenue à 65% de vapeur.

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Nomenclature

β = purity of limestone

E_{carb} = carbonation efficiency

F_{CaO} = molar flow rate of CaO from the calciner to the carbonator [kmol/h]

F_{CO2} = molar flow rate of CO_2 to the inlet of the carbonator [kmol/h]

F_{carb} = molar flow rate of CO_2 leaving the carbonator [kmol/h]

m_{CaCO3} = mass of calcium carbonate before calcination [mg]

m_{CaO} = mass of calcium oxide after calcination [mg]

M_{CaO} = molar mass of calcium oxide [g/mol]

M_{CO2} = molar mass of carbon dioxide [g/mol]

P_{eq} = equilibrium partial pressure of CO_2 [Pa]

W_0 = original sample mass [mg]

W_{calc} = mass of sample after calcination [mg]

W_{carb} = mass of sample after carbonation [mg]

X_{carb} = carbonation conversion

X_{calc} = carbonation conversion of sorbent at the outlet of the calciner

Acronyms

BET	Brunauer-Emmett-Teller
BFB	Bubbling Fluidized Bed
BJH	Barrett-Joyner-Halenda
CCS	Carbon Capture and Storage
CFB	Circulating Fluidized Bed
CFBC	Circulating Fluidized Bed Combustor

DC	Direct Current
GHG	Greenhouse Gas
LOF	Loss on Fusion
OECD	Organization for Economic Co-operation and Development
TG	Thermogravimetric
TGA	Thermogravimetric Analyzer
XRF	X-Ray Fluorescence

Chapter 1 - Introduction

1.1 - General Background

Fossil fuels continue to fulfill the majority of worldwide energy demands. Specifically, over 80% of total electric power is produced via thermal conversion of various carbon-based fuels such as coal, oil and natural gas.[1] Fuels such as natural gas are currently relatively inexpensive and since many countries have significant thermal power infrastructure it is likely that fossil fuels will continue to be significantly used in the coming century. However, the widespread use of carbon-based fuel combustion for the purposes of power generation results in significant greenhouse gas (GHG) emissions.

Greenhouse gases, such as CO_2, N_2O and CH_4, accumulate in the atmosphere and have been shown to contribute to climate change.[2] Although there are several greenhouse gases, carbon dioxide accounts for 93% of all anthropogenic emissions.[1] Worldwide CO_2 emissions from fuel combustion have increased by 15,714 Mt in the period between 1973 and 2011.[3] It has recently become an international priority to reduce GHG emissions in order to mitigate any possible future effects of climate change such as further melting of the ice caps, ecological changes and continued warming.[4,5] Many strategies have been proposed to reduce GHG emissions in the developed world. The options presented for power generation, comprising 75% of total OECD GHG emissions in 2011[6], primarily consist of transitioning our dependence on fossil fuels to renewable, low-emission options such as solar, wind and nuclear. However, many of these alternative power generation technologies either cannot currently achieve similar efficiencies or require significant capital expenditure. An alternate option, which allows for the continued use of existing thermal-power generation infrastructure, is carbon capture and storage (CCS).

Carbon capture and storage is a process in which CO_2 is removed from a carbon rich source, such as a coal-fired boiler flue gas, purified and sequestered in subterranean geological formations such as depleted oil reservoirs. As the total CO_2 sink capacity is finite, CCS is not a final solution to curbing GHG emissions. However, it will allow for a decrease in emissions in the near term while use of existing power generation infrastructure continues. As the current systems reach end-of-life, they can be replaced with low-emission options which will continue to be developed in the interim, significantly reducing the cost. Several CCS technologies have been proposed, many of which can be integrated with existing power generation facilities. Amine scrubbing is the most developed of the proposed processes. It utilizes an amine solution to remove CO_2 from a flue gas at ambient temperature which is regenerated at 100°C - 120°C, releasing the CO_2.[7] While this process is effective at decarbonizing a flue gas stream, it has a large energy penalty as it is a low-temperature process requiring a large energy input for sorbent regeneration. In contrast, calcium looping is an emerging technology which utilizes low cost, non-toxic limestone as a sorbent and potentially has a 5% net lower energy penalty than the amine scrubbing.[8]

1.2 - The Calcium Looping Process

The calcium looping process is based on the reversible reaction between calcium oxide and carbon dioxide, shown in equation 1-1.

$$CaO_s + CO_{2_g} \leftrightarrow \; CaCO_{3_s} + 178.2\ \frac{kJ}{mol} \tag{1-1}$$

When limestone is heated above 850°C in air, CO_2 is released via calcination, the reverse reaction in equation1-1. The lime that is produced can then be used to capture CO_2 via the carbonation reaction. Figure 1-1 shows the conversion of CaO to $CaCO_3$ over time for a typical carbonation reaction.

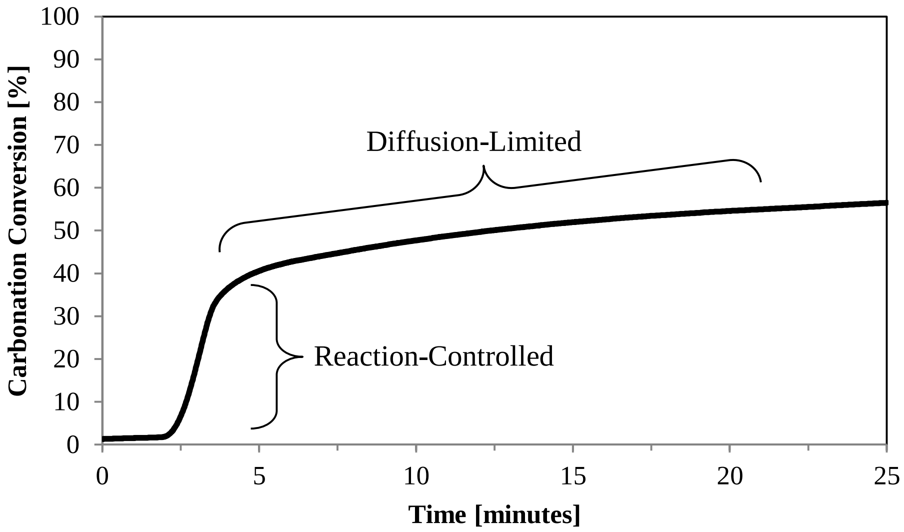

Figure 1-1 - Carbonation conversion over time for the reaction of CaO with CO_2 at 650°C in 15% CO_2, balance N_2, after initial calcination of limestone.

The carbonation reaction proceeds in two phases: reaction-controlled and then diffusion-limited. During the first phase, the rate of reaction is limited by intrinsic reaction kinetics as there is nothing restricting the CO_2 from diffusing into the pores of the sorbent and reacting at active surface sites. However, as the reaction continues, a shell of $CaCO_3$ begins to form around the sorbent particles. This shell restricts the access of the bulk CO_2 to the remaining active CaO sites in the mesoporous structure. The rate of reaction then becomes limited by the diffusion of the CO_2 through the product layer to the active sorbent at the core of the particles. Typically, the reaction kinetic-controlled phase lasts between 1 and 2 minutes. The sorbent will continue to react in the diffusion-limited phase, theoretically, until complete conversion. Conversely, calcination proceeds very rapidly and to full conversion provided the temperature is sufficiently above equilibrium (>900°C in a CO_2-rich environment). The CO_2 capture process that was developed using limestone as a sorbent is shown in Figure 1-2.

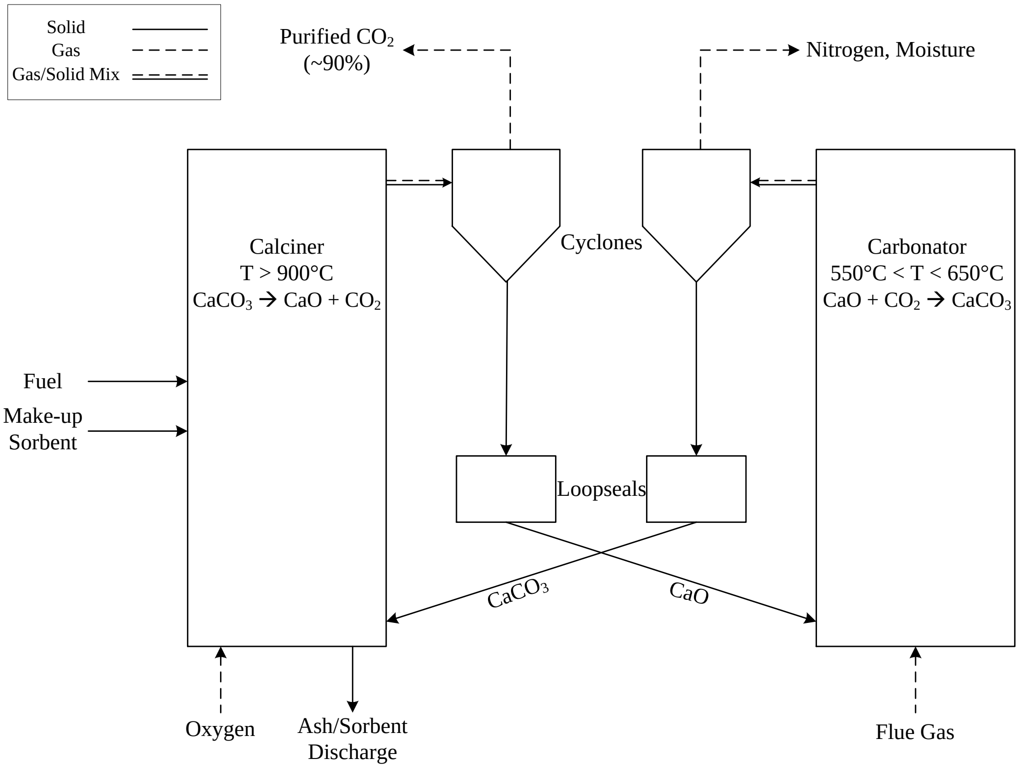

Figure 1-2 - Process flow diagram of the calcium looping process.

Shimizu et al.[9] proposed a process based upon two interconnected fluidized beds. Flue gas from a power station or other large point-source is fed to the carbonator reactor. The carbonator bed is composed of CaO. The CO_2 in the flue gas reacts with the CaO, partially converting it to $CaCO_3$. The carbonator is typically operated as a circulating fluidized bed which implies that the bed material travels along the length of the reactor, is separated from the gases via a cyclone and is either returned to the bed or transferred to the other bed via the loop-seal. The high velocities required to circulate the particles result in a relatively low average residence time, on the order of seconds. The lime is primarily converted in the reaction kinetic-controlled carbonation phase which allows for a fast reaction rate, optimizing conversion for a short residence time. The carbonator typically operates between 550°C and 650°C. Carbonation is exothermic which allows the reaction to be self-sustaining in a sufficiently insulated system. Additional energy can be removed from the carbonator in the form of steam via an in-bed heat exchanger which can be used to moderate the bed temperature and recover excess energy.

The partially carbonated sorbent is transferred to the calciner for regeneration. The sorbent is heated to temperatures in excess of 900°C to allow calcination to proceed. Like the carbonator, the calciner is typically operated as a circulating fluidized bed. The short residence time in this reactor is allowed by a rapid calcination reaction rate.[10] Combustion is needed to supply the heat required for the endothermic calcination reaction and to heat the incoming solids from the carbonator. Typically, solid fuels such as coal, biomass or petroleum coke are used. Fresh sorbent addition, spent sorbent removal and ash removal are also carried out in the calciner. There is also the possibility of recovering additional heat from the calciner exhaust gases as they are at very high temperatures (>900°C).

Any viable CCS process must produce a purified stream of CO_2 in order for the captured carbon to be effectively sequestered. To accomplish this, the calciner is operated as an oxygen-fired (oxyfuel) combustor. Unlike traditional combustion processes, oxyfuel combustion is performed with nearly pure O_2 rather than air. The flue gas is recycled to moderate temperature. The use of oxygen instead of air combined with a flue gas recycle results in a high CO_2 concentration (~90%) and very little nitrogen at the outlet of the combustor. Oxyfuel flue gas is comprised primarily of CO_2 and H_2O, with some excess O_2 and other trace contaminants (SO_2,

NO_x, N_2). The calciner exhaust stream contains the CO_2 removed from the flue gas in the carbonator and any produced from combustion in the calciner. This stream can be easily purified by condensing any remaining water and utilizing typical flue gas clean-up operations such as desulfurization, particulate filters, and selective catalytic reduction. The refined CO_2 stream can then be compressed and sequestered.

1.3 - Sorbent Reactivity Decay

Although calcium looping has the potential to be one of the most energy efficient processes for post-combustion CCS, there are several developmental hurdles to overcome. The most prevalent issue, and the focus of much of the research in this area, is to reduce or eliminate the drastic sorbent reactivity decay which occurs after repeated carbonation-calcination cycles. Figure 1-3 shows a typical sorbent reactivity decay curve based on a model developed by Grasa and Abanades.[11]

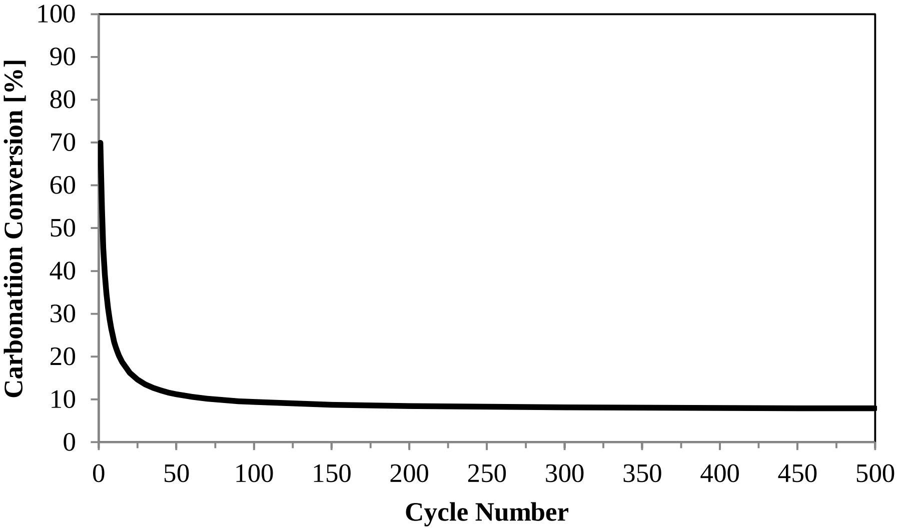

Figure 1-3 - Limestone reactivity decay relationship.

The conversion of CaO to $CaCO_3$, also referred to as carbon carrying capacity, decays rapidly in the first 50 cycles. After approximately 300 cycles the change in carrying capacity stops decreasing with increased cycle numbers. This is denoted as the residual conversion level. The residual conversion after hundreds of capture and release cycles is below 10% for many limestones studied in literature.[11] Although the sorbent will continue to reliably achieve residual conversion, this level does not allow for an economic reactor design. At a residual carbonation conversion of 7.5%, the sorbent is only able to remove 0.06 kg CO_2/kg CaO. This low carrying capacity would demand high solid transfer rates between the two fluidized beds and a large carbonator bed inventory to strip a sufficient amount of CO_2 from the flue gas. To raise the average reactivity of the calcium oxide in the system, fresh limestone is continually fed and spent sorbent removed. This make-up flow reduces the average residence time of sorbent within the system which results in a higher mean carrying capacity. The required sorbent make-up represents a significant operating expense, regardless of the low cost of limestone. Handling large quantities of limestone can also create logistic challenges for power station retrofits. In addition to the fluidized bed system, a large facility would be required to process and store limestone. Transport of the limestone to the site could also entail additional expense.

Reducing the sorbent make-up rate is thus key to further reducing the cost of the calcium looping process to make it a more attractive CCS technology. To develop a technique to counteract the decay in carbon carrying capacity, the cause(s) must be identified. Several phenomena are known to contribute to the decay in reactivity of CaO with CO_2, such as sulphation and sintering. Lime can react with sulfur dioxide, a common by-product of combustion, to produce calcium sulfate ($CaSO_4$). Unlike calcium carbonate, calcium sulfate will not decompose at temperatures present in the calcium looping process. Sulphation reduces the carrying capacity by permanently reducing the amount of CaO available to react with CO_2. The impact of sulphation on reactivity decay can be minimized by removing sulfur species from the flue gas before the carbonator and utilizing low sulfur fuels in the calciner. The primary source of the decay in calcium oxide reactivity can then be attributed to particle sintering.

Sintering is defined as a change in the morphology of the surface of a particle at that is being held at high temperature. The various peaks and ridges that form the pore structure of a particle consolidate and form simpler more compact shapes.[12,13] This results in a reduction in surface area and pore volume. In the case of CaO, the carbon carrying capacity decreases as there are fewer sites available for reaction due to the reduced surface area. Calcination typically is carried out above 900°C exposing the sorbent to an environment conducive to sintering. It has also been demonstrated that the gaseous atmosphere present can enhance the sintering effect. Borgwardt[14] demonstrated that carbon dioxide and steam, relative to air or nitrogen, enhance the sintering of CaO. The majority of the reactivity decay observed can be attributed to sintering because the sorbent experiences high temperatures and a carbon dioxide rich atmosphere with steam present in the calciner.

Several methods have been proposed to increase the sintering resistance of calcium oxide and produce a more reactive sorbent. Doping the sorbents with various acids and producing calcium oxide pellets with a cement binder have been shown to increase sorbent reactivity under certain conditions at the bench scale.[15] However, the modified sorbents still decay significantly with time. These techniques also increase the complexity of the process, increase the cost of the sorbent and potentially introduce toxic substances such as acids to power generation facilities. As the goal is to reduce costs, alternatives which utilize existing infrastructure and inexpensive feedstocks are preferable.

Sintering of naturally occurring limestone can potentially be reduced by changing the operating conditions, such as temperature and gas environment, in one or both of the reactors. For example, steam has been shown to be advantageous to the calcium looping process in several different ways. It was demonstrated that steam in the carbonator increased the extent of reaction during the reaction-controlled carbonation phase and increased the rate of reaction during the diffusion-limited phase.[16,17] A detailed description of the proposed mechanisms for this effect from literature is presented in section 3.1. Similarly, it was proposed to hydrate calcium oxide periodically before carbonation.[18] The subsequent dehydration upon heating opened up the pore structure resulting in increased surface area and pore volume, creating a more reactive sorbent. While hydration is able to regenerate the carrying capacity of spent sorbent, the physical strength/integrity was greatly reduced making it unsuitable for use in circulating fluidized beds. Regardless, steam clearly has the ability to increase the carbon carrying capacity of calcium oxide. To date, little work has been done to investigate the effect of having different levels of steam present in the calciner. Steam is already present in the calciner due to the combustion of fuel needed for calcination; however additional steam can be injected without major changes to the process as steam is easily condensed out of the flue gas by cooling. Steam can be used to dilute the high CO_2 concentration in the calciner which could potentially reduce the severity of sintering in the calciner thus significantly increasing the carrying capacity of limestone. Donat et al.[19] reported an increased carrying capacity for natural limestones when steam was present during calcination. The authors utilized a bench-scale bubbling fluidized bed reactor and evaluated steam concentrations up to 20% during calcination. They proposed that the steam shifted the pore volume to larger diameter pores resulting in a more reactive sorbent. However, to fully understand the mechanism and any possible changes to the operation of the process, further work is required involving a wider range of steam concentrations and realistic calcination conditions such as high CO_2 concentrations and very high heating rates. Other factors present in a full-scale commercial system, such as high gas velocities, combustion and different gas-solid contacting, could also influence the results and need to be evaluated.

1.4 - Thesis Objectives

The purpose of this thesis is to examine the impact of steam injection in the calciner on the performance of naturally occurring lime sorbents used in the calcium looping process. To that end, the specific goals for the work are as follows:

- Determine the effect of diluting the calciner gas with various levels of steam on the gas-solid reaction rates and the carbon carrying capacity in subsequent carbonations.
- Compare the effect of steam present during calcination versus carbonation and any resulting change in sorbent reactivity.
- Use pilot plant testing to assess the advantages and disadvantages of steam addition to a fluidized bed calciner and evaluate any impact on sorbent make-up rates.
- Present a mechanism for the changes observed in the gas-solid reaction resulting from steam presence during calcination.

The experimental equipment and the dual-fluidized bed pilot plant used in this work are described in Chapter 2. Chapter 3, entitled **"Influence of Steam Injection during Calcination on the Reactivity of CaO-Based Sorbent for Carbon Capture",** investigates the effect of the presence of steam during the calcination reaction on the subsequent gas-solid carbonation reaction. A pilot plant test campaign involving three levels of steam in the calciner and the resulting changes in sorbent make-up rates are presented in Chapter 4, entitled **"Steam Addition to Calcination for the Enhancement of CaO-Based Sorbent Reactivity for CO_2 Capture: A Pilot Study"**. Furthermore, a mechanism for the observed sorbent reactivity changes at the bench and pilot scale is presented. Finally, Chapter 5 contains concluding remarks and recommendations for future work.

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Chapter 2 - Experimental Methods

2.1 – Thermogravimetric Analysis

Thermogravimetric analysis involves observing the change in mass of a sample which is exposed to a controlled gas atmosphere and temperature. The thermogravimetric analyzer (TGA) used for the work presented in Chapter 3 is shown in Figure 2-1.

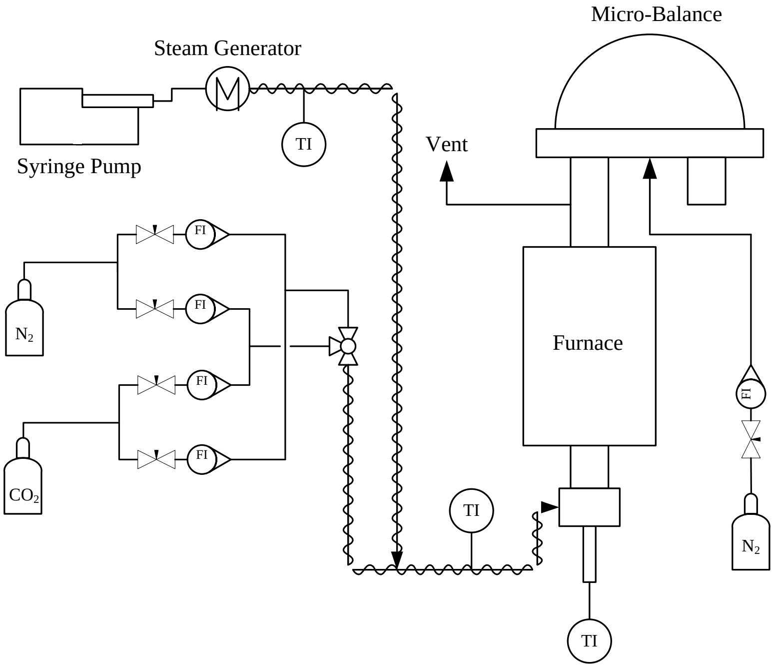

Figure 2-1 - Schematic diagram of a thermogravimetric analyzer modified for use with steam.

A Perkin Elmer TGA 7 modified to allow for the injection of steam with other reactive gases was used. It is capable of operating at temperatures up to 1000°C with heating rates between 5 and 50°C/min. The solid sample is suspended from a micro-balance at the center of the furnace in a platinum pan. The micro-balance used to measure the sample weight has a sensitivity of 0.01 mg. A typical sample mass appropriate for analysis is between 5 and 50 mg. The gas atmosphere is controlled by an automated three-way valve and a bank of rotameters. The automated valve allows one to switch between two unique atmospheres during a test. The micro-balance requires a nitrogen purge to keep the mechanism cool and free of any condensation or corrosive species. A steam generator and syringe pump are used to produce and deliver the steam for testing. The steam is mixed with the other reactant gases after the three-way valve and all lines containing steam are heat traced to eliminate any possibility of condensation. The syringe pump is controlled by a timer which allows for intermittent steam injection during tests. This allows for multiple reaction conditions to be evaluated, with or without steam, during one test. This ability is necessary to accurately emulate both calcination and carbonation conditions. The TGA is controlled by computer software which allows setting the heating rate, temperature, gas atmosphere and duration for each step of the test. The TGA records the mass and temperature of the sample over time. The analysis of this data for the purposes of calcium looping cycles is detailed in section 3.2.

2.2 – Dual Fluidized Bed Pilot Plant

The 100 kW_{th} dual-fluidized bed pilot plant located at CanmetENERGY in Ottawa, Ontario was used for the pilot plant experimental campaign. This section provides a description of the calciner, carbonator and the auxiliary systems used for testing. A schematic diagram of the pilot plant is shown in Figure 2-2 below.

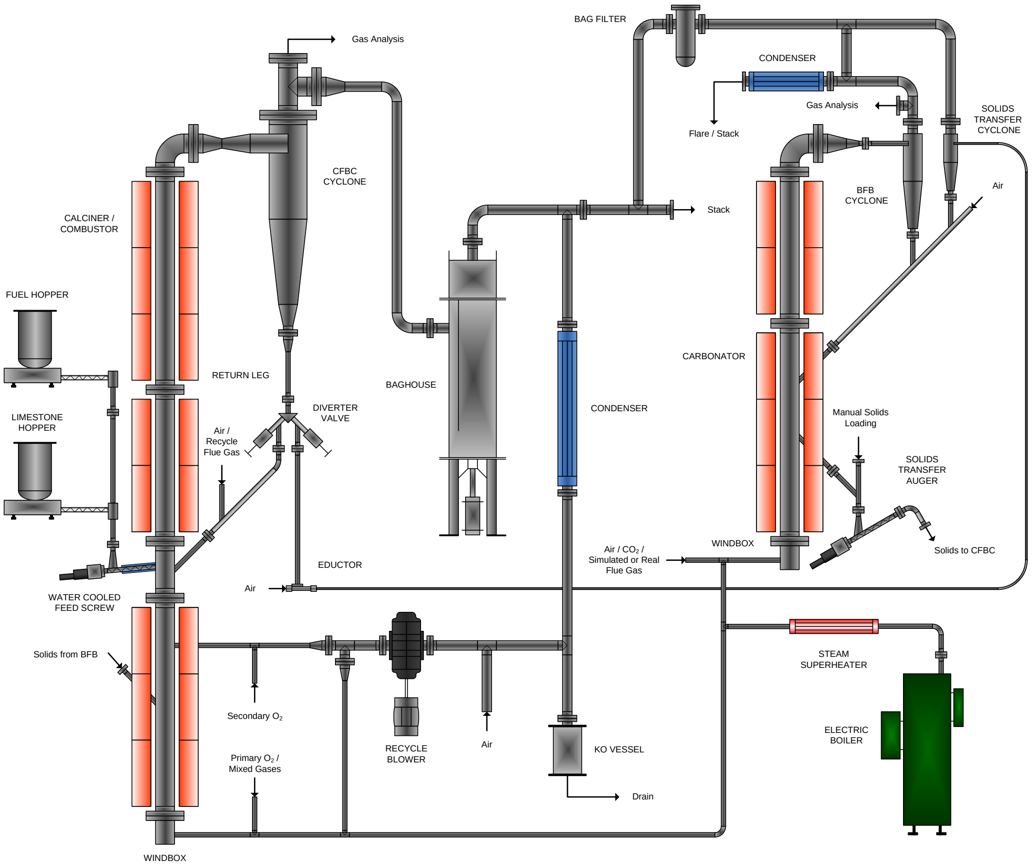

Figure 2-2 - Schematic diagram of the dual-fluidized bed calcium looping pilot plant.

2.2.1 – Calciner

The calciner reactor is a circulating fluidized bed combustor. The specifications of the reactor are outlined below.

Table 2-1 - Design specifications for the circulating fluidized bed calciner.

Design Specification	Value
Height	5.0 m
Inner Diameter	0.1 m
Operating Temperature	ambient - 1050°C
Operating Pressure	-10 kPa – 5 kPa
Superficial Gas Velocity	< 6.0 m/s

The calciner is lined with electric heaters. These heaters are used to pre-heat the reactor to a temperature suitable for the combustion of solid fuel. The majority of the heat required for calcination is provided by combustion; however the heaters are used to maintain a consistent temperature along the entire reactor. A loss-in-weight feeder with a water cooled screw is used to feed solid fuels to the calciner. The system is capable of burning various feedstocks including coal, petroleum coke and biomass. The inlet gas is supplied to the windbox by mass flow controllers. A nozzle-type distributor is used to distribute the gas flow throughout the bed material. Air can be supplied to the calciner from a compressor or a rotary lobe positive displacement blower. Oxygen (99.9%) is supplied from a bulk tank and can be mixed with up to 3 additional gases from cylinders. In addition, steam can be injected into the calciner. An electric boiler generates saturated steam at 690 kPa which is superheated to 190°C prior to being mixed with the other gases. A cyclone is fixed to the outlet of the calciner. This separates the majority of the solids from the gas stream and returns them to the reactor, allowing for operation as a circulating fluidized bed. Solids can be removed from the bottom of the bed through a 0.05 m channel in the distributor. Thermocouples are located every 0.25 m along the height of the reactor. Pressure transmitters are located before the distributor and at heights of 0.25, 0.76, 1.5, 3, 4 and 7 m. The differential pressure is also measured across the distributor and between each of the measured pressure points. The differential pressures are used to estimate the height of the bed in the reactor and the total bed inventory.

2.2.2 – Carbonator & Combustor

The carbonator is a bubbling fluidized bed reactor. The specifications of the reactor are outlined below.

Table 2-2 - Design specifications for the bubbling bed carbonator reactor.

Design Specification	Value
Height	3.0 m
Inner Diameter	0.1 m
Operating Temperature	ambient - 1050°C
Operating Pressure	-10 kPa – 5 kPa
Superficial Gas Velocity	< 2.0 m/s

The entire height of the carbonator is lined with electric heaters which provide the sole source of heat for the reactor. Gas is supplied to windbox via several mass flow controllers. Any combination of air, CO_2, SO_2 or other bottled gases can make up the inlet gas flow. The gas is fed to the reactor via a sintered steel plate used to distribute the flow evenly throughout the area of the reactor. A 0.02 m hole is present in the center of the distributor plate. This is closed by a ball valve and is used to discharge the reactor bed material. A cyclone is fixed to the outlet of the reactor as the primary gas-solid separation step. Any solids separated are returned to the reactor. The exhaust of the carbonator is passed through an induced draft fan. Thermocouples are located every 0.25 m along the height of the reactor. Pressure transmitters are located before the distributor and at heights of 0 m, 1.5 m and 3 m. The differential pressure is also measured across the distributor and between each of measured pressure points.

Although the carbonator is equipped to use mixed bottled gases to simulate flue gas, the use of real flue gas was desired for this work. Little experimentation has been done with pilot plants of this scale using flue gas produced from fuel combustion. Using a flue gas generated from combustion ensures all species, specifically moisture, are present in realistic quantities. To accomplish this, a natural gas combustor was designed to produce an adequate volume of flue gas suitable for carbonator operation. A schematic of the natural gas combustor vessel is shown in Figure 2-3.

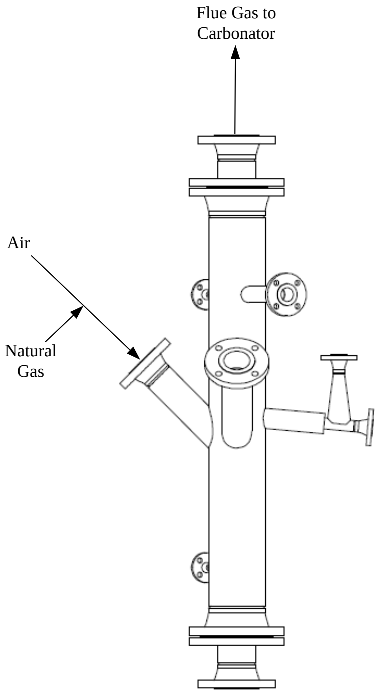

Figure 2-3 - Schematic of natural gas combustion vessel used to generate flue gas.

The vessel is composed of stainless steel, is 1.8 m in height and has a 0.15 m outer diameter. A 0.02 m thick layer of alumina bubble-cast refractory lines the inner surface. Refractory was used to ensure the outer steel shell was maintained at a safe operating temperature. The 8 kW_{th} nozzle-mix burner is mounted at a 45° angle and fires into the vessel. An infrared flame scanner is used to measure the intensity and stability of the flame after ignition. The scanner is interlocked with solenoid valves on the natural gas feed to shut off the fuel automatically in the event the flame is lost. The natural gas feed is controlled by a valved rotameter and a governing regulator is used to control the air flow and maintain a constant fuel-to-air ratio. The flue gas generated by the burner needs to be fed to the carbonator at a pressure high enough to overcome the pressure drop created by the distributor and the bed material. Unfortunately, the burner operates at a pressure of only 3 kPa which is insufficient to overcome the 26 kPa pressure drop across the distributor.

To overcome the pressure drop and allow consistent flow to the carbonator a heated diaphragm pump is used. The pump is heated to ensure that there is no condensation prior to the flue gas entering the carbonator. A moisture analyzer and a CO_2 analyzer are attached to the outlet of the vessel to monitor the composition of the flue gas. Moisture and carbon dioxide are the primary components of flue gas that impact the performance of the carbonator.

2.2.3 – Solid Transfer

The rate at which sorbent is transferred between the calciner and the carbonator is a key metric when evaluating the performance of the calcium looping process. From an operational perspective, it is also important to balance the bed inventory between the two reactors which requires good control of the solid transfer rates. This system utilizes two different methods for transferring solids from the carbonator to the calciner and from the calciner to the carbonator.

A 0.02 m diameter shaft-less screw conveyor is used to transfer the sorbent from the bubbling bed carbonator to the calciner. The material is transferred to the screw conveyor via an overflow port 0.25 m high on the carbonator. The rate at which the sorbent is moved to the calciner is controlled by a DC motor. The conveyor needs to be calibrated with the desired sorbent before a test so that the operators know what motor speed equates to the desired mass flow rate. Relationships between the motor speed and the mass flow of several materials, including calcium oxide at various carbonation conversions, were determined by weighing the solids discharged by the screw over a fixed time period at a several speeds. These linear relationships were used to select a motor speed based on a desired mass flow of sorbent. In addition to transferring solids between the reactors, the screw conveyor is also used to add new sorbent to the system. Batches of fresh sorbent were added via a 0.05 m port with a ball valve which is attached at the base of the conveyor where the solids drop in from the carbonator.

A gas-solid eductor is used to transfer the sorbent from the circulating fluidized bed calciner to the carbonator. The eductor is connected to the solids outlet of the cyclone; therefore solids are transferred to the carbonator after being circulated out of the calciner. Air is flowed through a converging then diverging nozzle in the eductor which creates a vacuum between the two nozzles. The solids are pulled into the eductor by the vacuum and entrained in the air flow. The mixed gas-solid flow is sent through a tube to a second cyclone attached to the carbonator. The solids from the eductor are removed by the cyclone and sent to the carbonator and the gas is vented to avoid diluting the carbonator atmosphere. The solid mass flow rate is controlled by the volume and pressure of the eductor air. Bucket tests were completed with various materials, including calcium oxide, to correlate the eductor gas and solid mass flow.

2.2.4 – Gas Treatment & Sampling

The composition of the gas leaving each reactor is the primary metric used to analyze the test results and operate the equipment safely. Therefore, the exhaust gas from the calciner and carbonator are both cleaned and analyzed before being released through the stack. After leaving the cyclone, the gas from the calciner is sent to a baghouse to remove any remaining particulate which was not removed by the cyclone. After leaving the baghouse, the gas stream is split. Part of the gas is sent to the stack and the remainder is recycled back to the inlet of the reactor. The gas which is recycled passes through a condenser and is cooled to approximately 20°C with cooling water. This removes the majority of the moisture from the gas which is required for operation of the recycle blower. The calciner flue gas is analyzed by extracting a sample through a 1µm sintered filter located at the top of the cyclone. A filter is required here to prevent particulate from being entrained in the sample gas and damaging downstream analytical equipment. The sample slipstream is dried before being pumped to an analyzer rack. Analyzers were used to measure and log the instantaneous O_2, CO_2, CO, SO_2 and NO_2 concentrations.

Similarly, the carbonator exhaust gas is passed through a single bag filter after leaving the cyclone. Unlike the calciner, a large baghouse is not required as the velocities are significantly lower in the bubbling bed (~1.5 m/s compared to ~4 m/s) therefore much less particulate has the required momentum to leave the bed. The carbonator exhaust is sent to the stack after passing through the bag filter. A sample of the carbonator exhaust gas is taken via a 1 µm sintered filter located at the top of the cyclone. The sample gas is dried before being pumped to an analyzer rack where the O_2, CO_2, CO and SO_2 concentrations were measured and logged.

2.3 – Solid Sample Analysis

Solid samples were collected during and at the end of each test. After a test was completed, samples were taken from both reactors, the screw conveyor and the baghouse. All solids were removed from the system and weighed to perform a mass balance on the sorbent. During operation, samples were regularly collected from the eductor transfer line to evaluate the condition of the calcined sorbent. Samples were also regularly collected from the screw conveyor to evaluate the sorbent at the outlet of the carbonator. The mass of the extracted samples was between 60 and 80 g which is a sufficient quantity to allow for several different analyses.

The samples were analyzed to determine the conversion of the sorbent leaving the carbonator and to characterize the morphology of the sorbent leaving the calciner. The samples taken from the carbonator were analyzed with a TGA. The samples were heated from ambient to 900°C at 50°C/min in an inert nitrogen atmosphere. This results in complete calcination. An example of the resulting weight-loss curve is shown in Figure 2-4.

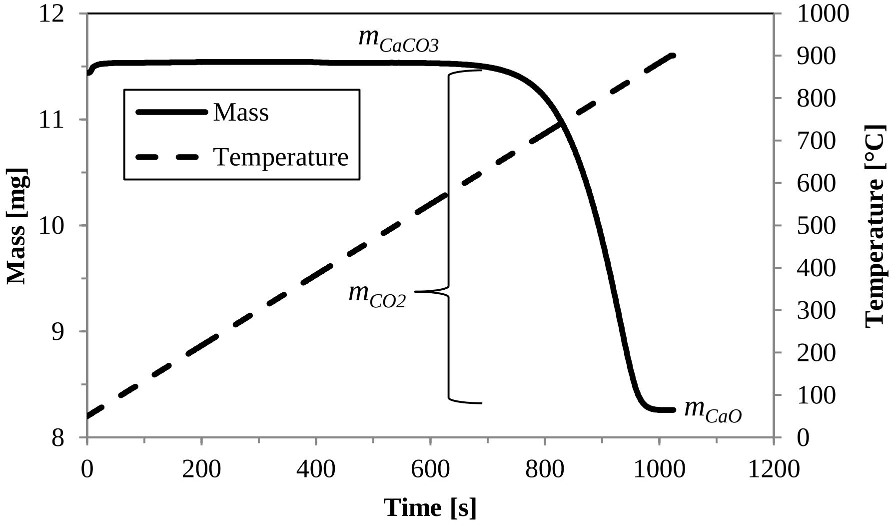

Figure 2-4 - Calcination in a TGA under a nitrogen atmosphere of a limestone sample taken from the pilot-plant carbonator.

The conversion of calcium oxide to calcium carbonate is determined by assuming all loss in weight is due to release of carbon dioxide from the calcination reaction. The remaining mass after calcination, m_{CaO}, is assumed to be primarily calcium oxide. The carbonation conversion was evaluated via equation 2-1.

$$X_{carb} = \frac{m_{CaCO_3} - m_{CaO}}{m_{CaO}\beta} \frac{M_{CaO}}{M_{CO_2}} \tag{2-1}$$

Here, m_{CaCO3} is the mass of calcium carbonate, m_{CaO} is the mass of calcium oxide, M is the molar mass of each species and β is the purity of calcium oxide. The TGA test utilizes small sample masses, approximately 10 mg. To ensure the TGA results represent the bulk of the bed inventory at the time the sample was taken, the calcination was repeated in a muffle furnace with a larger mass of approximately 5 g. Samples were weighed before and after being heated in the furnace using a laboratory balance with a sensitivity of 0.1 mg. The samples were heated to 850°C in air and held at temperature for 1.5 hours. The conversion was again calculated using equation 2-1. The TGA and furnace results were compared to ensure the analysis is representative of the bulk solid mixture in the reactor when the sample was taken.

The particle structure of the calciner samples was also analyzed to gain insights on the resulting reactivity of the sorbent. The surface area and pore volume were assessed via the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methodologies, respectively.[1] The nitrogen adsorption analysis was done with a Micromeritics TriStar II.

2.4– References

1. Rouquerol, F. *Adsorption by powders and porous solids principles, methodology and applications,* 2nd ed.; Academic Press: Amsterdam; Boston, 2014.

Chapter 3 - The influence of steam injection during calcination on the reactivity of CaO-based sorbent for carbon capture

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3.1 - Abstract

Calcium looping is an emerging CO_2 capture technology based on cyclic calcination/carbonation reactions using calcium-based sorbents. Steam is typically present in flue/fuel gas streams from combustion or gasification and in oxy-fuel combustors used for sorbent regeneration. The effect of steam in the calciner on sorbent performance has not been extensively studied in the literature. Here, experiments were conducted using a thermogravimetric analyzer (TGA) to determine the effect of steam injection during calcination on sorbent reactivity for carbonation. Two Canadian limestones, Cadomin and Havelock, were tested. Various levels of steam (up to 40%) were injected in the sorbent regeneration process throughout 15 calcination/carbonation cycles. All concentrations of steam were found to increase sorbent reactivity for carbonation for both sorbents. A level of 15% steam with calcination had the largest impact on carrying capacity for both sorbents. Steam changes the morphology of the sorbent while calcination is occurring, likely causing a shift from smaller to larger pores, resulting in a structure which increases carrying capacity. It was also demonstrated that steam addition has a larger impact on sorbent reactivity with carbonation than for calcination.

3.2 - Introduction

Power generation systems using fossil fuels and carbon capture techniques are typically classified into three categories: post-combustion, pre-combustion and oxy-fuel combustion. Post-combustion systems employing wet scrubbing of flue gas using liquid amine solutions are thought to be the most commercially-promising process for CO_2 separation.[1,2] However, the drawbacks of wet scrubbing include high energy demand for solvent regeneration (e.g., low process efficiency), relatively high operational and maintenance costs, potential solvent degradation, and solvent instability at high temperature.[2,3] In contrast to solvent-based processes, solid sorbent-based processes can be carried out under more flexible operating conditions with higher energy efficiency.[4] This work examines the effects of steam on calcium looping, which is usually a high-temperature solid sorbent-based post-combustion CO_2 capture technology that employs cyclic calcination/carbonation reactions with calcium-based sorbents.[4,5]

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{3-1}$$

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} \tag{3-2}$$

The calcium looping process is promising for either new or retrofit applications for CO_2 capture from flue gas. A relatively high-purity CO_2 stream is produced in the sorbent regeneration step (calcination) suitable for compression and sequestration. The advantages of such a process, compared to other proposed technologies, include a lower energy penalty, use of mature fluidized bed technology, an inexpensive and nontoxic sorbent derived from limestone, lower operating costs and potential synergy by using the spent sorbent in the cement industry.[6,7] The bench- and pilot-scale work to date indicates that the technology is reliable and promising, but with the major drawback of significant decay in the reactivity of the naturally-occurring lime-based sorbents, such as limestone and dolomite, after multiple CO_2 capture-and-release cycles.[4,8] Phenomena known to influence the sorbent reactivity and conversion include sintering, reaction with flue gas or syngas impurities (primarily sulphur species), and deposition of fuel ash onto the sorbent surface.[9,10,11]

In the Ca-looping processes, steam is typically present in the gas streams from either combustion or gasification in the carbonation reactor and from oxy-fuel combustion in the calciner for sorbent regeneration. Therefore, understanding the influence of steam for both calcination and carbonation is essential to understanding sorbent performance. Steam addition in the carbonation step was first examined by Symonds et al.[12] for CO_2 capture from syngas in a thermogravimetric analyzer (TGA) and at the pilot scale.[13] TGA studies were carried out at high enough temperatures to ensure that steam did not actually react with CaO, as is the case of steam hydration, but nonetheless sorbent performance was improved in the presence of steam and the effect is more pronounced after multiple reaction cycles.[15] CaO also enhances the water-gas shift reaction as a catalyst promoting H_2 production and enhancing CO_2 capture.[12] Experiments similar to the previous TGA studies[12,15] were repeated in a pilot-scale dual fluidized bed unit and the enhancement of sorbent conversion was confirmed whenever steam was added in the initial fast reaction step of carbonation or even later on (60 min) in the slow diffusion-controlled carbonation reaction regime.[13] This phenomenon may be interpreted in several ways including catalytic improvement of the capture process through the hydration of CaO at the surface of sorbent, forming $Ca(OH)_2$ as a transient intermediate since $Ca(OH)_2$ is not thermodynamically stable at typical carbonation temperatures (>600°C).[10] This would explain the increase in macroporosity for the carbonated samples and increased initial CO_2 capture due to a prolonged fast reaction phase of carbonation.[13] The enhancement of CO_2 mobility due to a reduction in diffusion resistance arising from the presence of steam also explains the increased sorbent conversion when steam is added in the middle of a carbonation step.[12-14]

There have been several recent studies on the addition of steam for the carbonation reaction.[15-18] Manovic and Anthony[15] studied seven limestones with an original size of 250-425 μm and carbonation temperature from 350 to 800°C in the presence of steam (10-20%) and reported that sorbent reactivity was improved, especially for the most sintered samples, and at relatively low temperature. This finding is attributed to the effect of steam in accelerating solid state diffusion. Dou et al.[16] investigated the effect of steam addition in the carbonation reaction in a fixed-bed reactor and reported an improvement of CO_2 capture with steam addition. In this case, the authors suggested that the enhancement of sorbent utilization with steam was due to the conversion of CaO to $Ca(OH)_2$ which reacted directly with CO_2. Yang and Xiao[17] studied the effects of steam addition on CaO carbonation performance in a pressurized TGA. In contrast to Dou et al.[16], these authors reported that steam increased CaO carbonation performance significantly, even if $Ca(OH)_2$ is not formed prior to carbonation. They suggested that this effect should thus be attributed to steam catalysis of the reaction between CaO and CO_2. Recently, Arias et al.[18] looked at the effect of steam in the initial carbonation period, where the reaction is under the fast kinetic-controlled regime, for two limestone samples at typical carbonation conditions in two TGA systems. Their results showed that while the presence of steam (20%) can improve the overall sorbent performance by increasing conversion with cycling, steam has no influence on the initial reaction rate constant. Similar kinetic rate constant values were obtained with and without steam present in the reacting gas.

Similarly, the addition of steam in the sorbent regeneration step has also been examined to simulate the flue gas produced by burning any hydrocarbon fuel for sorbent calcination. Reported data from recent studies showed, in general, a positive influence on sorbent performance by reducing the extent of CaO sintering in the presence of steam.[19,20] This contrasts with earlier reports of the negative effect of steam which enhanced sorbent sintering in the calcination reaction.[21,22] Borgwardt[21] found that, compared to N_2, sorbent sintering could be promoted by the addition of other components in the combustion flue gases, including water vapour and carbon dioxide. Each gas strongly augmented the sintering process, and their combined effects were even more severe. Porosity reduction was found to be accelerated by the presence of either H_2O or CO_2 in the sintering atmosphere and follow the Coble logarithmic law for sintering at 800–1000°C.[21]

Recently, Wang et al.[19] investigated limestone (250–500 μm) decomposition in an increasingly diluted atmosphere (20-100% steam in CO_2). They reported an increase in calcination conversion over 40 minutes corresponding to increasing steam concentration for the calcination due to enhanced heat transfer from gas to solid. The CaO produced from steam dilution showed a significant reduction of the time required for subsequent complete hydration ($CaO \rightarrow Ca(OH)_2$) and as well an improved reactivity in the carbonation reaction compared to that for CaO produced without steam. Donat et al.[20] examined the effect of steam (1–20%) in calcination for four naturally-occurring limestones and reported that steam enhanced sorbent carbonation reactivity at a steam concentration as low as 1%. Above that concentration they observed no further significant effect. The improvement correlates with promoted sintering that actually results in a more stable pore structure for most pores larger than 50 nm in diameter, which typically evolves when no steam is present.[22] By comparing the results from the addition of steam in carbonation, they suggested that the changes of sorbent morphology due to the presence of steam in calcination could have a more pronounced influence on sorbent reactivity than the presence of steam in carbonation.[20]

More work is obviously needed to better understand the mechanisms of the effect of steam on the reactivity of CaO for CO_2 capture in the high-temperature calcination/carbonation looping process. This work examines the effects of steam on calcination at concentrations consistent with solid fuel combustion and at higher levels to determine if there is any practical advantage in additional steam injection in the calciner. Results are presented for tests conducted with steam concentrations from 0 to 40% in calcination over 15 cycles.

3.3 - Experimental

Cadomin (Alberta, Canada) and Havelock (New Brunswick, Canada) limestones were tested at the 250-425 µm particle size range. Tests were also done using a smaller size fraction (45-106 µm) of Cadomin. Table 3-1 shows the chemical composition, derived from X-ray fluorescence (XRF) analysis, of the limestones tested. It should be noted that the smaller particles, which are ground from the same batch of larger particles, contain higher levels of impurities, indicating the heterogeneity of the sample particles.

Table 3-1 - Limestone compositions as tested (250-425 μm and 45-106 μm size fractions)

Component (wt.%)	Cadomin 45-106 μm	Cadomin 250-425 μm	Havelock 250-425 μm
SiO_2	2.09	1.44	0.73
Al_2O_3	1.12	0.30	0.27
Fe_2O_3	0.79	0.35	0.21
TiO_2	0.07	<0.03	<0.03
P_2O_5	<0.03	<0.03	<0.03
CaO	52.60	52.27	54.81
MgO	1.52	1.54	0.23
SO_3	2.72	<0.10	<0.10
Na_2O	<0.20	<0.20	<0.20
K_2O	0.17	0.09	0.05
Ba	257	<250	<250
Sr	296	258	171
V	97	<50	<50
Ni	257	<50	<50
Mn	261	80	936
Cr	779	<50	<50
Cu	2418	<30	32
Zn	158	<30	33
LOF	38.5	43.96	43.55

The performance of the sorbent under varying levels of steam addition for the calcination was studied using a TGA (Perkin-Elmer TGA-7). All samples used were approximately 5 mg, to avoid mass transfer limitations. Steam was produced using a steam generator and the injection rate controlled by a syringe pump. The steam system was controlled by a timer to allow intermittent steam injection, for instance, in the cases when steam was required only in the calcination step. The other gas flow rates were controlled using rotameters.

The calcination was carried out for 5 min at either 875 or 925°C to examine the benefits of adding steam to lower calcination temperature in a high CO_2 environment. Calcinations took place in a gas mixture of 60% CO_2, with H_2O varying from 0 to 40% (balance N_2). The carbonation step was carried out at 620°C for 20 minutes in a simulated coal-fired flue gas environment (15% CO_2, balance N_2). Steam was injected in some carbonation tests at 15% to investigate the effect of adding steam in both the calcination and the carbonation steps. All tests employed 15 calcination/carbonation cycles. Carbonation conversion was calculated based on the degree of mass change recorded, assuming all increases in mass are attributed to $CaCO_3$ formation, using the equation shown below:

$$X(\%) = \frac{(W_{carb} - W_{calc})}{W_0\beta}\frac{M_{CaO}}{M_{CO_2}} \times 100 \tag{3-3}$$

where W_{carb} is the mass of the sample after carbonation, W_{calc} is the mass of the sample after calcination, W_0 is the original sample mass, β is a purity factor (52.27% for the larger Cadomin samples here) and M is molar mass. It should be noted the conversion values shown in the figures below are calculated based on the mass at the end of the 20-minute carbonation regime. The duration of the carbonation reaction and the point in time at which conversion is calculated will nonetheless affect the observed results.

3.4 - Results and Discussion

Steam effects on the physical characteristics of the sorbent during calcination will impact the carbonation reaction. For example, if the sorbent surface area decreases as calcination proceeds, the subsequent carbonation should show a decreased conversion. Unfortunately, the sample mass (~5 mg) used in this work is insufficient to perform detailed chemical and physical analysis on sorbent characteristics, such as Brunauer-Emmett-Teller (BET) analysis; therefore, the impact of steam injection with calcination is evaluated based on any change in conversion for the subsequent carbonation. The effect of steam addition for calcination was investigated by introducing steam for calcination alone while all other variables were kept constant. The final carbonation conversion after each cycle for tests using Cadomin limestone with calcination performed at 925°C with varying levels of steam are shown in Figure 3-1. The standard deviation based on triplicate runs for the 0%, 15% and 40% cases, for any individual conversion value presented in Figure 3-1 ranges from 0.06 to 1.8%. The maximum difference between duplicate runs for the 5% condition is 3.2%.

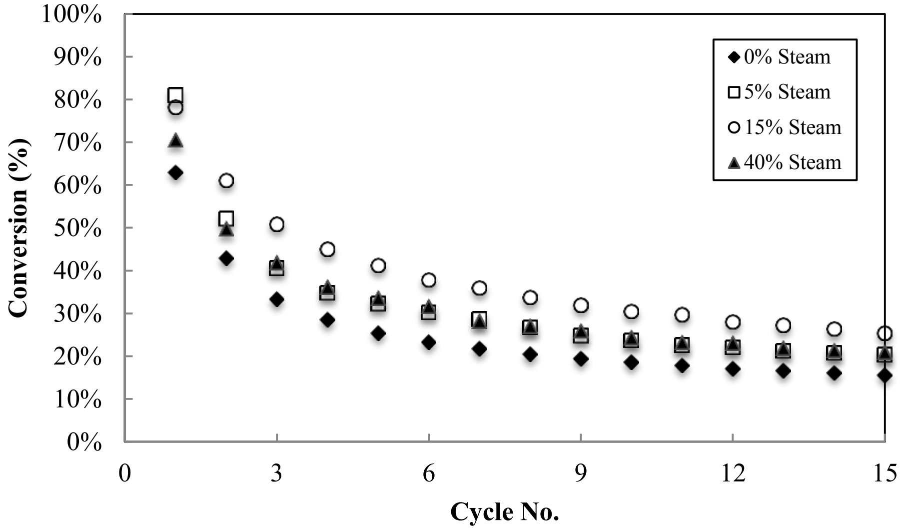

Figure 3-1 - Carbonation conversion from TGA tests performed on Cadomin limestone (250-425 μm) with calcination at 925°C, 60% CO_2 and varying steam levels (balance N_2) followed by carbonation at 620°C (15% CO_2, balance N_2)

The addition of steam while calcination is proceeding has an overall positive effect on the carrying capacity of Cadomin. Interestingly, the performance at 5% (by volume) and 40% steam is very similar, with the best performance in these tests seen at ~15%. The final carbonation conversion after each cycle for tests using Havelock limestone with calcination performed at

925°C with varying levels of steam are shown in Figure 3-2 and are very similar to the results seen with Cadomin.

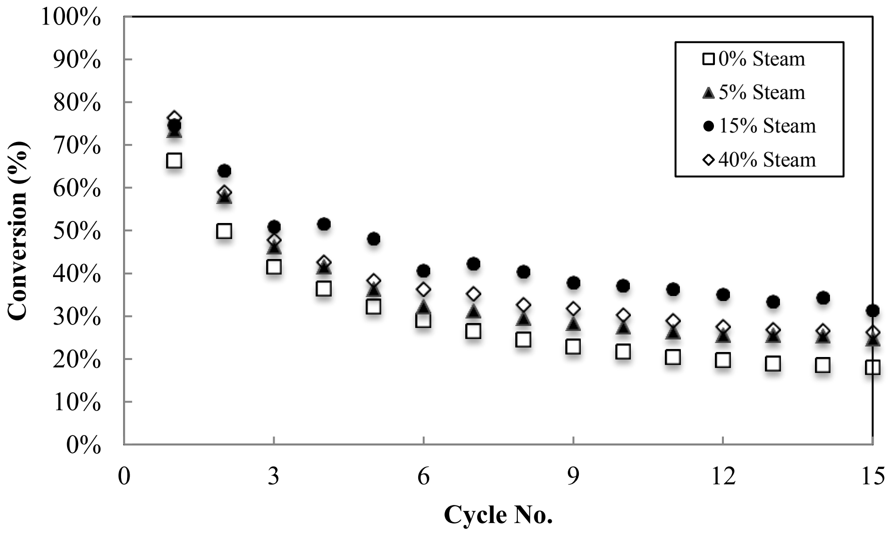

Figure 3-2 - Carbonation conversion from TGA tests performed on Havelock limestone (250-425 μm) with calcination at 925°C, 60% CO_2 and varying steam levels (balance N_2) followed by carbonation at 620°C (15% CO_2, balance N_2)

As seen in the Cadomin tests, all concentrations of steam tested in calcination increase the carbon carrying capacity. Again, 5% and 40% by volume steam show very similar performance. The best performance here is also seen at 15% steam addition.

Donat et al.[20], who used a small bubbling bed unit, also observed an increase in carrying capacity resulting from steam injection with calcination and noted that steam enhances sorbent reactivity at concentrations as low as 1% with no significant improvement at higher concentrations. By contrast, this work shows that, for both sorbents tested here, steam concentrations in excess of 1% continue to enhance the sorbent carrying capacity. The increased carrying capacity can be explained by a change in sorbent morphology during calcination. At a given temperature, steam is known to enhance sintering of CaO to a greater degree than other calcination gases, such as N_2.[21] Steam injection is expected to produce a larger average pore diameter and reduced particle surface area resulting from an increase in particle sintering.[20] A reduced particle surface area would adversely affect CO_2 adsorption at the surface; but, larger pores would lower diffusional resistance caused by carbonate formation at the surface, allowing higher overall conversion. Phalak et al.[23] observed such a shift, from smaller to large pores, while investigating reactivation via hydration. Their work demonstrated that this shift resulted in a higher capture capacity. This would indicate that the particle pore size, rather than the surface area, could be more influential in assisting the diffusion of reactants (such as CO_2) deeper inside the particle where there are still active CaO sites, thus increasing sorbent conversion. This mechanism would potentially explain the results presented in this study; however, a BET analysis would be required for confirmation of this hypothesis. Figure 3-3 shows the degree of carbonation versus reaction time for TGA experiments on Cadomin with varying levels of steam present for the calcination at 925°C. The relative performance of different steam concentrations is consistent throughout all 15 cycles and for both limestones tested (not shown here).

Both the fast, kinetically-controlled reaction regime and the diffusion-limited reaction regime are affected by steam injection with the calcination. An increase in the steam partial pressure results in an increased extent of reaction for the fast regime, up to a maximum at a steam concentration of 15%. The rate of reaction in the fast regime is the same for all steam compositions. This implies that any change the sorbent undergoes is related to the concentration of steam present. Above an optimum level, the steam has a negative impact on the sorbent's ability to react in the fast carbonation reaction. The best results observed in this work are for 15% steam; however, no attempts were made to determine the optimal level of steam addition more precisely but, these results are consistent with the hypothesis that steam causes the pore size to increase.[20]

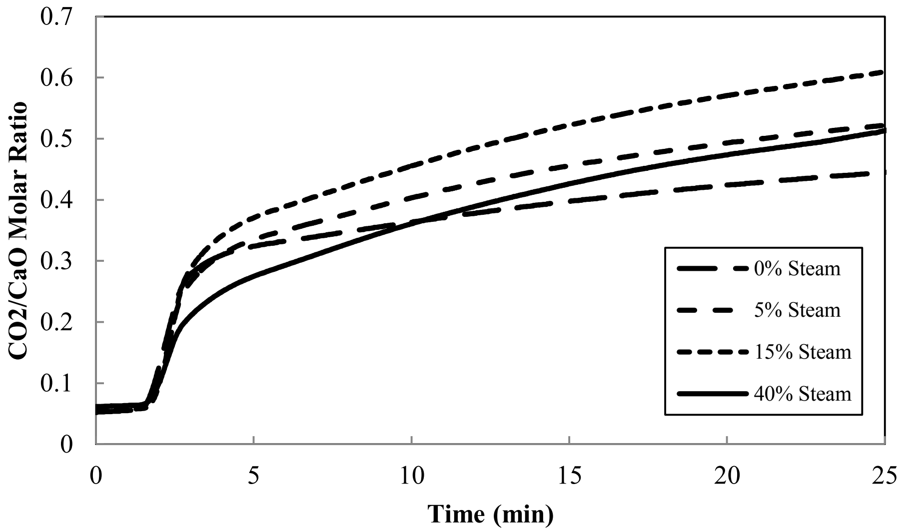

Figure 3-3 - Second carbonation from TGA tests performed on Cadomin with calcination at 925°C, 60% CO_2 (balance N_2) and varying steam levels

If high steam concentrations (e.g., 40%) enhance sintering of the sorbent beyond the point where it is advantageous, the pore size must shift to become larger than the optimal 50 nm which would significantly reduce the total surface area.[20] This reduction should result in a lower conversion for the fast reaction regime, where the calcine particle surface is preferentially converted. This mechanism would explain the reduced extent of reaction for the fast carbonation period for the 40% steam case.

The rate of carbonation for the diffusion-limited regime increases as the steam concentration increases, to a maximum at 15%. Concentrations of 15% and 40% steam allow for similar carbonation rates for this regime. Although steam present in calcination has a clear impact on the diffusion-limited reaction period, this effect would be hard to incorporate into an industrial-scale carbonator due to typically short residence times of the particles. For example, at a concentration of 40% steam, carbonation time must be longer than 10 minutes to achieve a conversion similar to the no-steam case (Figure 3-3). In an industrial-scale fluidized bed, the majority of carbonation is expected to be due to the initial fast reaction period, making it difficult to take advantage of any increase in reactivity for the slow reaction regime. Therefore, of the concentrations tested, 15% steam is considered optimal because it shows the highest carbonate conversion for the fast reaction period.

Tests were carried out at 925°C to simulate the required operating temperature for an oxy-fuel calciner. A temperature 25-50°C higher than the equilibrium temperature is required for rapid calcination since the CO_2 concentration is higher at the particle surface than in the bulk gas.[25] Steam injection in the calciner would lower the CO_2 partial pressure and enable calcination at lower temperatures. Tests were carried out at 875°C which will allow for rapid calcination in a 60% CO_2 environment. Figure 3-4 shows TGA results for 15 cycles with calcination at 925 and 875°C in 60% CO_2/40% steam, 60% CO_2/40% N_2 and 100% CO_2.

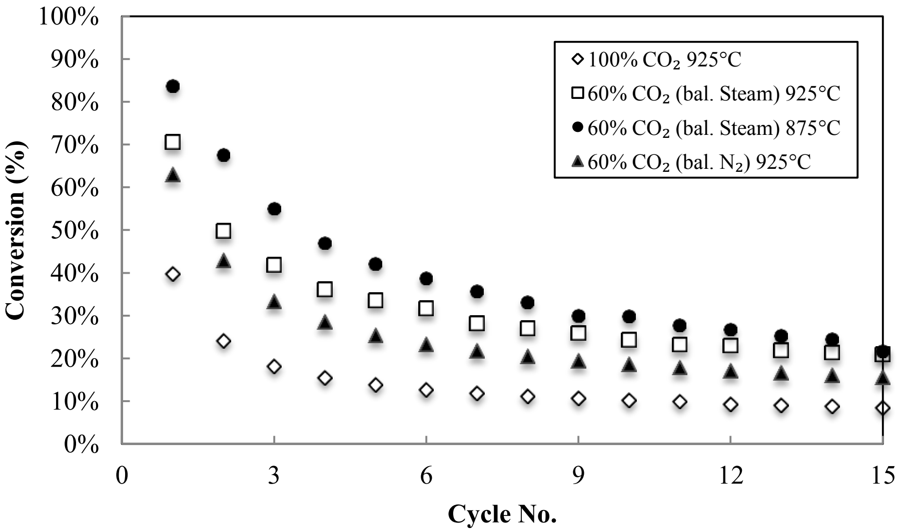

Figure 3-4 - Carbonation conversion from TGA tests performed using Cadomin with varying calcination temperatures with 60% CO_2 (balance steam or N_2), compared to the oxy-fuel case (100% CO_2, 925°C)

The highest conversion is achieved with calcination at 875°C with 40% steam, balance CO_2. The steam cases (60% CO_2, 40% H_2O) show only a minor performance increase compared to the no-steam case (60% CO_2, 40% N_2) by the 15th cycle. At 60% CO_2, the conversion decreases more rapidly after cycling at 925°C than at 875°C; however, the performance is very similar after 15 cycles. Rapid calcination likely started before the sample reached 925°C due to the decreased CO_2 concentration. This is true regardless of steam concentration. Steam injection causes a lower CO_2 partial pressure, resulting in a significantly higher carbonation conversion compared to the oxy-fuel-based case (100% CO_2). The oxy-fuel case is the 'worst case' scenario, as it requires a higher calcination temperature corresponding to the increased CO_2 partial pressure. The high temperature and high CO_2 level both enhance the sintering of CaO[21,25], resulting in the most sintered sorbent and the worst carbonation performance. A lower CO_2 concentration reduces the severity of the particle sintering, resulting in better carrying capacity from the tests with 60% CO_2 in calcination. The rapid decline in initial performance of the 925°C cases at 60% CO_2 results from the extended exposure of the CaO to higher temperature after calcination is complete. Steam injection for the sorbent regeneration will increase the carbonation conversion of the sorbent as shown above. Additionally, from a practical point of view, steam injection can lower the CO_2 partial pressure in the calciner, allowing for lower operating temperatures. This has the potential to decrease process energy requirements, while lowering the rate of sorbent deactivation.

A limited series of tests was carried out using a smaller particle size (45-106 μm) of Cadomin, to determine if the effects of steam are independent of particle size. Figure 3-5 shows a comparison of the effects of sorbent particle size on CO_2 conversions after carbonation with and without steam addition with calcination at 875°C and a steam concentration of 40%. At all conditions tested, the large (250-425 μm) particles outperformed the smaller particles (45-106 μm) over all 15 cycles. This is counterintuitive because smaller particles should have more surface area available for carbonation, resulting in an increased extent of reaction and therefore a higher final conversion. It is interesting to note that the drop in reactivity observed with the small particles occurs very rapidly in the first 5 cycles. This rapid drop in sorbent reactivity is observed in tests with and without steam present in the carbonation. This could be a result of higher levels of impurities(Si, K, Mn, Cu, etc.) in the smaller particles (Table 3-1), which are suggested to reduce sorbent reactivity by enhancing sintering.[25,26] Smaller particles have more surface area per unit mass than larger particles and, similarly, have fewer internal sites for carbonation due to a decreased radius. Thus, it can be assumed that most of the carbonation of the smaller calcine particles takes place at the particle surface. Smaller particles are, therefore, more susceptible to the effects of surface sintering, resulting in a rapid drop in sorbent reactivity. Figure 3-5 represents typical performance curves for all conditions tested in this study, comparing the results of both particle sizes.

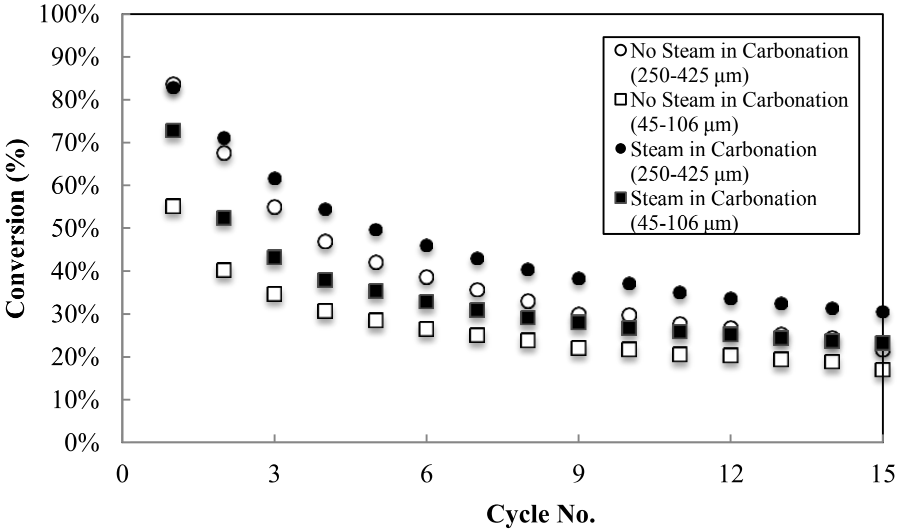

Figure 3-5 - Carbonation conversion from TGA tests performed using Cadomin with calcination at 875°C (60% CO_2 and 40% H_2O) at two different particle sizes with and without steam in carbonation

It is now clear that the addition of steam with carbonation enhances the carrying capacity of the sorbent.[12,13,15,18] This work has shown that the presence of steam for calcination can also increase the carrying capacity of the sorbent. This is presumed to be caused by changes in sorbent morphology.[20] To determine the relative magnitudes of these effects, TGA tests were conducted with steam injected with both calcination and carbonation to compare with steam injection for calcination alone. The resulting performance curves over 15 cycles with calcinations performed at 925°C (60% CO_2) are shown in Figure 3-6.

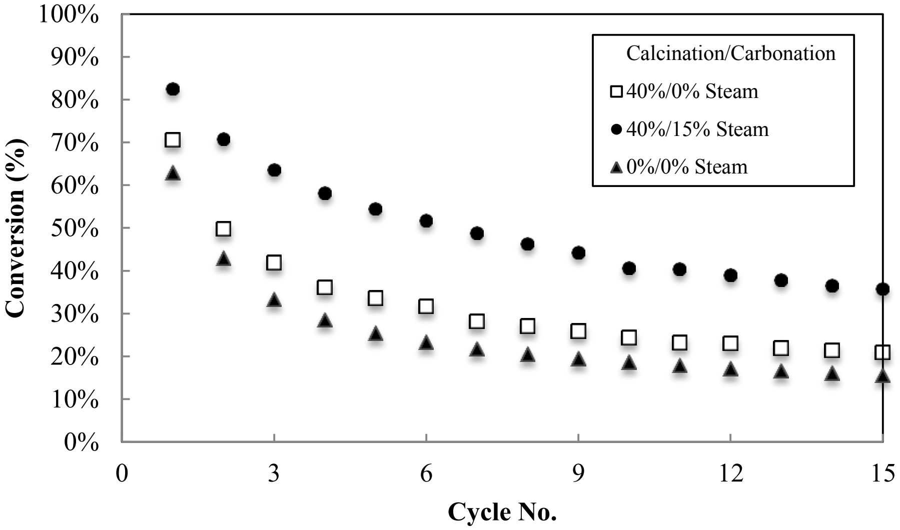

Figure 3-6 - Carbonation conversion from TGA tests performed using Cadomin with calcination at 925°C and 60% CO_2 (balance N_2) with steam in calcination only; and in calcination and carbonation

Steam injection with carbonation results in a much larger increase in carrying capacity compared to steam injection for calcination. A concentration of 15% steam for the carbonation results in a 15 percentage point increase in conversion after 15 cycles. However, a concentration of 40% steam for calcination only results in a 5 percentage point increase after 15 cycles. The different levels of improvement from steam injection for either calcination or carbonation imply that the carrying capacity is impacted via two distinct mechanisms.

To show that steam injection for calcination and carbonation impact sorbent carrying capacity via different mechanisms, steam was injected only for calcination and during calcination/carbonation after 11 dry cycles for comparison. The results are shown in Figure 3-7.

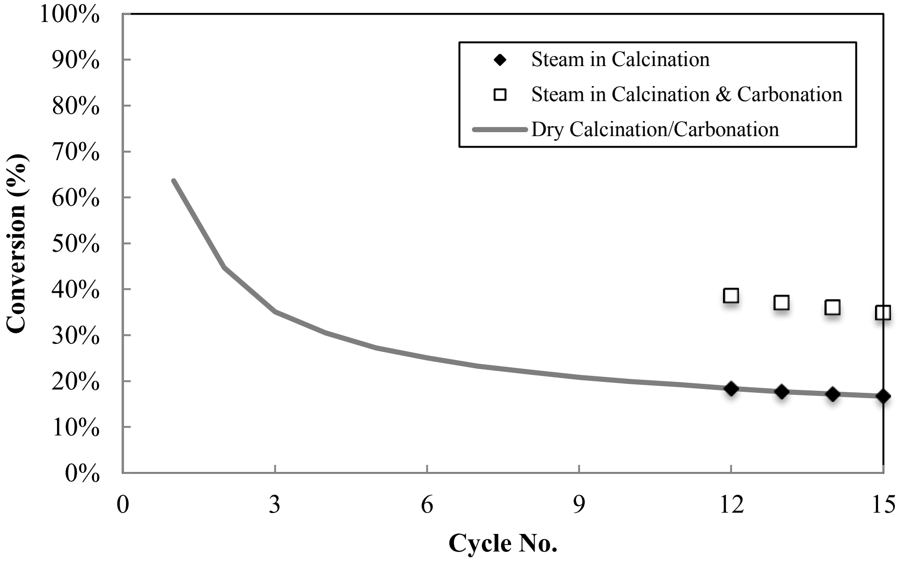

Figure 3-7 - Carbonation conversion from TGA tests performed using Cadomin with calcination at 925°C, 60% CO_2 (balance N_2) with steam injected after 11 cycles

Steam injection for calcination after 11 cycles had no impact on the carrying capacity. This can be explained based on sorbent morphology. After 11 cycles, the sorbent has undergone severe thermal sintering. If steam were influencing the pore structure via sintering as suggested, the steam would have to be present starting at the first cycle to have an impact. Once the structure is altered via thermal sintering, it is unlikely that the steam can further restructure the sorbent. Steam injection with both calcination and carbonation, however, shows a significant increase in conversion even after 11 cycles without steam. The observed performance increase is due to the introduction of steam for carbonation since the delayed injection of steam with calcination was shown to have no effect. Previous work done with steam addition for carbonation suggests that the extent of reaction in the fast regime and the slow diffusion reaction rate, and thus carrying capacity, are increased.[12,17,20] These results fit well with such mechanisms. Finally, it is important to reiterate that these mechanisms are quite different from those previously researched for the effects of hydration on sulfation[27,28], which require the formation of $Ca(OH)_2$ and should be clearly distinguished from them.

3.5 - Conclusions

The effect of steam injection on limestone calcination on sorbent CO_2 capacity has been studied. Steam introduced with calcination has been shown to increase sorbent reactivity at the temperatures studied (925 and 875°C), particle size fractions (250-425 μm and 45-106 μm) and for both sorbents tested. For the steam concentrations tested, a concentration of 15% was found to have the largest impact on sorbent carrying capacity. Steam injection for calcination was found to have a smaller effect on sorbent carrying capacity than injection for carbonation. Steam was shown to affect the reactivity of the sorbent via two distinct mechanisms during calcination and carbonation. The sorbent morphology is changed by steam in calcination resulting in a structure that increases carbonation reactivity, likely via a shift from smaller to larger pores. Steam in carbonation was also shown to influence the reaction directly resulting in a larger increase in conversion.

3.6 - References

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Chapter 4 - Steam Addition to Calcination for the Enhancement of CaO-Based Sorbent Reactivity for CO_2 Capture: A Pilot Study

Manuscript prepared for publication in an academic journal.

4.1 - Abstract

Calcium looping is a post-combustion carbon capture technology which uses natural limestone as a sorbent. The reactivity of the natural limestone, as CO_2 absorbent, decays with each calcination/carbonation cycle. Steam has been shown to decrease the reactivity decay and can also be used to reactivate spent sorbent. A testing campaign with continuous CO_2 capture and various levels of steam in the oxy-fired calciner was completed in a 100 kW_{th} dual-fluidized bed pilot plant. The calciner was operated with steam concentrations of 0%, 15% and 65% at the inlet of the windbox. The increase in steam in the calciner decreased the fresh sorbent make-up rate; for instance a 78% reduction in make-up was observed with 65% steam in the calciner. The increased carrying capacity of the sorbent is due to the increase in pore volume and surface area resulting from the increase in steam concentration as well as the corresponding reduction in CO_2 concentration and possible decrease in calcination temperature, which would reduce thermal and CO_2-induced sintering.

4.2 - Introduction

Coal and other fossil fuels continue to provide over 80% of global energy production.[1] Carbon Capture and Storage (CCS) technologies will be instrumental in the coming years to curb greenhouse gas emissions while fossil fuels will remain as a major resource for the continually increasing world-wide energy demand. Calcium looping is an emerging carbon capture technology which utilizes mature fluidized bed technology and has applications in both pre- and post-combustion capture. The calcium looping process utilizes natural limestone, which is abundant and inexpensive, to capture CO_2 from flue or fuel gas. The reversible carbonation/calcination reaction shown below is the basis for the process.

$$CaO_s + CO_{2_g} \leftrightarrow CaCO_{3_s} + 178.2\ \frac{kJ}{mol} \quad (4\text{-}1)$$

There are many proposed configurations for this process;[2,3,4] however the most common one for post-combustion is a dual-circulating fluidized bed system. The process at atmospheric pressure is illustrated in Figure 4-1. Carbon rich flue gas from a fossil-fuel fired power plant is fed into a fluidized bed, the carbonator, where it reacts with lime resulting in an exhaust composed primarily of N_2 and H_2O. The resulting $CaCO_3$ is circulated back to the other fluidized bed, the calciner, which regenerates the sorbent by releasing the captured CO_2. The calciner operates as an oxy-fuel combustor which provides the energy necessary for calcination and produces a concentrated CO_2 exhaust which is suitable for compression and sequestration.

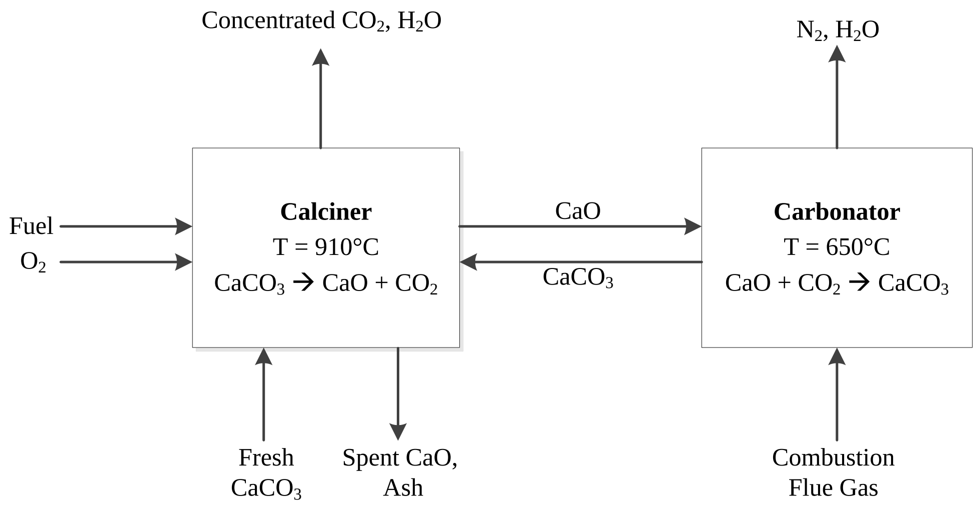

Figure 4-1 - Calcium looping process diagram.

The effectiveness of the process is represented by the carbonation efficiency (E_{carb}) which is defined by equation 4-2.

$$E_{carb} = \frac{F_{CO2} - F_{carb}}{F_{CO2}} \tag{4-2}$$

Where F_{CO2} is the molar flowrate of CO_2 entering the carbonator and F_{carb} is the molar flowrate of CO_2 leaving the carbonator. In addition to being able to effectively produce a purified CO_2 stream from a comparably dilute flue gas, this process potentially has a 5% lower energy penalty when compared to more developed, competing technologies such as amine scrubbing.[5] This is due to the additional electric power which can be produced from the high temperature processes required for both calcination (>900°C) and carbonation (650°C). However, calcium looping also has several limitations which must be overcome before the process can be scaled up and commercialized.

One of the primary developmental hurdles is the decay in sorbent reactivity with increased numbers of carbonation/calcination cycles. The CO_2 carrying capacity of limestone sorbents decays due to various mechanisms such as thermal sintering, sintering due to gaseous atmosphere, sulphation and ash deposition. The sorbent structure is most impacted by the harsh conditions involved in calcination (high temperature, high CO_2 partial pressure, sulfur and ash present from combustion).[6] A make-up flow of new sorbent is required to maintain an average activity in the carbonator which is adequate for the desired level of CO_2 removal. This make-up flow could represent a significant operating expense.

Research has focused on reducing the reactivity decay of natural limestone by changing operating conditions, increasing the carrying capacity via sorbent modification and manufacturing novel synthetic sorbents.[7,8,9] Sorbent modification and synthetic sorbents have the potential to be costly and to add complex and possibly hazardous unit operations to the process. However, there are opportunities to optimize the operating conditions or procedures which could reduce the decay in sorbent carrying capacity and therefore reduce sorbent make-up and operating costs.[10]

It has been shown in literature that steam addition in the carbonator or calciner can result in increased sorbent carrying capacity. Symonds et al.[11] and Manovic and Anthony[12] have shown in a TGA (Thermogravimetric Analyzer) and at the pilot scale that steam injected into the carbonator results in an increase in sorbent carrying capacity. Donat et al.[13] have reported that steam injection in a small fluidized bed during calcination and carbonation both result in increased sorbent reactivity. The authors attribute the increased sorbent activity due to a shift in pore volume to larger pores enhanced by the steam which results in a pore structure advantageous for carbonation. Champagne et al.[14] investigated the impact of steam during calcination in a TGA. The authors stated that steam injection during calcination results in a greater extent of carbonation without affecting the rate of reaction. It was also noted that steam must be present from the first calcination onward for the effect to be observed. To date, the effect of steam injection during calcination has been clearly defined at the bench scale. However, it has been shown that a TGA does not adequately emulate all aspects of larger scale operation, such as gas-solid contacting and heating rate.[15] Therefore, any benefits from steam addition to the calciner must be demonstrated at the pilot-scale before any economic or operational benefits can be assessed.

The goal of this work is thus to determine if the observed advantages of steam injection during calcination at the TGA scale will result in meaningful operational improvements at the pilot scale. The calcium looping process has been demonstrated at various pilot facilities varying in scale from 10 kW_{th} to 1.7 MW_{th}.[11,16,17,18] The pilot studies in literature have focused on the viability of the process, identifying operational challenges and getting data crucial for scale up such as solid circulation rate, sorbent make-up rates, bed inventories, carbonation efficiency and fuel consumption. No pilot studies have been completed with moisture levels in the calciner in excess of that resulting from combustion.

This study presents results from continuous operation of the CanmetENERGY dual-fluidized bed pilot plant with various levels of steam injection in the oxyfuel calciner. Tests were conducted with naturally occurring limestone and various levels of steam addition in the calciner to evaluate any changes in particle morphology caused by the steam which result in an increase in carrying capacity. The calciner was oxygen-fired with CO_2 concentrations >80% to fully evaluate the impact of harsh operating conditions on particle sintering. In addition to realistic calcination conditions, a natural gas burner was used as the flue gas source for the carbonator. Natural gas was chosen as a fuel for ease of operation and to eliminate SO_2 and ash being sent to the carbonator. The flue gas is not treated before being sent to the carbonator which results in a realistic level of moisture and CO_2. This configuration was designed to resemble, as closely as possible, a commercial-scale plant as the calciner will be oxygen-fired with flue gas recycle and moisture will be present in appropriate quantities in the carbonator.

4.3 - Experimental

4.3.1 - Dual-Fluidized Bed Pilot Plant

The dual-fluidized bed pilot plant used for this work is shown in Figure 4-2.

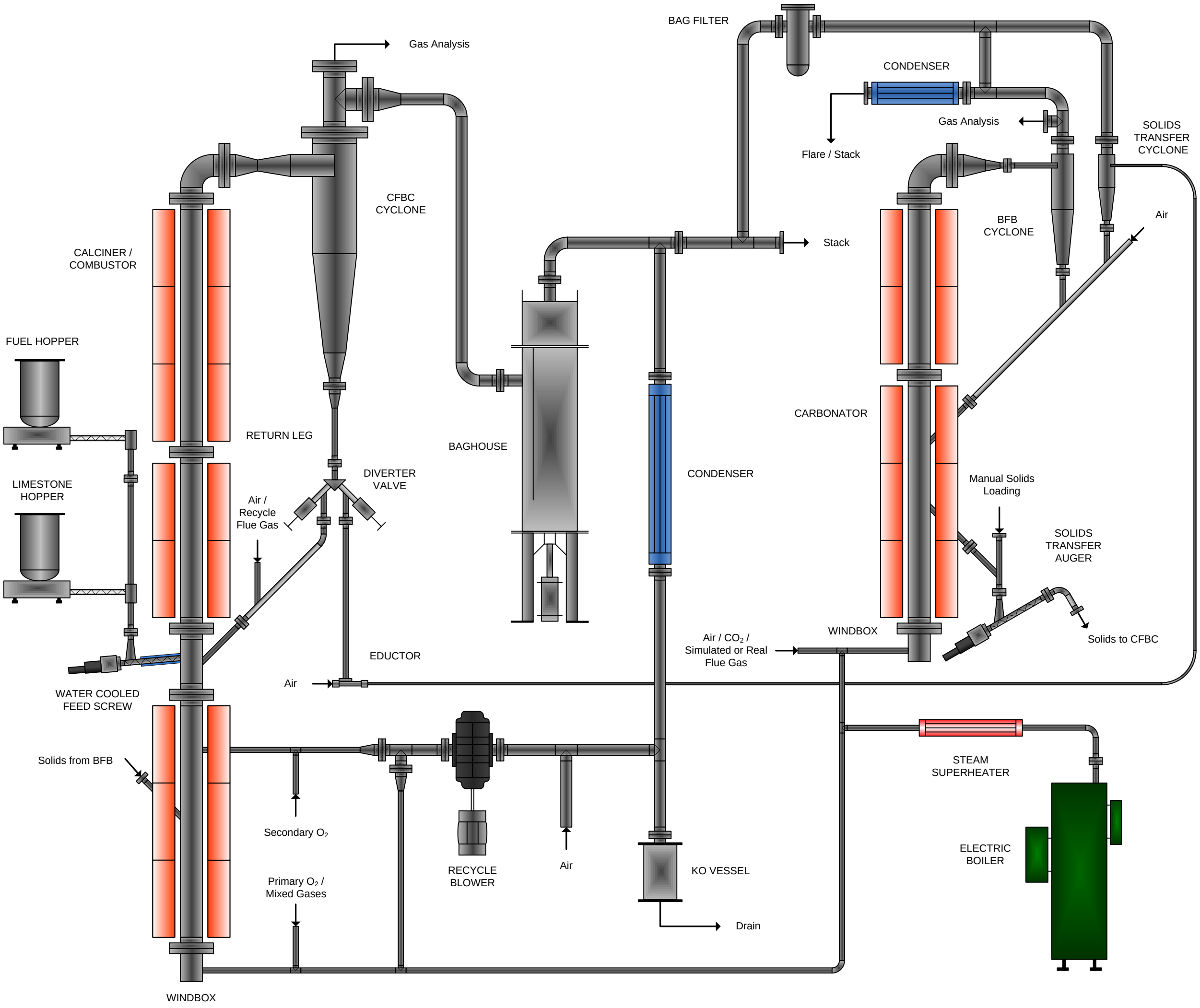

Figure 4-2 - Dual-fluidized bed pilot plant schematic.

The calciner is operated as a circulating fluidized bed (CFB) and the carbonator as a bubbling bed (BFB). Both reactors are lined with electric heaters. Additional energy for calcination is supplied by the combustion of solid fuels; for this work hardwood pellets were used as they have a low sulfur (<0.05 wt%) and ash content (0.68 wt%) which reduces the impact of sulphation and ash deposition on sorbent performance. The calciner contains a bed of inert material (olivine sand) which remains in the reactor to help absorb and distribute heat as there is no other mechanism to remove heat from the system. Oxygen is supplied to the calciner from a bulk tank and the flue gas is recirculated via a blower after passing through a baghouse to remove fine particles and condenser to remove moisture. Steam is supplied to the calciner by an electric boiler and is superheated to 190°C before being mixed with other gases at the windbox. Gas analyzers continually monitor O_2, CO_2, CO, SO_2 and NO_2 concentrations in the calciner exhaust and O2, CO_2, CO and SO_2 in the carbonator exhaust.

As stated earlier, the flue gas supplied to the carbonator is generated using a natural gas burner. The burner is air fired with 57% excess air. The flue gas was sent to the carbonator via a heated diaphragm pump and entered the windbox at 175°C. The burner is fired at the same conditions for all tests and the outlet CO_2 and moisture levels are continuously monitored and recorded. The resulting flue gas composition is shown in Table 4-1.

Table 4-1 - Natural gas burner flue gas composition.

Composition (vol% wet)		
CO_2	**H_2O**	**O_2**
8.59	15.80	2.04

4.3.2 - Operating Conditions & Procedures

The primary objective of this work is to evaluate the impact of injecting various levels of steam into the calciner; thus three levels of steam are chosen to be evaluated. The key calciner operating conditions for the three pilot tests are shown in Table 4-2.

Table 4-2 - Calciner operating conditions.

Test Condition	T (°C)	CO_2 (%vol dry at outlet)	H_2O (%vol at windbox)	Fuel Feed Rate (kg/h)	Oxygen Flow Rate (SLPM)
Base-case	910	>80	0	4.1	55
15% Steam	910	>80	15	4.1	55
65% Steam	850	>80	65	4.1	55

A test was conducted with no additional steam injected to the calciner to use as a base-case comparison for the other tests. It should be noted, however, that steam was inherently present in all tests due to the fuel combustion in the calciner. To minimize this impact on the overall steam concentration in the calciner, similar fuel feed rates and oxygen feed rates were used for all tests. A test was conducted with 15 %vol steam at the inlet of the calciner to emulate levels that would be present in a calciner operating under fuel combustion alone, i.e. without electric heaters, with a moderately wet flue gas recycle. Lastly, a test was conducted at 65 %vol steam to evaluate any possible advantages arising from significant reduction in CO_2 partial pressure in the calciner.

The temperature at which the calciner must operate to allow for rapid and complete calcination is determined by the CO_2 partial pressure in the reactor. The governing equilibrium relationship is shown below.[19]

$$P_{eq} = 4.137 \times 10^{12} exp\left(-\frac{20474}{T}\right)\ [Pa] \qquad (4\text{-}3)$$

It was decided to run the calciner approximately 20°C above equilibrium to allow for calcination to proceed rapidly due to the relatively short residence time in the CFB calciner. As all tests required the calciner to be oxy-fired, a minimum CO_2 concentration of 80 %vol(dry) was considered to be acceptable. The carbonator was operated at 650°C for all tests which results in a predicted outlet equilibrium CO_2 concentration of 0.95 %vol.

All conditions were run for a minimum of 5 hours of continuous, steady-state operation. The bed inventory, solid circulation rate and superficial gas velocities were kept consistent between tests. Solid circulation rates were estimated by calibrating the auger used for solid transport and verified by occasional bucket tests. The carbonator was loaded with 5 kg of limestone at the beginning of each test. The pilot system is not configured for continuous sorbent make-up at a relatively low make-up rate, thus 1 kg of fresh limestone was added to the system when the carbonator outlet CO_2 concentration reached 1.5 %vol. It was desired to maintain capture levels as close to equilibrium as possible throughout all three tests. Sorbent samples were taken from the calciner and carbonator once an hour. These samples were used to determine sorbent utilization via TG analysis and to evaluate the sorbent surface area and pore volume via nitrogen adsorption analysis.

4.3.3 - Sorbent Properties

Cadomin limestone (Alberta, Canada) was used as the sorbent for all tests. The size distribution is shown in Table 4-3. The Sauter mean diameter of the limestone after crushing is 342 µm. This sorbent has a $CaCO_3$ purity of 94% and a detailed analysis can be found in Champagne et al.[14]

Table 4-3 - Partial size distribution of Cadomin limestone.

Mean Aperture Size (μm)	212	231	275	362.5	512.5	600
Mass Fraction	0.0022	0.2928	0.3717	0.2072	0.0669	0.0592

4.4 - Results

4.4.1 - Base-case No Steam Test

The first test performed was a continuous CO_2 capture test with an oxy-fired calciner and no additional steam present. This test was used as the basis for comparison with other tests that did include steam levels above those present due to combustion. The bed temperatures, calciner CO_2 concentration, carbonator outlet CO_2 concentration and carbonation efficiency profiles are shown in Figure 4-3.

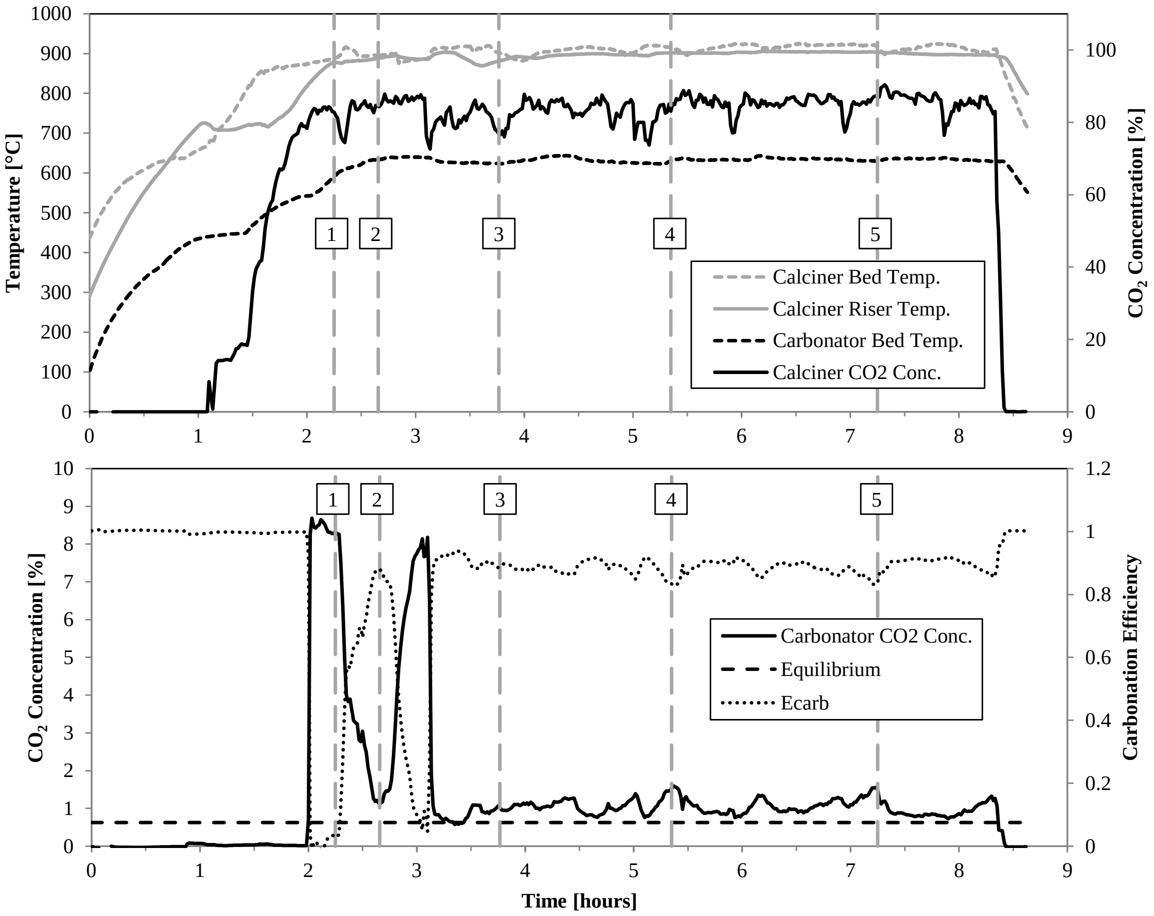

Figure 4-3 - Calciner and carbonator bed temperatures, CO_2 outlet concentration and carbonation efficiency profiles for the steady state operation without additional steam in the calciner.

Start-up occurs during the first 2 hours of the test. Flue gas recirculation in the calciner was started 1.5 hours into the test. The CO_2 level in the calciner reached 90% approximately 0.5 hours after this. During startup, there is no solid circulation between the two fluidized beds. Solid circulation began approximately 2 hours (point 1) into the test after the two beds reached the required temperatures.

A failure in the auger used to transfer sorbent from the carbonator to the calciner at point 2 in Figure 4-3 caused the CO_2 peak shortly after. As sorbent was no longer being calcined, the sorbent in the system was quickly saturated and the overall amount of CO_2 being captured rapidly decreased. Solid circulation was re-established 3 hours into the test. After this initial problem, the system ran at steady state for approximately 5 hours. Fresh limestone was added, 1 kg at a time, at points 3, 4 and 5 shown in Figure 4-3. Samples were taken from the carbonator and calciner each hour once the system reached steady state. Due to the scale of the system, sorbent discharge from regular solid sampling was able to effectively maintain a consistent bed inventory for the make-up rate used in this test. An average bed inventory of 3.8 kg was maintained in the carbonator, resulting in an average residence time of approximately 10 minutes. Any minor fluctuations in bed inventory due to sorbent addition or sampling had little observable effect on the carbonation efficiency. Similarly, the pilot plant provided good control of the solid looping rate due to the use of a speed-controller auger governing the solid flow from the carbonator to the calciner. As a result, the average calcium looping ratio (F_{CaO}/F_{CO2}) was 9.22.

As shown in Figure 4-3, the carbonator outlet CO_2 level was maintained near equilibrium for the duration of the test which resulted in carbonation efficiencies between 80% and 90%. Any increases in the CO_2 concentration are primarily due to a decay in sorbent reactivity, which is overcome when a batch of fresh sorbent is added. Smaller fluctuations result from various inconsistencies in operation which influences the reaction kinetics or the solid circulation rates such as changes in carbonator temperature, sorbent make-up and solid sampling. It is interesting to note that the outlet CO_2 level in the carbonator reached 1.5 %vol, requiring sorbent addition, approximately every 1.75 hours throughout this test. This indicates a consistent rate of decay in sorbent carrying capacity, as seen in literature.[20] However, it also validates the test methodology used to estimate a make-up rate for a given system and a desired level of capture.

4.4.2 - 15% Steam Test

The next test was performed with a steam concentration of 15 %vol at the windbox. This is in addition to the steam generated by the combustion of biomass in the calciner resulting in a slightly higher overall steam concentration in the reactor. All other variables were kept consistent with the no-steam test. The bed temperatures, calciner and carbonator outlet CO_2 concentration and carbonation efficiency profiles are shown in Figure 4-4.

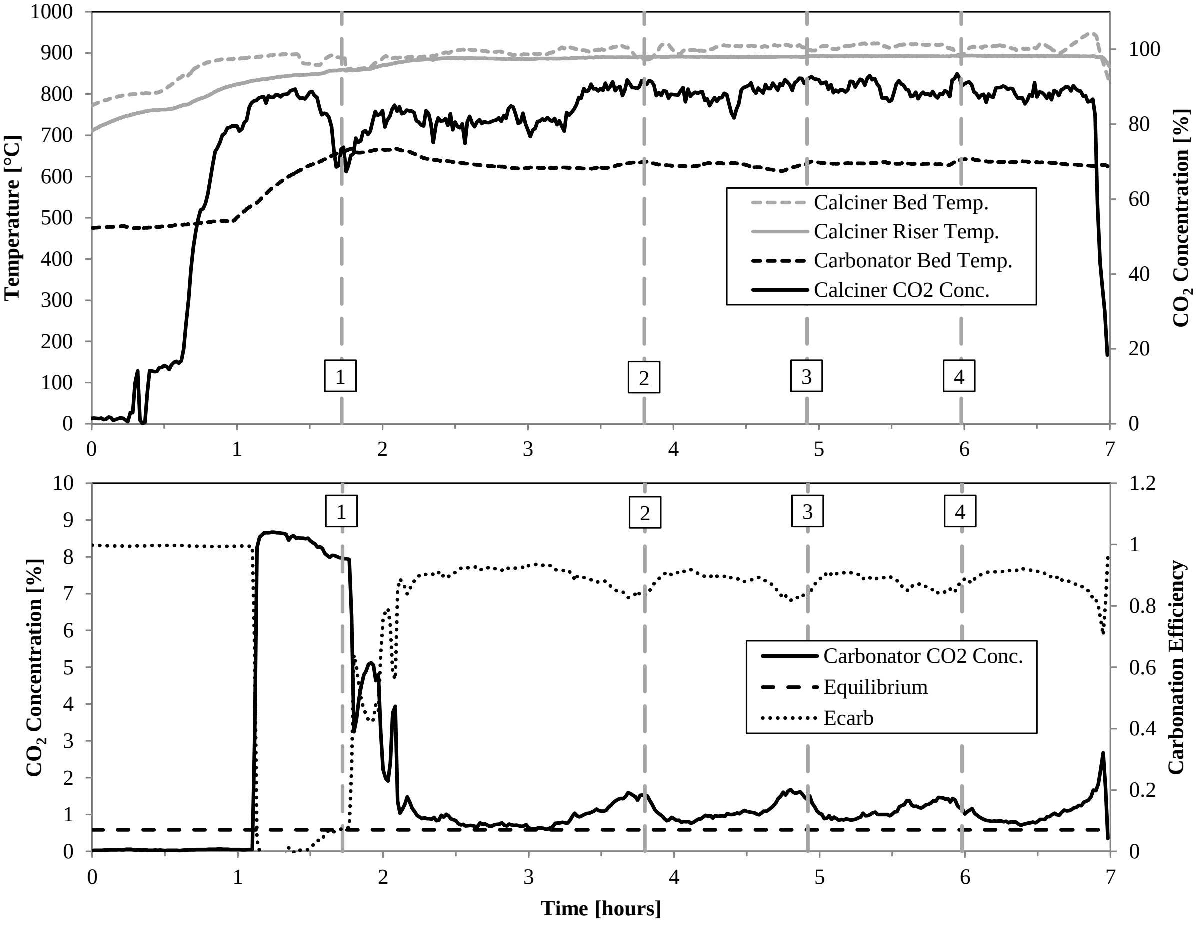

Figure 4-4 - Calciner and carbonator bed temperature, CO_2 outlet concentration and carbonation efficiency profiles for the steady state operation with 15% steam at in the calciner inlet.

The same start-up procedure described for the base case test was followed here, however it is important to note that steam was added to the calciner inlet before solid circulation was started between the two reactors. A suitable oxy-fired condition of 90 %vol(dry) CO_2 was attained within half an hour of recycling calciner flue gas. The calciner CO_2 level dropped to an average of 80 %vol(dry) when the solid looping began (point 1). This dilution was caused by air-ingress due to a pressure imbalance between the cyclone and the injector used to transport solids to the carbonator. This imbalance was corrected 3.5 hours into the test. Although the gas analyzers reported a CO_2 concentration in the calciner of 90 %vol, it should be noted that the actual concentration within the reactor was closer to 75 %vol due to the additional steam. According to equation 4-3, the equilibrium temperature required for calcination at 75 %vol CO_2 is 876°C, compared to 888°C for 90 %vol CO_2. This, in theory, should allow the calciner to operate at a lower temperature without impacting the calcination efficiency. However, in practice, temperatures in excess of 900°C were still required for complete calcination of the sorbent. It was, therefore, decided to operate the calciner at the same temperature as the base-case test (910°C) in order to have similar levels of thermal sintering on the sorbent while allowing for full calcination conversion.

Solid looping between the calciner and carbonator was started at point 1 in Figure 4-4. After that point, the system was run for 5.2 hours at steady state. An average carbonator bed inventory of 3.8 kg was again maintained throughout the test. The solid looping rate was consistent throughout the test with an average value of 9.6 kg/h. The resulting average CaO/CO_2 ratio was 9.74, which is similar to the base-case condition. Make-up of 1 kg of fresh limestone was added to the system at points 2, 3 and 4 in Figure 4-4. Unlike the base-case, the original loading of sorbent maintained the required level of capture for over 2 hours before requiring the addition of fresh sorbent. This could be attributed to the lower CO_2 level in the calciner during the majority of this 2 hour period. A lower partial pressure of CO_2 present during calcination can result in less sintered sorbent particles resulting in a comparably higher reactivity.[21] It could also be attributed to the addition of steam impacting the sorbent morphology and reactivity, as will be discussed later. For the remainder of the test, fresh sorbent was added every hour. Between make-up batches, the carbonation efficiency was maintained between 90% and 93%.

4.4.3 - 65% Steam Test

The final test was performed with a steam concentration of 65 %vol at the inlet to the calciner. The bed temperature, calciner and carbonator outlet CO_2 concentrations and the carbonation efficiency profiles are shown in Figure 4-5.

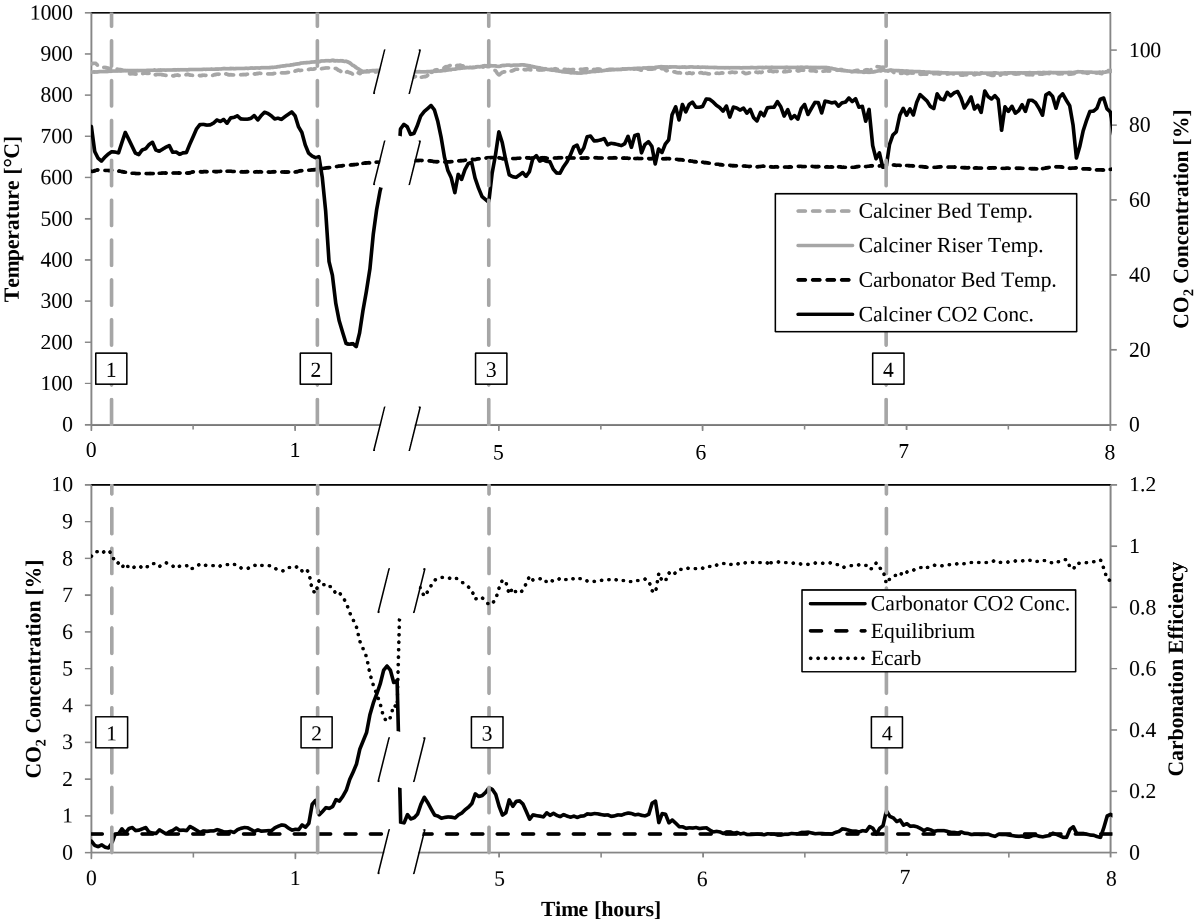

Figure 4-5 - Calciner and carbonator bed temperature, CO_2 outlet concentration and carbonation efficiency profiles for the steady state operation with 65% steam at in the calciner inlet.

The pilot plant start-up procedure is similar to that used in the previous two tests with one exception; flue gas was not sent to the carbonator before solid circulation had started (point 1 in Figure 4-5). The two were done simultaneously; therefore there was no initial spike in carbonator outlet CO_2 concentration. It should be noted that Figure 4-5 shows only the steady state operation time during the test. The screw conveyor used to transfer sorbent from the calciner to the carbonator failed at point 2, resulting in the reduction in capture observed immediately afterwards and a total of 3 hours of process interruptions. Steady state was re-established approximately 5 hours into the test. Minor interruptions in sorbent looping occurred at points 3 and 4; however they were recovered from quickly. A total of approximately 5 hours of operation at the desired condition and at steady state were achieved.

This test condition involved the majority of the calciner inlet gas being composed of steam. This greatly dilutes the carbon dioxide in the reactor to a concentration below 35 %vol. The equilibrium temperature for calcination at that concentration is 830°C. Applying the same 20°C margin which was used in the no-steam test, it was decided to operate the calciner at 850°C. This allows for a similar driving force for calcination as the no-steam case. However, both the temperature and gaseous atmosphere were changed for this test, relative to the other cases. This was chosen for two reasons: first, regardless of the temperature of the calciner, calcination will proceed once equilibrium allows, which is approximately 850°C for this case. Thus, sintering will be different regardless of the operating temperature as calcination will start as the sorbent is being heated. Second, from a commercial perspective, it does not make sense to operate a reactor at a higher temperature than necessary for good performance. This would increase fuel consumption. Regardless, the calciner operated well at the lower temperature and still allowed for complete calcination of the sorbent. The lower CO_2 concentration and temperature have the potential to substantially reduce particle sintering.

Unlike the previous two tests, essentially no make-up sorbent was required to meet the objective of maintaining an outlet CO_2 concentration below 1.5 %vol. However, 1 kg of fresh sorbent was added at point 2 to make up for the material lost while recovering from the solid transfer auger failure. While the addition of that fresh sorbent increased the average activity of the sorbent somewhat, it is still notable that the carbonation efficiency remained above 90% for the remaining 3.5 hours of the test without any additional make-up. Clearly, the sorbent activity decayed much more slowly than in previous tests.

There were, however, some important differences in operation to note for this high-steam test condition. Solid sampling resulted in a progressive decrease in bed inventory due to the lack of sorbent make-up. To keep the experimental methodology consistent between conditions, additional sorbent was not used to increase the bed inventory provided the outlet CO_2 concentration was below 1.5 %vol. While this did not impact carbonation efficiency, there is minimum allowable carbonator bed inventory required for solids to be transferred from the carbonator to the calciner. As the carbonator is operated as a bubbling bed, an overflow port is used to feed the screw-conveyor that transfers the carbonated sorbent to the calciner. If the bed inventory drops below 2 kg, an insufficient amount of material reaches the overflow port causing a stoppage in solid circulation. In order to maintain a large enough bed inventory in the carbonator to continue operation, the solid looping rate was increased 5.8 hours into the test. This resulted in an increase in the bubbling bed inventory due to a fixed residence time and ‘once-through’ configuration used in the calciner, i.e. sorbent does not recirculate within the calciner. The average solid circulation rate during this period was 17.8 kg/h compared to 9.6 kg/h for the first 5.8 hours of the operation. The resulting average CaO/CO_2 ratio with the higher looping rate was 18 compared to 9.7 during the lower looping rate period. The increased looping rate also resulted in a 15°C drop in the carbonator temperature due to the increased flow of cold solids from the calciner transfer line. This drop in temperature caused a 5% increase in carbonation efficiency due to the lowered equilibrium partial pressure of CO_2. The equilibrium line shown in Figure 4-5 is based on the average bed temperature in the carbonator. The period from 5 to 5.8

hours is still equilibrium capture but resulted in lower carbonation efficiency due to the higher than average temperature.

4.5 - Discussion

The calcium looping process must produce a high purity CO_2 stream that can be sequestered, therefore injecting any gases which cannot be easily separated from CO_2, regardless of the impact on the process, is not advisable. Steam was chosen as a diluent as it has been shown to change the morphology of the sorbent resulting in an increased carrying capacity and it is easily separated from the calciner flue gas via condensation. The goal of the pilot test campaign was thus to evaluate the impact of diluting the calciner atmosphere with steam on carbonation efficiency and sorbent performance. Solid samples were taken from both reactors to evaluate the performance of the limestone sorbent during the three pilot tests. The carbonation conversion (X_{carb}) was determined by TG analysis on the samples taken from the carbonator. The resulting conversions are summarized in Table 4-4.

Table 4-4 - Carbonation conversion for limestone samples taken from the carbonator during steady state operation.

Sample Time (h)	Carbonation Conversion (%)		
	No Steam	15% Steam	65% Steam
1	38.9	41.5	49.1
2	37.2	39.7	45.1
3	33.6	40.6	30.7*
4	32.7	37.7	28.0*

* Higher solid circulation rate

The carbonate conversion values from this work are consistently greater than those presented in literature from similar pilot plants.[11,18] First, it should be noted that although calcination efficiency was high (>95%) for all tests performed, some re-carbonation occurred at the outlet of the calciner due to a low temperature zone and highly reactive sorbent. Regardless, the majority of the discrepancy in sorbent utilization can be attributed to a combination of factors including differences in the pilot plant configuration, sample intervals and the effects of steam. The CanmetENERGY calcium looping plant utilizes a bubbling bed carbonator. This significantly increases the residence time compared to a circulating fluidized bed, which is the configuration used by many other calcium looping pilot facilities.[22] The increased residence time in the carbonator will result in a higher average sorbent utilization as the sorbent will continue to react, albeit at a reduced rate as the reaction becomes diffusion limited. Similarly, the extent of reaction will be higher in this configuration due to the presence of moisture in the flue gas sent to the carbonator, which is lacking in other facilities typically utilizing bottled CO_2. Steam present during carbonation has been shown to increase sorbent carrying capacity during both the reaction- and diffusion-controlled regimes.[11,12] Other fluctuations in the reported conversion could be a function of the times at which samples were taken relative to the times at which new sorbent was added. As a batch make-up scheme was used, if a sample was taken recently after new sorbent had been added the average activity should be higher as the new sorbent had not yet decayed significantly.

To ensure the accuracy and consistency of these results, a carbon mass balance was performed to compare the amount of CO_2 removed from the gas stream entering the carbonator and the amount of $CaCO_3$ formed. The gas-solid mass balance is summarized in equation 4-4.

$$CO_2\ Removed\ from\ Gas = CaCO_3\ Formed\ in\ Solids$$

$$F_{CO2}E_{carb} = F_{CaO}(X_{carb} - X_{calc}) \tag{4-4}$$

The gas mass balance is based upon the carbonation efficiency which is calculated from the carbonator outlet composition. As the outlet is continually monitored by gas analyzers, this value is assumed to be accurate. Conversely, the solid mass balance is based on the amount of CO_2 that has reacted with the sorbent at the outlet of the carbonator (X_{carb}), the amount that remains after exiting the calciner (X_{calc}) and the solid circulation rate (F_{CaO}). As all of these parameters are measured intermittently and the samples are assumed to represent the bulk bed inventory, the error is inherently larger. To reduce the influence of these measurement errors, a mass balance was performed at each point at which there was a sample taken. The results are summarized in Figure 4-6.

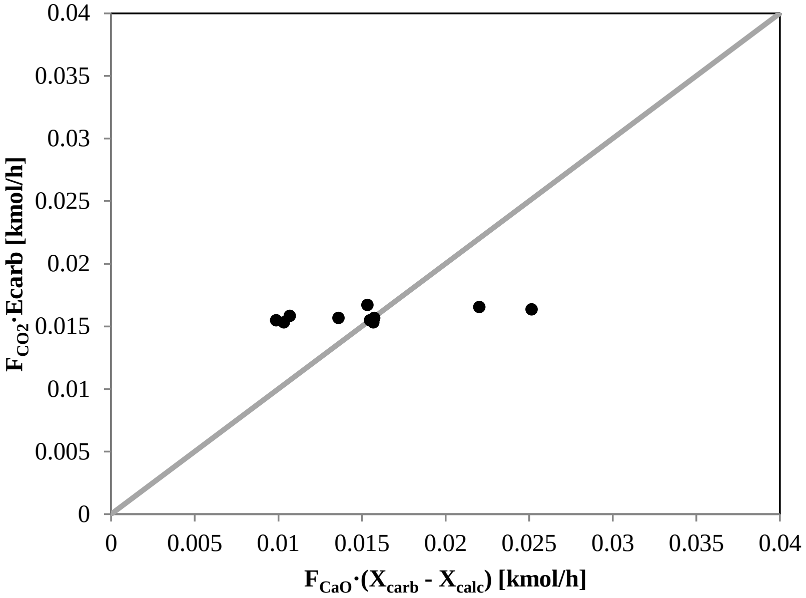

Figure 4-6 - Gas and solid carbon balance.

All points lie relatively close to the 45° line indicating a good closure of the carbon balance. The percent difference between the gas and solid carbon balance is 10% or less for each sample point.

Several trends emerged from the sorbent conversion analysis. Firstly, the average sorbent utilization increased with the amount of steam present in the calciner. This is true for all sample points except for samples taken at hours 3 and 4 for the 65% steam case. These are lower as the solid circulation rate was higher than the other test conditions, as discussed earlier. The second trend is that the rate of decay in carbon carrying capacity decreases with an increase in steam concentration in the calciner. However, as fresh sorbent make-up was used, the decay in reactivity must be discussed in parallel with the make-up rates. The average make-up rates, estimated using the intervals between 1 kg additions, were 0.926 kg/h for the no-steam case, 0.799 kg/h for the 15% steam case and 0.200 kg/h for the 65% steam case. As the level of steam in the calciner is increased, the rate of sorbent reactivity decay decreased, resulting in a lower sorbent make-up rate. The 15% steam case shows a minor improvement over the no-steam case, reducing the make-up rate by 13.7%. However, a much larger improvement is seen in the 65% case, reducing the make-up by 78% compared to the base-case.

Different phenomena have been shown to decrease the carbon carrying capacity of lime-based sorbents, including sulphation, ash deposition and sintering. The difference in sorbent carrying capacity observed in the tests performed here is primarily attributed to sintering as a low sulfur, low ash fuel was used in the calciner and a sulfur-free fuel (Natural Gas) was used to generate the flue gas to be treated. Sintering is the process by which parts of the particle fuse together, reducing the surface area available for reaction with gaseous species, such as CO_2. It has been shown in literature that the sintering of lime-based sorbents takes place via two unique mechanisms: thermal sintering and atmosphere-induced sintering. Thermal sintering results from the sorbent being exposed to high temperatures during regeneration.[23] Similarly, sintering can be enhanced by the atmosphere the particles are exposed to; CO_2 and H_2O have both been shown to enhance sintering of CaO, relative to N_2.[24] To clarify which sintering mechanisms had the largest impact on sorbent performance, BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) analyses were carried out on the sorbent samples taken from the calciner. The results are summarized in Table 4-5.

Table 4-5 - Surface area and pore volume of calciner sorbent samples after 1 hour of steady state operation.

BET Surface Area (m^2/g)			BJH Pore Volume (cm^3/g)		
No Steam	**15% Steam**	**65% Steam**	**No Steam**	**15% Steam**	**65% Steam**
4.50	5.78	5.53	0.009	0.017	0.019

A significant increase in surface area was seen with the addition of 15% steam; however further increasing the steam concentration resulted in a small decrease. Conversely, the pore volume consistently increased with an increase in steam concentration; however the largest increase is between the 15% steam case and the baseline with only a small increase between the 15% and 65% steam cases. For both pore volume and surface area, the largest difference was observed between the no steam and 15% steam cases. Figure 4-7 compares the distribution of surface area between the three pilot test cases which has evolved after 1 hour of continuous operation. The distribution for Cadomin limestone after one calcination in air is shown for reference.

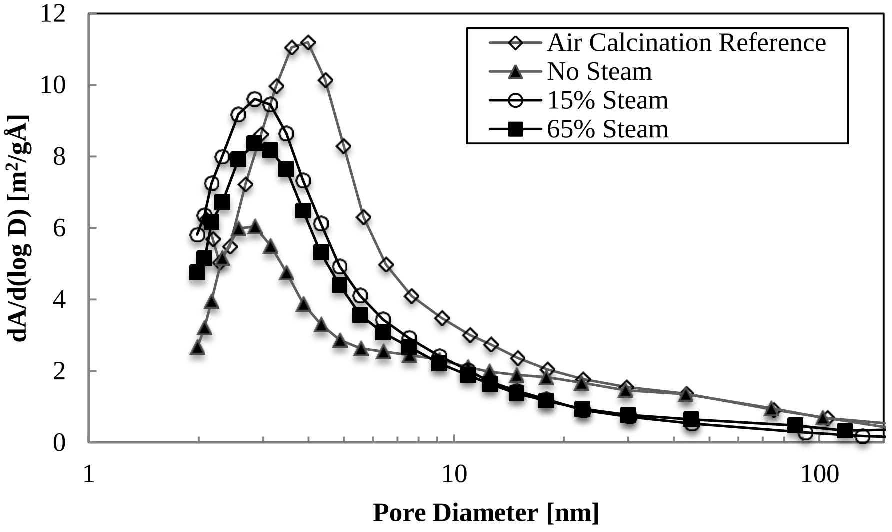

Figure 4-7 - Surface area distribution of calcined CaO samples after 1 hour of steady-state operation with varying steam concentrations.

The gains in surface area observed in the tests involving additional steam in the calciner are primarily in pores between 2 nm and 10 nm in diameter. Surface area found in pores with a diameter larger than 10 nm decreased at both levels of steam addition. As smaller pores have a larger influence on carbonation conversion, the increased surface area in the 2 to 10 nm range explains the increased carrying capacity observed in the 15% steam case.[25] However, the 65% steam case resulted in a similar surface area to the 15% steam case but resulted in higher carbonator conversion. Figure 4-8 compares the distribution of pore volume between the three pilot test cases which has evolved after 1 hour of continuous operation. The distribution for Cadomin limestone after one calcination in air is also shown for reference.

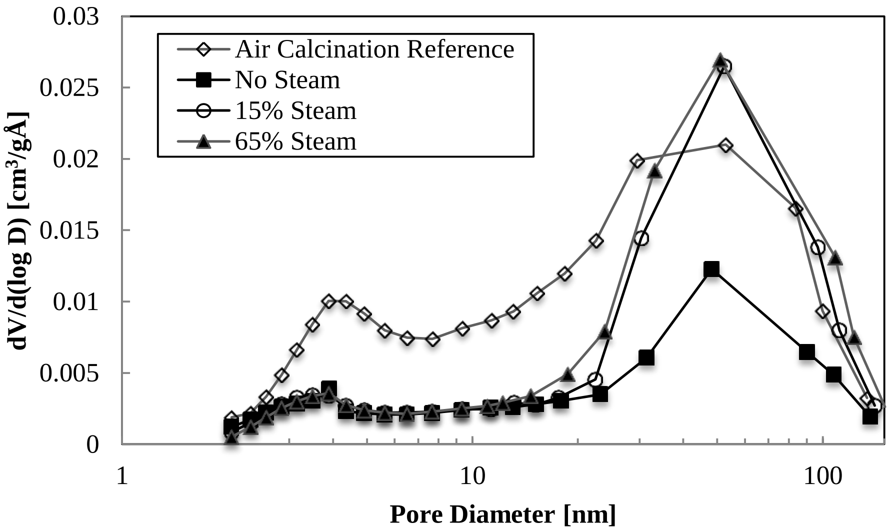

Figure 4-8 - Pore volume distribution of calcined CaO samples after 1 hour of steady-state operation with varying steam concentrations.

First, it is clear that all conditions resulted in a similar pore volume distribution with maxima of ~50 nm. Compared to the reference, there is a general shift towards larger pores. As some steam is present in all tests due to combustion in the calciner, this shift is consistent with previous work.[13] The combination of increased pore volume in larger pores and increased surface area in smaller pores allows for an increased carrying capacity. The pore volume of the larger pores(~50 nm) reduces diffusion resistance and pore blockage allowing more effective use of the evolved surface area contained in the smaller pores (2-10 nm). A similar mechanism has been reported for sulphation of CaO.[26]

While the changes in particle morphology were clearly documented, it is more difficult to determine which sintering mechanism, or combination thereof, had the largest influence. Although both steam and CO_2 have been shown to enhance the sintering of CaO, it has been reported that CO_2-induced sintering has a greater negative impact on sorbent reactivity. Wang et al.[27] reported enhanced carbonation conversion in CaO samples that were calcined with steam dilution when compared to a pure CO_2 atmosphere at the same temperature. This is in agreement with previous work involving steam diluted calcination.[14] However, thermal sintering has also been shown to have a detrimental impact on sorbent carrying capacity.[28]

Similar pore structures evolved in both the 15% and 65% steam cases, however the sorbent decayed much more slowly in the 65% steam case. This is likely due to a combination of effects, including the increased steam concentration, the lower temperature and the increased solid looping rate. The sorbent from the 65% steam condition has a similar surface area but larger pore volume than that from the 15% steam condition. The 65% steam case allowed for a decrease in calcination temperature of 60°C due to the lower CO_2 partial pressure, potentially reducing thermal sintering significantly. Similarly, Rodriguez-Navarro et al.[23] reported that calcination at 850°C, compared to 900°C, resulted in a similar evolved surface area but a slight increase in porosity in the mesoporous structure of CaO. It is possible that the increase in pore volume, evolved at larger diameters, further reduced diffusional resistances and pore blocking, allowing a higher conversion without a larger surface area.

It is also conceivable that the combined lower temperature and CO_2 concentration in the 65% steam test severely reduced the negative impacts of sintering, allowing the sorbent to maintain a high surface area over more calcination/carbonation cycles than other cases. This would cause the sorbent to decay much more slowly and greatly reduce the make-up rate, as observed here. However, as make-up sorbent was used in the other two tests, there is not sufficient data to compare the decay in surface area over time. It would also be important to examine the impact of additional steam on sulphation as it has been demonstrated that steam can enhance indirect sulphation of CaO which could result in a reduction in carbonation conversion.[29]

4.6 - Conclusions

Continuous CO_2 capture using the dual-fluidized bed system at CanmetENERGY has been demonstrated with up to 65% steam present in the oxy-fired calciner. A minimum carbonation efficiency of 80% was maintained during all test conditions, with some conditions reaching 95%. The calciner was successfully operated at a temperature of 850°C at the highest level of steam addition. Diluting the calcination atmosphere with steam was shown to increase the carbon carrying capacity of lime thus decreasing the fresh sorbent make-up flow required to maintain equilibrium capture levels. The increase in carrying capacity resulted from an increase in surface area present at small pore diameters (2-10 nm) and a corresponding increase in pore volume at larger diameters (~50 nm). These variations in pore structure were seen at both the 15% and 65% steam case. The change in sorbent morphology was attributed to less severe sintering due to the decreased CO_2 concentration in the calciner. A lower calcination temperature in the 65% steam case was also shown to potentially reduce thermal sintering and significantly decrease the rate of sorbent reactivity decay. In commercial operation, the increase in steam concentration could be achieved by taking a slip stream of low quality steam from the steam cycle or by operating a wet flue gas recycle system, depending on the desired extent of dilution. An economic analysis would have to be completed to determine which method and what level of steam results in the optimal process configuration.

4.7 - References

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Chapter 5 - Conclusions & Recommendations

The goal of this work was to evaluate the influence of steam in calcination on the carbon carrying capacity of naturally occurring CaO-based sorbents, identify any resulting advantages or disadvantages which arise during continuous CO_2 capture at the pilot scale and present a mechanism for the observed phenomena.

The impact of steam during calcination on the gas-solid carbonation reaction was studied in a TGA. Tests consisted of 15 calcination/carbonation cycles. Calcination was performed at 875°C and 925°C with steam concentrations of 0%, 5%, 15% and 40% vol. with a fixed CO_2 partial pressure of 61 kPa. Carbonation was carried out at 650°C with an inlet CO_2 concentration of 15% vol. for all tests. Some tests were also done with a steam concentration of 15% vol. present during carbonation. The addition of steam in calcination resulted in an increased carbonation conversion after 20 minutes for all levels of steam tested. The global rate of reaction during the reaction kinetic-controlled carbonation phase was not affected by the steam in calcination however the extent of reaction increased. The rate of reaction during the diffusion-limited carbonation phase increased proportionally to the amount of steam injected in calcination. Interestingly, the maximum carbon carrying capacity was observed with the sorbent that was calcined in 15% steam. The 40% steam case performed similarly to the 5% steam case. This indicates there is an optimum concentration of steam in calcination which produces the most reactive sorbent and above which the reactivity starts to decrease with increasing steam concentration. It was concluded that the presence of steam in calcination at a fixed temperature, up to an optimal value, reduces the degree of sintering the sorbent experiences resulting in a mesoporous structure conducive to higher carbonation conversions.

As discussed, steam in carbonation has also been shown to increase carbon carrying capacity. To compare the relative impact of steam present during calcination or carbonation, tests were carried out using a TGA with steam in only calcination, in only carbonation and in both reactions. While the presence of steam in either reaction resulted in an increase in carrying capacity after 15 cycles, a larger increase was observed when steam is present for only carbonation. However, the effects are synergistic and the largest increase was seen when steam is present for both reactions. It was discovered that for steam in calcination to have an effect on the sorbent, it must be present from the first calcination onward. In contrast, steam in carbonation increased the carrying capacity whenever it was present, even if introduced after several cycles without steam.

The impact of these effects was studied at the pilot-scale in a dual-fluidized bed system. Continuous CO_2 capture was demonstrated with 0%, 15% and 65% steam in an oxy-fired calciner. Each test consisted of a minimum of 5 hours of continuous, steady-state operation and carbonation efficiency was maintain above 80% for the duration of all runs. As predicted by the TGA trials, the addition of steam to the calciner slowed the decay in carbon carrying capacity resulting in a decrease in the fresh limestone addition rate. The sorbent make-up rate required to maintain equilibrium-level capture with 15% steam in the calciner was reduced by 13.7% compared to the no-steam case. Interestingly, the sorbent make-up rate with 65% steam in the calciner was reduced by 78% compared to the no-steam case. Unlike in the TGA, the best performance was achieved with the highest steam concentration. Thermal sintering is expected to be more severe in the pilot plant, compared to the TGA, for all steam concentrations due to the significantly greater heating rate. Thus, the optimal level of steam injection for the pilot plant will be different from that observed in the TGA.

The reduction in make-up rate is due to an increase in average carbonation conversion and a decrease in the rate of decay in reactivity. Carbonation conversion increased from 38.9% in the no-steam case to 41.5% and 49.1% for the 15% and 65% steam cases, respectively. Additionally, it was possible to operate the calciner at 850°C due to a lower carbon dioxide partial pressure resulting from the steam dilution. The 60°C reduction in calcination temperature could potentially reduce fuel consumption and particle sintering.

The sorbent samples extracted during the pilot plant experiments were analyzed to gain insight into the mechanism behind the observed increase in reactivity. Overall, the addition of steam in the calciner resulted in sorbent with larger surface area and pore volume which substantiates the increase in reactivity. The increase in surface area occurred in pores 2 to 10 nm in diameter. Conversely, the steam shifted the majority of the pore volume to larger pores, with the maxima at 50 nm. The increased pore volume in larger pores is proposed to reduce diffusion resistance and pore blockage allowing more effective use of the increased surface area evolved in the smaller pores. This change in sorbent morphology was attributed to a reduction in particle sintering due to a lower CO_2 concentration in the calciner. The 65% steam case resulted in the most stable sorbent with the highest average carbonation conversion. The combination of the lower calcination temperature and the lowest tested CO_2 concentration resulted in the least severe sintering atmosphere and therefore the best performing sorbent.

The following list summarizes suggestions for future work involving the addition of steam to calcination in the calcium looping process:

- Complete process simulation of cases involving various levels of steam addition in the calciner and a sensitivity analysis to determine the optimum steam concentration based on the cost of steam and the reduction in fuel and sorbent make-up.
- A detailed heat integration is required to evaluate the most practical and economical source of the steam to be used in this process. Various sources should be evaluated including the power plant primary steam cycle, the calcium looping steam cycle and running a wet recycle on the calciner.
- Investigate the impact of sulphation on the pore structure evolved during calcination with steam at the bench and pilot scale.
- Perform pilot scale tests using commonly available fuels proposed for calciner operation such as coal and petroleum coke.