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Carbon dioxide capture from fossil fuel power plants using dolomite

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Carbon Dioxide Capture From Fossil Fuel Power Plants

Using Dolomite

by

Drupatie Latchman

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering
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LIST OF SYMBOLS

| | |
|-------------------------------------|---|
| CaO | Calcium Oxide |
| CaCO ₃ | Calcium Carbonate |
| CO ₂ | Carbon Dioxide |
| CO | Carbon Monoxide |
| CaMg(CO ₃) ₂ | Calcium Magnesium Carbonate |
| IPCC | Intergovernmental Panel on Climate Change |
| LANL | Los Alamos National Laboratory |
| MEA | Monoethanolamine |
| PBI | polybenzimidazole |
| TGA | Thermogravimetric Analyzer |
| USEPA | United States Environmental Protection Agency |

CARBON DIOXIDE CAPTURE FROM FOSSIL FUEL POWER PLANTS USING DOLOMITE

Drupatie Latchman

ABSTRACT

The main objective of this research is to develop a simple and cost effective separation method that captures CO₂ from power plant flue gas, as a pure stream that can be stored using regenerable dolomite (calcium magnesium carbonate) as the sorbent. The developed dolomite sorbent was evaluated for CO₂ capture capacity using multi-cycle tests of cyclical carbonation/calcination experiments in the thermogravimetric analyzer (TGA) model SDT 600. The variables controlled in the experiment were weight of calcium oxide and sintering time of the sample. The dolomite materials investigated were from two sources Alfa Aesar and Specialty Minerals. The prepared sorbent, after conditioning, is in the oxide form and can adsorb CO₂ to form the carbonate and be regenerated back to the oxide.

The results showed that the dolomite sorbent developed can be used for reversible CO₂ capture. The data from 8 multi-cycle TGA experiments show that the reversible capacity reduced in the first few cycles; however it stabilized to an average value of 34% after an average of 10 cycles and an average conditioning time of 15 hours. Data from two multi-cycle TGA experiments show that the dolomite sorbent is capable of an

average stabilized conversion of 65% in an average of 13 cycles at a conditioning time of 87 hours.

CHAPTER 1. INTRODUCTION

1.1 Carbon Dioxide Emissions

Carbon dioxide (CO₂) is a clear colorless gas that is present everywhere in the atmosphere. It is one of the most important gases essential to life because plants use CO₂ to produce food and in the process oxygen is released. However, CO₂ has been implicated as major cause of climate change because it is a known greenhouse gas and its atmospheric concentration has significantly increased over the last four decades (Figure 1). Most of this increase has been attributed to global industrialization. The United States and China alone account for more than 40% of the world's CO₂ emissions (Figure 2) [1]. Climate change is expected to have profound effects on the environment and on human socioeconomic systems. This has prompted the United States Environmental Protection Agency (USEPA), for example, to classify CO₂ as a pollutant in 2009, which would trigger measures to reduce the quantity released into the atmosphere [2].

There are many approaches to reducing CO₂ emissions from industrial sources, particularly from power generation facilities. These include switching to alternative fuels (low carbon or carbon-free fuels) sources and improving process efficiency. However, many trends indicate that fossil fuels, especially coal and natural gas, will continue to serve as the predominant energy source for decades and therefore carbon capture and storage is an important approach currently being investigated. There are several

technologies available to capture CO₂, but they are currently costly to install and operate. They can be installed in pre- or post-combustion processes. All capture technologies are based on trapping the gas in a suitable medium, solid sorbent or liquid absorber. CO₂ emissions can to be addressed via: capture and storage of future man-made carbon dioxide emission, reducing the existing quantities of carbon dioxide from the atmosphere, and restoring the carbon- cycle to pre-industrial era.

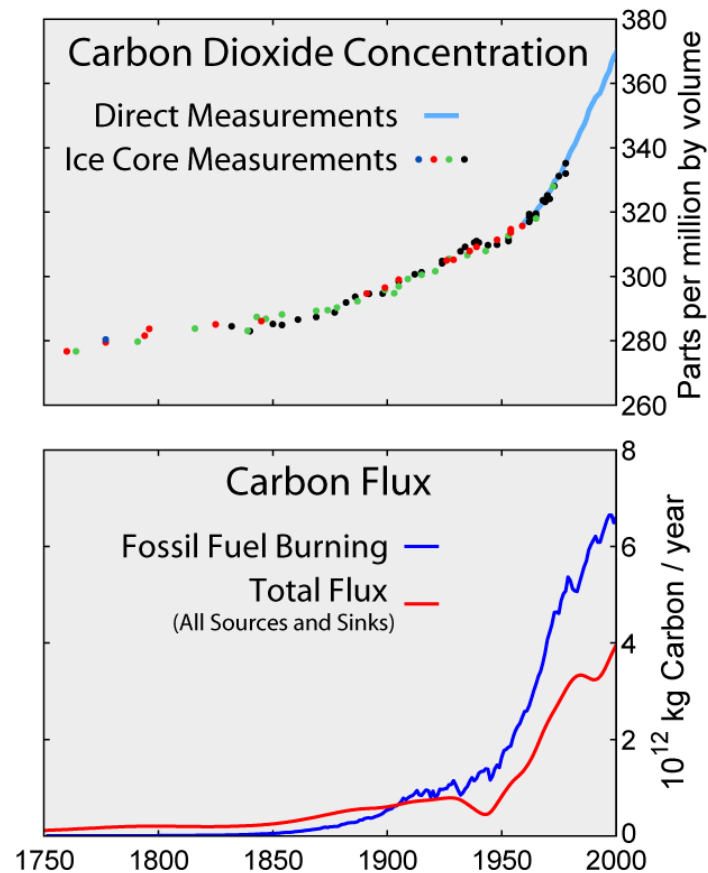


Figure 1. Carbon Dioxide Concentration [3]

Capture and storage technology of future man-made carbon dioxide emission has made some advancement; however, no single technology exists today that addresses the pollution problem.

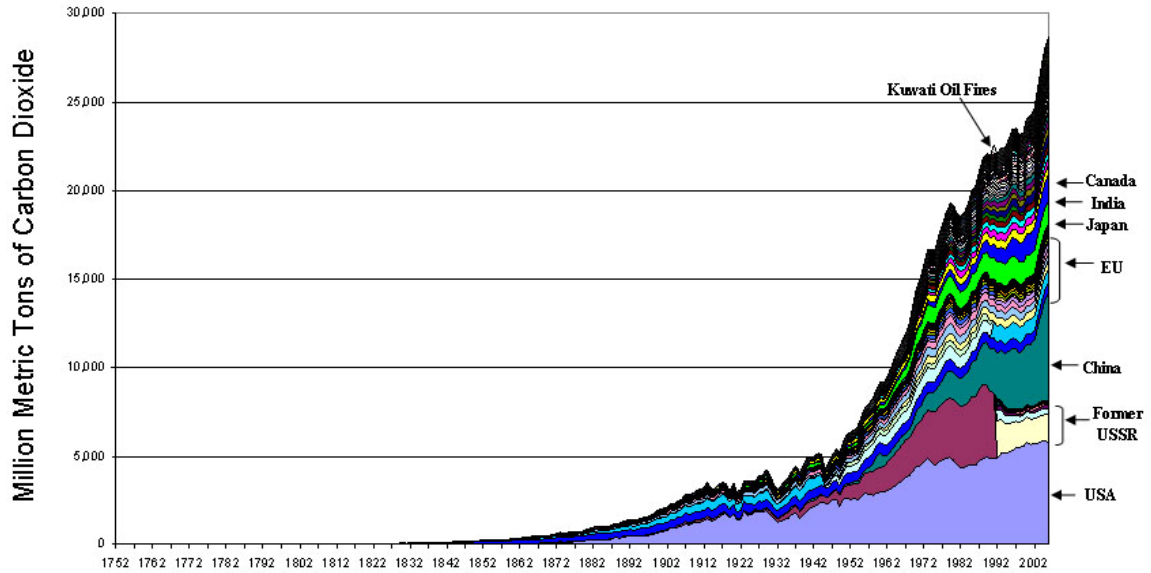


Figure 2. World Carbon Dioxide Levels [4]

According to the Intergovernmental Panel on Climate Change (IPCC) Special Report on CO₂, the following is a profile of CO₂ emissions by process or industrial activity of worldwide large stationary CO₂ sources with emissions of more than 0.1 million tons of CO₂ (MtCO₂) per year [5].

Table 1. Global CO₂ sources (taken from [5]).

| Process | Number of sources | Emissions |
|------------------------------|-------------------|----------------------------|
| | | (MtCO ₂ per yr) |
| Fossil fuels | | |
| Power | 4,942 | 10,539 |
| Cement production Refineries | 1,175 | 932 |
| Iron and steel industry | 269 | 646 |
| Petrochemical industry | 470 | 379 |
| Oil and gas processing | Not available | 50 |
| Other sources | 90 | 33 |
| Biomass | | |
| Bioethanol and bioenergy | 303 | 91 |
| Total | 7,887 | 1 ,466 |

The above table shows that electricity production worldwide is the largest contributor to CO₂ emissions. It is clear that developing technologies to capture and store CO₂ from these large point sources will have the biggest impact on CO₂ emissions. Metz [5] also states that other options to control CO₂ emissions are energy efficiency improvements and implementation, use of lower carbon fuels, nuclear power, renewable energy sources, enhancement to biological sinks, and reduction of other greenhouse gases.

Currently, CO₂ is used in many processes, but CO₂ is often produced for use in these processes instead of using the existing CO₂ supply in the atmosphere because of purity requirements. According to Edwards[6], CO₂ is used in the manufacturing of products, such as chemicals, fertilizers, carbonated beverages, food preservatives, fire extinguishers, and it is even injected into oil and petroleum wells to improve production and aid recovery. Edwards [6] goes on to state that the rate at which CO₂ is consumed is less than the quantity currently emitted, therefore an impact will not be seen, but every

molecule of CO₂ recycled and removed from the atmosphere, along with the elimination of new CO₂ produced from fresh feedstock, will go a long way in helping to reduce CO₂ levels.

Fossil fuel combustors are the major contributors of CO₂ emitted into the atmosphere (Figure 3). Power plants are the largest subset of fossil fuel combustors that are CO₂ polluters. Fossil fuel provides approximately 85% of the energy the world needs [7]. Steps can be taken to control CO₂ levels by capture and storage of emissions, using alternative sources of energy and using energy efficiently. Lee et. al.[8], developed a CO₂ capture method using immobilized calcium oxide (CaO) on yttria and alumina substrates. The method showed with a 23 weight% sample the conversion was 75% and with a 55 weight% sample the conversion was 62% over 13 and 10 cycles respectively. This research is a continuation of the Lee et. al.[8] research; however, dolomite according to Silaban et. al. [9] dolomite would have a higher capacity without increasing the cost.

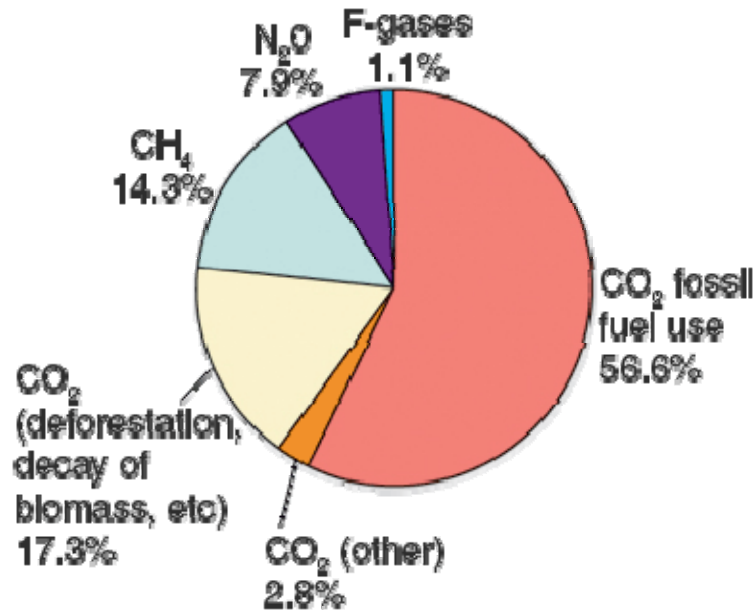


Figure 3. Carbon Dioxide Emission Sources [4]

1.2 Research Objectives and Scope

The overall objective of this project was to develop an inexpensive and efficient sorbent to capture CO₂ and the design a reactor that uses the sorbent to capture CO₂ emissions from power plants. The central hypothesis of the project was that dolomite would be a more efficient sorbent for the capture of CO₂ than pure calcium carbonate in the given configuration because the magnesium carbonate decomposition in the dolomite would increase the surface area after sintering, which would increase the capacity to adsorb CO₂. The rationale for this project is that the development of an effective sorbent for CO₂ will allow scientists and engineers to design systems capable of capturing the gas and thereby contribute to the overall reduction of greenhouse gas emissions. The main focus of the research was the capture of CO₂ emissions from power plants. However, the results of this project may be applicable for CO₂ capture from other processes.

The overall research objective was accomplished through the following plan. The first objective was to develop a sorbent using a method developed by Lee et. al. [10] to impregnate dolomite onto a ceramic fabric to capture CO₂. It involves impregnating a ceramic fabric (alumina or yttria) with pure calcium carbonate. However, dolomite was used in this work instead of calcium carbonate. It is hypothesized that the inert magnesium in dolomite increases the surface area of the material during sintering, and thus the capacity to adsorb more gas. This occurs because magnesium carbonate has a lower melting point than calcium carbonate and, when the sorbent is sintered during preparation, the magnesium particles decompose and leave pores in the sorbent so that the CO₂ molecules can reach the internal calcium oxide particles and react with them, instead of just the surface calcium oxide particles.

The second objective was to quantify the conversion, determine the regeneration time needed, and evaluate the cyclic performance of the sorbent. CO₂ molecules from flue gas react with the calcium oxide in the sorbent to form calcium carbonate. Heat is then used in the regeneration process to drive the CO₂ molecules from the sorbent leaving a pure stream of CO₂ that can be captured and reused or stored.

CHAPTER 2. CARBON DIOXIDE CAPTURE TECHNOLOGIES

The development of new and innovative technologies is critical in resolution of the carbon dioxide pollution problem. Power plants have a huge role in curbing carbon dioxide emissions as they are the largest carbon dioxide emitters. The captured carbon can then be transported to an injection site for long-term storage in geologic formations for example. These technologies are currently being researched with some technologies in the early stages of research and development [11].

There are several ways to capture CO₂, but it must first be separated from other combustion gases [5]. The following are the three main capture technologies from power plants:

1. Pre-combustion
2. Post-combustion
3. Oxyfuel combustion

Pre-combustion systems developed to capture CO₂ are designed for Integrated Gasification Combine Cycle (IGCC) units [5]. Due to the nature of this process, it is easiest to remove pollutants prior to combustion. The fossil fuel is reacted with steam and air /oxygen at very high temperatures to produce a gaseous fuel that can be combusted in the turbine. This gaseous mixture is “synthetic gas” or “syngas” consisting of carbon monoxide (CO), hydrogen (H₂), methane (CH₄), and water vapor (H₂O). The CO can

then undergo a water-gas shift reaction, which will convert the CO to CO₂ and H₂. The CO₂ is then captured in the reactor using carbon capture technology. Therefore, CO₂, like sulfur dioxide (SO₂) and other pollutants, is removed before the syngas is fired in the turbine, preventing these pollutants from being emitted into the atmosphere. The benefit of pre-combustion CO₂ capture is the ability to manipulate the concentration and pressure of carbon dioxide prior to burning of the fuel. This leads to a reduction in the capture equipment size and cost.

The syngas can then be treated to remove pollutants and contaminants, leaving a clean, efficient fuel. For IGCC plants water-gas shift reactions equipment would need to be installed, for existing and new units, to produce a CO₂ stream that can be separated and captured. Existing solvents and capture technology can effectively remove CO₂ because the high pressure syngas stream has high CO₂ content [12].

Post-combustion CO₂ capture system, on the other hand, removes CO₂ after the combustion process. According to Metz et. al. [5], a liquid organic solvent such as monoethanolamine (MEA) would be used to capture the CO₂ in the flue gas. This means of CO₂ capture is more challenging as the concentration of CO₂ is very low and there are other pollutants present in the flue gas, which makes separation very costly and difficult [11].

In the case of oxyfuel combustion systems, oxygen is used for combustion of the fossil fuel and it produces mostly water vapor and CO₂ [5]. The high concentration of CO₂ (greater than 80% by volume) can be captured after the water vapor is separated by cooling and compressing the flue gas and other pollutants are removed. This method of CO₂ capture is very cost prohibitive as the equipment needed for air separation and the

production of oxygen is very expensive. Each of the three CO₂ capture categories discussed above can utilize any of the three CO₂ separation technologies or a mixture of CO₂ separation technologies to attain an efficient capture system. The three CO₂ separation technologies are: solvents, membranes, and sorbents. However, chemical looping combustion, oxy-combustion, and cryogenic separation can also be used in the fight to reduce CO₂ emissions and are briefly described.

2.1 Solvents

The process of solvent absorption uses the reversible nature of the chemicals to remove the CO₂ from the flue gas stream either physically or chemically [13, 14]. The solvent can then be regenerated by changing the operating conditions, that is, the temperature or pressure in the system [14]. Both physical and chemical solvents can be used to capture CO₂.

Physical solvents remove the carbon dioxide selectively by absorbing the gas without any chemical interaction, usually organic liquids [11, 14]. Selexol and Rectisol, KS-2, and propylene carbonate are examples of physical solvents [15]. Here the CO₂ partial pressure is proportional to the capacity of the absorbing capability of the physical solvents according to Henry's law [11, 14]. Researchers are working to improve physical solvents by finding different and better solvents, manipulating pressure, temperature and other conditions of both the flue gas and solvent stream, and improving the selectivity of the solvent to CO₂. Physical solvents use less energy for regeneration, but, they work best at low temperatures [11].

Chemical solvents, on the other hand, facilitate a chemical reaction to strip or extract the carbon dioxide from the flue gas stream and are usually aqueous solutions [13, 14]. MEA is example of a chemical solvent and is currently the most matured technology used to capture CO₂ [15, 16]. Scholes et al., [12] also investigated the use of hot potassium carbonate solvent system. MEA and amine solvents have a high removal percentage, but they use a lot of energy to regenerate and also decrease the electric output of the unit by about 15 to 60 percent depending on the type of generating unit [13, 17]. Amine solvents degrade quickly and cannot be reused. They are also corrosive in nature, which affect the construction material of equipment [12].

Applications of solvents for high pressure and high temperature are being researched as part of the DECARBit project [17]. Technological advancement to amine systems are currently being developed by Fluor, Mitsubishi Heavy Industries (MHI), and Cansolv Technologies [11]. Modifications and improvements to amine systems aim to reduce pressure drop, increase contacting, increase heat integration to reduce energy requirements, reduce corrosion, and improve regeneration procedures [11].

Ammonia wet scrubbing can also be used as a solvent to capture CO₂ and it is similar to amine systems, but has lower energy requirements, higher CO₂ capture capacity, lack of degradation, is tolerant to oxygen in the flue gas, low cost, and potential for regeneration at high pressure [11, 18]. Yeh et al. [18] compared aqueous ammonia solution to MEA. The study showed that the energy required for regeneration using aqueous ammonia instead of amine could be reduced by approximately 62% [18]. However, ammonia has a higher volatility than MEA, which is one of the main concerns about this solvent, as the flue gas must be cooled to improve absorption [11]. Figueroa et

al., [11] also states that other technical issues that must be overcome to make this technology more attractive than using amine.

Ionic liquids are liquids that are mostly made up of ions instead of molecules [11, 19]. This solvent can dissolve gaseous CO₂ and is not lost into the gas stream [19]. Therefore, the flue gas does not have to be cooled before the solvent can come into contact with the flue gas, however the absorption capability of CO₂ needs improvement [11]. Olivier-Bourbigou et al., [20] discusses and reviews ionic liquids, their applications, and their properties in detail.

2.2 Membranes

Membranes are semi-permeable materials that selectively allow molecules to pass through them [21]. Membrane separation can be a combination of adsorption and absorption. Polymer-based membranes are showing promising results in the fight to lower the energy requirement and cost of carbon separation and capture. According to researchers at DOE's Los Alamos National Laboratory (LANL), a polybenzimidazole (PBI) membrane has shown signs that it can be durable in coal fired power plants [11]. Researchers at the NETL in collaboration with the University of Notre Dame are working on a liquid membrane, which will selectively remove the CO₂ molecules [11]. The membrane is made of an advanced polymer substrate and an ionic liquid [11].

Another concept under development is the use of an inorganic membrane. Researchers are developing a micro-porous membrane to allow for the separation of CO₂ from the flue gas [11, 22]. This modification allows the strong interactions between the permeating CO₂ molecules and the amine functional membrane pores [11]. While in the

New Mexico Institute of Mining and Technology, zeolite membranes are being developed. Zeolites are micro-porous structures of aluminosilicate minerals [11, 23]. Enzyme based membranes are also being investigated. Carbonic anhydrase is an enzyme that is contained in a hollow fiber [11]. Demonstrations show 90% CO₂ capture followed by regeneration at ambient conditions. Limitations include membrane boundary layers, pore wetting, surface fouling, loss of enzyme activity, long-term operation, and scale-up [24]. Ravanchi et al. [21] review membrane separation in great detail and lists the advantages and disadvantages of this technology.

2.3 Sorbents

Solid reactants can be used to react with CO₂ to form stable compounds. The reactant can also be regenerated to release the absorbed CO₂ [11]. These solid reactants range from metal oxides and carbonates such as calcium oxide, potassium carbonate, dolomite (CaMg(CO₃)₂), and other carbonate systems. The metal oxide will react with the CO₂ to form a carbonate. While in the carbonate system, it will react with CO₂ and water to form bicarbonate. The main disadvantage of mineral CO₂ capture are the calcinations temperatures and slow reaction rate for lithium-containing sorbents, which shows the most promising sign for high temperature capture [25]. Of the many metal oxides that exist or can be modified, each has its drawbacks. For example, metal oxides such as sodium and potassium work best at low temperatures, which requires the flue gas be cooled significantly prior to CO₂ separation; or for magnesium oxide the temperature range is 350 to 500°C, which makes it a suitable material for conventional post-combustion capture; while calcium based oxides work best in temperatures greater than

600°C, making ideal for pre-combustion capture and is being investigated in this work [26, 27].

Researchers are also working on an amine-enriched sorbent [28]. Here the amine compounds are immobilized on a high surface area material, the amine then reacts with the CO₂ to form a carbamate in a two-step process [11]. Microporous and mesoporous materials are also being researched and is discussed by Zelenak et al. [29] whose work studies the modification of these materials with amine to improve the efficiency and regeneration time. Zeolites, types of mesoporous and microporous materials, are also being loaded with amine to produce novel adsorbents [23]. However, since these are synthetic materials the cost of preparation is high and a modified zeolite that would work at high temperatures is still being researched.

Metal organic frameworks (MOFs) are also a new class of sorbents being researched. The hybrid material built from metal ions and organic compounds in geometrically organized structures [11]. MOFs require low energy for regeneration; they have good thermal stability; they are tolerant to contaminants and they are also low cost [11]. According to Millward et al. [30] MOFs offer the advantages of being totally reversible and flexible.

Hydrotalcite sorbents are also being studied by researchers. Hydrotalcites are a class of clay, layers of double hydroxides [31, 32]. According to Iwan et al. [25] hydrotalcites showed the most promise in high temperature capture of CO₂, possessing both a good adsorption capacity and rate.

2.4 Chemical-looping Combustion

Chemical looping combustion uses a solid oxygen carrier to supply the oxygen needed for combustion. According to researchers at the University of Kentucky Center for Applied Energy Research, chemical looping provides two major advantages [33]:

1. A high-purity CO₂ stream, which would make separation more efficient
2. The conversion efficiency would be greatly improved compared to that of using solvent for separation of the CO₂ or oxy-combustion.

Chemical looping combustion is in the early stages of process development. The major advantages of this technology is that air separation equipment is not required [11]. Research has to be focused on handling of multiple solid streams and the development of adequate oxygen carrier materials. Rubel et al. [33] discusses the oxidation/ reduction chemistry of several oxygen carriers and determined that iron oxide powder and catalyst showed the most promise.

Researchers at Ohio State University are working on three novel chemical looping gasification processes: Syngas Chemical Looping(SCL), Coal Direct Chemical looping (CDCL) process, and Calcium Looping Process (CLP) [34]. The SCL process utilizes conventional coal gasification technology to produce a hydrogen stream for electricity production and a CO₂ stream in two different reactors, which would lead to a system that does not require CO₂ separation [34]. The CDCL process on the other hand does not produce a syngas, but uses coal as the feedstock. CDCL promises reductions in oxygen consumption and process intensification [34]. A resulting solid iron and ash stream is produced and a gas stream of CO₂ and H₂O, again requiring no separation of the CO₂ prior to sequestration. The last process CLP offers the same advantages as the SCL and

the CDCL, but can be installed on a conventional gasification system removing the need for syngas cleanup after the shift reaction. Ryden et al. [35, 36] and Chiesa et al. [11] discuss in detail chemical-looping combustion for natural gas with similar advantages.

2.5 Oxyfuel Combustion

In this technology pure oxygen is used for combustion instead of air and it is combined with a recycle flue gas stream [37]. This will produce a 70% CO₂ rich flue gas that can be easily purified [37]. According to a literature review conducted by Buhre et al. [37] research work has shown that oxyfuel combustion is a viable option to producing a sequestration ready stream of CO₂, but when compared to pre- and post-combustion capture technologies it depended on the combustion unit retrofitted and the systems on the unit. Buhre et al. [37] as discusses in the literature that unit availability and reliability of an oxy combustion unit was still in question as no full-scale plant has been demonstrated and built. In 2009, McCauley et al. [38] presented favorable results from the Babcock & Wilcox Company (B&W), through its Power Generation Group, and Air Liquide oxy combustion demonstrations.

Even though oxy combustion is a very favorable technology for CO₂ sequestration there are many issues that still need to be resolved operationally and this can be very costly option as an air separation unit will be needed to produce the pure oxygen required for combustion [11].

2.6 Cryogenic Separation

Cryogenic separation is applied to CO₂ capture by cooling and drying the flue gas to a temperature where solid CO₂ is formed and can be separated [39]. Burt et al. [39] also points out that the capture efficiency is dependent on the expansion pressure and temperature. Research is still continues on cryogenic technology to reduce the amount of energy required to operate the systems [11]. The flue gas is cooled from 60°C to temperatures between -90 to -137°C, then the pressure is changed until the CO₂ is below its triple point, where it exists as a solid [40]. Tuinier et al. [41] discusses cryogenic CO₂ capture using packed beds and the advantages of cryogenic technology are chemicals are not required and the disadvantage is that expensive water separation is required to moved all traces from the gas.

CHAPTER 3. CARBON DIOXIDE CAPTURE USING DOLOMITE

3.1 Dolomite

Dolomite is a metastable mineral material composed of calcium magnesium carbonate $\text{CaMg}(\text{CO}_3)_2$. Vast amounts of the mineral are found in geologic deposits in lakes, shallow seafloor, and other sites [42]. According to Warren [42] it can be formed in many ways: a primary precipitate, a diagenetic replacement, or a hydrothermal/metamorphic phase. Warren [42] also states that dolomite tend to be ferroan and its crystals are saddle-shaped.

Goldsmith et al.[43] defines an ideal dolomite as one having a 1:1 molar $\text{CaCO}_3:\text{MgCO}_3$ ratio. However, the study showed that a number of natural dolomite samples were not ideal, as the CaCO_3 content was in excess of the 1:1 molar ratio[43], the mole percent of the CaCO_3 in the dolomite were discovered to be more along 55%.

3.2 Capture of CO_2 with Carbonates

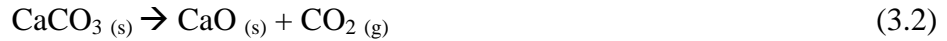
In general, calcium-based oxides react with CO_2 to form the metal carbonates. The carbonate can then be decomposed to form the metal oxide for continued capture of CO_2 . The main disadvantage of using calcium-based oxides is that they degrade rapidly [44]. Lee et al. [10] previously studied the calcium oxide in the use of CO_2 capture by preparing a solid sorbent made of precipitated calcium carbonate impregnated unto a ceramic fabric as the starting material. Lee's newly developed method for the preparation

of the sorbent showed a maximum conversion of approximately 55-59% [8]. The following are the reactions for CO₂ capture using a metal oxide:

Reaction for the carbonation of calcium oxide to calcium carbonate:



Reaction for the calcination of calcium carbonate to calcium oxide:



Lee [8] goes on to state, in his dissertation that degradation seen from his experimentation and the works of Barker and Borgwardt [45, 46] need to be addressed. Results from the literature review of calcium-based oxide for use in CO₂ capture showed dolomite as being more promising than calcium carbonate [15, 47]. Hence, this research aimed to use Lee's newly developed preparation of the calcium oxide sorbent and the results of the literature review to produce a dolomite sorbent that had the flexibility of Lee's sorbent and an improvement to the degradation of the calcium carbonate sorbent.

Dolomite and calcium carbonate are both abundantly available and naturally occurring resources, which reduces the material cost of CO₂ capture, if these products were utilized [48]. The literature states that if 50% conversion of calcium oxide takes place cyclically then 393 grams of CO₂ per kilogram would have been captured [48].

Senthoorselvan et al. [48] states that the temperatures at which calcium carbonate and dolomite undergo carbonation/calcination are applicable to power plant exit flue gas temperatures and well suited for CO₂ capture. The sorbent has a maximum capacity that beyond which it degrades drastically, due to pore closures, and the inability of the CO₂ molecules to reach inner calcium oxide molecules. The decomposition of the magnesium carbonate molecules at 750°C is believed to leave micropores for the CO₂ molecules to

penetrate into the material and reach calcium oxide molecules. This feature of dolomite was the main reason it was considered in this study.

The decomposition of magnesium carbonate, at lower temperatures than calcium carbonate, impedes its ability to participate in the CO₂ capture, but allows the magnesium molecules to stabilize the particle structure and create void space for the CO₂ molecules to pass through [48]. The calcinations of calcium carbonate occurs at 750°C and 385°C for magnesium carbonate [15].

According to Gupta et al. [15] the carbonation of calcium oxide goes through a two step mechanism, a rapid heterogeneous chemical reaction and a slower second step which involves the penetration of calcium carbonate layer formed [15]. The extent of conversion for calcium oxide, according to the literature, ranges anywhere from 30% to 93% [15], while Lee's sorbent showed conversion in the 62-75% range.

CHAPTER 4. SORBENT PREPARATION

4.1 Sorbent Preparation

Dolomite was immobilized on alumina fabric using the method described by Lee [10]. Dolocron 4512 (pulverized dolomite limestone) was selected as a starting material, as it was commercially available as a nano-powder. Precipitated calcium carbonate was added to the mixture to help the material to adhere to the fabric well. This acted as a surfactant and helped immobilize the dolomite to alumina.

The general procedure for the preparation of the sorbent began by turning on the small furnace and setting the temperature to 700°C. The alumina fabric was then cut into strips. The alumina strips of fabric were placed in the furnace for 15 and 30 minutes respectively to remove any moisture, coating or binders. Fifteen milliliters (15mL) of ethyl alcohol was placed into a 50mL centrifugal tube. Half a gram (0.5g) of dolomite and 0.1g of precipitated calcium carbonate were added to the ethyl alcohol. The mixture was placed on a vortex for 3 minutes and then sonicated with a Sonic Dismembrator for 10 minutes. The fabric was then removed from the furnace and weighed. The mixture of sorbent and ethyl alcohol was applied to one side of the fabric and dried at 150°C for 10 minutes. The material was removed from the furnace and the solution of mineral and alcohol was applied to the uncoated side. The sorbent material was then placed in furnace at 800 °C for 12, 18, 55, 72 and 87 hours respectively. The sample was then weighed after sintering.

4.2 Calcination-Carbonation Cycling Experiments

The sorbents were tested in a TGA to obtain data on the carbonation/calcinations cycles. All tests were performed under isothermal conditions at 750°C using 200ml/min CO₂ in nitrogen during the carbonation cycle during the carbonation phase. Pure nitrogen was supplied to the TGA during the calcinations phase. The system was programmed to operate automatically with carbonation and calcinations running for 20 minutes each. The data was collected by the computer data logger and stored for future use. The software recorded the change in weight of the sample as CO₂ was cyclically adsorbed and released in the TGA chamber.

4.3 Material Characterization

The sorbent materials were characterized by x-ray diffraction analysis to confirm the material composition. The compound provided by Specialty Minerals used in this research is dolomite and sintering does remove the CO₂ content of the dolomite leaving a compound made up of the oxides.

CHAPTER 5. RESULTS AND DISCUSSION

5.1 The Effect of Preparation Method on Capture

The sorbent was first made with dolomite rocks purchased from Alfa Aesar (Ward Hill, MA). The rock had to be crushed and milled in the laboratory before it could be used. The crushed dolomite was then mixed with ethyl alcohol. The dolomite did not adhere to the fabric and fell off very easily. The conversion efficiency for the sorbent prepared by this method was very low (Figure 4).

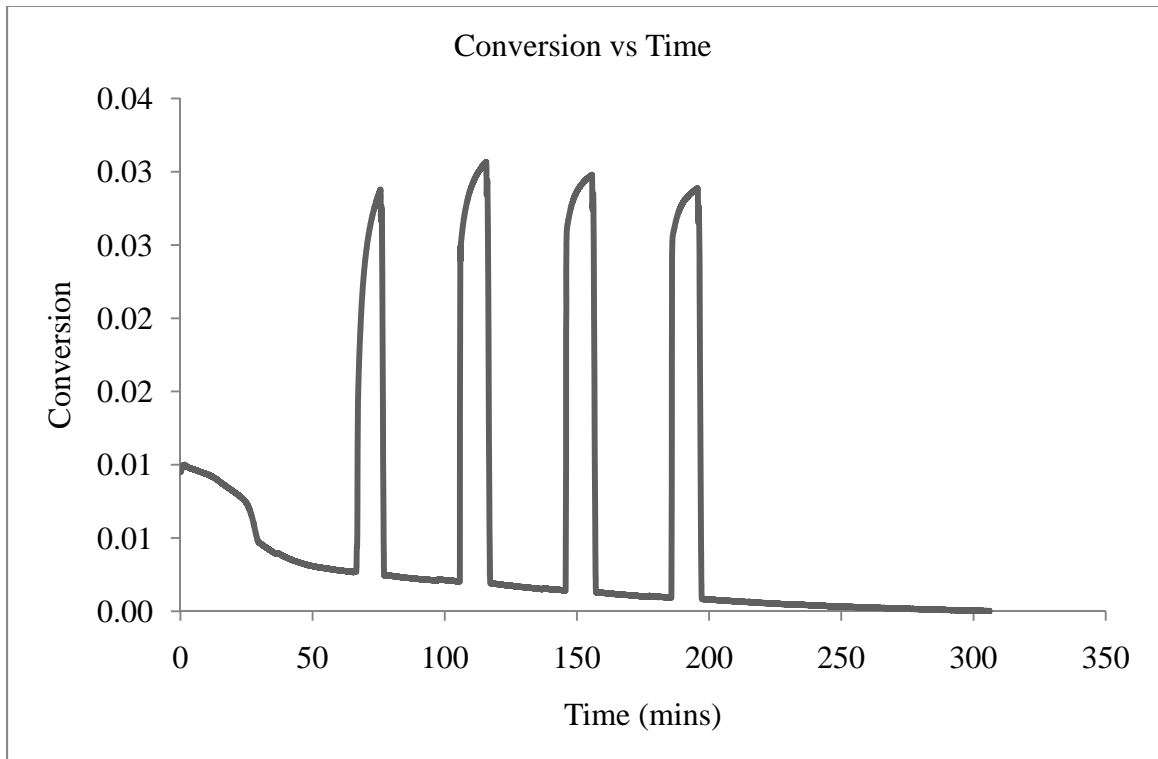


Figure 4. Conversion Cycles for Alfa Aesar Dolomite

The maximum conversion achieved with this method was 3.6% which means very little of the dolomite actually adhered to the alumina fabric.

In a second approach, acetone replaced ethyl alcohol as the solvent to determine if changing the solvent would allow the dolomite to be impregnated onto the fabric. The results indicated that the solvent had no effect on the material preparation in this case. The same results were obtained in terms of the physical appearance with low attachment of the sorbent to the ceramic material.

A search for a surfactant that would not affect or change the properties of the dolomite was undertaken. Fuller's earth, a clay-like material, made up of mineral oxides was chosen because it would inertly bind the dolomite to the fabric [49]. Different weights for Fuller's earth were used to make the sorbent and it was usually inspected to determine the stability of the sorbent. The initial method was modified by adding 0.25g of Fuller's earth to 0.5g of dolomite with ethyl alcohol as the solvent.

Since the preliminary data showed promise for the development of the dolomite sorbent, a new source of dolomite was found. Dolocron 4512 was supplied by Specialty Minerals (Allentown, PA), the same provider of the precipitated calcium carbonate used in Lee's work [8]. Dolocron 4512 is a brand of dolomite powder that had a mesh size of 325 (approximately 44 microns) and did not require further processing in the laboratory.

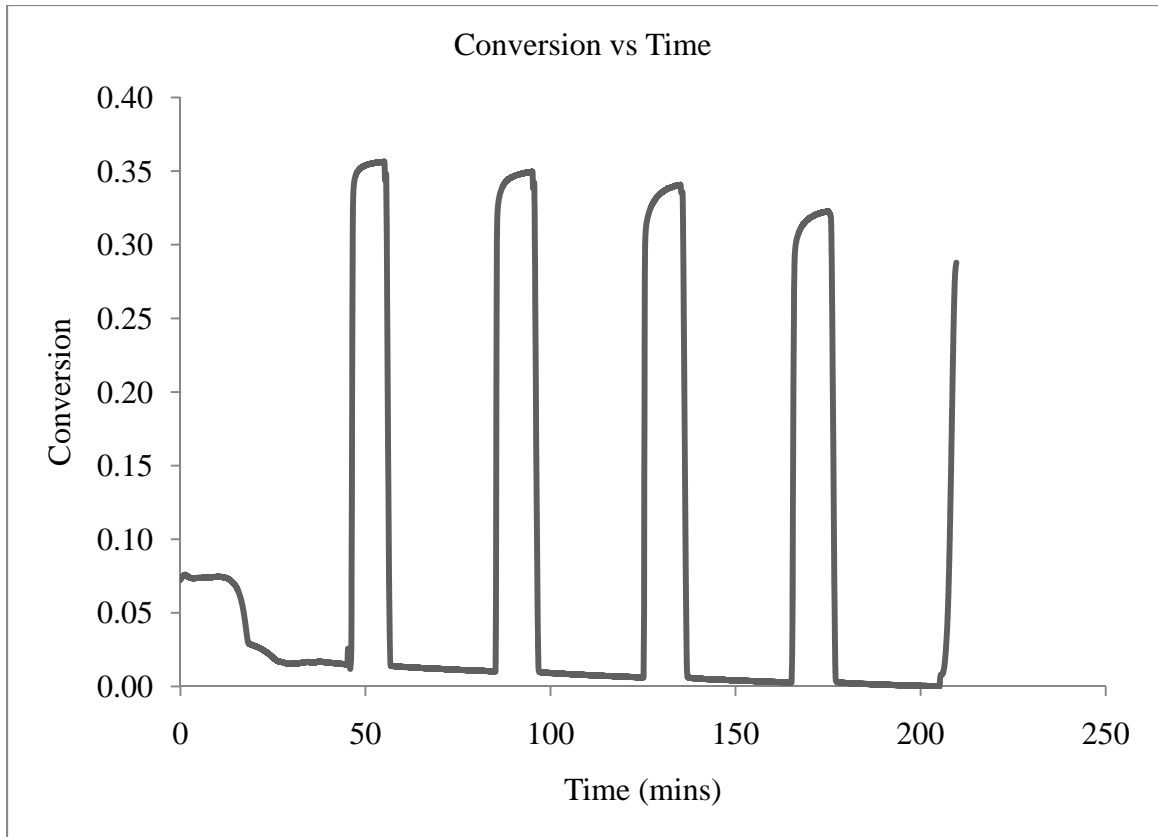


Figure 5. Conversion Cycles for Dolocron 4512 and Fuller's Earth

Figure 5 shows an increase in the conversion of calcium oxide to calcium carbonate from the Alfa Aesar dolomite. The maximum conversion achieved was 35% and the average conversion of the four cycles of data was 34%. This results are similar to those obtained in the literature [15].

Although the data was within the range for the Dolocron and Fuller's earth mixture for conversion, this work looked at ways to improve the conversion and get it closer to the 62-75% conversion seen in Lee's work [8]. This was achieved by investigating mixtures of the Dolocron 4512 and the precipitated calcium carbonate Lee

used in his research. The sorbent was made using the materials and procedure from Section 3.2.

The Dolocron-calcium carbonate sorbent was prepared adding 0.06g of the precipitated calcium carbonate. The graph below shows the conversion with respect to time for this sorbent preparation method.

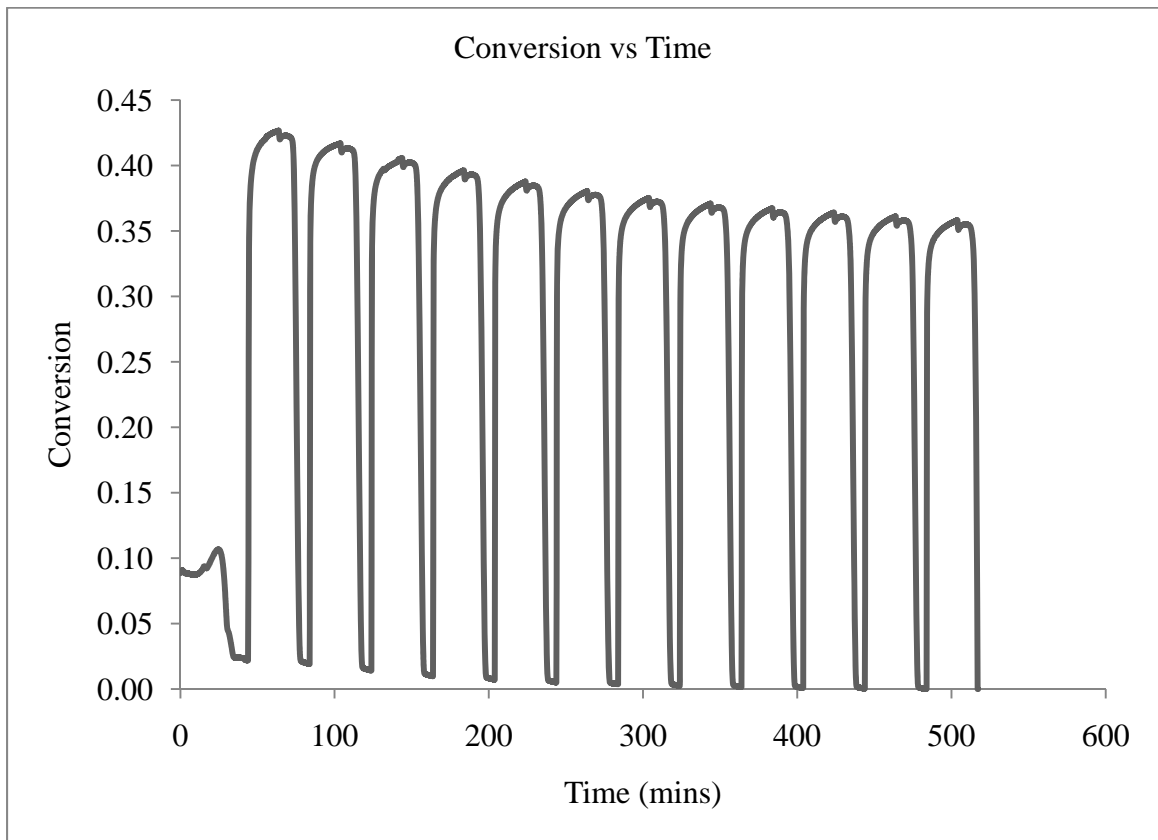


Figure 6. Dolocron 4512 and Precipitated Calcium Carbonate

Figure 6 shows a maximum conversion of 53%, which indicated that the change from Fuller's earth to the precipitated calcium carbonate was beneficial. The precipitated calcium carbonate made the Dolocron adhere even better than the Fuller's earth and had

the positive effect of added calcium oxide sites for CO₂ adsorption, instead of the inert Fuller's earth.

5.2 Effect of Conditioning Time on Capture

The effect of conditioning time on conversion was studied. The results indicate that conditioning time has a significant effect on the conversion. Conversion increases with conditioning time (Figure 7). Longer conditioning times drive off more CO₂ increasing the potential of gas uptake during carbonation, which is clear from the data shown in Tables 2- 4 and Figure 7.

Table 2. Conditioning Time of 12 Hours

| Weight Percent | Conditioning Time (Hours) | Stabilized Conversion | Number of Cycles |
|----------------|---------------------------|-----------------------|------------------|
| 39% | 12 | 29% | 5 |
| 77% | 12 | 35% | 12 |
| 62% | 12 | 38% | 12 |
| 84% | 12 | 32% | 9 |
| Average | | 34% | 10 |

Table 3. Conditioning Time of 18 Hours

| Weight Percent | Conditioning Time (Hours) | Stabilized Conversion | Number of Cycles |
|----------------|---------------------------|-----------------------|------------------|
| 33% | 18 | 40% | 9 |
| 33% | 18 | 33% | 12 |
| 35% | 18 | 32% | 18 |
| Average | | 34% | 11 |

Table 4. Conditioning Time of 55 Hours

| Weight Percent | Conditioning Time (Hours) | Stabilized Conversion | Number of Cycles |
|----------------|---------------------------|-----------------------|------------------|
| 82% | 55 | 36% | 12 |
| 37% | 55 | 37% | 21 |
| 37% | 55 | 40% | 12 |
| Average | | 37% | 15 |

Table 5. Conditioning Time of 72 Hours

| Weight Percent | Conditioning Time (Hours) | Stabilized Conversion | Number of Cycles |
|----------------|---------------------------|-----------------------|------------------|
| 32% | 72 | 53% | 20 |
| 21% | 72 | 64% | 21 |
| 23% | 72 | 51% | 20 |
| Average | | 56% | 20 |

Table 6. Conditioning Time of 87 Hours

| Weight Percent | Conditioning Time (Hours) | Stabilized Conversion | Number of Cycles |
|----------------|---------------------------|-----------------------|------------------|
| 24% | 87 | 68% | 8 |
| 24% | 87 | 63% | 18 |
| Average | | 65% | 13 |

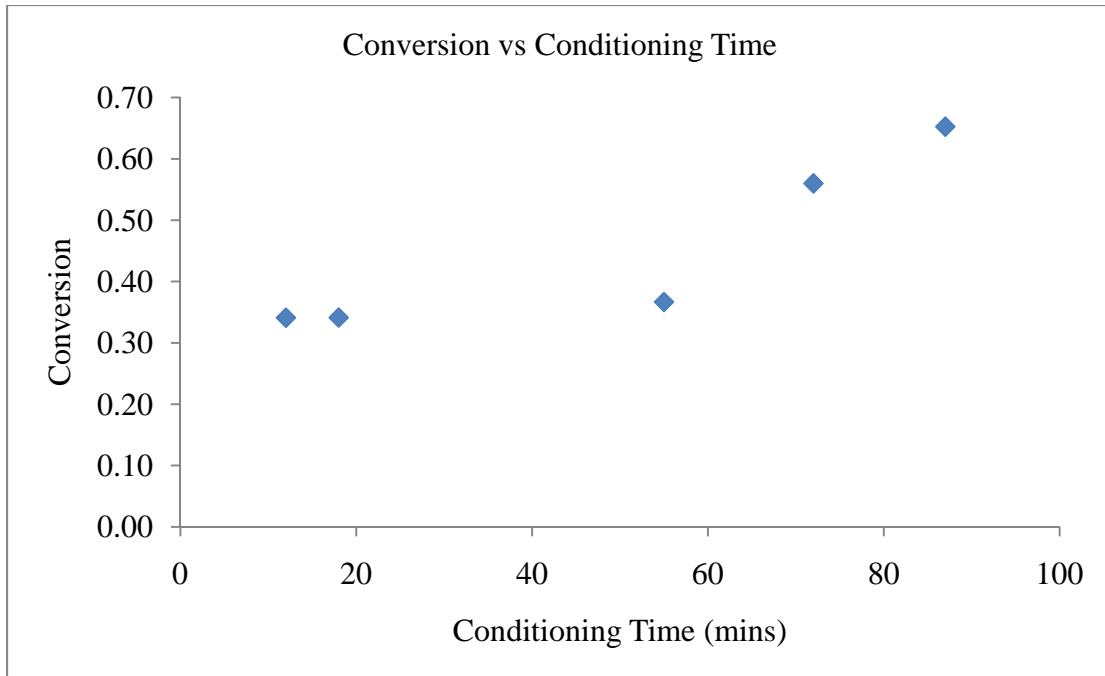


Figure 7. Effect of Conditioning Time on Conversion

The conversion at 87 hours of is double that at 12 hours (Figure 8 and Figure 9). The results indicate that as conditioning time increased the conversion increased. A maximum threshold for conditioning exists, however further experimentation at higher conditioning time is needed to determine this value.

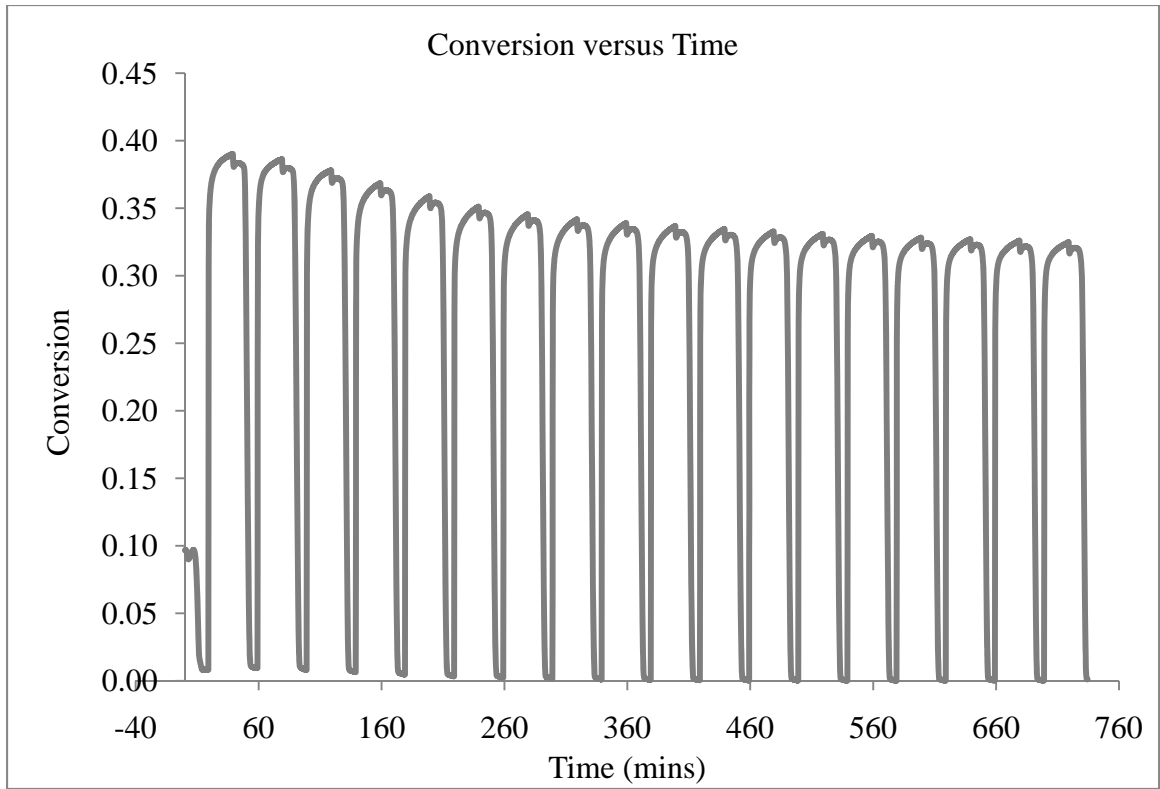


Figure 8. Dolomite Sorbent Conditioned for 12 Hours

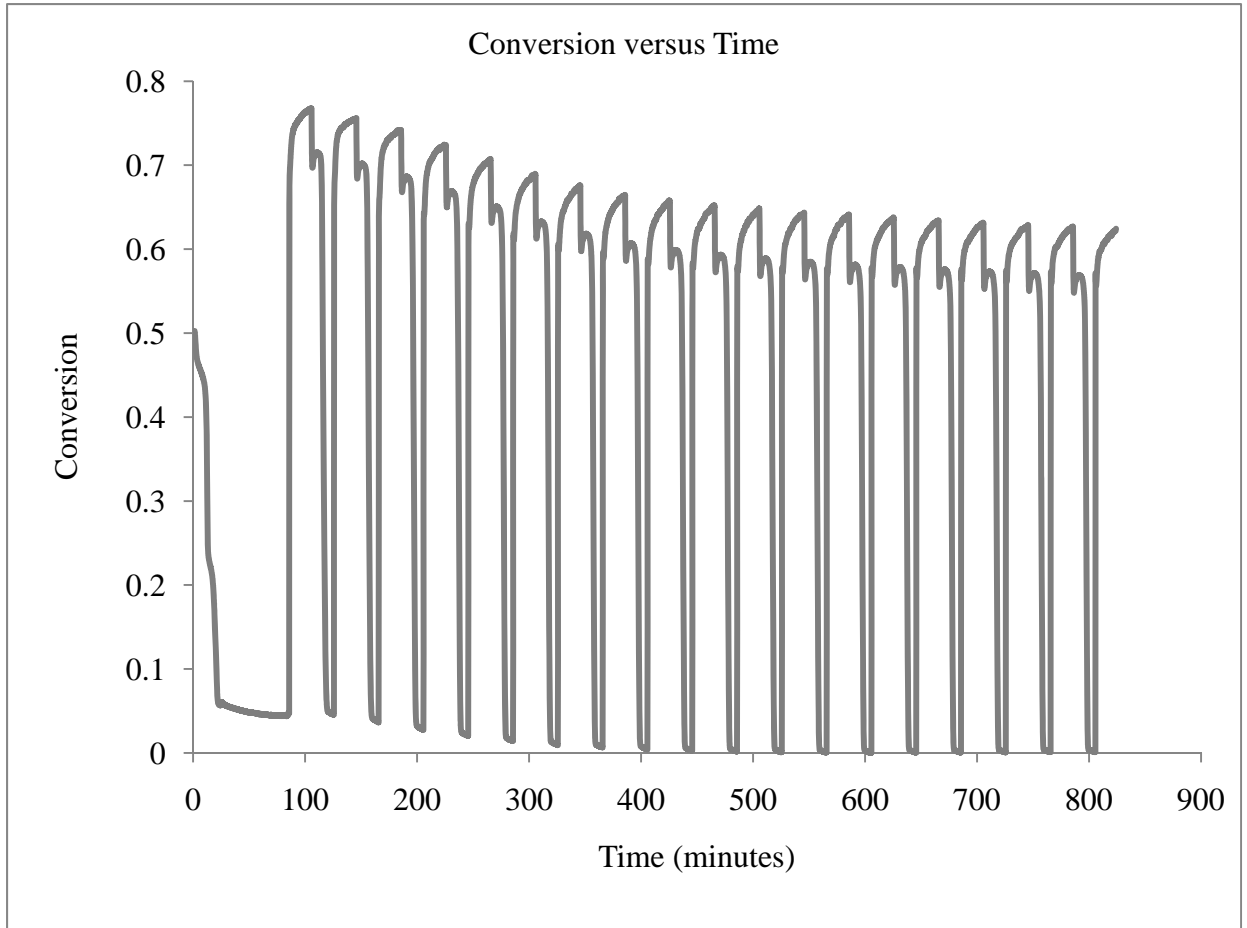


Figure 9. Dolomite Sorbent Conditioned for 87 Hours

5.3 Overall Capture Efficiency and Material Stability

Conversion data was calculated for more than 10 experiments using the Dolocron 4512 and precipitated calcium carbonate blend. The stabilized conversion seen for the dolomite sorbent is anywhere from 30-68%, which shows that the dolomite can be used for CO₂ capture.

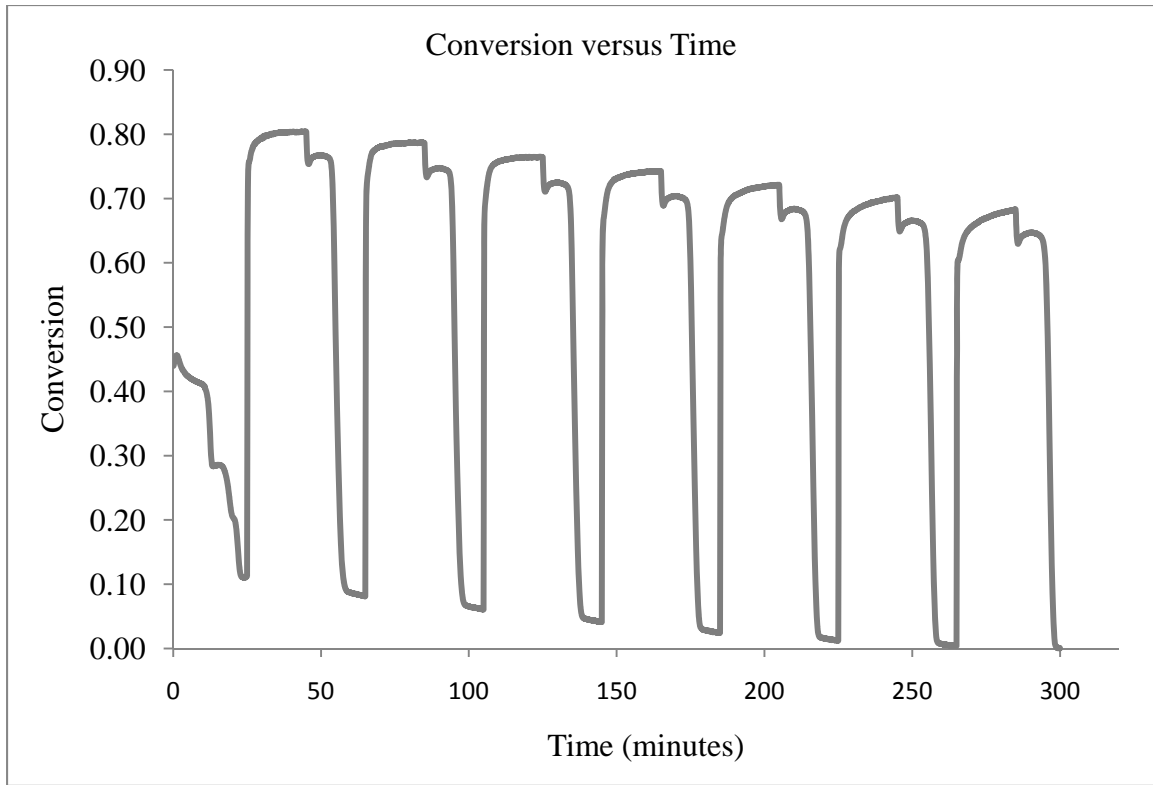


Figure 10. Dolocron 4512 and Precipitated Calcium Carbonate

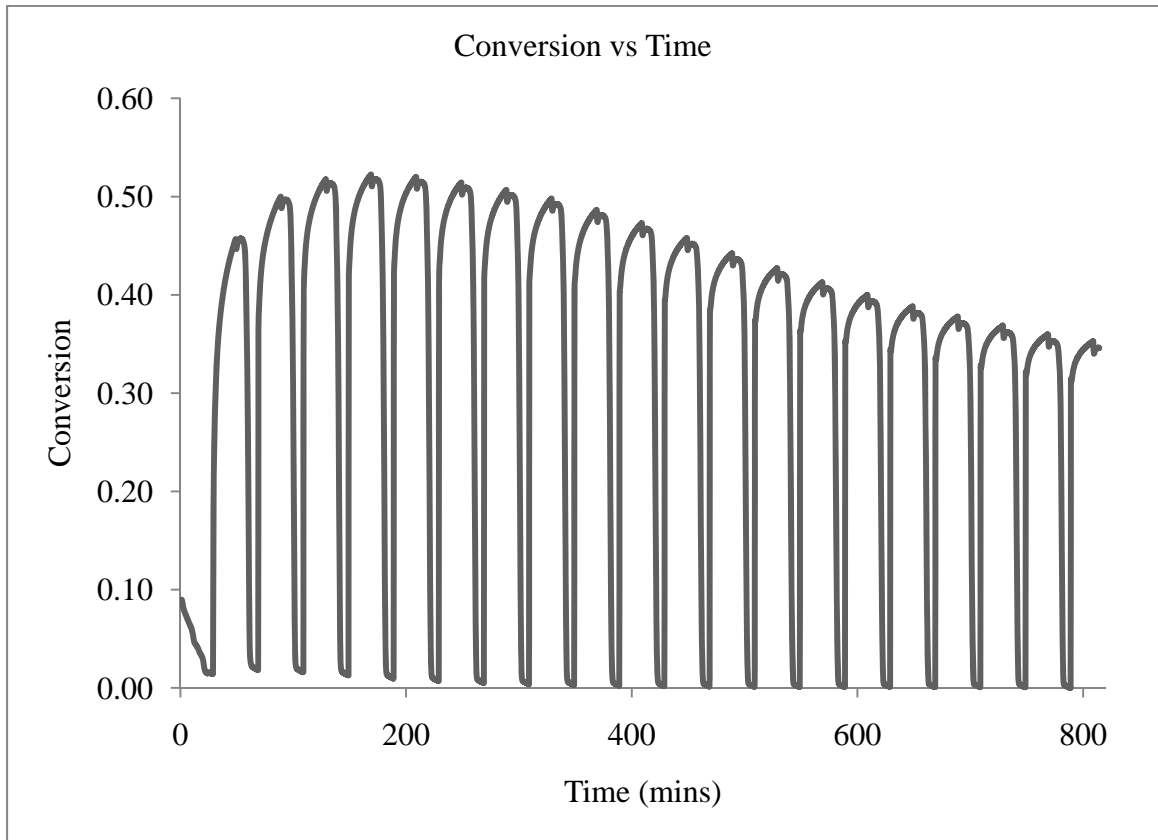


Figure 11. Precipitated Calcium Carbonate

Comparison of Figures 10 and 11 shows that dolomite capacity may be stabilizing after 10 cycles while precipitated calcium carbonate’s capacity continues to decrease even after 19 cycles. However, in both cases the number of cycles is too few to make a conclusion.

5.4 Regeneration Time

The regeneration time was investigated in three experiments. The first experiment used the 10 minute calcinations regeneration time from Lee’s dissertation [15]. However, this proved to be an inadequate amount of time. The time was then increased to 15 minutes and this was still not enough time. The experiments were then performed at 20

minute regeneration intervals, which allowed the sorbent to completely regenerate prior to the next carbonation cycle.

5.5 Cyclic Performance

Figure 10 below shows schematic of the carbonation/ calcinations cycle for a pre-combustion units, namely IGCC.

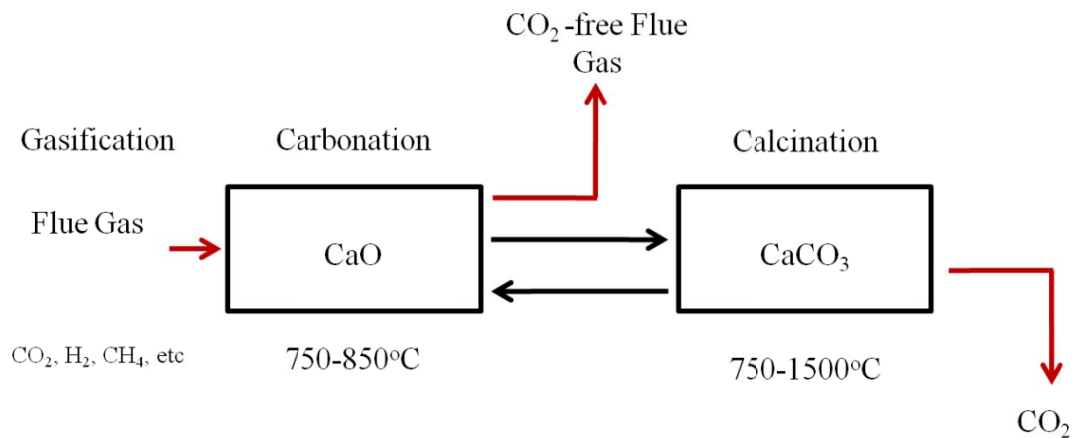


Figure 12. Carbonation/Calcination Cycle

The data shows that although dolomite has a higher uptake of CO_2 for the first couple of cycles, the cyclic capabilities become stable and almost constant, around 34%, for future carbonation/calcinations cycles as can be seen in Table 2 and Figure 13.

Table 7. Stabilized Conversion

| Weight Percent | Conditioning Time (Hours) | Stabilized Conversion | Number of Cycles Stabilized Conversion Determined |
|----------------|---------------------------|-----------------------|---|
| 39% | 12 | 29% | 5 |
| 77% | 12 | 35% | 12 |
| 62% | 12 | 38% | 12 |
| 84% | 12 | 32% | 9 |
| 85% | 18 | 32% | 5 |
| 33% | 18 | 40% | 9 |
| 33% | 18 | 33% | 12 |
| 35% | 18 | 32% | 18 |
| Average | 15 | 34% | 10 |

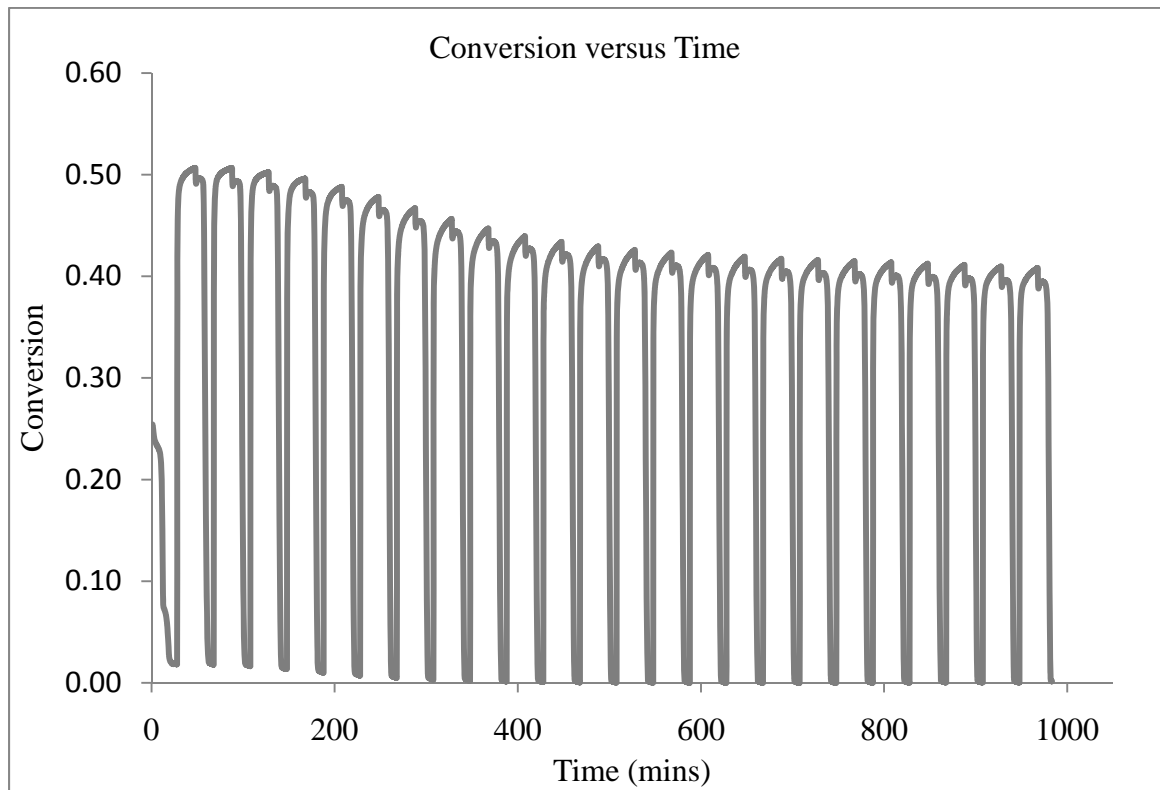


Figure 13. Cyclic Carbonation/Calcination of Dolomite

The cyclic performance shows that carbonation is an exothermic process, while calcination is an endothermic process and needs energy for the process to take place. The

stability of dolomite can be clearly seen from Figure 13. Although, the dolomite adsorbs less CO₂ than the calcium carbonate sorbent it showed promise of being more stable, although longer cyclical experiments would be needed to be sure.

CHAPTER 6. CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This aim of this research was to develop an inexpensive and efficient sorbent to capture CO₂ and the design a reactor that uses the sorbent to capture CO₂ emissions from power plants. The sorbent was developed using an earlier developed method to impregnate dolomite onto alumina fabric. This sorbent was successfully used to capture CO₂. However, this research shows that the capacity of dolomite is about the same as calcium carbonate, although additional multi-cycle experiments are needed to draw a conclusion.

This work was also able to quantify the capture conversion, the regeneration time, and cyclic performance of the sorbent, although for a small number of cycles. The dolomite sorbent effectively captured CO₂ and its capture capacity degraded initially, but became stable at 34% after 10 cycles.

Based on the experimental results in the cyclic reactions, the dolomite immobilized on the fibrous alumina fabric had continuous conversion in the carbonation/calcination cycles and was comparable to that of calcium carbonate.

6.2 Recommendations

The dolomite sorbent showed continuous high reactivity in the cyclic carbonation/calcination cycle at 750°C, however further experimentation is required at different operating and conditioning times, CO₂ flow rates, weights of dolomite immobilized on the alumina fabric, and different fabrics, for example yttria. With additional experimentation and data, reactor design can be completed.

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