High Pressure Steam Reactivation of Calcium Oxide (CaO) Sorbents For Carbon Dioxide (CO_2) Capture Using Calcium Looping Process

THESIS

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Abstract

Calcium looping is a sorbent based chemical looping process that uses calcium oxide or similar calcium sorbent precursors for pre-/post-combustion carbon dioxide capture. Extensive study of this process at the Ohio State University has led to the development of two variants of this process: Carbonation-calcination reaction (CCR) process for post-combustion carbon capture in electricity generation and calcium looping process (CLP) for pre-combustion carbon capture in hydrogen production and electricity generation. CCR is a cyclic post-combustion carbon capture process, demonstrated at a 120 KW_{th} scale at OSU. This demonstration achieved more than 90% carbon dioxide removal and over 99% sulfur dioxide (SO_2) removal. It has been shown through process simulations that CCR process induces less energy penalty than the conventional amine/oxy-combustion based carbon dioxide capture technologies. This process involves carbonation-calcination-steam hydration of calcium sorbents. Steam hydration is a reactivation step which mitigates the effect of sintering of sorbents during calcination, regenerates the sorbent surface, and retains carbon capture capacity over a large number of cycles. High pressure steam reactivation of calcium sorbents was investigated and the dependence of hydration rate on steam pressure is obtained. Higher steam partial pressure allows for higher temperatures (500-550ºC) to get higher hydration conversions. The reaction being highly exothermic (-109 kJ/mol), high temperature gives high quality heat which can be used elsewhere in the process. Reaction kinetics of steam hydration for four different limestone based sorbents was studied using high pressure thermogravimetric analysis. Elevated pressures (1-3.5 atm) and high temperature (500-530ºC) were used in this study. Steam hydration of PG Graymont limestone sorbent experimentally showed second order with respect to steam pressure driving force ($P_{H2O} – P^*_{H2O}$). Rate constants for each operating conditions were calculated and activation energy of the reaction was computed from these calculations. The activation energy obtained from this study is 5.18 KJ/mol. Nitrogen physisorption studies were performed for characterization of the sorbents and their reactivity was compared via the steam hydration studies in the TGA at 500ºC and P_{H2O} 1.5 atm. CaO sorbent derived after hydration shows the highest surface area and pore volume, which is more than 6-10 times that of the sorbent derived by calcination of $CaCO_3$. This study is a strong indication that hydration with water/steam regenerates the sorbent morphology, in process reactivating the sorbents with high porosity. It is believed, however, that initial particle size has little or no bearing on the reactivation process or sorbent reactivity in the multi-cyclic studies as hydration causes particle breakage.

This study is significant in regard to the post-combustion and pre-combustion carbon capture calcium looping processes developed at OSU as the hydration temperature would be comparable to the carbonator temperature as it is expected to make the processes economically viable. There exists a trade-off however for the steam pressure to be used for hydration. Very high steam pressure would incur high compression costs and affect the energy penalty of the process. This could deter the compensating effect of heat recovered from the hydrator and in turn make the process more energy intensive. This study is limits the pressure to 4-5 times the atmospheric pressure and still obtain higher conversions.

This document is dedicated to my guru and to my parents for their incredible support and encouragement.

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Fields of Study

Major Field: Chemical Engineering

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Chapter 1: Introduction

Anthropological activities since the advent of industrial revolution have caused an unprecedented increase in carbon dioxide concentration in air from 285 ppm before the arrival of the industrial revolution to the current level of 405 ppm[1]. This is the result of unabated and to a certain extent profligate consumption of available fossil fuels like coal, oil, and natural gas. Electricity generation using coal has helped light up even the remotest areas of the globe at a frugal cost, but it continues to be an acute source of carbon dioxide emissions. In the United States, coal combustion contributes nearly a third of the total carbon dioxide emissions while providing half of total electricity generated. Worldwide, 42% of the total CO_2 emissions come from the burning of coal while it accounts for just 41.3% of the total power generated. While natural gas can replace coal for firing the power plants, coal continues to be an economical fuel for electricity generation. There is a concerted effort worldwide to develop effective and efficient CO_2 capture systems, which concentrate the dilute CO_2 in flue gas for storage through sequestration.

United States Electricity Generation by Fuel Type[51]

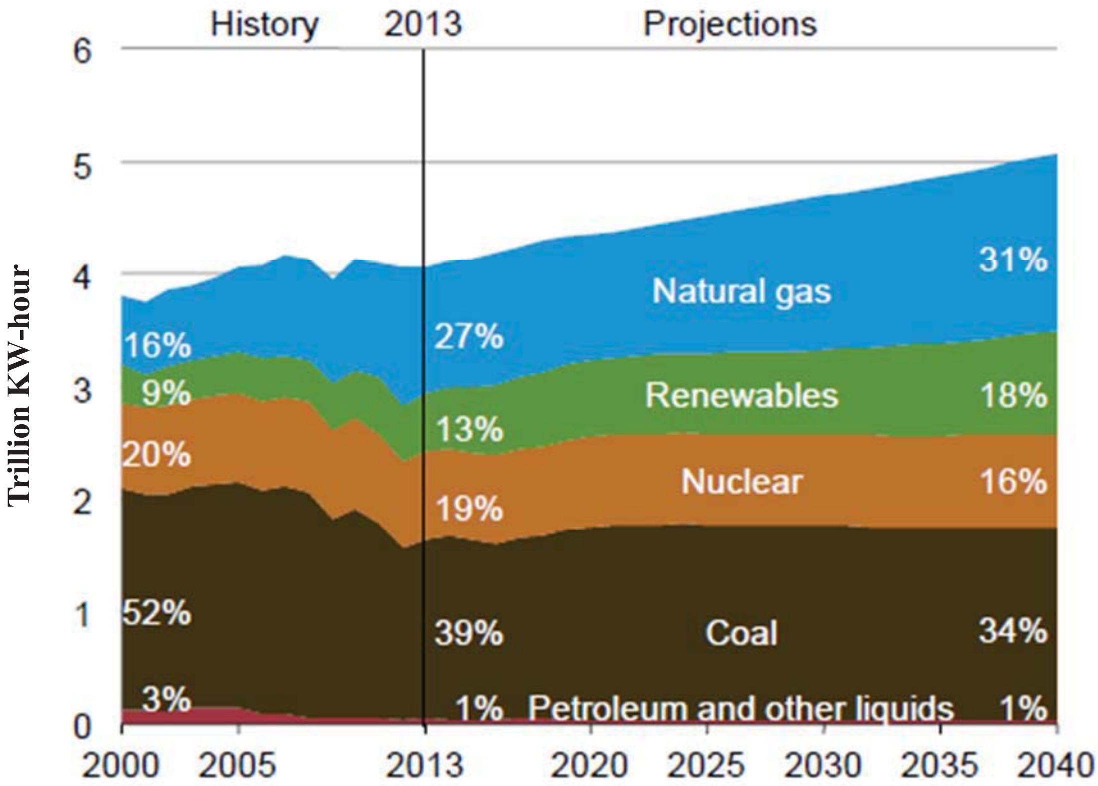


Figure 1.1 United States Electricity Production by Fuel Source

Figure 1.1 shows the estimated contribution of currently used fuels for electricity production in the United States. According to these projections, natural gas and coal will be the primary sources of fuel for electricity generation in 2040. More than half of the electricity produced in the United States in 2040 is estimated to come from fossil fuels. Although the contribution of natural gas towards electricity production will be more than that of coal, clean coal conversion is equally necessary for cheaper and reliable supply of electricity. Moreover, variation in natural gas prices is significant as compared to the prices of fuel. Thus, a process designed for carbon capture from coal-fired power plants would be economically realistic. Though the current prices of natural gas (2$/mmBTU) are lucrative, the variation in prices over the last 5 years has been high and the prices had soared up to 6.5$/mmBTU at the start of 2014 while coal prices have remained stable at around 1.9$/mmBTU for the last 5 years, with the current price being 1.57$/mmBTU. Coal mining is still a major boost for the local economy in the United States and generates a large number of jobs across the United States. Any reduction in the usage of coal adversely affects the coal miners and the people dependent on the coal production, processing, and distribution chain. This is one of the reasons that coal mining and coal utilization are largely supported by the federal and state governmental agencies like the Department of Energy (DOE) and Ohio Coal Research Consortium (OCRC). Their strong financial support and initiative for clean coal research have led to the development and successful demonstration of the post-combustion Carbonation Calcination Reaction (CCR) process for carbon capture at Ohio State University.

The U.S Environmental Protection Agency (EPA) has recently set new regulations for carbon dioxide emissions from new and existing power plants fired with coal or natural gas. These rules mandate a minimum of 20% wt. CO_2 capture from the existing power plants and 30-40% by wt. CO_2 capture from new natural gas or coal-fired power plants. CO_2 emission limit has been set at 1400 pounds per MW-hour of gross electricity generated in the existing coal power plants and 1000 pounds per MW-hour of gross electricity generated from natural gas-fired power plants[3]. With the current amine-based carbon capture technologies for existing power plants, the Levelized cost of electricity (LCOE) increases by more than 80% than that for the subcritical pulverized coal boiler without carbon capture. Preliminary techno-economic analysis of the three step carbonation-calcination reaction (CCR) process developed at Ohio State University indicates a 32% increase in the LCOE as compared to the base case (subcritical PC boiler with no CO_2 capture). Thus, the calcium looping process has a great potential as a post-combustion carbon and sulfur capture technology with relative ease of integration in the process[4,5]. Extensive research in the calcium looping process for pre-/post-combustion carbon capture has shown that calcium based sorbents, especially limestone are suitable for high-temperature carbon dioxide capture in both pre-/post-combustion configurations[6,7,8,9,10,11]. Calcium based sorbents are also effective in completely capturing sulfur dioxide as well as acid gasses like hydrochloric acid (HCl) from flue gas streams in pre-combustion configuration[12]. Along with lab-scale experiments using thermo-gravimetric analyzer (TGA) and fixed bed reactor systems, calcium looping process has been demonstrated at OSU on a sub-pilot 120 KW_{th} scale In the post-combustion CCR process configuration[11]. This post-combustion CO_2 demonstration using coal/natural gas co-fired stoker which produced coal-boiler type flue gas composition was successfully demonstrated. Various aspects of the process like sorbent reactivity, process integration, and process economics were extensively researched[4,11]. Promising outcomes of this demonstration and research elsewhere led to 1.7 MW_{th} demonstrations of this technology.

1.1 Limitations of the two-stage calcium looping process

Calcium looping process for carbon dioxide capture in pre-post-combustion configuration has been extensively researched as two-step process – carbonation and calcination which uses a single reversible reaction of calcium oxide (CaO) with carbon dioxide (CO_2) to form calcium carbonate ($CaCO_3$) at temperatures ranging from 550-700°C and the same $CaCO_3$ is calcined back to CaO. Using this idea a number of processes were developed worldwide and most of them were successfully demonstrated up to pilot scale, for example the Ohio State University (OSU) Calcium Looping Process (CLP)[13] for high purity hydrogen and electricity production from syngas, the Hydrogen Production by Reaction Integrated Novel Gasification (HyPr-RING) process[14,15], ALSTOM's Hybrid Combustion-Gasification Process[16], the GE-Fuel Flexible Process[17], and CO_2 acceptor process[18,19]. A major challenge with the scale-up of the two-step process is to maintain the sorbent reactivity and recyclability. For example, the results of a test conducted on a sorbent obtained from the Pleasant Gap quarry from Graymont shows that the CO_2 capture capacity goes down drastically over multiple cycles[20] as seen in Figure 1.2. CO_2 capture capacity is given by the simple equation

$$\text{Weight Capture (\%)} = \frac{(W_t - W_0)}{W_0} \times 100$$

Where W_t is the weight after carbonation, W_0 is the initial weight before being subjected to carbonation. Thus, the theoretical maximum of the capture capacity is 78.5 % by wt.

The decrease of CO_2 capacity of the sorbent after multiple cycles has been widely reported[21,22,23]. High calcination temperature of the order of 900-1300°C leads to a detrimental effect on the sorbent morphology which adversely affects the reactivity of the sorbent. This effect is called 'sintering'[7,21,24,25]. Loss of reactivity due to sintering occurs after a few cycles of carbonation and calcination as the sorbent surface turns smooth, pores fuse together thus hindering the diffusion of CO_2 inward. Sintering is a combined effect of multiple factors like calcination temperature, the design of the calciner, the residence time in the calciner, heat transfer in the reactor etc[26]. Rotary drum reactor is has been determined to be one of the best calciner reactors regarding minimizing the sintering effect on the sorbents. Other types of calciner are a fixed bed calciner or a kiln commercially used for the production of quicklime. However, this design is not preferred in the two-step carbon dioxide capture process due to higher levels of sintering of the sorbents.

To improve the reactivity of the sorbents, several methods have been proposed and experimented in the past among which, steam hydration is the most viable and cost-effective alternative. Synthesis/modification of the sorbents doped and supported sorbents, reactivation through steam/water hydration are some of the techniques that have been attempted for reactivation of the sorbents[27], as seen in Figure 1.2 and Figure 1.3.

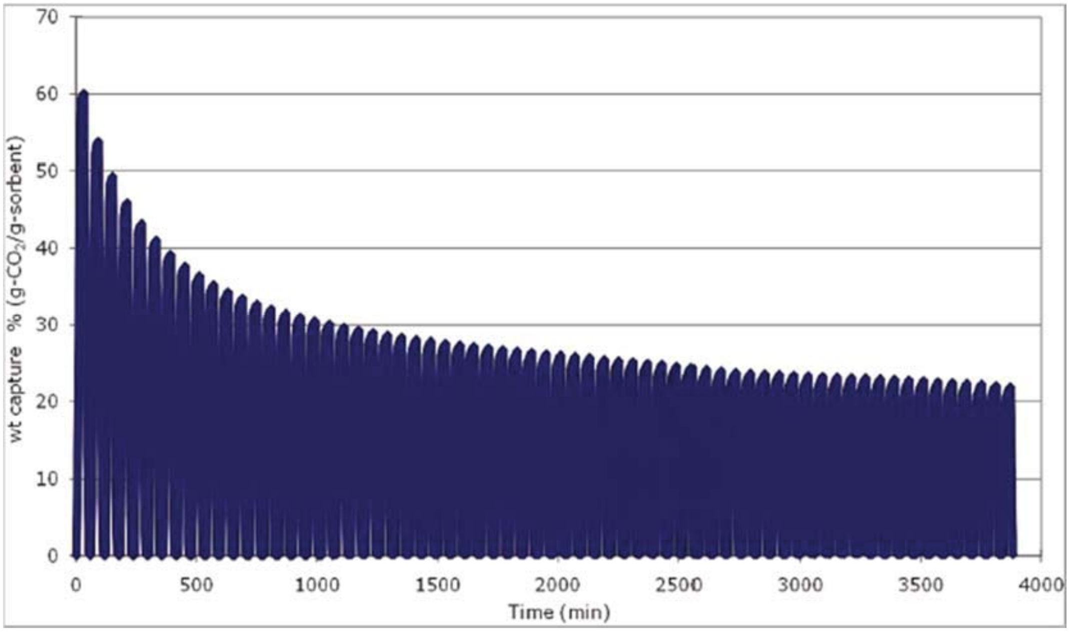


Figure 1.2 Carbon dioxide (CO_2) capacity w.r.t time in multi-cyclic CCR process

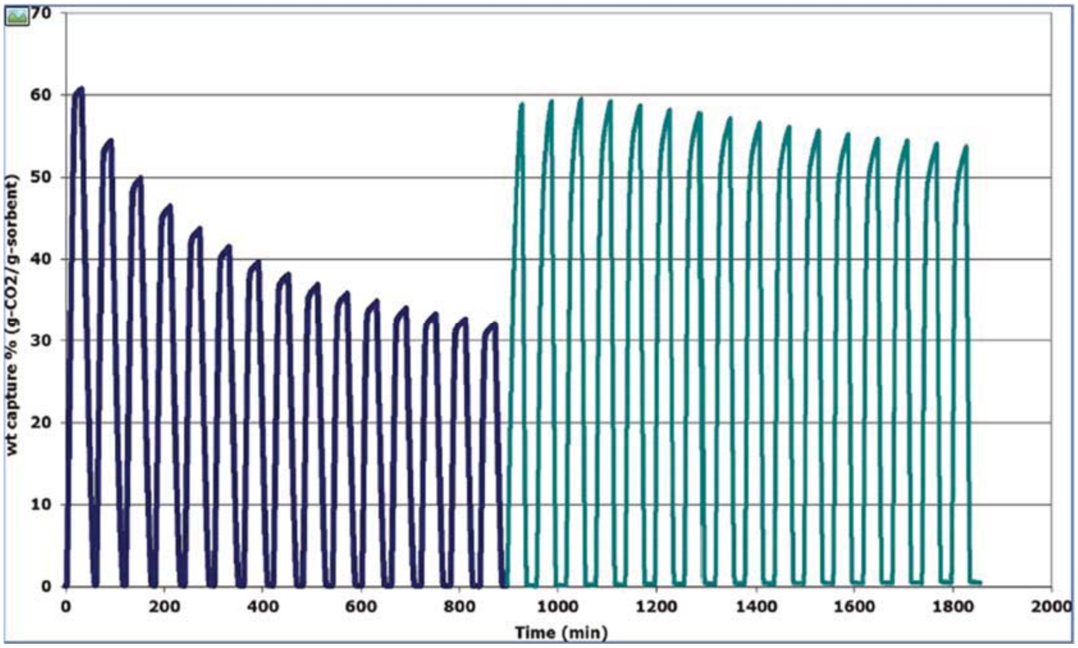


Figure 1.3 Carbon dioxide (CO_2) capacity for three step CCR process involving steam hydration reactivation

1.2 Sorbent Reactivation Techniques

1.2.1 Synthesis of calcium-based sorbents from precursors

Sorbents having a high surface area and pore volume have higher activity as it is relatively easier for gas molecule diffusion and formation of $CaCO_3$. Precipitated Calcium Carbonate (PCC) with a large surface area can be synthesized by bubbling CO_2 through a $Ca(OH)_2$ slurry. Morphology of the sorbent can be tailored by using an anionic dispersant (N40 V) to obtain unique mesoporous structure (5-30 nm). This sorbent can maintain a high reactivity over several cycles. PCC was used in a sulfur removal in the Ohio State Carbonation Ash Reactivation (OSCAR) process[28,29]. High reactivity of calcium oxide (CaO) can also be obtained from inorganic and organometallic precursors like calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$), calcium acetate ($Ca(CH_3COO)_2$), calcium propionate ($Ca(C_2H_5COO)_2$), calcium acetylacetonate ($Ca(CH_3COCHCOCH_3)_2$), calcium oxalate ($Ca(COO)_2$), calcium 2-ethylhexanoate ($Ca(C_7H_{15}COO)_2$), and calcium D-gluconate monohydrate. CaO derived from calcium acetate, calcium propionate, and calcium D-gluconate monohydrate exhibited a higher CO_2 capture capacity due its mesoporous and macroporous structure[30]. CaO sorbents modified with ethanol solutions showed higher CO_2 capture capacity. Although sorbents could be changed in many different ways using organometallic precursors, the ability of higher CO_2 capture using these modified sorbents has only been tested in the thermo-gravimetric analyzer (TGA) and not in actual process systems. Thus, their applicability against the cost of materials is debatable.

1.2.2 Doped or supported calcium oxides

Sorbents doped with calcium aluminate cement were tested for 1000 cycles of carbonation/calcination retaining 22% by wt. Residual capture capacity. Dolomite derived CaO performs better-regarding capture capacity (24 wt. % after 1250 cycles) due to the support of MgO[31,32]. Dopants or supports make the sorbents mechanically and morphologically stronger, but the overall CO_2 capture capacity is affected due to lower CaO content[33]. Solids circulation rate required to capture the same amount of CO_2 with doped or supported sorbents may be very high as compared to unsupported CaO sorbent. Thus, the impact on process material and energy balances would also have to consider thoroughly for every doped sorbent as the amount of support/dopant would decide the amount of inert circulating in the loop. The cost of these sorbents may also be higher as compared to limestone precursors.

1.2.3 Steam/water hydration

A unique aspect of carbonation-calcination reaction (CCR) process developed at OSU has been the demonstration of calcium hydroxide ($Ca(OH)_2$) based sorbent for post-combustion CO_2 capture. $Ca(OH)_2$ based sorbent was obtained by high-temperature steam hydration at 450-510ºC using a bench scale fluidized bed hydration. $Ca(OH)_2$ based sorbent mitigates the loss of reactivity over multiple cycles caused by high temperature (900-1300ºC) calcinaton which is known to cause 'sintering' of the sorbent. 120 KW_{th} demonstration of the CCR process achieved >90% CO_2 capture and 100% SO_2 capture using $Ca(OH)_2$ sorbent with Ca:C mole ratio of 1.43:1 as against 10:1 with CaO sorbent. Intermediate hydration of the sorbent helps in retaining the CO_2 capture capacity, thus minimizing the solid circulation and sorbent make-up rate which gives higher overall process efficiency[11]. Hydration of calcium-based sorbent is a highly exothermic reaction which when performed at higher temperatures using superheated steam provides high-quality heat. With proper heat integration, the energy penalty induced due to the calciner operation could be minimized. With $Ca(OH)_2$ based sorbent demonstration, the overall energy penalty can be retained at 17.5% with the use of Pulverized coal (PC).

$CaO + H_2O \longrightarrow Ca(OH)_2 \quad \Delta H^0 = -109$ kJ/mol

An almost instantaneous reaction with water at room temperature, hydration of calcium oxide (CaO) is limited by thermodynamics when performed with superheated steam at high temperature. Figure 3.1 on page 31 shows the relationship between temperature and equilibrium steam partial pressure (P^*_{H2O}) at high temperature. Steam hydration at temperatures comparable to the carbonator temperature (550-700ºC) in the calcium looping process would have to be operated at elevated steam pressure (>1 atm) for effective conversion and higher rates of reaction in the hydrator. The operation of the hydrator at higher temperatures would allow for extraction of high-quality heat usable in the steam turbine cycle of the power plant[4].

Figure 1.4 shows three-stage post-combustion CCR process that could be retrofitted to a coal/natural gas fired power plant. Reactions colored red indicate endothermic reaction which requires energy to overcome the activation barrier while reactions colored in green are exothermic reactions.

$CaO + CO_2 \longrightarrow CaCO_3 \; \Delta H^o = -174$ kJ/mol

Pre-combustion calcium looping process (CLP) generates high purity H_2 and electricity from syngas obtained from a coal gasifier[8]. This process produces hydrogen through water gas shift reaction while CaO sorbent takes up the CO_2 generated in the reaction. This shifts the reaction equilibrium to the right according to Le Chattelier's principle.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

It uses intermediate hydration reaction scheme like the CCR process to retain the sorbent reactivity.

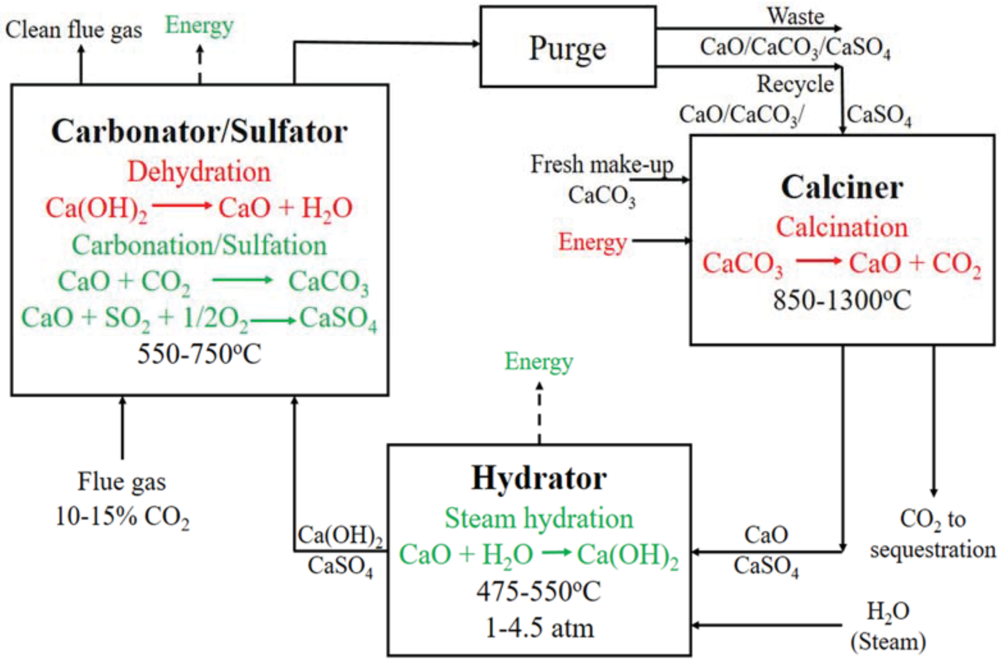


Figure 1.4 Schematic of post-combustion carbon capture CCR process

Carbon dioxide capture capacity has been shown to drop drastically over multi-cyclic operation in the CaO sorbent based process which decreases the process efficiency and also necessitates the use of water-gas shift (WGS) reaction for H_2 production[34]. $Ca(OH)_2$ based process not only obviates the need for a water gas shift catalyst but also removes other acidic gasses like hydrogen sulfide (H_2S), hydrogen chloride (HCl), carbonyl sulfide (COS), etc. in a single step[8,12,13]. As the operating temperature of the carbonator is sufficiently large for dehydration of the $Ca(OH)_2$ from the hydrator, the resulting steam generated is available for the WGS reaction, thus waiving the additional steam requirements for WGS. $Ca(OH)_2$ as sorbent would decrease the solids circulation rate and the fraction of make-up solids in the calciner[13]. Pre-combustion calcium looping process has been studied for high pressure and shows higher CO conversion with highly pure hydrogen (>99%) in the product stream when operated at high pressures (11-20 atm)[12]. Moreover, due to the inherent requirement of steam in the pre-combustion process for hydrogen production, the introduction of steam hydration may not affect the economics of the process to a great extent. At higher pressures, hydration of CaO is much more favorable due to larger driving force. Thus pressurized steam hydration at a higher temperature could be integrated into the pre-combustion calcium looping process with relative ease. Figure 1.5 shows the schematic of pre-combustion carbon dioxide capture process.

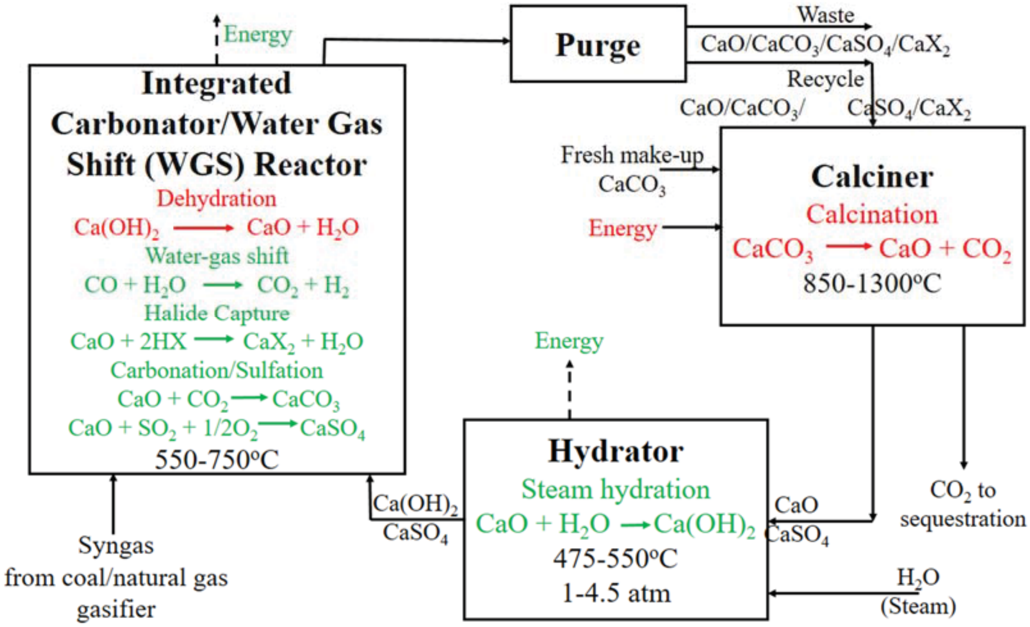


Figure 1.5 Schematic of pre-combustion carbon capture CLP process

For both pre- and post-combustion carbon capture processes, there are common advantages for using $Ca(OH)_2$ based three-stage calcium looping process.

$Ca(OH)_2$-CaO as the sorbent has superior morphological properties (surface area, pore volume, porosity) thus making it more reactive than CaO and could be used as a sorbent in the carbonator which could make use of extremely small residence times in the carbonator (even few seconds). Along with improving the reactivity, this will allow for fast fluidization operation in the carbonator. Thus, the residence time for carbonator could be reduced against that required for a carbonator operating in a bubbling or circulating fluidized bed. This would enable faster and greater CO_2 capture by maintaining lower solid circulation rates and same reactor size. Ca:C ratio as low as 1.3 was observed for >90% carbon dioxide capture in the CCR process using $Ca(OH)_2$ based sorbent as against 10 for Graymont lime in the same study[4,11]. Lower Ca:C molar ratio allows for designing of smaller equipment thus minimizing the capital cost. This is even more favorable given the latest EPA regulation for 20% CO_2 capture in the new coal and natural gas-fired power plants[3]. Economics of the process could improve to a great extent by remodeling the three stage calcium looping process tuned in accordance with the latest regulations. This study aims to find the residence time and good operating conditions for steam hydration of sorbents regarding steam pressure and hydrator temperature. Reactivation by hydration of the sorbent was first proposed to improve sorbent performance for SO_2 capture in Fluidized Bed Combustion (FBC) systems as the expansion caused due to hydration of CaO to $Ca(OH)_2$–cracks up the $CaSO_4$, which otherwise may hinder CaO-CO_2 and CaO-SO_2 reaction[35],[36],[37],[38]. Re-carbonation of

$Ca(OH)_2$ based sorbent occurs in two ways according to the recent findings- direct carbonation and indirect carbonation. Indirect carbonation is the isothermal reaction of CaO derived from $Ca(OH)_2$ and CO_2. Direct carbonation with $Ca(OH)_2$ occurs in non-isothermal condition before $Ca(OH)_2$ dehydrates to CaO. Direct carbonation occurs without entering the slow diffusion regime characteristic of CaO-CO_2 reaction[39]. This allows for 100% conversion and would thus give maximum sorbent utilization in the process. By regenerating the sorbent surface, carbon dioxide capture capacity is restored nearly to its theoretical limit of 78.5 wt. % over multiple cycles. Direct carbonation observation has been confirmed by several researchers[9,39]. Moreover, the exothermic heat of reaction of hydration at high temperature in the hydrator could be directly used in the steam turbine cycle to generate more electricity[4]. These advantages of using steam hydration of sorbent as an intermediate step in calcium looping process, especially for processes developed at OSU, is a significant driving force behind the high-pressure steam hydration study.

Earlier studies on intermediate steam hydration of calcium sorbents have been performed at lower temperatures using wet gas instead of steam. For energy integration of hydration into the calcium looping process (either pre-/post-combustion), requires the reaction to be operated at intermediate process temperatures between 400-600ºC [4]. This allows for utilization of the heat of reaction while retaining the sorbent reactivity. Fixed bed and bench scale hydration studies performed with steam partial pressure (P_{H2O}) of 1.0 atm have an upper limit due to the thermodynamics of the reaction. At 512ºC, steam partial pressure at equilibrium (P^*_{H2O}) is 1.0 atm which requires the hydrator to be operated at temperatures lower or close to 500ºC. Bench scale hydrator studies performed at 473ºC showed 70% conversion in 30 minutes which needs to be further optimized by considering the implications on reactor design and capital cost. Kinetics studies at lower steam partial pressures (0.1-1.0 atm) show a substantially lower rate of reaction if (Teq – T) < 50ºC (Teq = equilibrium temperature for particular operating steam pressure and T = reaction temperature)[40]. To overcome the equilibrium barrier and to allow for higher reactor temperature, higher steam partial pressures could be used which would require a detailed kinetics study for better reactor design. Kinetics and Particle characterization studies for steam hydration at intermediate pressures (1 – 4.5 atm) and temperature between 475-550ºC are presented here. Steam hydration at elevated pressures has been studied for pre-combustion carbon capture integrated with a coal gasifier, similar in design to the HyPr-RING system[14]. Wang et al investigated the effect of particle properties using four types of Japanese limestone for steam partial pressures between 13-23 atm. It was observed that hydration rate of CaO is a function of steam pressure gradient ($P_{H2O} – P^*_{H2O}$) for particular operating temperature[41]. Thermogravimetric (TGA) studies on another Japanese limestone by Lin et al for steam pressures between 6.7 – 23 atm showed that rate of reaction is a function of second power w.r.t partial pressure gradient ($P_{H2O} – P^*_{H2O}$) [42]. It is evident from these studies that steam partial pressure substantially affects the reaction rate, however, such high temperatures and pressures would require additional capital and operating cost, frequent maintenance, and stringent safety standards compared to other units operating at a much lower pressure. For pre- and post-combustion calcium looping systems developed at OSU, hydration at intermediate steam pressures (1.0 – 4.5 atm) and temperature 500-600ºC is advantageous considering previous studies of process economics of CCR process and CLP process (500ºC and 2.0 atm P_{H2O})[13, 43, 44, 45]. Preliminary techno-economic analysis for the CCR process suggests performing hydration at a temperature close to 500ºC to maintain the overall energy penalty of the process at 17.5% while more electricity could be generated from the process[43]. Other parameters like particle size, surface characteristics, origin are also known to affect the hydration rate[46]. ASPEN process simulations studies which include steam hydration in both the pre- and post- combustion calcium looping process indicate a direct impact of sorbent reactivity and hydration extent on the process energy consumption, economics, and solids circulation rate. For instance, more than 90% CO_2 capture and >99% SO_2 capture could be achieved in the CCR process with the use of $Ca(OH)_2$ based sorbent at a Ca:C mole ratio of 1.3. Previous studies over steam hydration of CaO and process economics studies at OSU dictates the importance of kinetics study of hydration for intermediate steam partial pressures performed using TGA for four different limestones from quarries in Ohio, Pennsylvania, and Kentucky.

Theoretically, a pressurized steam hydrator should yield favorable reaction kinetics to reverse the adverse effect of sintering in the calciner thus retaining the sorbent reactivity over a large number of cycles, reduce solid circulation rate in the system, and minimize the Ca:C mole ratio to give higher carbon dioxide capture. This study has been performed to test steam hydration of calcium sorbents at achievable and feasible operating conditions of temperature and steam pressure which would not affect if not reduce the overall energy penalty of the current CCR process[47].

Chapter 2: Materials and Experimental Setup

2.1 Materials and Sorbent Preparation

Four types of calcite limestone samples were investigated in this study which was obtained from Graymont, Inc. and Hanson Aggregates. Graymont sample was procured from Pleasant Gap (PG), Pennsylvania and Hanson Aggregates samples came from Flemingsburg (FL), Kentucky, AA from southern Ohio, and Eagle (EA), Ohio. Though the selected samples may be different w.r.t formation and age from other limestone samples in the US, it is believed that results obtained from more than one sample allow for confident reporting of the results and interpretations drawn from them. PG sample is a pulverized sample while AA, FL, and EA were crushed and particles less than 140 μm in size were separated and used for this study. The phenomenon of particle attrition/breakage due to hydration has been reported through several studies[30,42,46]. Therefore, initial particle size has little or no bearing on the hydration experiments, especially in a multi-cyclic process. Four limestone samples obtained from different quarries in Ohio, Pennsylvania, and Kentucky were tested in Pyris1 TGA for quantifying the calcium content and extent of hydration of the sorbent with water at room temperature. Isothermal Decomposition in the completely inert atmosphere (100% N_2) at 700ºC was performed for each sample. Program for the TGA analysis was as follows: Sample was heated from 25 to 700ºC in N_2 and held isothermally for 30 min for both calcination of sample and dehydration of hydrated sorbent. The sample was cooled back to 25ºC. The rate of heating and cooling was controlled at 25ºC/min. In completely inert atmosphere, calcium carbonate ($CaCO_3$) in limestone sample starts calcining at ~600ºC. Holding the temperature at 700ºC for 30 min ensured complete calcination of the sample. While calcination starts at 600ºC, decomposition of the hydrate in the hydrated sorbent starts at a much lower temperature (350-400ºC). However, with the same program used for hydrated sorbents, usually two steps for weight loss were observed. Weight loss during temperature ramp-up was attributed to dehydration ($Ca(OH)_2$ to CaO) and isothermal weight loss occurring at 700ºC is attributed to calcination of residual calcium carbonate ($CaCO_3$) in the sorbent. Isothermal weight loss is a small fraction of the total weight loss during decomposition of hydrated sorbent. Carbon dioxide capture capacity of the sorbent is a direct function of the calcium content of the limestone sample. Thus, four limestone samples acquired from quarries around Ohio were tested in Pyris1 TGA. 20-25 mg sample was used for each analysis. Amount of calcium carbonate ($CaCO_3$) in the sample was calculated from the weight loss due to the release of CO_2.

$$\%CaCO_3 = \frac{\left(W_0 - W_{calcined}\right) * M_{CaCO3}}{W0 * M_{CO2}}$$

W_0 is the weight of the sample tested in the TGA and $W_{calcined}$ is the weight of the sorbent after 30 minutes of isothermal calcination at 700ºC in the TGA. All the limestone samples except AA have more than 90% calcium content. Limestone samples were calcined in the muffle furnace at 900ºC for 2 hours, and calcined samples were hydrated with a stoichiometric quantity of DI water at room temperature to check the extent of hydration. All the samples contained more than 70% hydrate and a small amount of uncalcined calcium carbonate along with the inherent inerts. This study showed the capability of steam hydration of the sorbents for the parametric thermo-gravimetric studies. Also, sorbents hydrated with water at room temperature were analyzed for pore size distribution and surface area studies using the nitrogen physisorption. The extent of hydration is known by calculating the extent of hydration of the sorbent. The weight loss curve for hydrated sorbents tested in Pyris 1 TGA using the same program as that used for calcination, is different from a single steep loss as seen in calcination. Weight loss due to dehydration of $Ca(OH)_2$ occurs at much lower temperatures (>400ºC) and is completed as the temperature reaches 700ºC. Two distinct weight loss patterns are observed in this study. The one occurring at a temperature lower than 700ºC is attributed to the weight loss due to dehydration of $Ca(OH)_2$. Extent of hydration is calculated as follows:

$$\%Ca(OH)_2 = \frac{(W0 - W1) * M_{Ca(OH)_2}}{W0 * MH2O}$$

The extent of hydration seen in these studies is not complete due to incomplete calcination of the sorbent in the muffle furnace. In the parametric TGA studies, limestone sample is calcined in the TGA and hydrated using steam. Thus, complete hydration was observed during these studies. Table 2.1 shows the composition of 4 limestone minerals regarding calcium carbonate content and extent of hydration.

Table 2.1 Composition of limestone sorbents and extent of water hydration

Company/ Quarry	**Sample**	**Location**	**Type**	**Acronym Used**	**%$CaCO_3$**	**%$Ca(OH)_2$ Water hydration**
Graymont	Pleasant Gap	Pennsylvania	Calcite	PG	97.43	75.56
Hanson Aggregates	Flemingsburg	Kentucky Ohio River Basin	Calcite	FL	91.74	72.80
Hanson Aggregates	Grayson	Kentucky Ohio River Basin	Calcite	AA	98.80	70.25
Hanson Aggregates	Eagle	Ohio Ohio River Basin	Calcite	EA	89.28	76.11

2.2 Experimental Setup and Procedure

2.2.1 Calcination

Calcination of the samples was performed in an oven (Fischer Scientific Isotemp Muffle Furnace) with a maximum capacity of 1100ºC. Samples were placed in a ceramic crucible for calcination. Samples were calcined at 700ºC and 900ºC for 2 or 3 hours. Due to a lower degree of calcination (<50 %wt.) at 700ºC, sorbents obtained for the studies presented here have been calcined at 900ºC for 2 hours. Loss of reactivity of the sorbents due to sintering is mainly a function of calcination temperature than the time for which samples were calcined[48]. Calcination of the sample was almost complete within 2 hours. To avoid hard burning of the outer structure of the sample, calcination time was limited to 2 hours.

2.2.2 Nitrogen physisorption studies

Physisorption studies were performed on the limestone sorbents using nitrogen gas to obtain the surface area, pore volume, and pore size distribution of the sorbent surface using the Braunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method on Quantachrome NOVA 4200e series analyzer from Quantachrome Instruments.

Solid surfaces must be free from contaminants such as oil and water before performing the analysis. Any impurity chemically or physically adsorbed on the surface can be removed by degassing the samples under vacuum or inert gas at high temperature (100-400ºC). The temperature for the degassing of the sample was selected based on the sorbent. Hydrated sorbent ($Ca(OH)_2$) was performed at 400ºC to decompose the $Ca(OH)_2$ to CaO to capture the effect of expansion of the pores and increase in surface area due to hydration. Fresh sorbent ($CaCO_3$) and calcined sorbent (CaO) was degassed at a lower temperature of 200ºC. Degassing was usually performed overnight or at least 8 hours, after which the samples were weighed and subjected to adsorption-desorption analysis. To maintain a constant temperature of the sample, liquid nitrogen bath was used which maintained the sample temperature at -196ºC. Small amounts of nitrogen gas are admitted in steps in the evacuated chamber. Adsorption of the gas on the solid surface tends to form a thin layer that covers the entire adsorbent surface. Based on the well-known BET theory, a number of molecules Nm adsorbed on the surface is computed. The product of Nm and cross-sectional area of an adsorbate molecule yields the sample's surface area. Continued addition of the gas molecules beyond monolayer formation leads to gradual stacking of the multiple layers. BJH method is used to compute the pore sizes from equilibrium gas pressures. Experimental isotherms of adsorbed gas volumes relative versus equilibrium pressures are converted to cumulative or differential pore size distributions.

2.2.3 Thermogravimetric Analysis (TGA) studies for high pressure steam hydration

Parametric studies for steam hydration of calcium oxide (CaO) sorbents by varying steam pressure and temperature were performed on the Rubotherm Magnetic Suspension Balance (MSB) (schematic in Figure 2.1). Rubotherm MSB is a thermo-gravimetric analyzer with provision for sending a gaseous mixture with 5 gases, can withstand a pressure up to 20 atm or 300 PSI. Cylindrical quartz sample holder weighing just more than 1g with a diameter 10 mm and a height of 20 mm was used. Sample holder was suspended from the magnetic balance using a titanium rod. Sample holder and the titanium is enclosed with an Inconel casing. Reactor system is heated with an electrical furnace programmed with a computer. VTI Flow software was used to set the test parameters, temperature for calcination and hydration temperature, equilibrium criterion for the test, data logging interval etc. Flow of gases was controlled independently using a Rubotherm gas manifold operated using pneumatic valves. For hydration experiments, nitrogen was used as the inert gas during calcination and as a carrier gas during steam injection.

Limestone sample being tested in the TGA was subjected to calcination and subsequent steam hydration. The samples were heated from 25 to 700ºC and held at 700ºC for 45 minutes after which they were cooled from 700ºC to the hydration temperature. Hydration temperature was varied from 450-550ºC for parametric steam pressure studies. Calcination of the samples was performed in 100% N_2 (inert) atmosphere. After the hydration temperature had been reached, steam injection was started. Steam generation consisted of a high precision syringe pump (ISCO 100DM), which delivered water at a set flow rate into the preheater zone. Preheater zone consisted of stainless-steel tubing with heating tapes over it and appropriate insulation. The temperature in the zone was maintained at 230-250ºC which instantaneously converted the inflow of water into steam. 50% vol. the flow of steam balanced with N_2 was injected into the reactor by the preheater zone. Delivery of water through the pump was performed in the intervals of 3 min for a duration of 5 min. This helped regulate a continuous flow of steam into the reactor without flooding the preheater zone. Water flow was stopped when more than 90% conversion was observed. Conversion of CaO to $Ca(OH)_2$ is calculated on a molar basis. Instantaneous conversion is computed from the increase in sorbent weight due to the formation of $Ca(OH)_2$. Let W_{CaO} be the instantaneous weight of the sorbent, W_{oCaO} be the weight of the sorbent at the start of the reaction, and M_k is the molecular weight of the molecule.

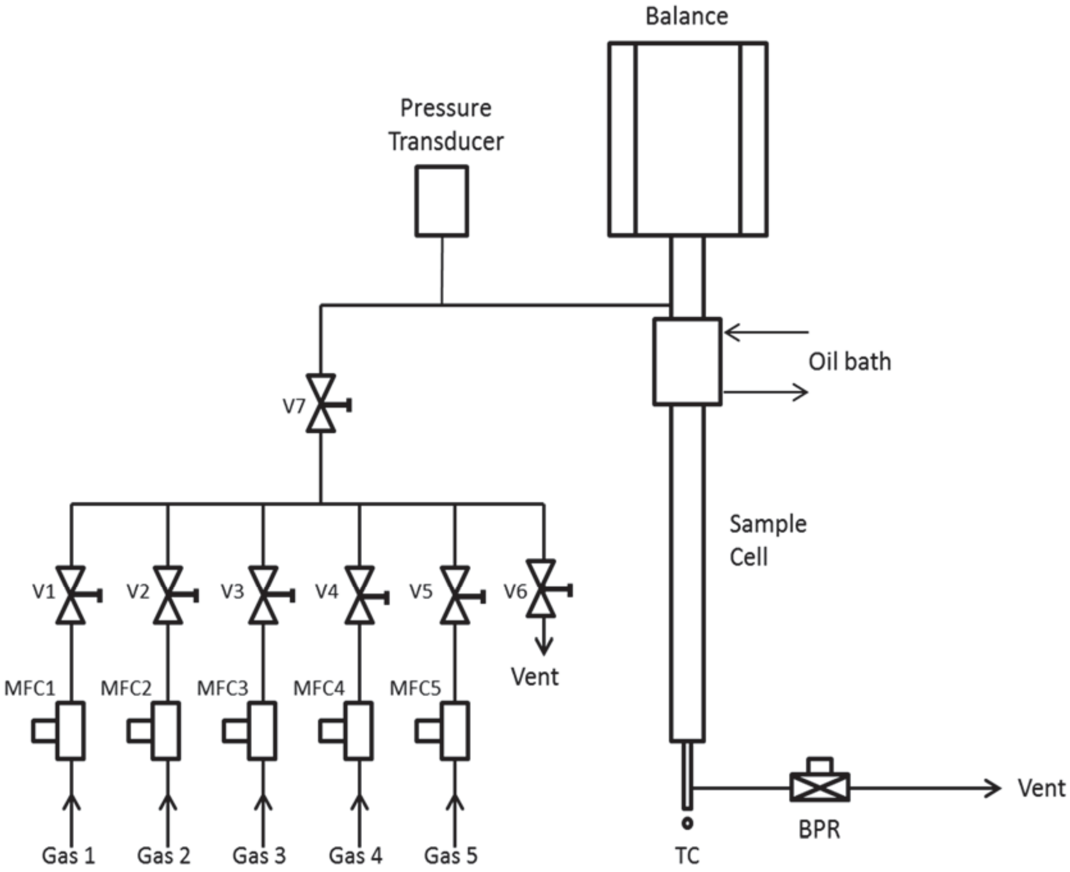


Figure 2.1 Rubotherm Magnetic Suspension Balance (MSB)

Figure 2.2 TGA setup in the laboratory

Conversion (%) $X_{Ca(OH)2} = \frac{(W_{CaO} - W_{oCaO}) * M_{CaO}}{W_{oCaO} * M_{H2O}}$

Aim of the thermogravimetric experiments was to investigate several factors affecting steam hydration of the sorbent which includes:

- Steam partial pressure and operating temperature of the reactor. At a particular operating temperature, the rate of hydration of the sorbent with steam depends on the driving force which is the difference between operating steam pressure and equilibrium steam pressure ($P_{H2O} - P^*_{H2O}$).
- Effect of limestone origin. To observe the behavior of origin of limestone, four different limestones were included in this study from quarries in and around Ohio.

2.2.4 Fixed bed studies for steam hydration and calcination

An existing fixed bed reactor system was modified to study the steam hydration of calcium sorbents. A preheater section was used for continuous steam generation and flow into the fixed bed reactor. The reactor itself consisted of a cylindrical ceramic tube 45-50 cm long with an ID of 1.27 cm. Approximately 5 grams of calcined sorbent, was used for the fixed bed experiments. Figure 2.3 shows the fixed bed reactor setup with the different sections labeled: water pump, preheater, reactor, heater, back pressure regulator, and condenser. A syringe pump, the same one used for water injection into the high-pressure TGA for steam hydration experiments, was used to inject continuously water for continuous steam generation. N_2 was used as a carrier gas for the steam into the reactor.

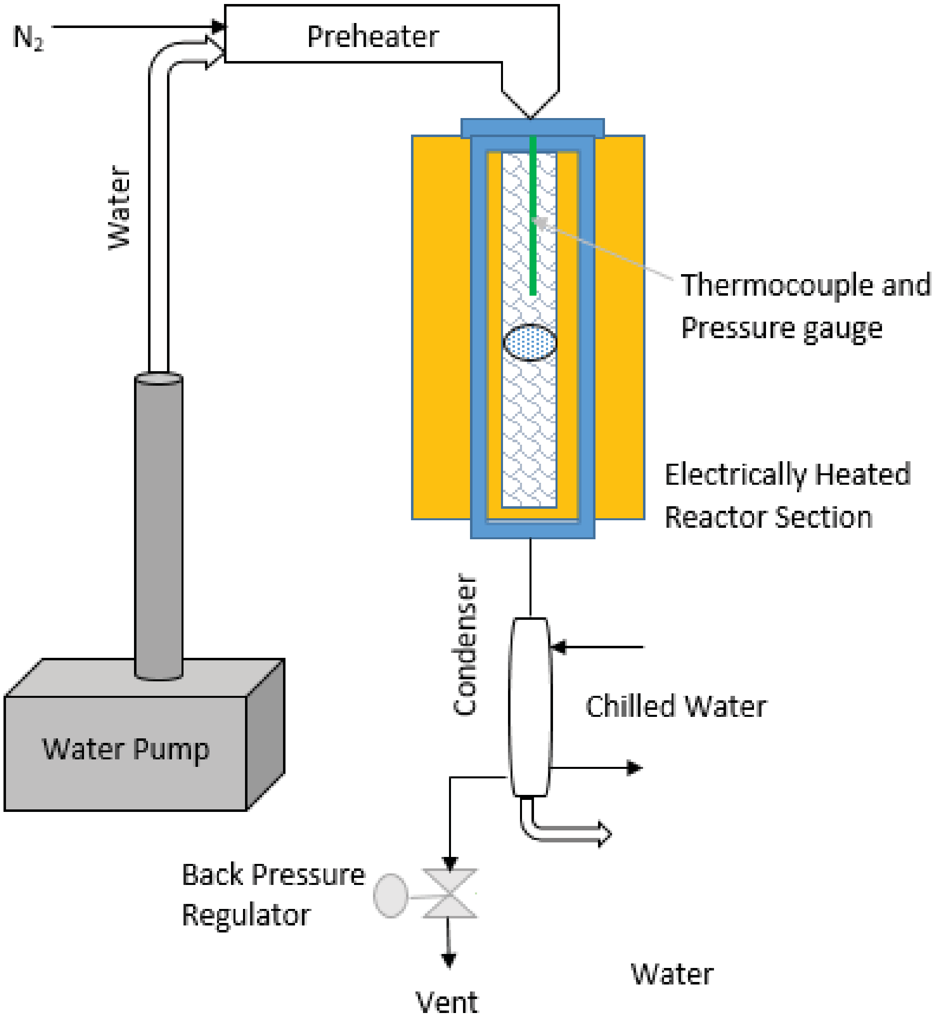


Figure 2.3 Fixed bed reactor setup for pressurized steam hydration of sorbents

Same fixed bed setup was also used for the calcination studies for sorbents subjected to different calcination conditions in the fixed bed. For this experimental setup, steam injection point, condenser and the back pressure regulator were removed. Particle bed was created using a long quartz cylindrical tube with a perforated quartz plate at the bottom. With dimensions of 12.5 mm for diameter and 150 mm tall, the quartz tube can hold up to 8 g of fresh limestone sorbent ($CaCO_3$). Ceramic reactor tube of the fixed bed was packed using quartz chips and quartz wool. Quartz cylindrical tube was placed over the quartz wool. The tubular quartz reactor was fabricated from the glass blowing workshop at OSU. It minimized the loss of sample that occurs due to the fines in the quartz wool.

Chapter 3: Results and Discussion

3.1 Reaction kinetics studies in the TGA

Parametric steam hydration studies were performed using a Rubotherm Magnetic Suspension Balance (MSB), a thermo-gravimetric analyzer as described in detail on page 24 under the experimental section. Steam hydration of calcium sorbents was demonstrated in the 120 KW_{th} sub-pilot post-combustion CCR process using superheated steam for hydration at 475ºC in a bench scale fluidized bed[11]. For a better hydrator design and process integration, thermo-gravimetric studies were performed at a particular temperature and steam pressure range. The equilibrium between steam partial pressure and temperature dictates the minimum steam partial pressure required for a particular temperature. For example, steam hydration at atmospheric pressure is limited in temperature by the minimum temperature needed for steam generation from the exothermic heat of reaction and the maximum temperature allowable for hydration to occur, which is 512°C (785 K). The design of experiments for the parametric study is described in Table 3.1. The Rubotherm high-pressure TGA is used to conduct hydration tests. The amount of sample used in the experiments is between 0.120-0.160 g. N_2 is used as an inert gas, also acting as a carrier gas for steam. A flow rate of 400 sccm was used along with 60% steam. Gas flow rate and water injected with a syringe pump are calibrated for each set point of temperature and pressure used for steam hydration. High-pressure experiments were performed using a back pressure regulator (BPR) to control the TGA reactor pressure and set before beginning water injection. Table 3.1 provides the temperature and partial pressure of steam at which four samples were tested. This study was performed in the third quarter and is included here to discuss the possible correlation of surface studies and reactivity of the sorbents tested in the TGA.

Table 3.1 Design of experiments for parametric steam hydration studies

Temp (^{o}C)	**Steam pressure (P_{H2O}) (atm)**
450	0.667, 1.0, 1.5
475	0.667
500	1.5, 2.0, 2.25, 2.5
520	2.0, 2.25, 2.5, 3.0, 3.5
530	2.0, 2.2, 2.4, 2.6, 2.8, 3.0

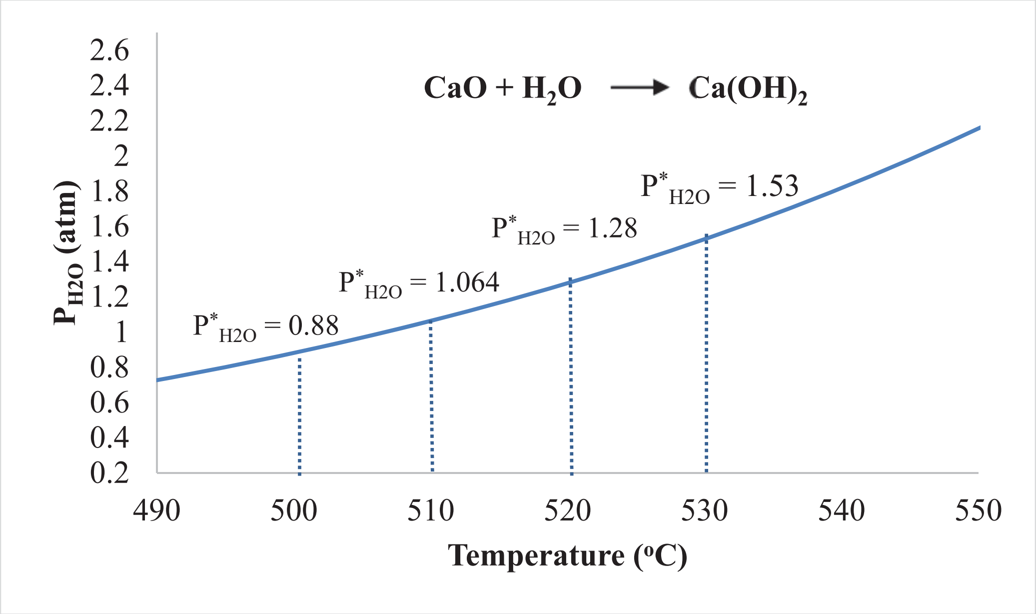


Figure 3.1 Equilibrium curve of steam partial pressure and reaction temperature

3.1.1 Effect of temperature

The temperature for performing the steam hydration reaction should be as high as possible to maximize heat recovery. The economics of post-combustion carbon capture using calcium looping process could be improved if the steam hydration of the calcium sorbent is performed at temperatures comparable to that of the carbonator. Because the hydration of calcium oxide is a highly exothermic reaction, high-quality heat can be obtained from the hydrator at a higher temperature if the hydrator is operated under elevated pressure. This heat could then be integrated into the process to reduce the energy impact on the process and potentially reduce carbon capture costs. Temperatures higher than 500ºC, specifically 520ºC and 530ºC were selected for TGA studies. Equilibrium partial pressure of steam at these temperatures are 1.28 and 1.53 atm respectively. TGA studies were performed at partial pressures greater than 2.0 atm. Maximum partial pressure of steam used in these studies is 3.0 atm. The cost of steam production increases as the partial pressure of steam is increased. It could be compensated for the hydrator operating at temperatures around 500ºC allowing for a superheated steam generation by directly utilizing the heat evolved from the exothermic hydration reaction. This may positively affect the process simulations of the CCR process by potentially reducing the energy penalty induced by the calciner. Also as the capture capacity of the sorbents will be retained, lesser solid circulation will be required thus decreasing which implies lower energy for the calciner. Thus higher temperature of the hydrator is expected to have a positive impact on the overall process efficiency and economics.

Steam hydration in the TGA is slower as the temperature increases. This could be attributed to the decreasing driving force as the reaction is performed at higher temperatures for same steam partial pressure. At 500ºC, equilibrium steam pressure is 0.88 atm while at 530ºC, equilibrium steam pressure is 1.53 atm. Effect of temperature on the rate of steam hydration was studied for two steam pressures 2.0 atm and 2.5 atm. The rate of the reaction computed at these temperatures indicate that steam hydration of calcium oxide is twice as fast at 500ºC than at 530ºC for P_{H2O} 2.25 atm. The rate of reaction at different temperatures is shown in Figure 3.2, Figure 3.3, and Figure 3.4. Reaction at 530ºC for steam pressure close to 2.25 atm shows that as the pressure is slightly increased from 2.2 atm to 2.4 atm, there is a significant increase in the hydration rate. This indicates a non-linear order of the reaction w.r.t steam pressure, explained in detail in the following section. This effect has been observed in one of the studies for steam hydration at high temperature (~1023 K) [42].

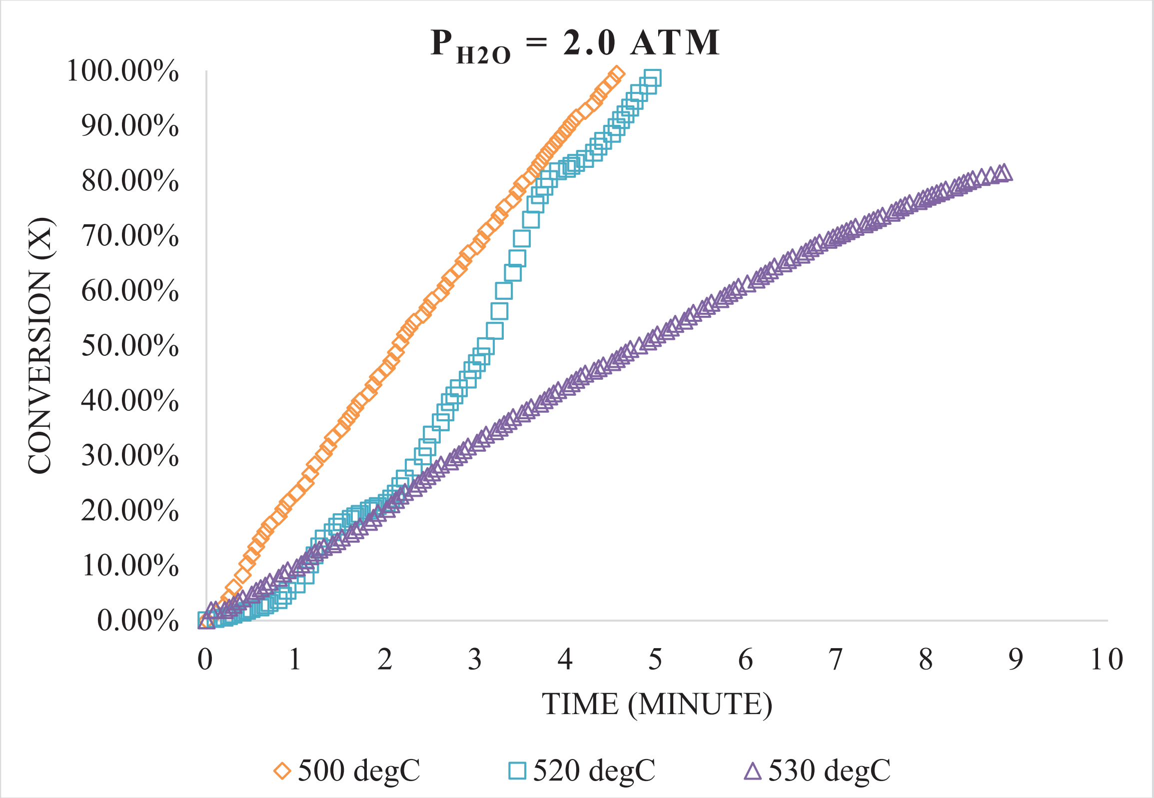


Figure 3.2 Steam hydration studies of PG sorbent for P_{H2O} 2.0 atm and reaction temperature: 500, 520, 530°C

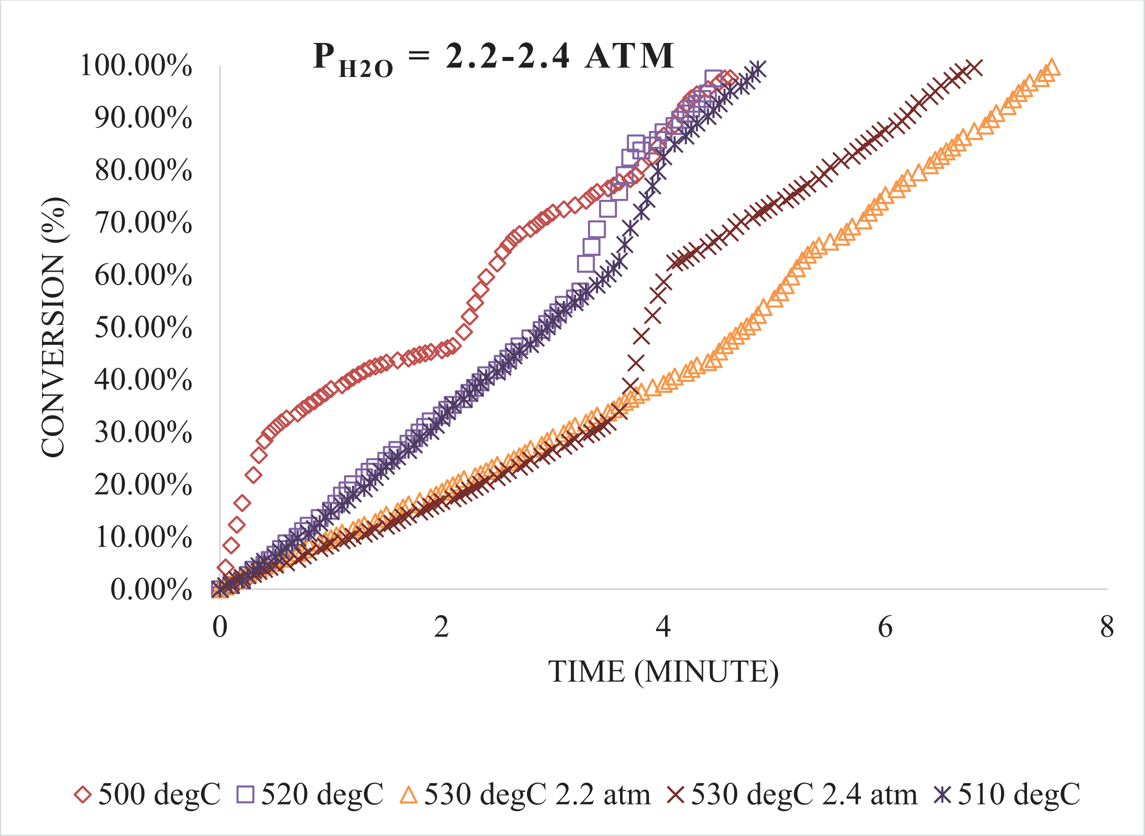


Figure 3.3 Steam hydration studies of PG sorbent for P_{H2O} 2.2-2.4 atm and reaction temperature: 500, 510, 520, 530°C

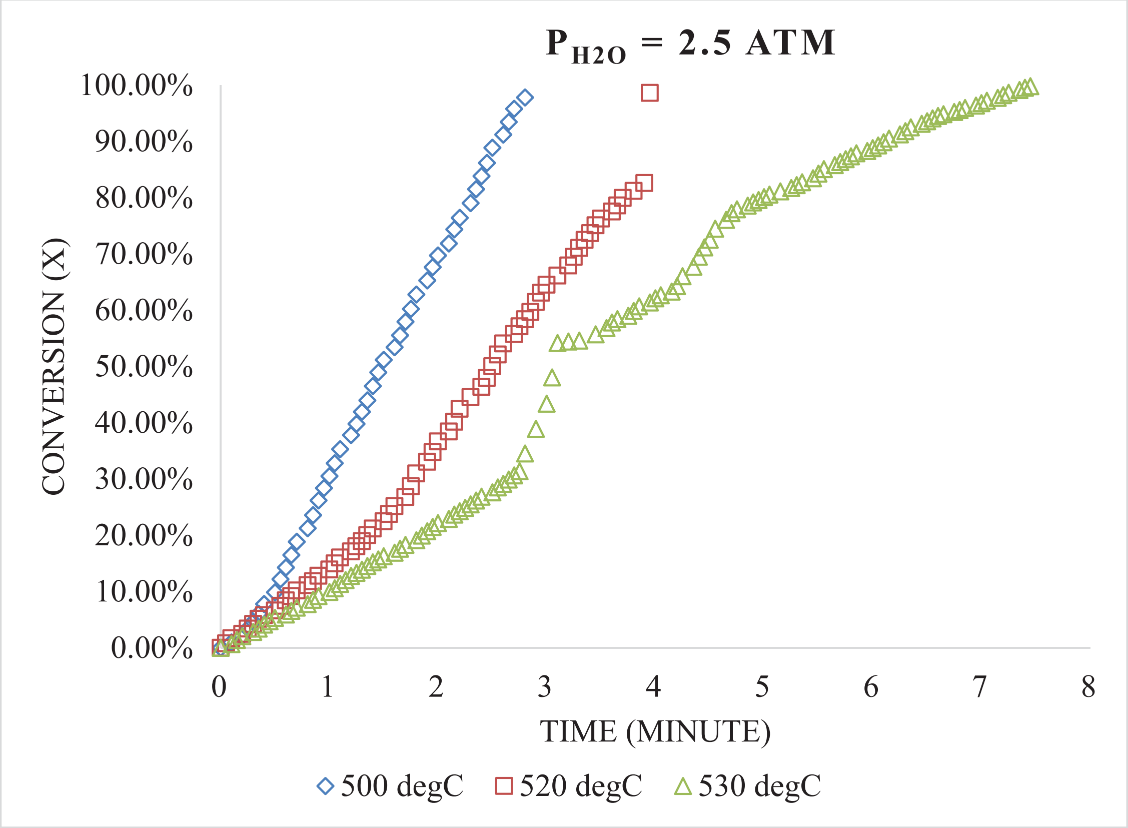


Figure 3.4 Steam hydration studies of PG sorbent for P_{H2O} 2.5 atm and reaction temperature: 500, 520, 530°C

3.1.2 Effect of steam partial pressure on reaction rate

As the partial pressure of steam increases, the rate of hydration also increases. This is due to the increase in the driving force ($P_{H2O} - P^*_{H2O}$). Steam hydration at pressures greater than 1 atm could be favorable for the economics of the calcium looping process as it will allow the hydrator to be operated between the temperatures of 500-550°C. Modifications made on the high-pressure TGA in this quarter fixed the problem of incomplete conversion during steam hydration and ensured continuous steam injection in the reactor. Thus, a new set of experiments were performed for three temperatures 500, 520, and 530ºC. Steam pressures used for these temperatures are given in Table 3.1. Results obtained from these experiments are interesting as they have revised the earlier estimate of residence time for conversion in the TGA. A large number of data points were generated for each run and reaction conversion occurs under a more stable, steady steam injection than before. For determining the order of the reaction w.r.t steam partial pressure, a detailed study with six pressure data points was performed at 530ºC (Figure 3.7), starting at 2.0 atm and increasing steam pressure by 0.2 atm, up to 3.0 atm. The rate and steam pressure relationship obtained at this temperature show a power law relationship with reaction order of ~2. Some of the modifications done on the instrument include uniform heating of the entire section through which gas carries the steam from preheater to the reactor. Steam concentration was limited to 50% with N_2 gas as balance. Thus, water flow rate from the syringe pump was slightly lesser. The temperature of all the sections of the preheater, top and middle portion of the TGA reactor was measured to ensure superheated steam at higher pressures. For steam pressures just over 4.5 atm, saturation temperature of steam exceeds 140ºC.

At 500ºC, equilibrium steam pressure is close to 1.0 atm. Thus, the reaction rate at 1.5 atm is significantly slower than that at 2.0 atm. It takes close to 9 minutes for complete conversion of the available CaO. For P_{H2O} of 2.5 atm, the same reaction is completed in less than 3 minutes. At 2.25 atm, the reaction is initially faster, TGA data showing 40% conversion in less than a minute. However, its progression is slower at higher conversions and goes to completion in about the same time as the one performed at 2 atm, as seen in Figure 3.5.

At 520ºC, equilibrium steam pressure is 1.28 atm. Thus, steam hydration carried out at pressures higher than 2 atm. The reaction is almost twice as fast at a steam pressure of 3.5 atm as compared to the reaction performed at 2.0 atm. The rate of the reaction does not vary to a large extent from 2 atm to 2.5 atm. However, the reaction is significantly faster at 3.0 atm and 3.5 atm, as seen in Figure 3.6.

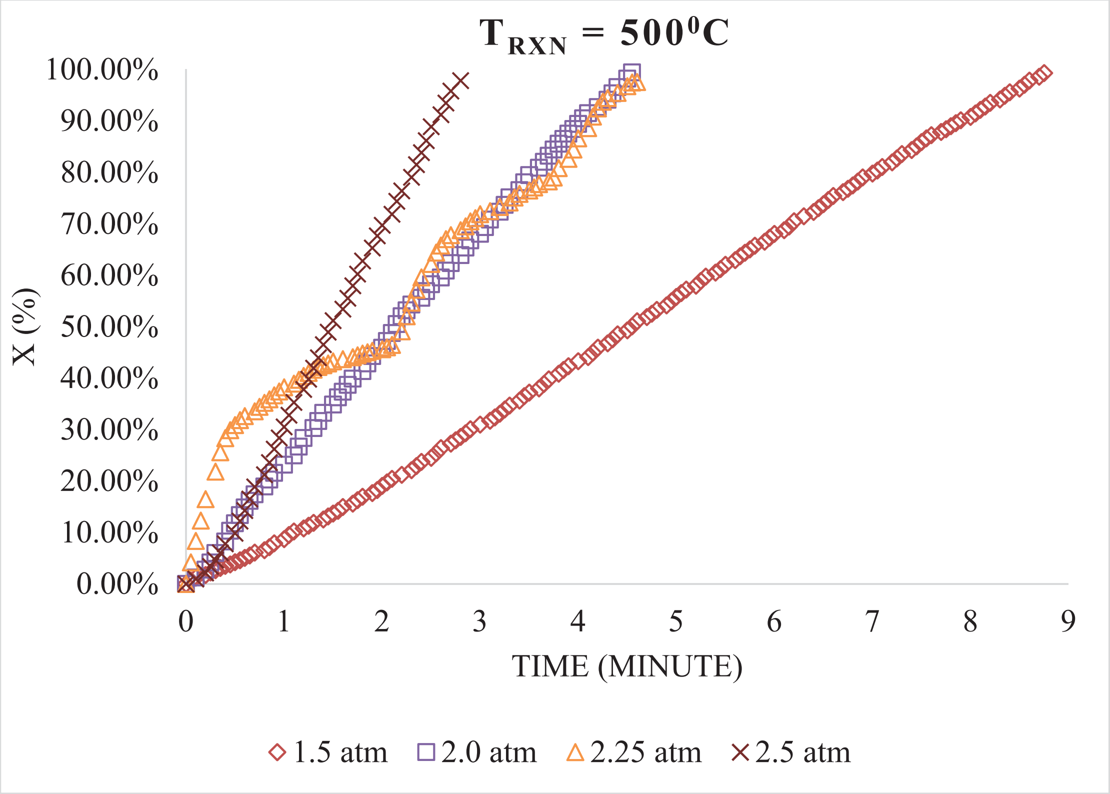


Figure 3.5 Steam hydration studies of PG sorbent for P_{H2O} 1.5, 2.0, 2.25, and 2.5 atm and reaction temperature: 500°C

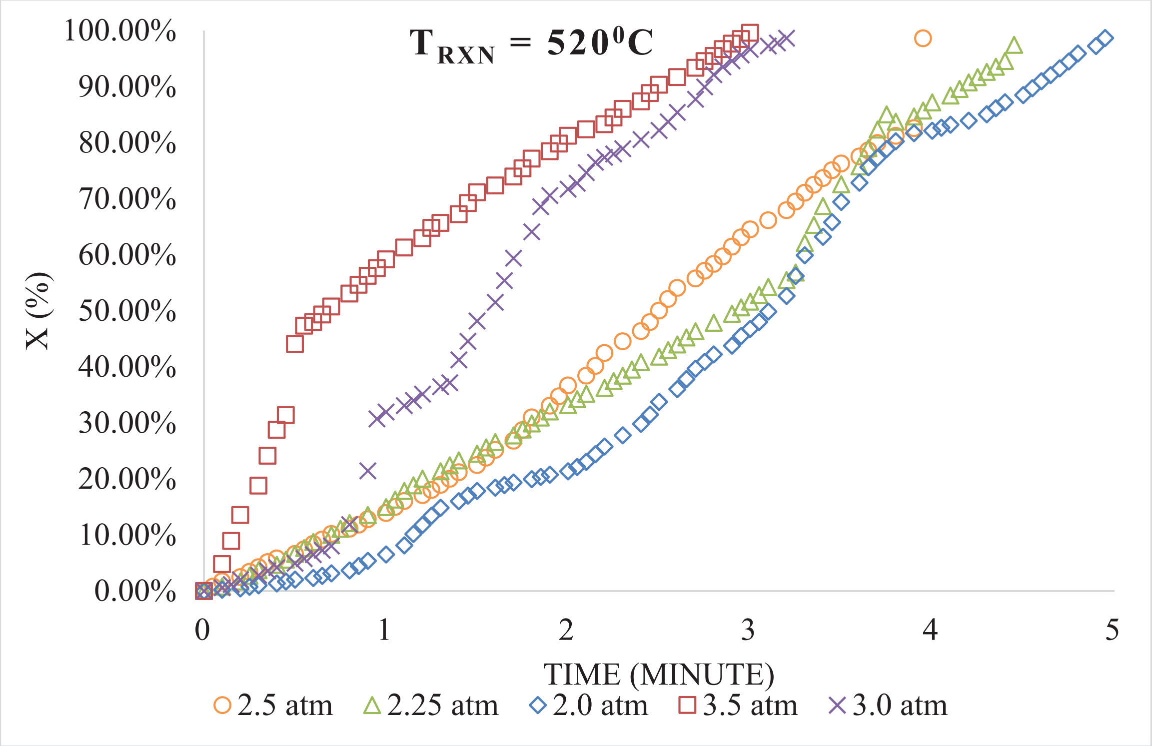


Figure 3.6 Steam hydration studies of PG sorbent for P_{H2O} 2.0, 2.25, 2.5, 3.0, 3.5 atm and reaction temperature: 520^{o}C

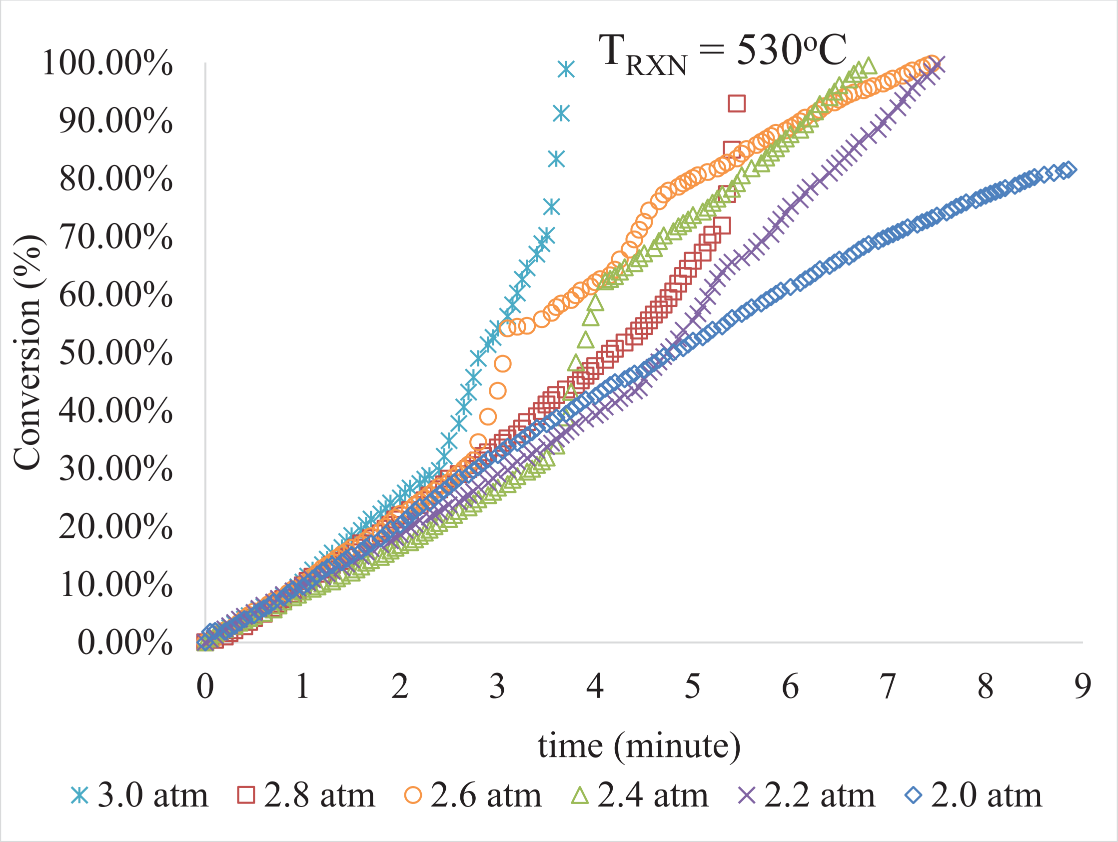


Figure 3.7 Steam hydration studies of PG sorbent for P_{H2O} 2.0, 2.2, 2.4, 2.6, 2.8, 3.0 atm and reaction temperature: 530^{o}C

3.2 Kinetics of steam hydration

Empirical data obtained for different steam partial pressures at different temperatures was analyzed and plotted together to empirically compute the order of the reaction. Assuming a power law relationship between rate of the reaction and ($P_{H2O} – P^*_{H2O}$) with power ‘n’, the value for n can be computed as follows:

$$n = \frac{(log(-r_{a1}) - log(-r_{a2}))}{(log(P_{H2O} - P^*_{H2O})_1 - log(P_{H2O} - P^*_{H2O})_2)}$$

From the plot shown in Figure 3.8, the order of the reaction w.r.t ($P_{H2O} – P^*_{H2O}$) is ~2.0. Thus, the rate constant for steam hydration can be given as follows:

$$k = \frac{-r_a}{\left(P_{H2O} - P^*_{H2O}\right)^2}$$

Rate constant computed for each steam pressure and the temperature is given in Table 3.1.

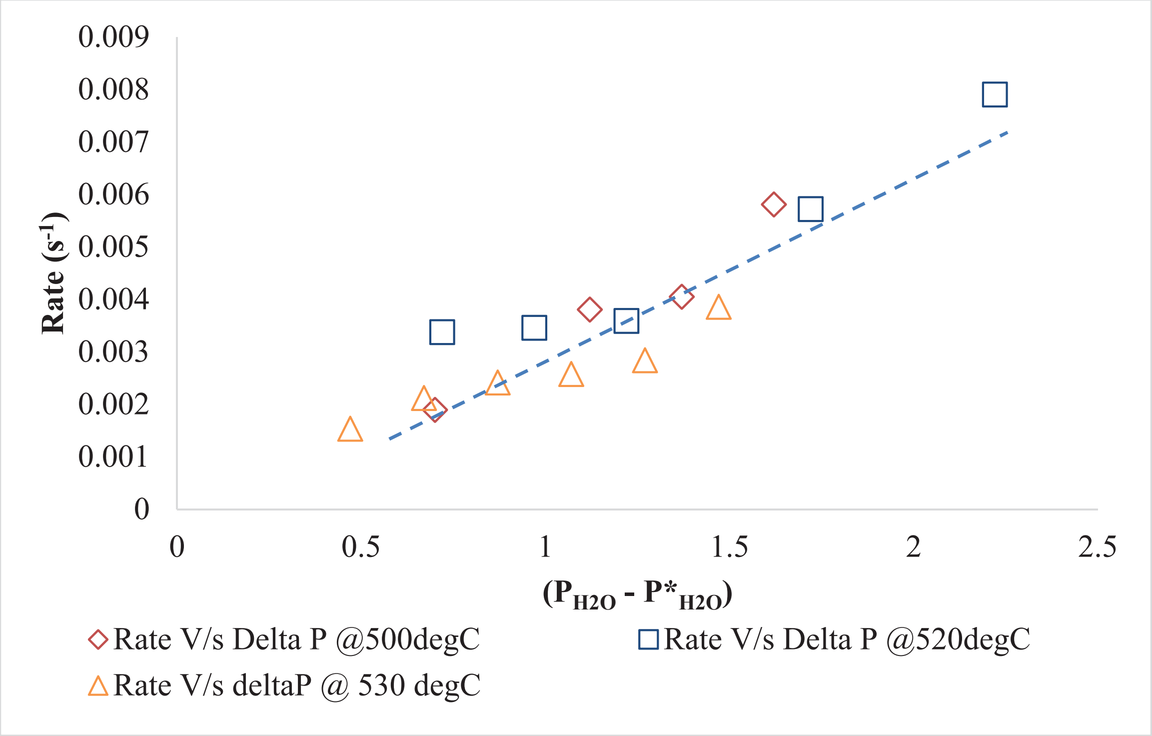


Figure 3.8 Rate of steam hydration of PG sorbents w.r.t steam pressure

Table 3.2 Rate constant for all temperatures and steam pressures

Reaction Temperature (T_{Rxn}) (°C)	Steam Pressure (P_{H2O}) (atm)	Rate Constant (k) ($MPa^{-2}s^{-1}$)
500	1.5	3.87E-05
500	2.0	3.04E-05
500	2.25	2.16E-05
500	2.5	2.21E-05
510	2.25	2.25E-05
520	2.0	6.51E-05
520	2.25	3.67E-05
520	2.5	2.41E-05
520	3.0	1.93E-05
520	3.5	1.6E-05
530	2.0	6.95E-05
530	2.2	4.72E-05
530	2.4	3.19E-05
530	2.6	2.25E-05
530	2.8	1.76E-05
530	3.0	1.79E-05

Equation 1 Rate equation for steam hydration

$$k = A*\exp(-E_a/RT) = -r_a / (P_{H2O} - P^*_{H2O})^2$$

Thus, the Arrhenius plot of rate constant (k) obtained from Table 3.2 is shown in Figure 3.9.

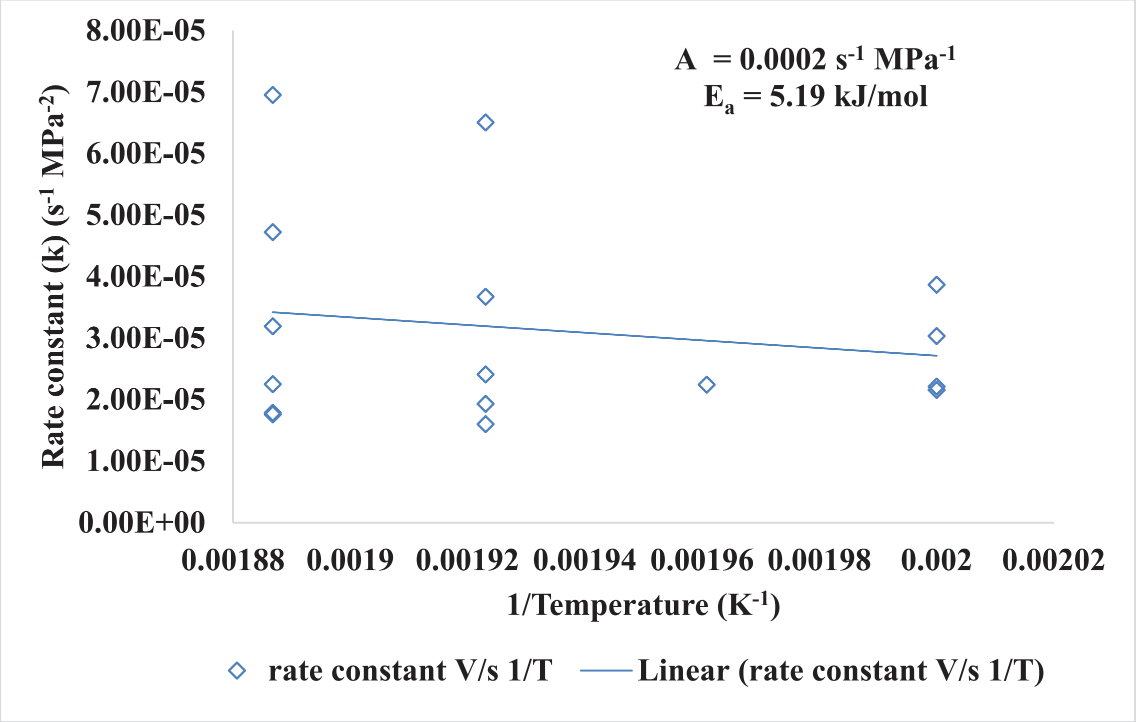


Figure 3.9 Arrhenius plot for rate constant for steam hydration reaction

Thus, the activation energy is computed to be 5.19 KJ/mol from the experimental calculations.

3.3 Sorbent characterization and reactivity studies

Surface morphology and pore distribution studies were performed in the Quantachrome NOVA 4200e series analyzer using the BET method as described in section 2.2.2 Nitrogen physisorption studies). Pore size distribution was obtained using the BJH pore size distribution method. These studies were performed for limestone samples in different forms. The high calcium sample (mostly $CaCO_3$), fresh sorbent (c-CaO), hydrated form (mostly $Ca(OH)_2$), and sorbent-derived from hydrated sample (h-CaO). The surface area of the samples in these forms, obtained from the Braunneaur-Elmett-Teller (BET) method is shown in Figure 3.10. Surface area of c-CaO (calcined) sorbent is important for in the initial cycles of solids circulation as it represents the available surface for the reaction with CO_2 from the flue gas. After 5-10 cycles when the reactivity carbon dioxide starts going down owing to sintering during calcination, solids circulation through the hydrator could be started. Thus surface area post-hydration and of the sorbents derived from $Ca(OH)_2$ is an important indication of the reactivation of the sorbents. Thus BET studies for these two forms is thus critical. Surface studies and pore volume studies are the indicators of reactivation of the sorbent as the surface becomes rough and develops cracks. Reaction with water/steam causes inward diffusion of water in the sorbent which expands the pores on the surface. This pore volume expansion allows the larger CO_2 to penetrate the sorbent surface during re-carbonation.

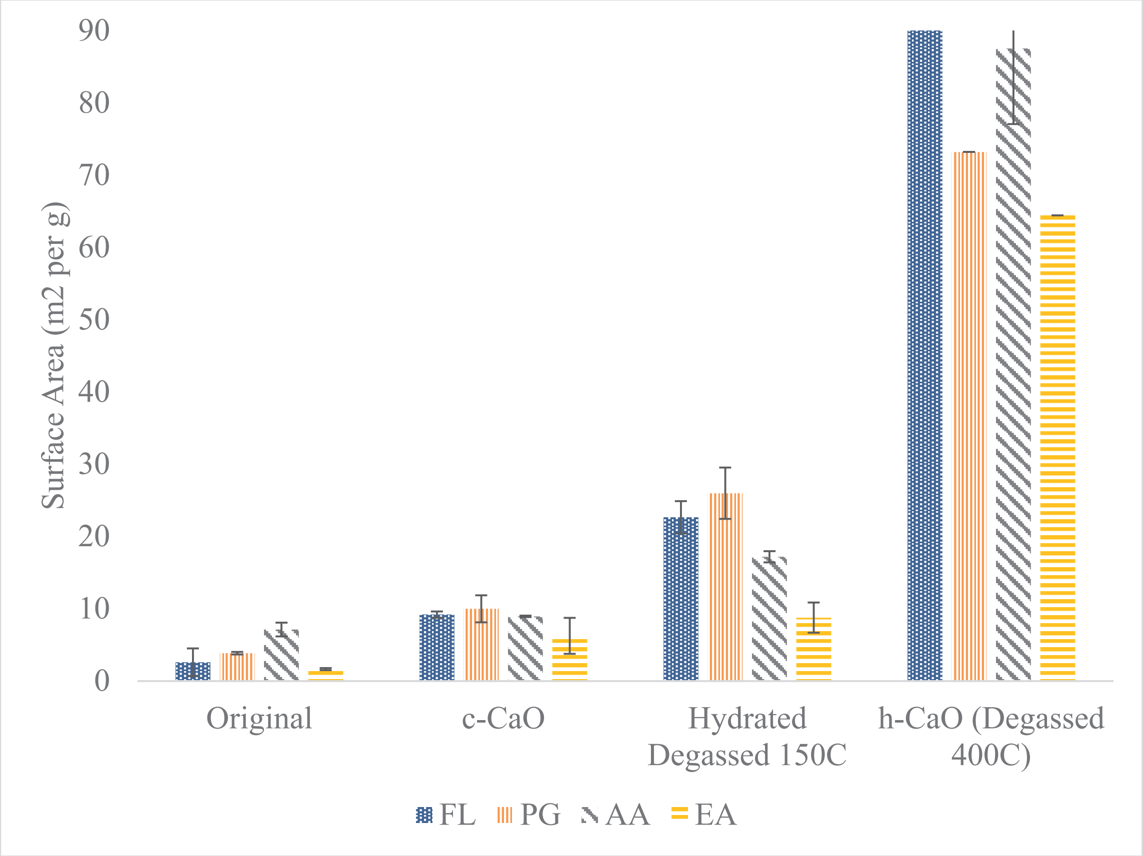


Figure 3.10 Surface area using BET method for nitrogen physisorption studies of PG, FL, AA, and EA sorbents

From Figure 3.10 it can be seen that the surface area of sorbents derived from calcium hydroxide (h-CaO) is 8-10 times more than that of the calcium oxide derived directly from calcium carbonate(c-CaO). The effect of hydration on particle size distribution for the Graymont limestone (PG) sample has been documented in the earlier studies. Large increase in the surface area post-hydration is an important indicator of the reactivation of the sorbent surface by effective mitigation of detrimental sintering effect caused by calcination. Steam hydration causes the expansion of pores in the sorbents derived from calcium hydroxide (h-CaO). Pore volume of h-CaO is 4-5 times that of c-CaO sorbents. This volumetric expansion occurs due to difference in molecular size of $Ca(OH)_2$ and CaO. Figure 3.11 shows the pore volume of the sorbents obtained from the same study. The reactivation effect due to hydration would be similar with steam hydration. Multiple sorbent reactivity studies in the TGA at 500ºC and P_{H2O} of 1.5 atm is shown in Figure 3.12.

Rate of steam hydration of sorbent is the highest for PG and lowest for AA. These sorbents were subjected to steam hydration for the first time. Thus, the surface area of the calcined sorbent (c-CaO) could be correlated with the reaction rate. Surface area of PG is highest for c-CaO sorbent, and that of EA is the lowest. TGA steam hydration experiments show the following order for the rate of hydration: PG > FL > EA > AA. This study was performed at a lower steam partial pressure (1.5 atm) and 500ºC.

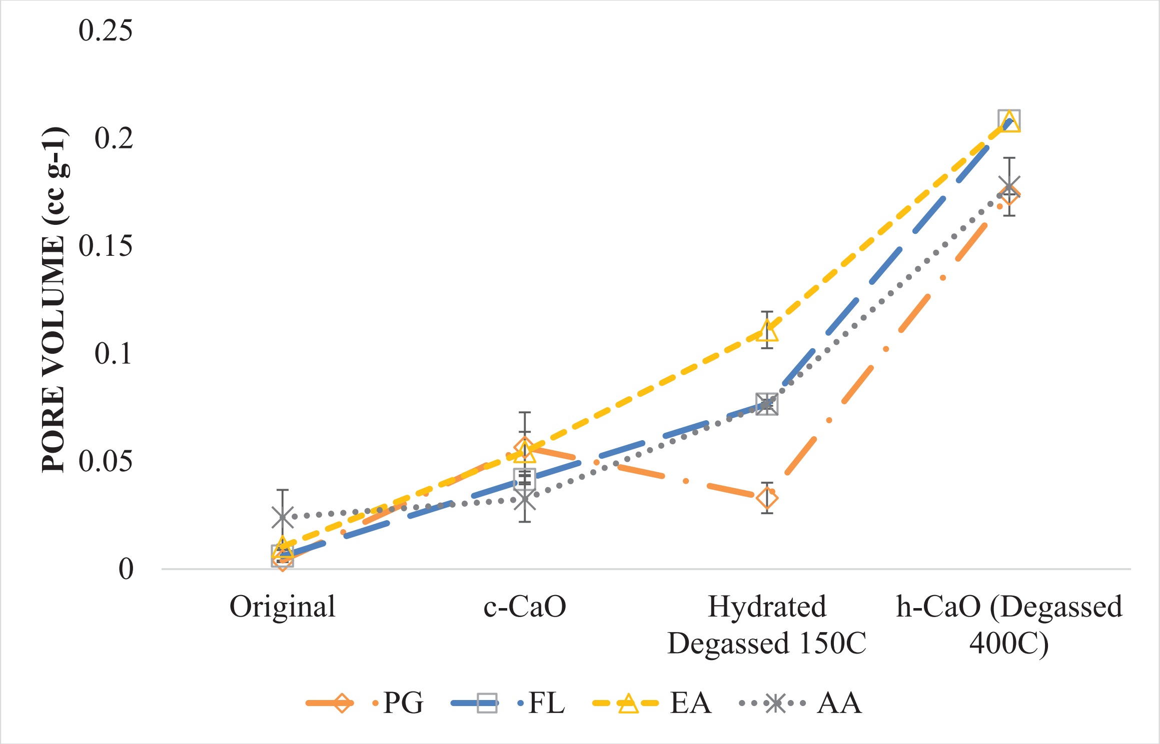


Figure 3.11 Pore volume of PG, FL, AA, and EA sorbents using BJH pore size distribution studies

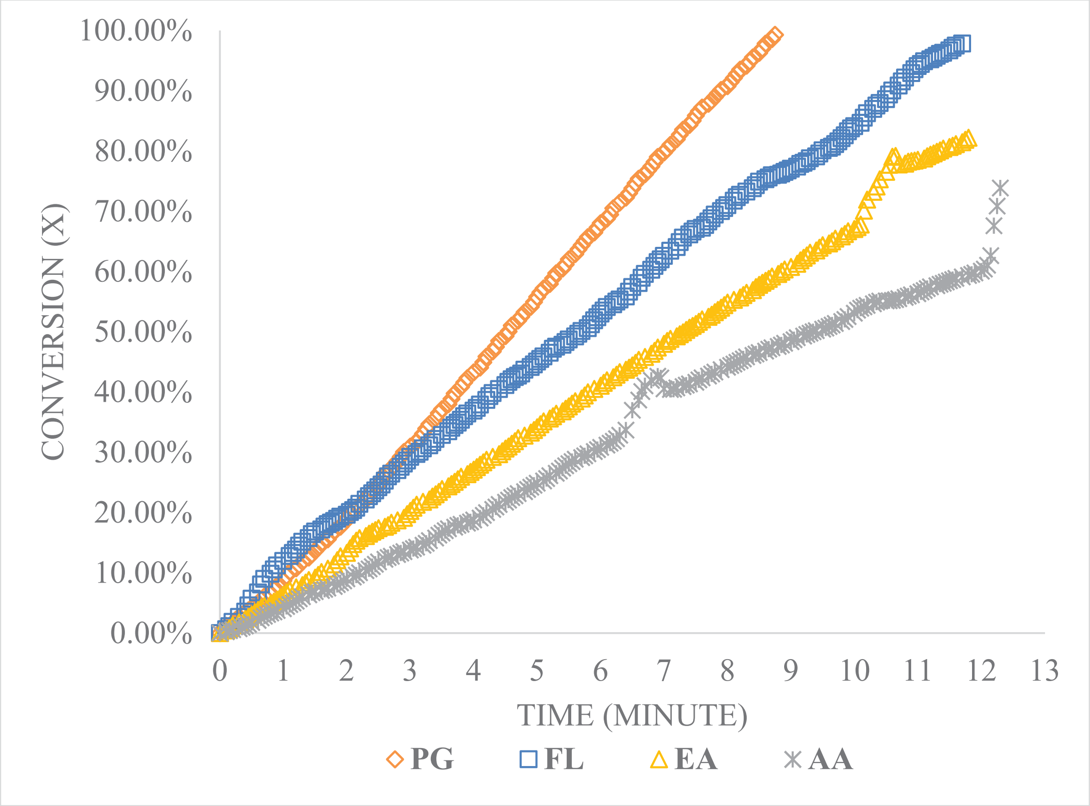


Figure 3.12 Sorbent reactivity studies for PG, FL, AA, and EA at 500°C and P_{H2O} 1.5 atm

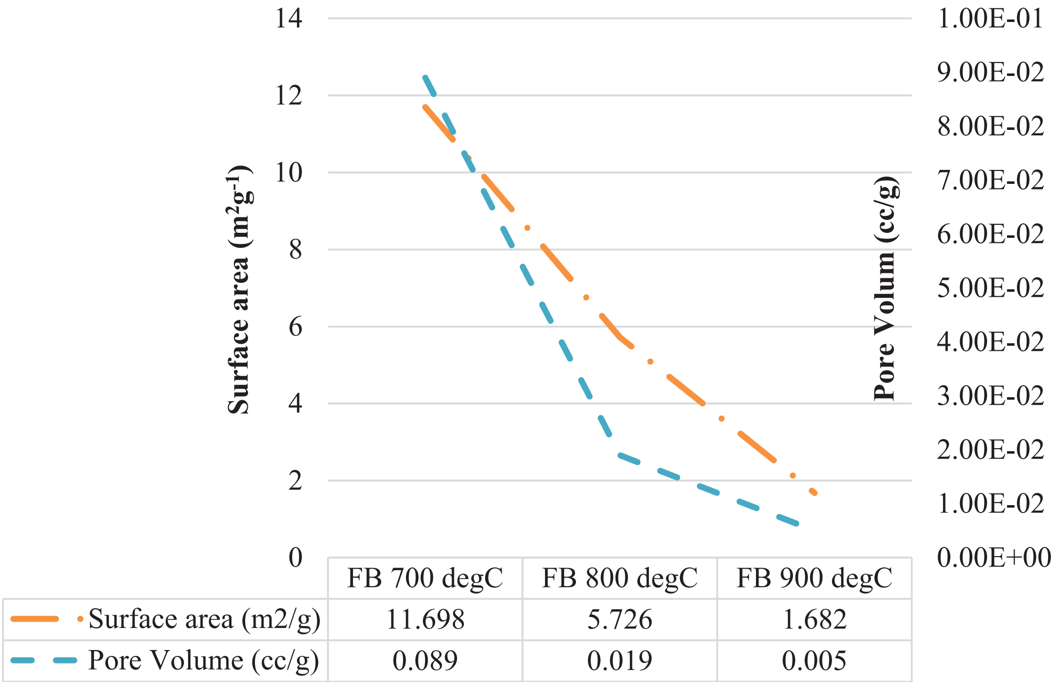
3.4 Effect of upstream calcination conditions on sorbent reactivity

Upstream calcination conditions may affect the reactivity of sorbents towards steam when hydrated. To see the effect of calcination on TGA reactivity of sorbents, limestone sample PG was calcined in the fixed bed at 700, 800, and 900ºC under partial/complete CO_2/air atmosphere. Conditions of air/CO_2 mixture were determined from the thermodynamics of calcination. Thus for 700ºC, calcination was performed under 100% air. At 800ºC, 20% CO2 – 80% air (by vol.) was used. Equilibrium CO_2 concentration at 800ºC is close to 0.15 atm. At a temperature slightly above 900ºC, 100% CO_2 atmosphere was used for calcination. Equilibrium partial pressure of CO_2 is 1.0 atm at 898ºC. This ensured steady isothermal calcination of the sample, causing hard burning of the sample which is more exposed to the heated surfaces of the reactor tube. The core of the bed remains uncalcined at 700ºC and partially calcined at 800ºC. However, at 900ºC more than 80% of the sample is calcined. Calcination experiments were performed in fixed Bed setup using an MTI Corporation high-temperature tube furnace. A quartz reactor was placed in the center of the ceramic tube of a 23 in long with an ID of 0.5 in and the bottom packed with quartz crystals. At the bottom of the quartz, the reactor was a porous plate to support the solids. Approximately 5 grams of PG limestone was used for the fixed bed experiments. The experiments were performed at three different temperatures for different CO_2 partial pressures based on the calcination thermodynamic equilibrium curve. The conditions and extent of calcination are shown in Table 3.3. An MFC was used to control the gas flow of air and CO_2 in the reactor. Figure 2.3 shows the fixed bed reactor setup with a preheater, reactor, and electric furnace. Since the experimental setup is comparable to the size of the TGA setup, a gas flow rate of 300 sccm was used to calcine the sample. Mass Flow Controllers (MFC) were used to control the flow rates of air and CO_2 sent to the fixed bed. The temperature in the furnace was ramped up in two stages to the set point. The samples were calcined for 3 hours. At 700°C, 300sccm of air flow rate was used. At 800°C, a flow rate of 60sccm CO_2 and 240 sccm air was used for calcination. At 900°C, the samples were calcined in 100% CO_2 atmosphere.

Table 3.3 Fixed bed calcination conditions

PG bed calcination	**Air (ml/min)**	**CO_2 (ml/min)**	**Extent of calcination**
700ºC	300	0	67.7%
800ºC	240	60	76.5%
900ºC	0	300	84.3%

Nitrogen physic-sorption studies were performed for the sorbents calcined in the fixed bed under the conditions given in Table 3.3. BET method for surface characterization and BJH pore size distribution method was used to obtain the surface analysis and pore volume of the sorbents after calcination. Results are presented along with the chart in Figure 3.13. Results indicate a decrease in the surface area and pore volume of the sorbents as the calcination temperature increases. This is an indication of the deteriorating effect of sintering of the sorbent due to hard burning. This may affect the reactivity for steam hydration in the TGA. Ongoing studies for the effect of upstream calcination conditions on the reactivity of steam hydration will be presented in the next quarterly report.



	FB 700 degC	FB 800 degC	FB 900 degC
Surface area (m2/g)	11.698	5.726	1.682
Pore Volume (cc/g)	0.089	0.019	0.005

Figure 3.13 Nitrogen physisorption studies for PG sorbent calcined at 700, 800, and 900^{o}C in the fixed bed reactor

Chapter 4: Conclusions

Parametric Thermogravimetric studies for higher hydrator reaction temperature and elevated steam partial pressure has produced reliable reaction kinetics results that could be applied for a better design of the hydrator using smaller residence times, higher temperature and appropriate steam partial pressure. Through this study, it is observed that the hydrator could be operated at a temperature close to 500ºC with steam partial pressure 1.5-2.5 atm to obtain higher conversions in relatively less time. The residence time for near complete conversion during hydration in the TGA varied from 120 seconds (2 min) to 600 seconds (10 min) for PG sorbent and residence time as high as 780 seconds (13 min) for sorbents showing lower reactivity to steam, at lower steam partial pressure. This shows that a commercial hydrator with 100% steam input, a residence time of 15-20 min should give fairly large conversions (> 70%), thus satisfactorily reactivating the sorbent. Order of the reaction with respect to the driving force available for reaction ($P_{H2O} - P^*_{H2O}$) is approximately 2. The experimentally computed activation energy for the reaction is 5.19 kJ/mol. Temperature could be increased further to 550-570ºC using a steam pressure of under 4 to 4.5 atm. At 550 and 570ºC, the steam partial pressure at equilibrium is 2.12 and 2.95 atm respectively. The Higher operating temperature of the hydrator will lead to better heat integration due to extraction and utilization of higher quality heat in the steam turbine. This cumulatively would further decrease the already lower energy penalty of the CCR process retrofitted in a coal power plant. Also, it decreases the sorbent make-up requirements and also the solids circulation rates due to replenished capture capacity of the sorbent in the each cycle. However operating cost of the hydrator should not be too high to increase the energy penalty of the process, as pressurized superheated steam is an expensive utility, especially for a commercial scale unit where the amount of solids processed could be in thousands of ton per day. Thus, there must be a trade-off with the operating conditions of the hydrator. If the steam hydration of the sorbents positively affects the process to reduce the Ca: C mole ratio to close to 1, then the process has immense economic advantages over other post-combustion carbon capture technologies currently in use or the development stage. This effect is proposed to be investigated with lab scale fixed bed continuous multi-cyclic three step carbonation calcination hydration studies that would use the conditions obtained from the TGA studies for hydration.

Chapter 5: Future Work

ASPEN simulation studies on the three step CCR process suggest that carbon capture capacity of the sorbent is highly sensitive to the hydration conversion[26]. The extent of hydration has a direct effect on the sorbent reactivity in the subsequent cycle. Regenerating the sorbent via hydration is important to minimize the Ca:C mole ratio for the same level of carbon/sulfur removal, thus operating the process at much lower solids circulation rate. Among other advantages of lesser solids circulation rate like smaller reactors, lesser operating costs, and higher processing capacity, lesser calciner energy requirement is the single most significant advantage. Calciner energy requirement has the highest contribution to the overall energy penalty of the post-combustion process as calcination is a highly endothermic reaction and is thermodynamically feasible at temperatures > 900-1000ºC. Decreasing the calciner size can significantly bring down the energy penalty. Moreover, the steam requirement for hydration is another important parameter in the energy efficiency of the process. It is important to minimize the steam: Ca mole ration for the process to be viable. If a pressurized steam hydrator can achieve higher conversion (70-80%) in lesser time, it can potentially enhance the process and energy efficiency[26]. Preliminary techno-economic analysis of the CCR process suggests a 32% increase in the Levelized Cost Of Electricity (LCOE) as compared to the base case[7]. A subcritical PC boiler without CO_2 capture was selected as the base case. CCR process was modeled on the same base case subcritical PC boiler. When an amine scrubber is modelled with the base case, it increases the LCOE by 80%. Moreover, these process simulations were designed for 90% CO_2 removal adhering the Department of Energy (DOE) standard[27]. With the current EPA regulations of minimum 20% CO_2 removal, the LCOE for carbon capture using the CCR process would not be too high as compared to that of the no carbon capture case. Thus the fixed bed multi-cyclic studies are important to know how intermediate high-pressure steam hydration affects the sorbent reactivity in multiple cycles.

Successful completion of the proposed work will provide a strong experimental basis for future scale up of the three step carbonation-calcination process as a viable carbon capture technology given its relative ease of integration with the existing coal/natural gas fired power plants. Without soaring up the cost of electricity to a large extent, the CCR process could be an economical option to meet the current EPA regulations. This lab scale multi-cyclic study will give valuable information and insights about the sorbent reactivity and performance, mechanical strength of the solid sorbent when subjected to high-pressure steam reactivation, operability, and viability of the cyclic process. Theoretically, a pressurized steam hydration should yield favorable reaction kinetics, produce reactive sorbents, and reduce the solids circulation rate. However, there exists a trade-off between high hydration conversion, steam consumption, energy required for high-pressure steam generation, and the cost of high-pressure superheated steam. All these parameters will could be judged with greater reliability and confidence after the completion of this study. If the current fixed bed setup allows for the proposed 20 cycles of CCR process, this demonstration will be longer than the fixed bed studies conducted at OSU till date. Multi-cyclic fixed bed studies for three step CCR process with hydration at atmospheric pressure and lower temperature, performed in 2010-2011 at OSU could reach only 15 cycles. However, this was due to loss of sample taken out for TGA analysis after every step. In this study, we propose to perform carbonation and calcination in continuous mode and hydration in a discontinuous mode. Sample would be taken out for TGA analysis only after hydration after a complete cycle. Thus, it should be possible to reach the target of 20 cycles.

One of the articles for steam hydration of calcium sorbents for the post-combustion CO_2 capture process predicts and describes a shrinking core model for steam hydration of the sorbents[49]. According to Blamey et al, hydration occurs at the interface of a porous and unreacted CaO core, and porous $Ca(OH)_2$ product layer[49]. Diffusion through the bulk phase to the particle surface follows the Chapman Enskong theory[49,50]. This could be verified by characterization studies of the sorbents used for performance tests in the multi-cyclic studies. Along with BET surface area and BJH pore size distribution studies, bulk phase of the sorbents could be analyzed using X-Ray Diffraction (XRD) techniques. Particle surface and core could be analyzed using advanced techniques like X-Ray Photoelectron Spectroscopy (XPS), depth profiling technique using XPS or Scanning Ion Mass Spectrometry (SIMS) techniques. Depth profiling using SIMS could be particularly useful in this case as it gives the composition of the material on the surface as well as the core by etching techniques.

Thus, the proposed studies are expected to validate further the conclusions obtained from the reaction kinetics studies of the sorbents as well as particle characterization studies. Significant outcomes are expected from the cyclic fixed bed studies of the three step CCR process using pressurized steam hydration. Independent studies at Ohio State University for the techno-economic analysis and economic viability of the three step process would use the reaction kinetics results obtained from this study for a better process modeling of the hydrator. Also heat recovery from the hydrator at high temperature will be studied and its application in the steam turbine cycle to generate more electricity will be simulated by modifying the existing ASPEN Plus simulations.

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