Investigation of Partial CO_2 Capture Using Ash from CFB Boilers with Limestone Injection

by

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ABSTRACT

Circulating Fluidized Bed (CFB) power plants have been gaining popularity globally due to its ability to utilize less expensive solid fuels, in-situ capture of SO_x, low NO_x emission and flexible operating characteristics. Higher CO_2 emission from sulfur capturing CFB plants, on the other hand, is a major shortcoming of this technology. Additionally, fly ash generated from CFB power plants contains high amount of sulphate and unreacted lime due to sulphur capture in the furnace, which restrict its use in many commercial applications. To turn these shortcomings into positive use, an investigation was conducted to explore if the fly ash produced in a CFB power plant can capture a part of the CO_2 released from it.

Present work found that unreacted CaO in fly ash from some CFB boilers can indeed be utilized to partially capture CO_2 in its flue gas. Experiments were conducted in a reactor with a batch of samples and continuous supply of simulated flue gas at 500-750 °C and 30-80 °C for dry and hydrated fly ash respectively from the 197 MWe Point Aconi power plant. It was shown that CO_2 capture through conversion into $CaCO_3$ was initially 100%, but decreased with time. The capture rate increased with temperature up to 700 °C for dry fly ash and 50 °C for hydrated ash; thereafter it started to reduce. Effect of partial pressure of CO_2 (17 kPa to 31 kPa) on carbonation reaction was minor, but, the duration of the high initial CO_2 capture was inversely proportional to the partial pressure. For baseline tests, the capture characteristics of high calcium lime were compared with that of CFB ash at the same conditions. In most cases, carbonation reaction in such lime followed a similar pattern as in fly ash. The capture characteristics were also similar for bottom ash (particle size, 116 μm to 275 μm) of CFB boiler, but the amount of CO_2 captured by bottom ash was significantly lower than that by dry fly ash at the same condition. Thus the present work showed its potential for use of dry or hydrated ash in reducing CO_2 emission from CFB power plants at low cost.

LIST OF ABBREVIATIONS AND SYMBOLS USED

CCS	Carbon capture and storage
MEA	Monoethanolamine
Syngas	Synthetic gas
IGCC	Integrated gasification combined cycle
CFB	Circulating fluidized bed
PF	Pulverised fuel
THF	Tetrahydrofuran
L/S ratio	Liquid to solid ratio
CCPs	Coal combustion products
FGD	Flue gas desulfurization
FBC	Fluidized bed combustion
RH	Relative humidity
PC	Pulverised coal
CO_2	Carbon dioxide
H_2	Hydrogen
N_2	Nitrogen
CO	Carbon monoxide
$CaCO_3$	Calcium carbonate
$CaSO_4$	Calcium sulfate
CaO	Calcium oxide
MO	Metal oxides

MCO_3	Metal carbonates
MgO	Magnesium oxide
$Ca(OH)_2$	Calcium Hydroxide
$MgCO_3$	Magnesium carbonate
$Mg(OH)_2$	Magnesium hydroxide
H_2O	Water
$CaSiO_3$	Wollastonite
Mg_2SiO_4	Olivine
H_2CO_3	Carbonic acid
SiO_2	Silica
$Ca(HCO_3)_2$	Calcium bicarbonate
Al_2O_3	Aluminium oxide
Fe_2O_3	Ferric oxide (iron)
K_2O	Potassium oxide
Na_2O	Sodium Oxide
SO_3	Sulfur trioxide
V_2O_5	Vanadium oxide
P_2O_5	Phosphorus pentoxide
LOI	Loss on ignition

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CHAPTER 1: INTRODUCTION

Coal played a major role in the Industrial Revolution of the 19th century, and steam powered rail engines fueled by coal were the major source of transportation during that period (U.S Department of Energy, 2013). Coal is abundant and has the highest reserve-to-production ratio of all fossil fuels (BP, 2016). It is estimated to be the source of 40% of the world's electricity generation (WCA, 2009), but coal-fired thermal power plants produce several harmful gases and several solid products, such as fly ash, bottom ash, boiler slag, and flue gas desulphurization residues, most of which are, to some extent, hazardous for the environment. About 42% of the global CO_2 emission originates from electricity production and heating from coal (IEA, 2015). Increasing global energy demands compound these issues, and by 2040, as much as 78% of global energy could come from fossil fuels (EIA, 2016).

1.1 CARBON CAPTURE AND STORAGE

Carbon capture and storage (CCS) is a generally accepted technology to capture CO_2 from a stationary source such as fossil fuel based power plants. The capture is followed by transportation and storage of CO_2 into an underground geological storage reservoir such as deep aquifers, coal bed methane, depleted gas reserves etc. or storage by ocean (Anderson and Newell, 2004). Figure 1 illustrates the three major CO_2 capture methods based on their operating principle from fossil fuel power plants: pre-combustion, post-combustion, and oxy-fuel combustion (D'Alessandro et al., 2010; Samanta et al., 2012).

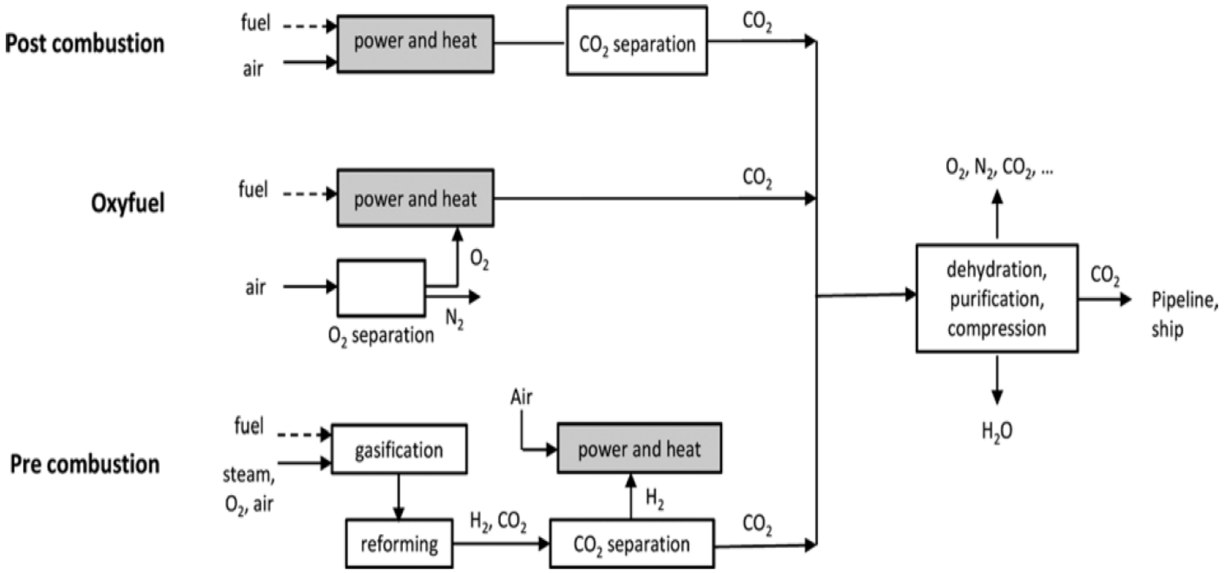

Figure 1: CCS process technologies[1]

1.1.1 Post-combustion Capture

Post-combustion capture involves capture of CO_2 after it is produced in the power plant. For capture of CO_2 from the flue gas, chemical absorption in monoethanolamine (MEA) is a widely used method, as it produces a pure stream of CO_2. However, this process is energy intensive and significantly increases the electricity production cost of a plant. For example, a coal fired power plant equipped with a post-combustion chemical absorption technology would increase the energy requirement of the plant by 30% - 60% (Anderson and Newell, 2004) and the increase in the electricity production cost by as much as 70% (Yang et al., 2008).

Adsorption process and use of membranes for CO_2 capture are other emerging post-combustion technologies. The CO_2 capture by adsorption is achieved by materials such as

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[1] Source: Markewitz et al. (2012)

activated carbon or molecular sieve through pressure or temperature swing operations. Membrane technology has a higher energy penalty than chemical absorption methods for post-combustion capture (IPCC, 2005).

1.1.2 Pre-combustion Capture

Pre-combustion capture involves a pre-treatment process that produces a fuel with higher hydrogen to carbon molar ratio, making it a less carbon intensive fuel. This can be achieved by producing syngas (CO and H_2 mixture) through steam reforming and partial oxidation or gasification process to the fuel before the combustion process. The produced CO is converted to CO_2 by water-gas shift reaction ($CO + H_2O = H_2 + CO_2$), and, the CO_2 can be separated through pressure swing operation.

Gasification process produces synthetic gas (syngas) from coal, which can be used in an integrated gasification combined cycle (IGCC) turbine to produced power. In an IGCC plant without CO_2 capture, the syngas can be directly burnt in the gas turbine. However, the water-gas shift reaction to convert, CO to CO_2 is applied to a plant with CO_2 capture facility, and the produced CO_2 can be separated, compressed, and stored while H_2 alone is burnt. If natural gas is the feed stock, syngas can be produced from methane steam reformation following the similar procedure, and carbon dioxide is separated before H_2 is burnt.

The capture and separation of CO_2 by pre-combustion methods in IGCC is less expensive than in post-combustion methods (by chemical absorption) (Yang et al., 2008). This is due to high (around 40%) CO_2 concentration in fuel gas in the pre-combustion process (Kenarsari et al., 2013) compared to less than 15% in the post combustion process in a typical coal fired power plant (IPCC, 2005). Physical absorption process using solvents such as Selexol and Rectisol, in pre-combustion process involves energy penalty of about 15% to the system (Anderson and Newell, 2004).

1.1.3 Oxy-fuel Combustion

A highly concentrated flue gas stream can be produced if nitrogen in the air is eliminated before combustion. Oxy-fuel technology works on this principle. Oxygen with recycled CO_2 gas and water is supplied to the furnace to limit the increase in temperature. This process gives capture efficiency as high as 100% and produces flue gas stream with CO_2 concentration of 80% to 98% after water removal depending on fuel and process parameters (IPCC, 2005).

The major drawback of this technology is the cost; oxygen separation from air using cryogenic distillation requires much energy. An oxygen separation plant for oxy-fuel combustion could require as much as 37% of the plant's energy and cost equivalent to chemical absorber in a post-combustion system (Yang et al., 2008). Membrane technology is also expected to be a promising option for oxygen production (Kenarsari et al., 2013).

1.2 CIRCULATING FLUIDIZED BED BOILER

Circulating fluidized bed (CFB) is an advanced means of solid fuel combustion. Such power plants have been expanding due to its ability to utilize low-grade fuel or mixtures of fuels (such as coal and petroleum coke), fuel flexibility, in-situ capture of SO_x, and low NO_x emission (Basu, 2015). According to 2012 data, there are around 600 coal firing CFB units in operation, and 180 units under construction (around 60 GW) including world's largest CFB power plant of 2200 MW in South Korea scheduled to be in operation in January 2017 (Peltier, 2016).

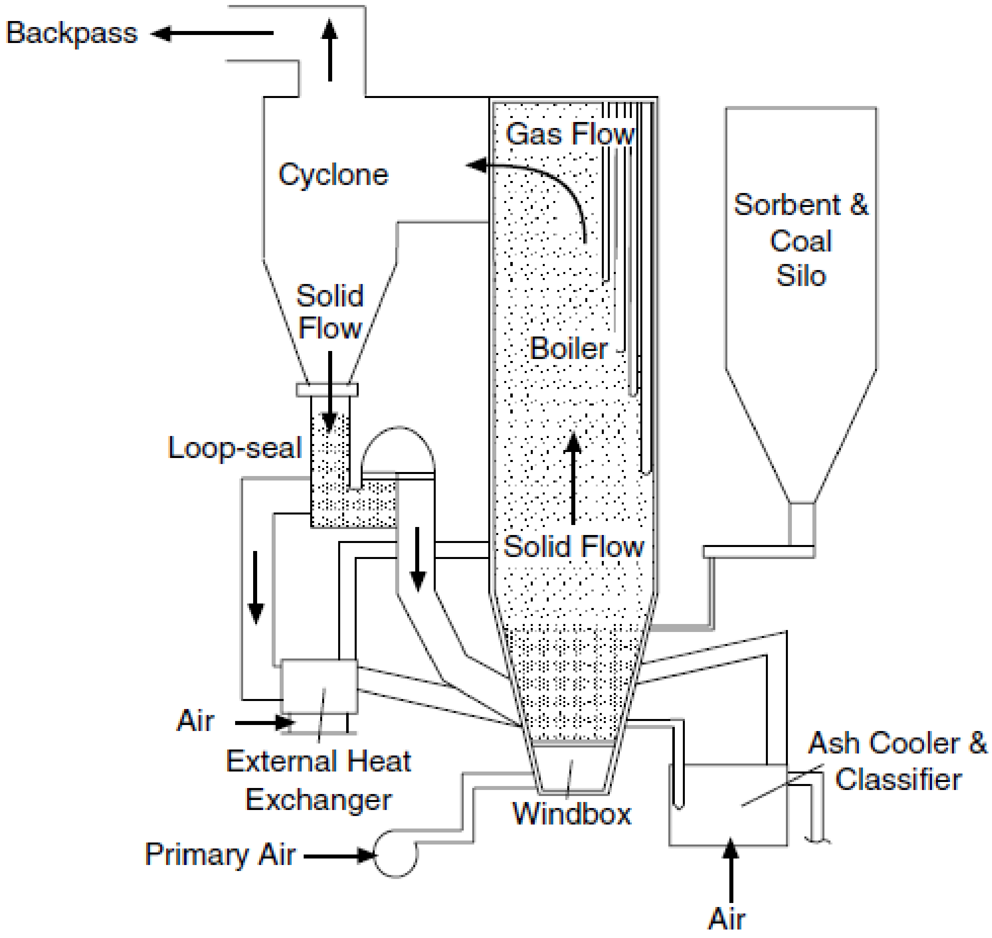

Figure 2: Schematic of a CFB boiler[2]

Basu (2015) defines a CFB boiler as “a device for generating steam by burning fossil fuels in a furnace operated under a special hydrodynamic condition: where fine solids are transported through the furnace at a velocity exceeding the terminal velocity of average particles, yet where there is a degree of refluxing of solids adequate to ensure uniformity of temperature in the furnace.” A schematic of CFB boiler is shown in Figure 2. A typical CFB boiler furnace circulates a large inventory granular (around 200 µm) solids that

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[2] Source: Basu (2006)

contains only around 1-3% combustible materials (Basu, 2015). The bed materials are fluidized by gas at a velocity above the terminal velocity of average solids and the entrained solids are recirculated back at a sufficiently high rate to create fast bed hydrodynamic conditions. Bed materials are well-mixed due to this hydrodynamic condition. Cyclone gas solid separator, returns the entrained bed materials to the furnace through a loop seal. However, very fine solid particles could leave the furnace, collected at a bag house or electrostatic precipitator located downstream; these particles being fine called fly ash. Evaporator tubes enclosed in the furnace, whereas other components, such as economizer, reheater, air preheater, are placed in the secondary section (back pass) of the CFB boiler. Hot gas leaving the cyclone transfers remainder of the combustion heat to the components in the secondary section.

Due to the excellent mixing of solids and large thermal inertia, CFB boiler can burn both good and low grade fuel with acceptably high combustion efficiency. Regional environmental laws limit the amount SO_x and NO_x that can be emitted to the atmosphere. In CFB boiler limestone could be fed into the furnace for in-situ sulfur capture. Limestone injection provides an attractive option to burn high sulphur fuels in CFB boiler. However, the CO_2 emission intensity of such a CFB power plant is higher than that of a pulverised-fuel (PF) fired power plant, as the limestone added to capture SO_x releases CO_2 during decomposition in the furnace as shown in equation (1) (Basu, 2015).

$$CaCO_3 + \frac{1}{2}O_2 + SO_2 = CaSO_4 + CO_2 \qquad (1)$$

Also, nitrous oxide a major GHG gas emission from CFB boiler is high. Although CFB boiler enjoys a number of practical benefits, high GHG emission often comes in the way for its use in some environment sensitive areas. The ash produced from CFB power plant firing higher sulphur fuels find little use in building materials due to its volumetric expansion when cured at normal temperature (Zhang et al., 2012). Thus, it is necessary to explore new cost effective and less energy-intensive practical methods for carbon capture.

This work explores if the ‘useless’ solid wastes from such CFB boilers can be utilized to reduce at least to some extend its GHG emission.

1.3 MOTIVATION AND OBJECTIVE

A major challenge in post-combustion CO_2 capture from a typical coal or petroleum coke fired power plant is the low partial pressure of CO_2 in flue gas stream. Carbon dioxide accounts for less than 20% of flue gas stream (Wang et al., 2008), which makes its direct compression, transportation and storage energy expensive and difficult. Limestone is added with the high sulphur fuel to capture SO_2 in CFB boiler, but only 35-40% the of lime feed is utilized in SO_2 capture (Wang et al., 2008). As a result, fly ash and bottom ash from a typical CFB power plant with limestone injection contain a significant amount of free CaO.

The objective of this work is to investigate cost-effective and low-energy intensive practical means for partial capture of CO_2 from CFB power plant utilizing the ash it produced. The CaO in ash can be utilized in carbonation reaction with flue gas to capture CO_2. Using CFB ash waste to capture CO_2 from the same power plant could be a sustainable approach in reducing greenhouse gas emission and making the CFB boilers more environment friendly.

1.4 ORGANIZATION OF THESIS

This thesis is organized in 5 chapters. Chapter 1 gives an insight to the need of CO_2 capture from fossil fuel power plants and principle CCS technology. A short introduction of CFB power plant and the objective of this research is included in this section. Chapter 2, Literature Review, gives information on current material, methods, and status of CCS technology with the potential of mineral carbonation in CO_2 capture and storage. Details on applications of coal ash is followed by discussion on current research conducted on CO_2 capture using coal ash. Chapter 3, Methodology, discusses experimental setup, ash analysis, test condition, sample information and experimental methods. Result and Discussion is given in chapter 4, which illustrates results of the experiments conducted and comparison of the results with reasoning. Chapter 5, Conclusion, summarizes the result and conclusion drawn. Lastly, Chapter 6 suggests possible future work on the development of the technology.

CHAPTER 2: LITERATURE REVIEW

Various methods and materials are being investigated for the carbon capture and storage technology. Figure 3 and Figure 4 illustrate a major group of technologies to separate CO_2 from the flue gas and their innovation stage with cost benefit associated (D'Alessandro et al., 2010). It is apparent from Figure 4 and Figure 5 that economically beneficial options such as chemical looping and membrane technology are at laboratory stage

Although chemical absorption methods such as amine scrubbing to capture carbon dioxide has been practiced in the industry for over 80 years (Rochelle, 2009), these methods are energy intensive and expensive. IPCC (2005) reported that increase in cost of electricity generation for post-combustion CO_2 capture from an amine scrubbing plant would be 40% to 70%, whereas it would be 20% to 55% in pre-combustion capture from a physical absroption based process.

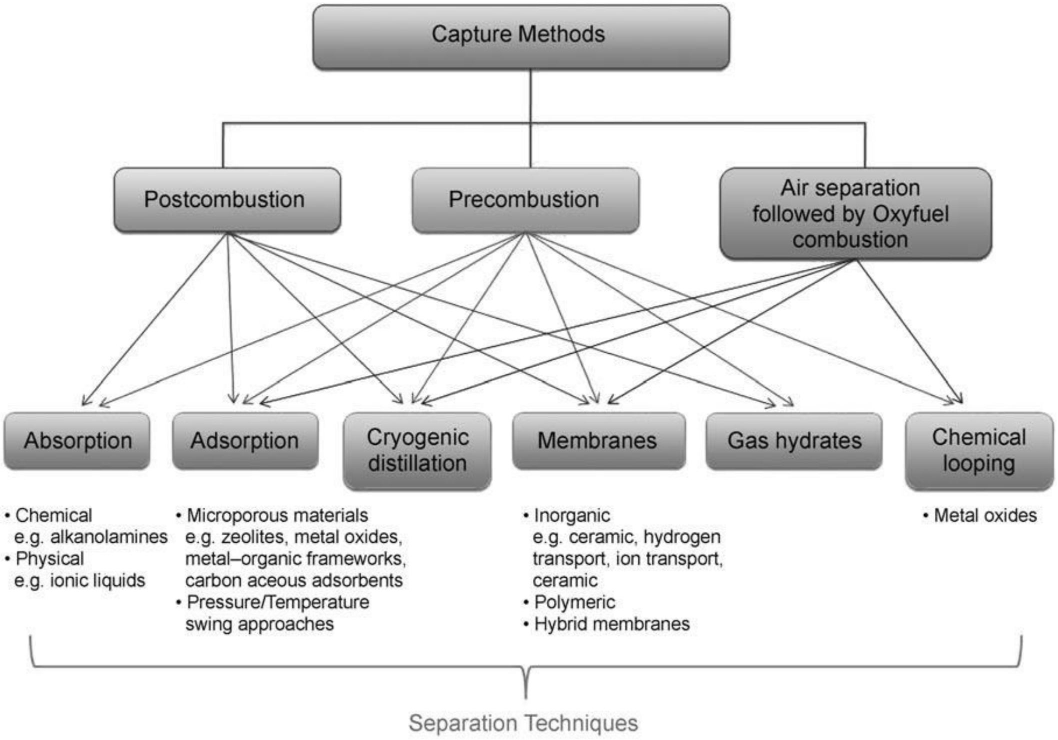

Figure 3: CO_2 capture methods and materials[3]

In adsorption process, CO_2 molecules are captured on the surface of microporous materials through chemical or physical interaction. The captured CO_2 can be separated after regeneration of adsorbent through temperature or pressure swing. Zeolite, metal organic framework, biochar, lithium based sorbent are some of the materials used for CO_2 capture by adsorption. Physical adsorption process requires less energy for regeneration. Hence, it has an advantage of cost reduction over absorption processes (Creamer and Gao, 2015). However, this technology is not commercially developed yet.

Cryogenic distillation is an air separating process to produce oxygen. A typical cryogenic air separation unit used in an oxy-fuel combustion plant for carbon capture reduces its

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[3] Adapted from D'Alessandro et al. (2010)

overall efficiency by 8% to 10%, which is similar to air separation by membrane (Pfaff and Kather, 2009)

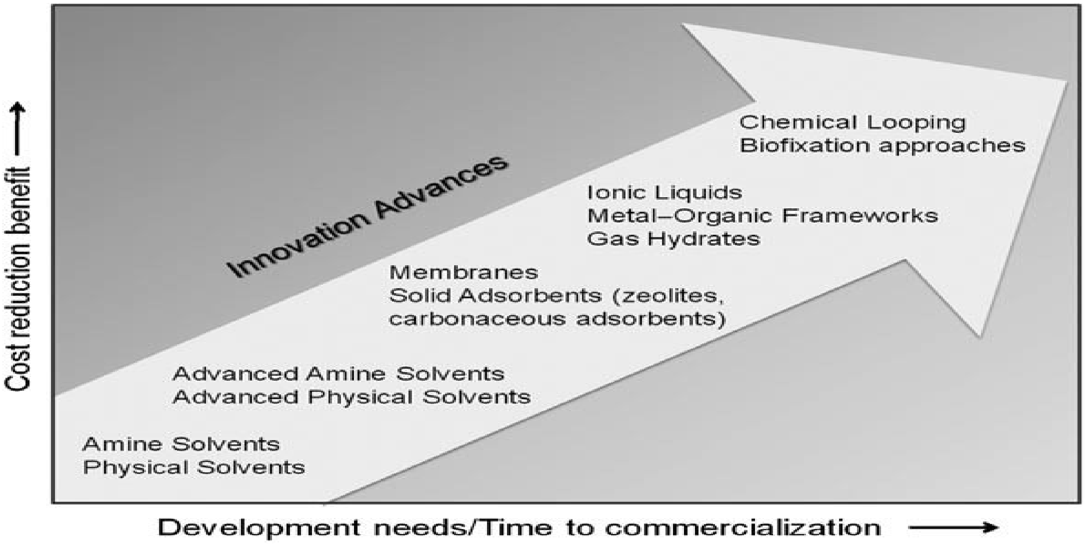

Figure 4: Status of different technologies[4]

Various organic and inorganic membranes are tested for CO_2 capture from gas mixture by diffusion and molecular sieving (D'Alessandro et al., 2010). Also, the possible use of ion transport membranes in oxygen separation from mixture of gases is being explored.

Gas hydrates methods are proposed to produce crystalized hydrate of CO_2 gas in post-combustion or pre-combustion system and capturing the CO_2 through hybrid hydrate membranes (Linga et al., 2007). Another method proposed by Lee et al. (2010) used tetrahydrofuran (THF) to produce gas hydrate of carbon dioxide and hydrogen to capture CO_2 from power plants based on integrated gasification combined cycle. CO_2 capture by gas hydrate methods require near zero temperature and high pressure, which are the main difficulties in the commercial implementation.

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[4] Source: D'Alessandro et al. (2010)

Photosynthesis process in micro-organisms such as micro-algae or bacteria could capture CO_2 and produce renewable fuels. Several investigations in this area of research were reported by Stewart and Hessami (2005).

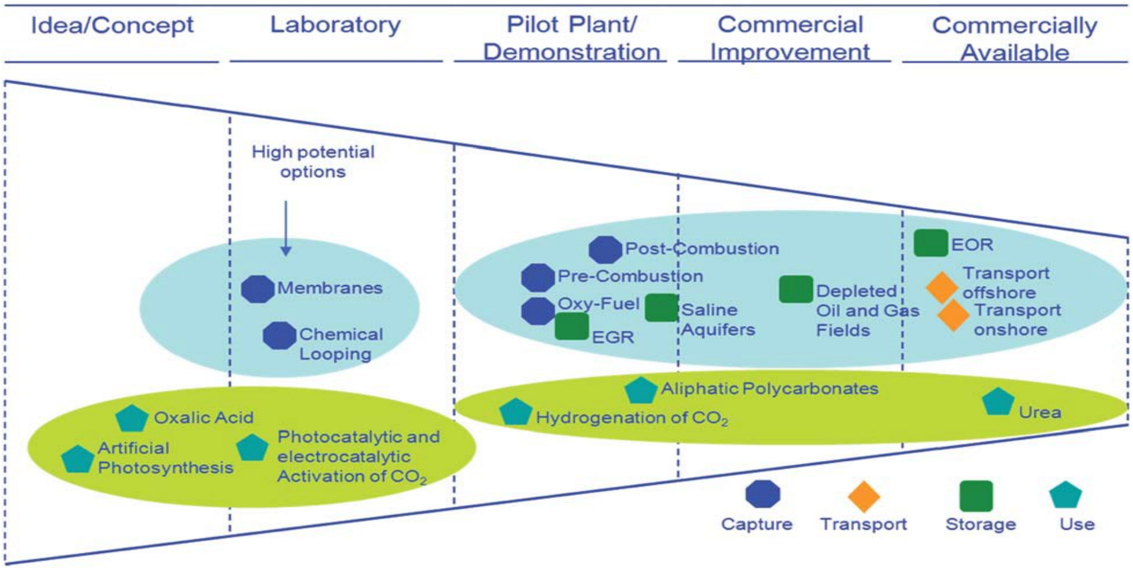

Figure 5: Current status of most CCS technology modules[5]

CO_2 capture by chemical looping combustion is technology that separates a single stage combustion system into two stage oxidation and reduction stage. Oxides of metals such as manganese, copper, nickel, and iron, can be oxygen carriers (Zafar et al., 2005) to separate oxygen from air which eliminates the requirement of expensive air separator units. In the reduction stage, metal oxides react with hydrocarbon fuel to produce heat and power. The produced flue gas stream mainly comprises carbon dioxide, water vapour and nitrogen. The reduced metals are oxidized again in the oxidation unit. The materials for chemical looping combustion technology are in laboratory stage (IPCC, 2005).

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[5] Source: Markewitz et al. (2012)

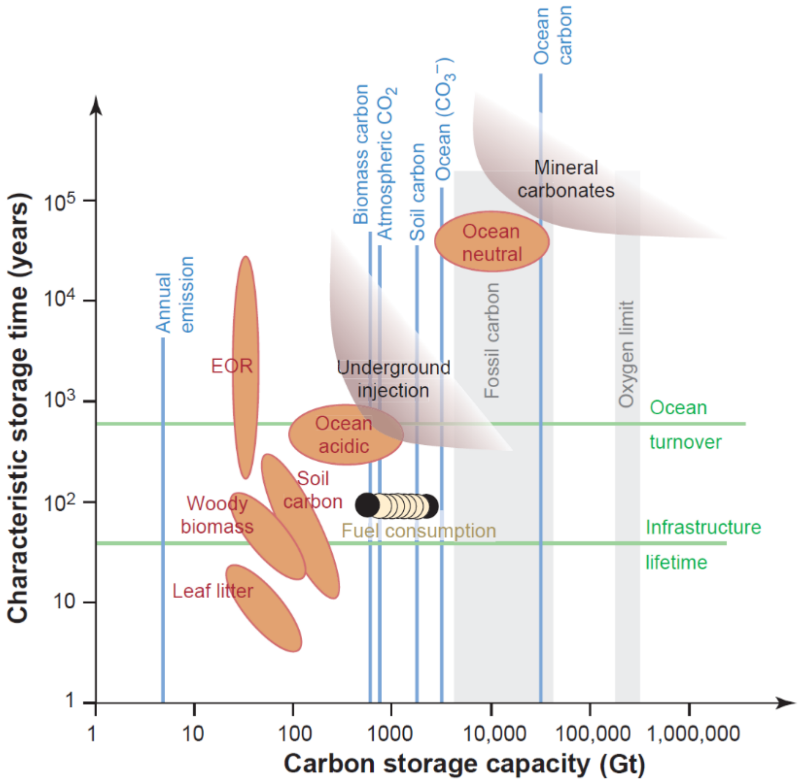

Figure 6: Estimated carbon storage capacity and time for CO_2 sequestration methods[6]

An estimation of CO_2 storage capacity and time required for each sequestration source was made by Lackner (2013) and shown in Figure 6. Carbon dioxide sequestration by enhanced oil recovery (EOR) has limited storage capacity compared to other methods. Methane hydrates formed under the ocean floor due to high pressure and near zero temperature were also considered in the 'fossil carbon' column in the figure with other fossil fuel carbon sources. Fossil fuels would require oxygen for the combustion, and the total fuel that would use all the oxygen available was represented by 'oxygen limit' column. 'Ocean acidic' was representation of the ocean's capacity to sequester carbon dioxide forming carbonic acid and 'ocean neutral' was shown for neutralization of the acid. Interestingly, carbon

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[6] Source: Lackner, (2013)

sequestration by mineral carbonation was estimated as the largest storage source with the longest storage time compared to other methods (Lackner, 2013).

2.1 MINERAL CARBONATION

Mineral carbonation is the accelerated form of natural silicate weathering, where alkaline metals of silicates react with atmospheric carbon dioxide and produce carbonates. In mineral carbonation, reaction takes place at considerably high CO_2 concentration with metal oxide or alkaline minerals such as serpentine, olivine, silicate rocks, and industrial wastes: slag from steel plant, fly ash, municipal solid waste incineration ash etc. (Sanna et al., 2014; IPCC, 2005). Equation (2) from IPCC (2005) gives general exothermic carbonation reaction in metal oxides (MO),

$$MO + CO_2 \rightarrow MCO_3 + \text{Heat} \tag{2}$$

The alkaline or oxide metals that could be used are lime, magnesium, wollastonite, olivine, serpentine etc.

Carbon dioxide sequestration through mineral carbonation can be achieved by in-situ carbonation or ex-situ carbonation. In in-situ mineral carbonation, CO_2 is injected into underground geological storage site of silicate rocks or alkaline aquifers where CO_2 can be trapped as insoluble carbonates (IPCC, 2005).

IPCC (2005) illustrated ex-situ mineral carbonation in a separate plant by industrial alkaline waste or silicate rocks (Figure 7). Mineral carbonation reactions of metal oxides or industrial alkaline residues can be divided in two major types: direct carbonation and indirect carbonation.

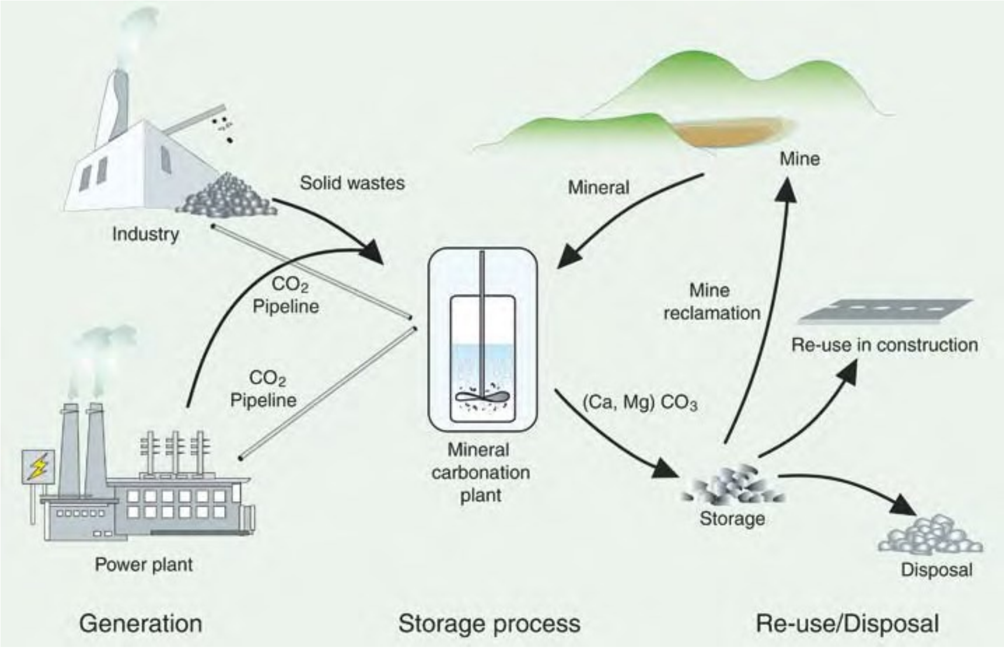

Figure 7: Ex-situ mineral carbonation[7]

Direct carbonation is a single step carbonation reaction, where CO_2 reacts with the metal oxide or alkaline minerals (or in aqueous solution). The single step simple approach of this process was outlined as a low cost method due to minimum activities required in process integration (Sipilä et al., 2008).

Indirect carbonation methods are multi-step reaction mechanisms to capture CO_2 in the reaction. The separation of reactive components from metal oxides (CaO or MgO) is the first step. The extracted ions react with CO_2 to form carbonate in either dry or aqueous process and in the presence of other additives, depending on the process (Sanna et al., 2014).

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[7] Source: IPCC, 2005

Mineral carbonation reaction can proceed through two routes: Dry (gas-solid) carbonation and wet (aqueous) carbonation. Exothermic gas-solid carbonation reactions in magnesium oxide and magnesium hydroxide are given in equation (3) and (4).

Magnesium oxide and magnesium hydroxide gas-solid carbonation (Pan et al., 2012):

$$\text{“}MgO + CO_2 \rightarrow MgCO_3, \Delta H = -118 \text{ kJ/mol } CO_2 \tag{3}$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O, \Delta H = -81 \text{ kJ/mol } CO_2\text{”} \tag{4}$$

Carbonation reaction in aqueous condition in wollastonite and olivine are given in equation (5) and (6) respectively (Erikson, 2014; Pan et al., 2012).

$$CaSiO_3 + CO_2 + 2H_2O \rightarrow CaCO_3 + H_4SiO_4 \tag{5}$$

$$Mg_2SiO_4 + 2CO_2 + 2H_2O \rightarrow MgCO_3 + H_4SiO_4 \tag{6}$$

Sanna et al. (2014) explained the aqueous carbonation route, for example in olivine, carbonic acid is formed due to dissolution of carbon dioxide in water as given in equation (7).

$$\text{“}CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{7}$$

H^+ ions liberates Mg^{2+} from olivine as given in equation (8), which react with the bicarbonate producing magnesite (equation (9)).

$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + SiO_2 + 2H_2O \tag{8}$$

$$Mg^{2+} + HCO_3^- \rightarrow MgCO_3 + H^+ \tag{9}$$

The carbonation reaction can be optimized by various operating parameters such as temperature, pressure, gas humidity, CO_2 partial pressure, surface area of particulate, alkaline material and liquid to solid ratio (Pan et al., 2012). Also, the liquid to solid (L/S) ratio defines the process route for direct carbonation reaction. A carbonation reaction at L/S ratio less than 0.2 can be considered as a gas solid reaction whereas l/s ratio over 5 follows wet (aqueous) carbonation route (Pan et al., 2012). However, Erikson (2014) stated that the optimum L/S ratio for each alkaline material varies with operating process parameters such as temperature, particle surface area and porosity, humidity levels and carbon dioxide concentration.

CO_2 capture and storage as carbonate through mineral carbonation was estimated to increase the energy requirement of a plant by 60% to 180% compared to a plant without CCS (IPCC, 2005). However, due to its abundance quantity in nature, reliability in storage (no leakage and no monitoring of disposal sites) and on-site availability for many process, research is being conducted in this area of CCS.

2.2 UTILIZATION OF COAL ASH

Coal as a fuel used in thermal power plants produces by-products also known as coal combustion products (CCPs), such as fly ash, bottom ash, boiler slag and flue gas desulphurization that are hazardous for humans and the environment. The fine ash travels with flue gases and is captured by electrostatic precipitator, cyclone or filter known as bag house. The fine ash is composed of extremely fine powdery spherical particles of inorganic combustion products known as fly ash. The bottom ash falls below the grate and has a sand like texture.

The utilization of ash is not a new concept; in AD 80 (2 centuries), it started with the world’s largest amphitheater construction, known as “The Roman Colosseum” (Wayman, 2011 and Guinness World Records). Although volcanic ash was used in this prestigious construction, the role of ash and its effect was proven in construction and building materials. Ash is an important part of modern construction industries for cement and concrete production. However, it is evident from Figure 8 and Figure 9 that there has been a large gap in the production and utilization of fly ash and bottom ash in the USA.

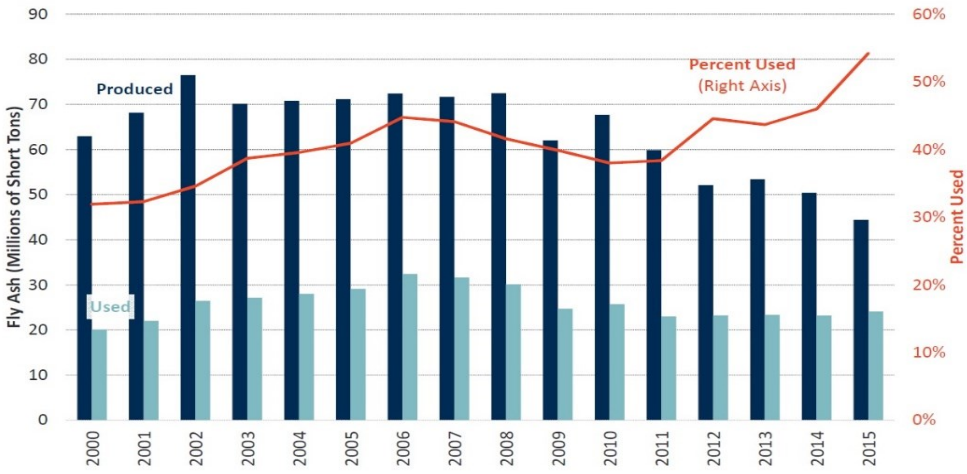

Figure 8: Fly ash production and utilization in the USA[8]

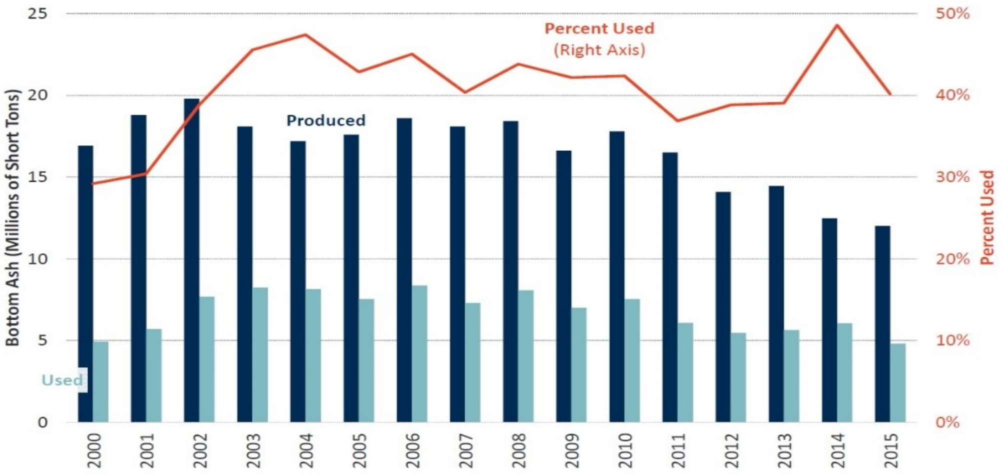

Figure 9: Bottom ash production and utilization in the USA[9]

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[8] Source: ACAA, (2016)

[9] Source: ACAA, (2016)

Coal combustion products (CCPs) can be utilized in number of applications. Some are in use and others are at the laboratory stage. The physical and chemical properties of ash vary with type, location, and method of coal combustion (Fatih and Umit, 2001). The pozzolanic and geotechnical characteristics of ash make it useful to construction industries for production of cement, concrete and brick. Some other uses can be in road construction, soil stabilization, and as a binder in different applications (Ahmaruzzaman, 2009). The physiochemical properties of ash make it suitable to use as an absorbent. As reaction of $Ca(OH)_2$ and fly ash containing amorphous silica, and alumina produces hydrates of higher surface areas, fly ash mixed with calcium hydroxide is reported to be more reactive for SO_2 than $Ca(OH)_2$ alone for SO_x absorption (Davini, 1996). The absorption of mercury and NO_x using unburned carbon of fly ash has been reported (Ahmaruzzaman, 2009). Several studies reported the utilization of ash in carbon dioxide capture (Arenillas et al., 2005; Muriithi et al., 2013; Reddy et al., 2011). Bayat (2002) experimented the absorption properties of fly ash for nickel, copper and zinc. For improvement in removal of organic and inorganic compound, fly ash can be chemically treated to convert it into zeolites (Wang and Wu, 2006). Fly ash can also be used in the synthesis of low grade zeolite (Ahmaruzzaman, 2009).

Major utilization of CCPs are in mining applications, concrete, concrete products and gypsum panel products which consumed over 65% of total CCPs utilized in 2014 (Larson, 2016). The highest portion of fluidized bed coal combustion ash, such as CFB ash, is utilized in mining applications (ACAA, 2016). Major CCPs being alkaline materials can be utilized in mine filling to neutralize acidic ground water produced from the chemical reaction of water and sulfur bearing material (Murarka and Erickson, 2006; Larson, 2016). Murarka and Erickson (2006) also stated that the use of CCPs in mine filling would not only reduce acid formation, but also would control its subsidence. Use of pulverised coal (PC) fired boiler fly ash material in Portland cement concrete production as a supplement material is a common practice in the modern construction industry. Pozzolanic characteristic of fly ash to react with calcium hydroxide ($Ca(OH)_2$) is utilized by the addition of fly ash to Portland cement, which increases strength and reduces the amount Portland cement required otherwise. Larson (2016) reported that use of fly ash in concrete has avoided greater than 150 million tons of greenhouse gas emission since 2000. They have also stated that another CCP, calcium sulfate, acquired from flue gas desulfurization (FGD) units finds major application as the wallboards materials as much as 33% in the U.S. It can also be used in soil amendment and Portland cement manufacture. Bottom ash could be utilized in road base, structure fill, light weight concrete production, asphalt, etc.

Recently there has been a great interest developed in the recovery of rare earth elements from CCPs (Hower et al., 2016; Phuoc et al., 2016). Figure 10 shows the 17 rare earth elements that could be separated from CCPs. Larson (2016) mentioned that these elements are important to the national security of the USA, field of energy and environment, state of the art technologies in electronics and communications, such as fiber optics, sensors, lasers, satellite communications, fuel cells, computer components, batteries, capacitors etc. (NETL, 2016).

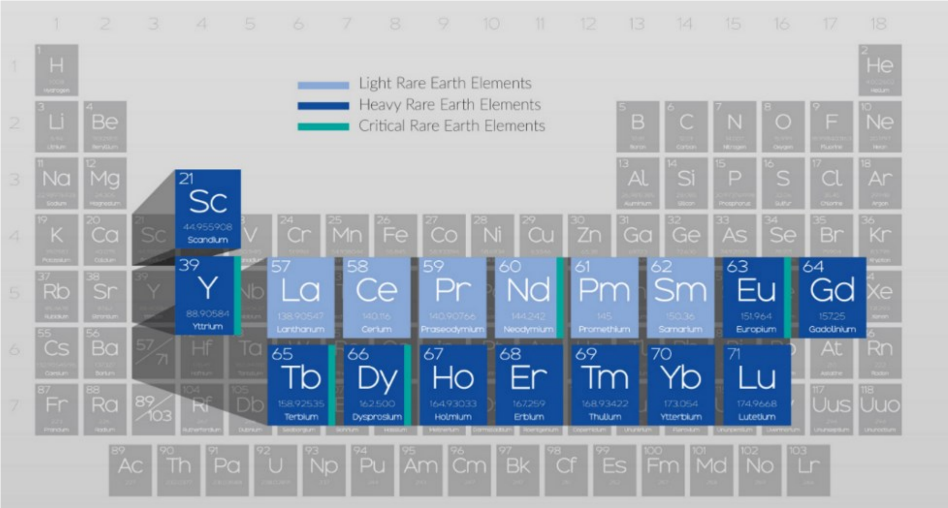

Figure 10: Rare earth elements in periodic table[10]

Figure 11 illustrates the use of rare earth elements in different applications; China was the biggest supplier of these elements with over 97% of the world's rare earth elements production in 2012 (Humphries, 2012).

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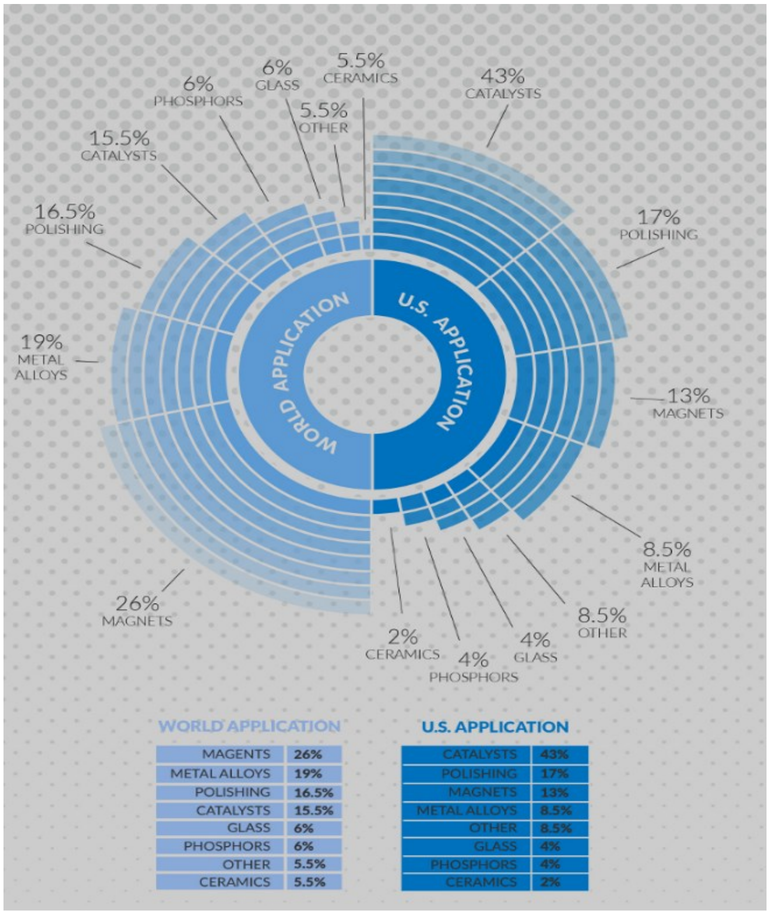
[10] Source: NETL (2016)



WORLD APPLICATION

MAGENTS	26%
METAL ALLOYS	19%
POLISHING	16.5%
CATALYSTS	15.5%
GLASS	6%
PHOSPHORS	6%
OTHER	5.5%
CERAMICS	5.5%

U.S. APPLICATION

CATALYSTS	43%
POLISHING	17%
MAGNETS	13%
METAL ALLOYS	8.5%
OTHER	8.5%
GLASS	4%
PHOSPHORS	4%
CERAMICS	2%

Figure 11: Applications of rare earth elements[11]

Larson (2016) presented a case study of a Wisconsin based company We Energies, which has been utilizing 100% of its total ash production in highway and building construction. Figure 12 shows that utilization of fly ash outreached its production in 2013. In that year, company had to remove the ash from land fill for its value added utilization. It has been stated that regulations of local government and their intention made possible the total utilization of coal ash in value added applications.

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[11] Source: NETL, (2016)

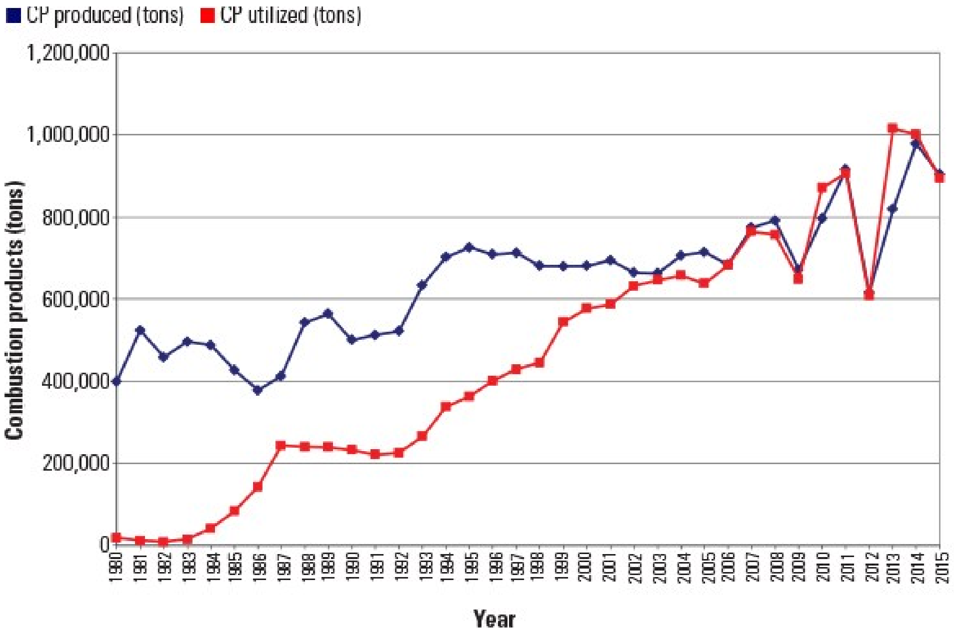

Figure 12: We Energies coal combustion production and utilization[12]

Although around 52% of total produced coal ash was utilized in various applications in the USA in 2015, fluidized bed combustion (FBC) ash was not utilized in any building material or construction application (ACAA, 2016). This is because bricks and cement produced from ash from fluidized bed combustion such as CFB boiler incorporates high SO_3 and free lime contents, which exhibit volumetric expansion of the structure cured at room temperature (Zhang et al., 2012). The expansion of construction materials made from CFB fly ash is due to the formation of dihydrate gypsum and ettringite (AFt) during curing (Anthony et al., 2002; Zhang et al., 2012). Sulfur in the fly ash is in the form of II-$CaSO_4$ whose reaction with water converts into gypsum with solid volume expansion up to 62%. In addition to this, its reaction with $Ca(OH)_2$ and alumina produces AFt with apparent expansion of 125% of initial solid volume (Zhang et al., 2012).

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[12] Source: Larson (2016)

The destructive expansion due to high free lime and SO_3 can be reduced if free lime from the CFB ash is carbonated (Anthony et al., 2002; Siriruang et al., 2016). A study on the comparison of mortar made from CFB fly ash before and after carbonation showed that the latter sample showed great reduction in the expansion compare to former (Siriruang et al., 2016). Compressive strength attained and the water requirement for both types of mortar specimen were almost the same. Thus, a sustainable process integration could be achieved, if fly ash from CFB ash could be utilized in building and construction application after carbonation.

2.3 CO_2 CAPTURE BY COAL ASH

Carbonation of alkaline solid wastes such as coal ash containing lime can proceed through two routes: dry (gas-solid) carbonation and wet (aqueous) carbonation (Pan et al., 2012)

In gas-solid carbonation, carbon dioxide reacts with available CaO in the ash to produce $CaCO_3$ as shown in reaction (10):

$$CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)} - 178\ \text{kJ} \tag{10}$$

In aqueous carbonation, CO_2 gas reacts with water and produces carbonic acid according to Reddy et al. (2011), Pan et al. (2012), Beruto and Botter (2000) and Samari (2014) by the following reactions:

$CO_{2\ (g)} + H_2O_{\ (moisture)} \rightarrow H_2CO_{3\ (carbonic\ acid,\ aq)}$

$$H_2CO_{3\ (carbonic\ acid,\ aq)} \rightarrow H^+ + HCO_3^-{}_{(bicarbonate)} \rightarrow 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \tag{11}$$

With increase in CO_2 partial pressure, its dissolution in water increases (Pan et al., 2012), but the dissolution of CO_2 is inversely proportional to the temperature (Tai et al., 2005).

And the solid phase reaction is:

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)} \rightarrow Ca2^{+}{}_{(aq)} + 2OH^{-} \qquad (12)$$

CO_3^{2-} ions from reaction (12) reacts with Ca_2^{+} to produce $CaCO_{3\,(nuclei)}$ which converts into $CaCO_{3\,(s)}$

$$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3\,(nuclei)} \rightarrow CaCO_{3\,(s)} \qquad (13)$$

The overall reaction can be written as,

$$Ca(OH)_{2\,(s)} + CO_{2\,(g)} + H_2O_{(l)} \rightarrow CaCO_{3\,(s)} + H_2O_{(l)} - 118\text{ kJ} \qquad (14)$$

In addition to the above reaction (14), there is the formation of calcium bicarbonate, which gives enhanced CO_2 diffusion due to its higher solubility (Samari, 2014).

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2 \qquad (15)$$

Calcium bicarbonate reacts with calcium hydroxide and forms calcium carbonate as shown in reaction (16):

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O \qquad (16)$$

Several studies were conducted for CO_2 capture and CaO utilization in carbonation reaction of fly ash or limestone derived materials. Wang et al. (2008) investigated carbonation reactions in CFB fly ash in oxy fuel condition (CO_2 concentration 80%) and observed that CaO utilization increased with increase in temperature and that below a critical temperature (less than 400 °C) there was no significant capture without water vapour. Steam enhanced the carbonation reaction even at low temperature (around 250 °C). Formation of $Ca(OH)_2$ was assumed to be as transient intermediate at where CaO and water vapour encountered above 400 °C, which increased the carbonation reaction.

Interestingly, there was no major difference in the carbonation conversion characteristics at different water vapour concentration between 8% and 15%. Reduction in the carbonation conversion rate compared to the start of the experiments was attributed to $CaCO_3$ product layer built up on the surface.

A pilot scale plant study at Jim Bridger power plant to investigate carbonation reaction in fly ash fluidized by flue gas at around 30-45 °C showed a reduction of CO_2 by about 3.5% in just 2 minutes of the start of the test (Reddy et al., 2011). It also showed that such direct mineral carbonation of fly ash also captured mercury and SO_2 from flue gas. The analysis of the mineral carbonation sample showed carbonates of Ca and other oxides with silicate minerals. This is due to the carbonation reaction of oxides and dissolution of amorphous silicate mineral in acidic pH flue gas. Research into optimization of process parameters was recommended for future study. A preliminary economic analysis of this process for the Jim Bridger unit-2, 532 MW, PC power plant which emits 4.9 million tonnes of CO_2 was conducted by Christensen (2010). It estimated that 90% of total CO_2 captured at a theoretical rate of 207 kg CO_2/tonne of fly ash would cost around \$11/tonne of CO_2. Based on this value it was estimated that increase in cost of electricity would be around \$12/MWh that is approximately 33.5% increase. Similar analysis at 50% capture level (103.5 kg CO_2/tonne of PC fly ash) showed increase in cost of electricity to around 64% (\$22/MWh).

The aqueous carbonation reaction in one tonne fly ash containing 4.1% CaO could capture 26 kg of CO_2 at 60-90 °C (Montes-Hernandez et al., 2009). Two step reactions, first, hydration of fly ash to convert CaO to $Ca(OH)_2$ followed by carbonation reaction were employed. Mineral carbonation of fly ash by pressure balance method revealed that efficiency was not dependent on initial pressure of carbon dioxide and it was as high as

82%. There was not a notable effect of temperature on the carbonation reactions. It should be noted that only CO_2 was supplied in the experimental study conducted by Montes-Hernandez et al. (2009).

Another study on the dry gas-solid carbonation reaction of coal fly ash with 32.4% lime and at 100% CO_2 concentration was carried out by Mazzella et al. (2016). Experiments were conducted at different CO_2 pressure and temperature; it was observed that at temperature 25 °C and 45 °C, CO_2 capture increased with temperature and pure CO_2 pressure up to 7.5 bar; however, between 7.5 and 15 bar the effect of temperature on the carbonation reaction was less evident. The maximum carbonation reaction observed was 74% in this study.

A similar study on the carbonation of class F fly ash (CaO < 10%) at ambient temperature and CO_2 pressure (100% vol.) under 10 bar showed that aqueous fly ash captured nearly double the mass of CO_2 than dry fly ash (Tamilselvi Dananjayan et al., 2016). The maximum efficiency of carbonation was around 68%. There was a significant influence of process parameters on the gas-solid and aqueous carbonation reactions of fly ash observed. Carbonation reaction increased with CO_2 pressure up to 10 bar and 4 bar for dry and aqueous experiments, after which there was no notable effect of pressure observed. The effect of the contact time on carbonation revealed that the rate of carbonation increased up to 1 hr and reduced thereafter in dry gas-solid carbonation tests. The reason for this effect was stated as passivation; a $CaCO_3$ layer phenomenon that inhibits the direct contact of CO_2 and available oxides. Similar reasoning was given by other (Silaban, 1993; Sun et al., 2007; Li et al., 2012). The optimum time of carbonation reaction in aqueous experiments observed was 2 hrs with liquid to solid ratio at 15.

Aqueous carbonation reaction in petcoke CFB fly ash at 100% CO_2 concentration at different temperatures (between 30 °C to120 °C) and solid to liquid ratios (S/L:6 to 50 g/l) showed that with increase in temperature carbonation reaction increased up to 90 °C, and it reduced at 120 °C (González et al., 2014). In aqueous carbonation, dissolution of alkaline materials such as lime and portlandite, increases the pH of the solution. The change in the pH values were shown as another indicator of carbonation reaction. It was observed that carbonation reaction works as neutralization process and the reduction of pH from 12.5 to 7.0 was observed with CO_2 capture. It was observed that at a fixed S/L ratio with increase in temperature, dissolution of Ca ions increases but CO_2 solubility decreases; thus, above a certain temperature carbonation reaction start to decrease. However, if the amount of water could be increased, higher carbonation reaction can be achieved at higher temperature. It showed that aqueous carbonation reaction at a particular temperature depends on the amount of water present in the system. It has also been mentioned that besides the process parameters, carbonation in aqueous condition would depend on alkaline material's minerology, pore surface area, chemical composition etc.

Ukwattage et al. (2015) studied the effect of temperature and liquid/solid (l/s) ratio on the wet carbonation in three types of fly ash samples by measuring the change in the CO_2 pressure, which was initially at 3 MPa. Water to solid ratio was explained as an important parameter for carbonation reaction, it was stated that greater amount of water than required blocks the solid pore restricting the dissolution of CO_2 and diffusion of Ca^{2+} to form carbonates. On the other side, less than required amount of water would leach out the calcium or the reaction would be a slow dry gas-solid. The optimum l/s ratio considered in this study was 0.2-0.3. Effect of temperature showed that increase in temperature up to 60°

C increased the reaction rate and further increase in temperature reduced the rate of carbonation. The reason for this was similar as explained by González et al. (2014). Ukwattage et al. (2015) also mentioned that aqueous carbonation required less energy than dry gas-solid carbonation.

Effect of water on the carbonation reaction of $Ca(OH)_2$ and CO_2 showed that it acts as a catalyzer and enhances the reaction further due to H_2O produced from the reaction (Pontiga et al., 2013). Investigation of the effect of relative humidity (RH) on the carbonation of $Ca(OH)_2$ revealed that the reaction could not take place below a critical RH (8%), and the influence of RH was higher than the temperature (Shih et al., 1999). Also, increased RH and temperature increased carbonation reaction rates, but there was no notable effect of CO_2 concentration observed.

Another study conducted at same temperature range (20 °C to 80 °C) compared aqueous mineral carbonation capacity of pulverised coal (PC) and fluidized bed lignite fly ash (Jaschik et al., 2016). The study concluded that mineral carbonation of fluidized bed fly ash of lignite coal had the highest carbonation potential due to highest CaO compared to PC based fly ash samples.

Comparison of naturally weathered carbonation and accelerated carbonation (at 4 MPa, 90 °C) of fly ash showed that the required time duration for about the same level of carbonation was 20 years for the former compared to 2 hours for the latter (Muriithi et al., 2013).

Although Wang et al. (2008) studied CO_2 capture by dry CFB fly ash in oxy-fired condition above 400 °C and in presence of water vapour above 250 °C, the reaction at low CO_2 partial pressure as expected in air fired CFB boiler, and, at low temperature for hydrated fly ash could differ considerably. Comparison of carbonation reaction characteristics of pure lime and CFB fly ash for similar operating condition could provide more insight into the effectiveness of CO_2 capture by CFB fly ash. As untreated CFB fly ash contains items like SO_3, CaO, LOI, Al_2O_3, SiO_2, a difference in the reaction characteristics of CFB fly ash and pure lime could exist.

González et al. (2014) investigated carbonation in aqueous condition at 100% CO_2 concentration, however, in typical air fired CFB boiler CO_2 accounts for less than 20% (Wang et al., 2008). Thus it is necessary to evaluate the effect of partial pressure of carbon dioxide on the carbonation reaction of CFB fly ash.

CHAPTER 3: METHODOLOGY

Fly ash for the experiments was collected from the 197 MWe Circulating Fluidized Bed (CFB) power plant at Point Aconi, Nova Scotia. This CFB power plant presently uses a mixture of petroleum coke and coal as fuel at the ratio of 80:20. Limestone is added for in-situ capture of SO_2. Table 1 gives the composition of fly ash.

Table 1: Fly ash analysis

Element	Weight (%)
Al_2O_3	1.7
CaO	37.25
Fe_2O_3	0.87
K_2O	0.32
MgO	0.45
Na_2O	0.11
SO_3	15.88
SiO_2	0.22
V_2O_5	0.22
P_2O_5	0.05
LOI	11.08

It shows that fly ash contains 37.25% lime, derived from limestone. Fly particle size distribution is shown in Figure 13, that shows that 95% of total volume of fly ash particle size falls under 120 µm bulk of it is centred around 40 µm.

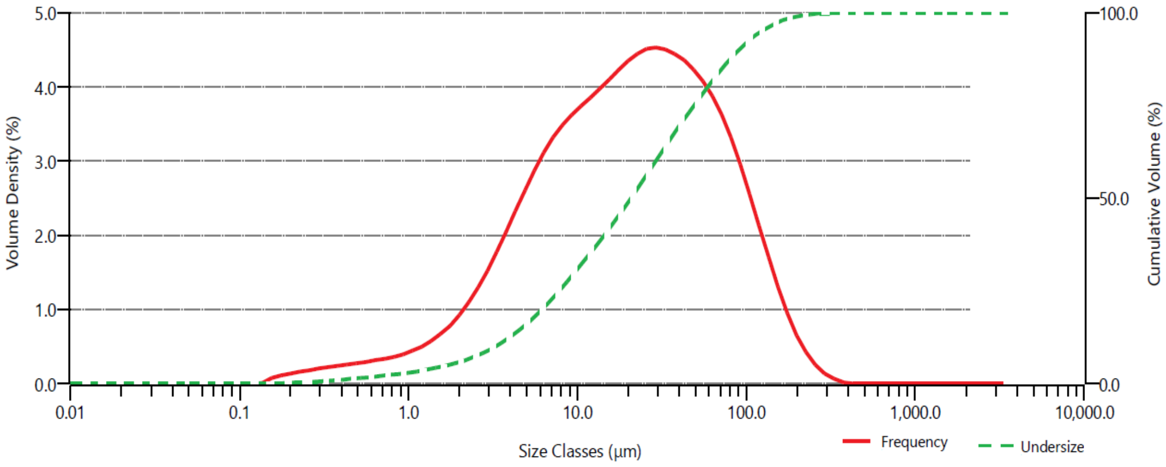

Figure 13: Fly ash particle size distribution

An experimental setup as shown Figure 14 in was prepared to investigate the CO_2 capture by fly ash and high calcium quicklime in carbonation reaction. A stainless steel cylindrical reactor of diameter 25 mm and height 300 mm closed at both ends served as the test reactor. It had a provision to insert a gas tube and thermocouple through the two end caps (Figure 14). To ensure uniform temperature distribution, the reactor was heated in a bubbling fluidized bed heater. During the experiment, mixtures of nitrogen (N_2) and carbon dioxide (CO_2) gases were introduced from the bottom end of the reactor. The exit gas passes through the cap on top of the reactor that also holds a thermocouple that continuously monitor interiors temperature of the reactor during experiments. A Testo 350-XL gas analyser continuously analyzed gases coming out of the reactor. Schematic is shown in Figure 14 while a photograph of the experimental setup is shown in Figure 15.

The aim of this study is to investigate carbon capture (carbonation) reaction in fly ash at different conditions and to compare that with high calcium quicklime. The high calcium quicklime was procured from Graymont Limited, Havelock, New Brunswick, Canada, which contains more than 90% CaO.

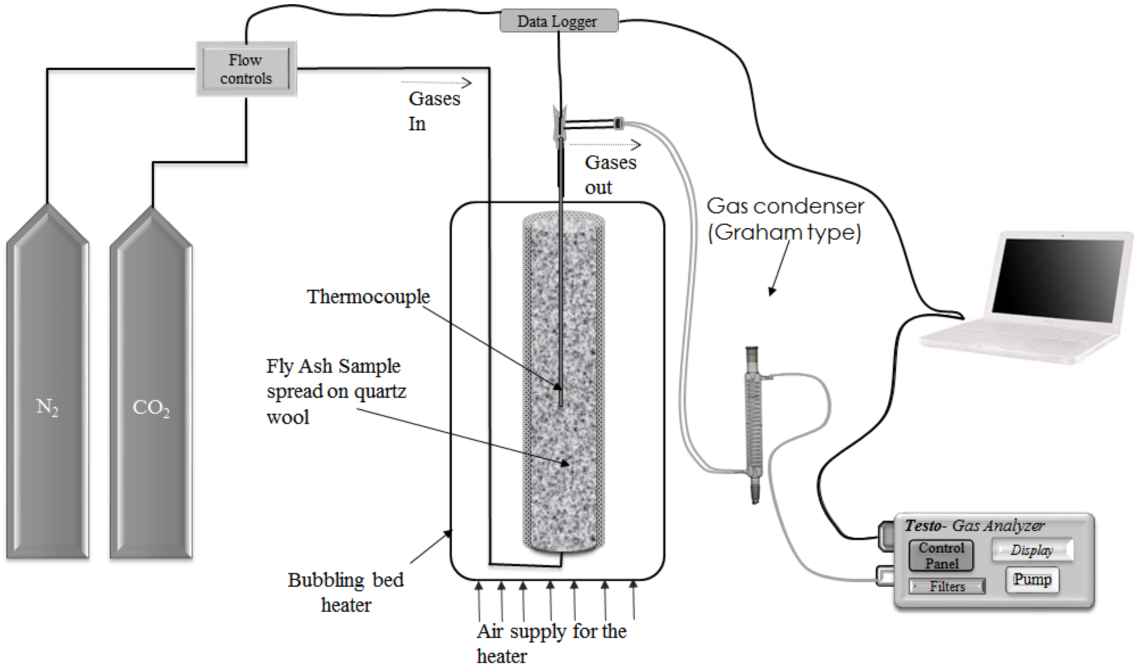

Figure 14: Schematic diagram of the experimental setup

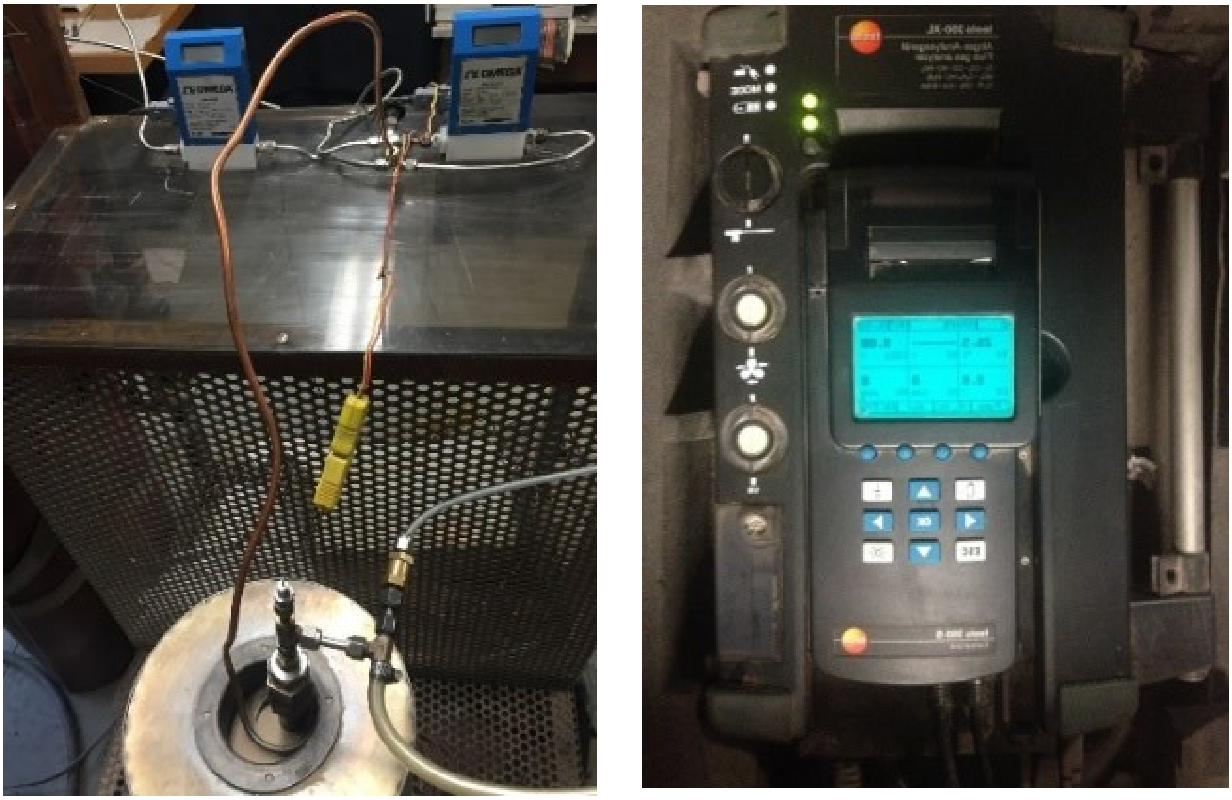

Figure 15: Photograph of the experimental setup

3.1 TEST CONDITION

In order to compare the results, two sets of experiments were conducted in different conditions. First set was experiments at dry conditions for both dry fly ash and dry quicklime. Other experiments were conducted at hydrated condition for hydrated fly ash and hydrated quicklime. As the reactor has a limited volume and the dry and hydrated samples have different density it was not possible to accommodate the same mass of hydrated quicklime sample in the reactor. Hydrated quicklime sample of smaller mass (i.e., 30 g) was selected, as shown in Table 2. The table also gives sample preparation information, such as weight of ash/lime and amount of water added.

Dry and hydrated test were performed at high temperature (above 500 °C) and low temperature (below 80 °C), respectively. Table 3 shows the test matrix prepared for this study. For all the experiments, nitrogen flow rate was maintained constant at 0.46 liters/min and the amount of water for hydration was kept constant at liquid to lime ratio of 0.65. Most experiments were repeated 2 to 3 times for the repeatability.

Table 2: Sample details

	Sample weight (g)	Water added (g)
Dry fly ash	50	0
Hydrated fly ash	50	12
Dry quicklime	50	0
Hydrated quicklime	30	19.5

Table 3: Test Conditions

Temperature	Hydrated fly ash	Hydrated quicklime	Dry fly ash	Dry quicklime
(°C)	CO_2 = 0.20 l/min (Vol: 30%), N_2 = 0.46 l/min (Vol: 70%)			
30	✓	✓	N/A	
40	✓	✓		
50	✓, *	✓, *		
60	✓	✓		
80	✓	✓		
500	N/A		✓	✓
600			✓	✓
700			✓, *	✓, *
750			✓	✓

*test conducted for CO_2 volume concentration: 16%, 22%, 30%, 36%

3.1.1 Effect of Temperature in Dry Conditions

Previous study (Wang et al., 2008) noted that gas solid carbonation reaction in CFB fly ash below 500 °C is insignificant even at CO_2 concentration as high as 80%, but that CO_2 capture increased with temperature. All experiments to investigate the effect of temperature in dry conditions were conducted in the temperature range from 500 to 750 °C, at significantly lower CO_2 concentration (16-36%) than that investigated by Wang et al. (2008). Fifty grams of un-treated dry fly ash or quicklime sample were spread on quartz wool and that was placed in the reactor. Quartz wool served as a highly porous support for the sample, with free access of gas from all directions. Nitrogen (N_2) was continuously supplied during the experiment, and, on reaching the desired reactor temperature, it was switched to a mixture of CO_2 and N_2 gases at 0.20 and 0.46 l/min (as volume: 30% and 70%) respectively. The product gas of reaction leaving the reactor was continuously cooled in a Graham (coiled type) condenser and then analyzed on-line by a gas analyzer.

3.1.2 Effect of Temperature in Hydrated Conditions

Carbonation of hydrated fly ash is conducted typically below water evaporation temperature to prevent steam from escaping, or to avoid an expensive pressurized carbonation vessel. It was noted later that under hydrated condition, a level of capture equivalent to dry sample at 500 °C or above can be achieved at temperature as low as 50 °C. This less energy intensive choice simplifies industrial processes and makes it cost-effective. So, the carbonation reaction in hydrated fly ash and hydrated quicklime was conducted at low temperature range (30-80 °C) following the same procedure as in dry cases.

3.1.3 Effect of CO_2 Partial Pressure

To investigate the effect of CO_2 partial pressure on carbonation reaction, tests were conducted at four CO_2 partial pressures at temperature 50 °C for hydrated and 700 °C for dry case while keeping all other parameter constant. The CO_2 partial pressures were 17, 22, 31 and 37 kPa (Volume: 16%, 22%, 30%, 36%) for a N_2 flow of 0.46 l/min.

3.1.4 Effect of Particle Size

In order to investigate the effect of particle sizes on the CO_2 capture, bottom ash of average particle sizes 116 µm, 196µm and 275 µm were selected and the capture results were compared with the same particle sizes of dry quicklime experiments carried out at similar operating conditions. Operating condition for all the experiments was fixed at temperature 700 °C and CO_2 partial pressure at 31kPa.

The novelty of this work is, firstly, the investigation of CO_2 capture by un-treated CFB fly ash at low CO_2 partial pressure and at different temperature in dry and hydrated conditions. Secondly, comparison of CO_2 capture with quicklime for the same experiments. Thirdly, study of carbonation reaction in CFB bottom ash of different particle size.

CHAPTER 4: RESULT AND DISCUSSION

Most experiments conducted in this study have shown an initial rapid sorbent conversion followed by a very slow reaction stage. All dry samples eventually dropped the capture level to around 50%, and, after that, it reduced very slowly. A similar observation has been seen in studies by Bhatia and Perlmutter (1983), Dedman and A.J. Owen (1962), Silaban (1993), Stanmore and Gilot (2005) and Mess et al. (1990). The rapid reaction is essentially a surface reaction of CO_2 with CaO, which was kinetically controlled due to the high gas-exterior surface mass transfer. This produced a $CaCO_3$ product layer on the exterior surface of the fly ash particles, which restricts further direct contact of CO_2 with available CaO beneath, as noted by Sun et al. (2007), Li et al. (2012), and Agrinier et al. (2001). This mass transfer restriction slows down the reaction, and thus the reaction is controlled by diffusion of CO_2 gas into pores to react with CaO (Agrinier et al., 2001; Nikulshina et al., 2007; Silaban, 1993). The CO_2 diffusion was very slow in the second stage phase of carbonation of lime. The total CO_2 capture is nearly independent of CO_2 partial pressures, as noted in this research and by others studies (Mess et al., 1990; Grasa and Abanades, 2006; Silaban, 1993).

4.1 **EFFECT OF TEMPERATURE**

Several experiments were conducted to investigate the effect of temperature on CO_2 capture by fly ash and quicklime at different conditions. Experimental results of dry and hydrated conditions for CFB fly ash and quicklime are shown in the following subsections.

4.1.1 Dry Test

Figure 16 shows the percentage capture of the CO_2 entering the reactor in the temperature range 500 °C to 750 °C by the as received dry fly ash from Point Aconi plant. It is apparent from the figure that initial level of CO_2 capture increased with the increase in flue gas temperature up to 700 °C. This result agrees with the tests by Wang et al. (2008), where with increase in temperature CaO utilization increased. However, after the initial capture, all the sample showed that capture reduced slowly below around 50% capture level. At 750 °C there was a reduction in CO_2 capture in the rapid reaction regime. This could be because above 700 °C, Gibbs free energy would be approaching zero at the partial pressure of CO_2 of the present experiments, and, hence, the carbonation reaction could not take place (Li et al., 2005). Li et al. (2005) explained that at 10 kPa CO_2 partial pressure, change in Gibb's free energy becomes zero at 720 °C and there could not be any carbonation reaction. It could be stated that at 750 °C and at 31 kPa CO_2 partial pressure change in Gibb's energy approached to zero and the reaction approached to calcination reaction. Thus, at 750 °C very little carbonation reaction took place in the kinetically controlled regime.

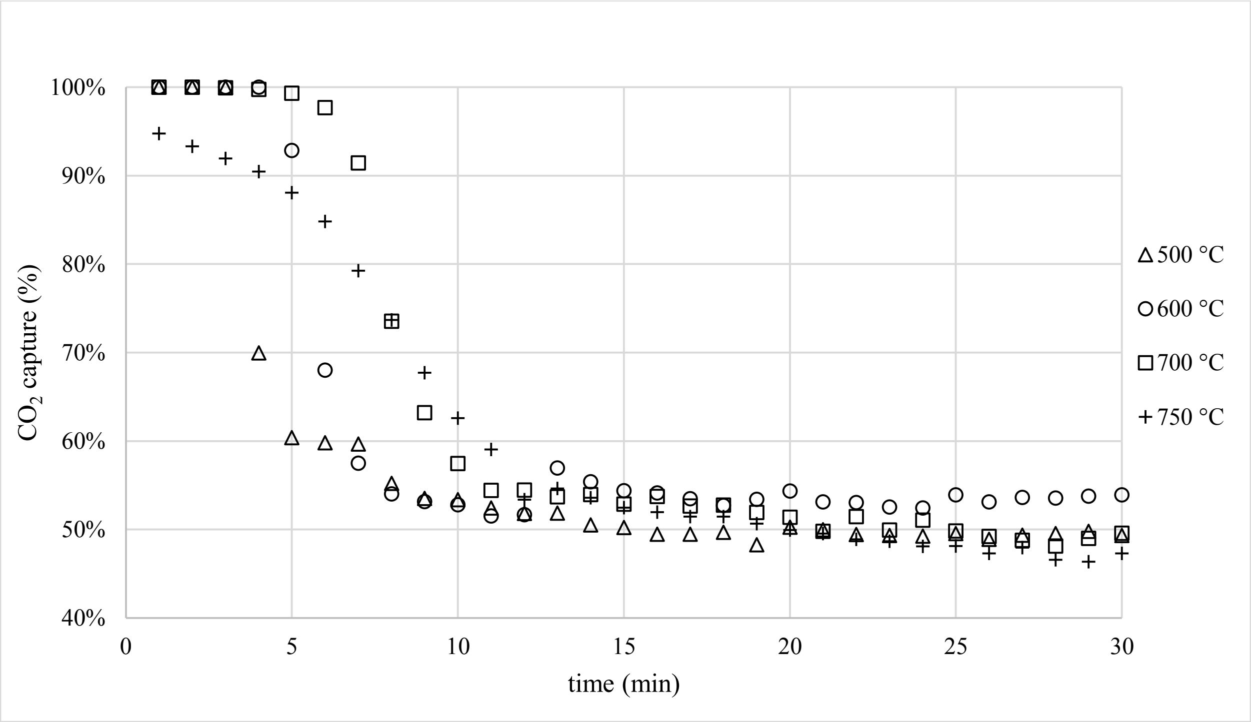

Figure 16: CO_2 captured by 50 g of dry fly ash

Figure 17 shows similar experiments with high-calcium quicklime instead of fly ash. The sample of dry fly ash contained 37.25% lime in comparison with quicklime sample which had more than 90% CaO available for the carbonation reaction. Temperature had therefore, significant effect on the carbonation of quicklime. To drop to 50% capture level, the test at 500 °C took around 10 minutes; at 600 °C, 50 minutes; at 700 °C around 100 minutes; and more than 160 minutes at 750 °C, while the tests with dry fly ash it took only 10-15 minutes.

Similarly, to the case of dry fly ash, the initial rate of CO_2 capture by quicklime increased rapidly with increased temperature up to 700 °C and only gradually reduced to its steady-state slow reaction stage. For similar reason, there was a significant reduction in the duration of first-stage initial rapid kinetically controlled carbonation stage at 750 °C, and, thus, the initial highest capture noted in both the cases was at 700 °C.

During the initial rapid surface carbonation reaction stage (kinetically controlled regime), a significant amount of CO_2 was captured followed by a very slow diffusion controlled regime. However, in latter stage of slow reaction stage, there was not a noticeable effect on temperature on the amount of CO_2 capture was observed.

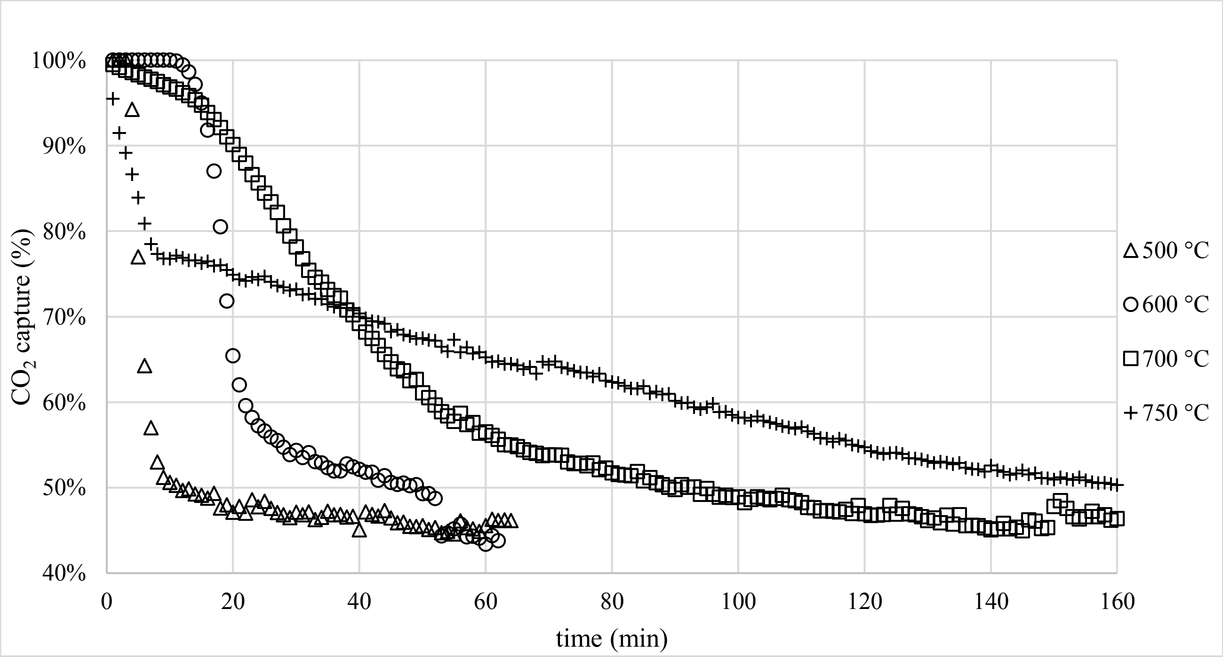

Figure 17: CO_2 captured by 50 g of dry high calcium quicklime

This rapid transition could be considered taking place at around 95% CO_2 capture level. Figure 18 shows the amount of CO_2 captured per unit mass of the sample in the kinetically controlled regime at different temperatures. For dry fly ash, the highest CO_2 captured was around 0.04 kg per kg sample at 700 °C, and the minimum was around 0.01 kg per unit sample at 750 °C. The highest value translates into 14% conversion of the CaO in ash. Per unit mass capture was higher for dry quicklime, it was around 0.1 kg CO_2 per unit mass of quicklime at both 600° and 700 °C, then it dropped to the same level as dry fly ash at 750 °C. Interestingly this translate into lower (12.8%) conversion of the CaO in quicklime; a lower level of CaO utilization noted here in case of lime.

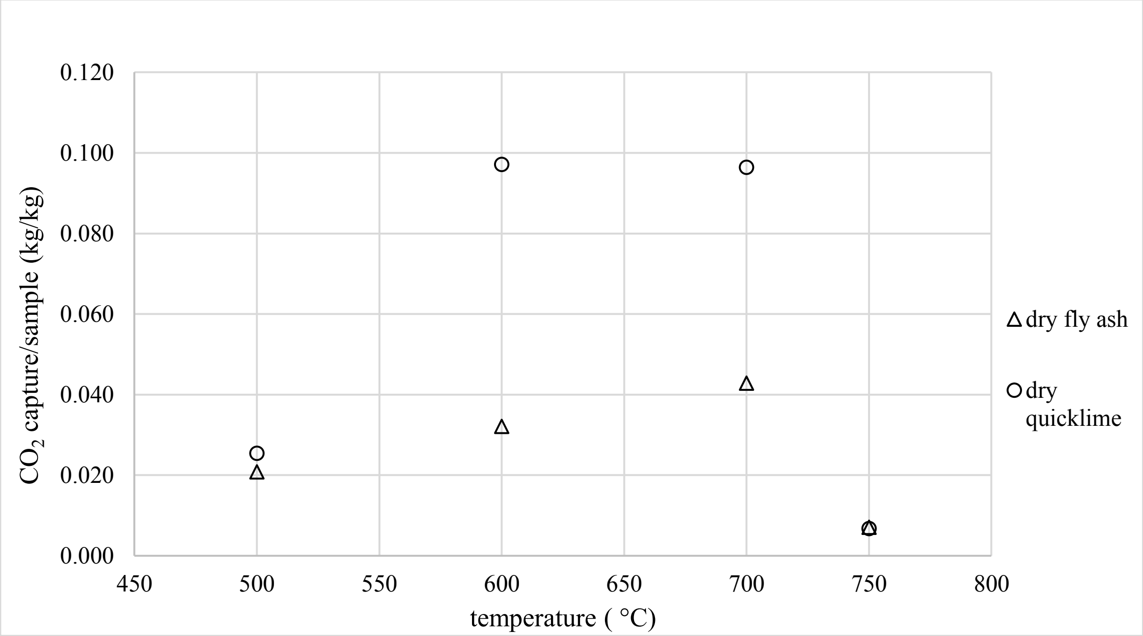

Figure 18: CO_2 captured per unit mass of sample during rapid reaction stage

4.1.2 Hydrated Test

It can be assumed that part of the available CaO in fly ash and quicklime was converted to $Ca(OH)_2$ through hydration. However, it was not possible to verify the extent of $Ca(OH)_2$ conversion by measurement of mass change as significant amount of water was taken up in the reaction to form phases such as hydrated aluminosilicates (Gora et al., 2006). Hence, for hydrated fly ash experiments, free CaO or $Ca(OH)_2$ may be expressed as CaO.

The reaction between CO_2 and $Ca(OH)_2$ is dependent on the amount of moisture present in the reaction environment. There could be no reaction if CO_2 and water were not present simultaneously above a particular relative humidity (Yang et al., 2003). On the surface of $Ca(OH)_2$, nano size-droplets of water or a liquid like layer were necessary for the reaction to take place at a reasonable rate. The initial first stage rapid reaction could be considered as gas-liquid-solid process (Yang et al., 2003; Beruto and Botter, 2000). Figure 19 illustrates this reaction on surface of $Ca(OH)_2$ particle. According to Samari (2014), at the start of the reaction, CO_2 reacted with sorbent in presence of water droplets and formed a product layer of $CaCO_3$. This product layer on the surface of sorbent hindered further carbonation reaction resulting in transition to a slow second stage reaction that was controlled by diffusion of CO_2 into the pores.

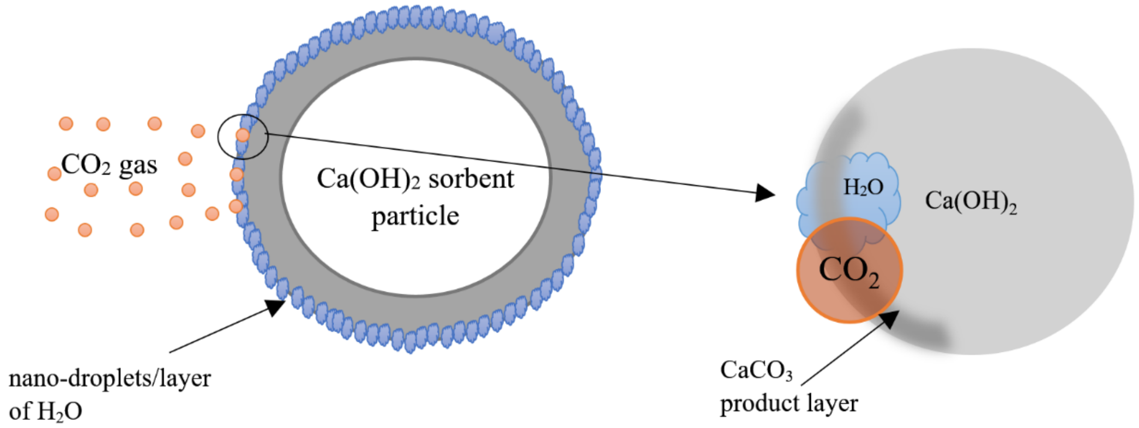

Figure 19: $Ca(OH)_2$ particle carbonation reaction

The time variation of CO_2 capture by hydrated fly ash and hydrated quicklime for the temperature in the range of 30 °C to 80 °C is shown in Figure 20 and. Figure 21 respectively. It can be seen that CO_2 capture increased with increase in temperature but only up to 50 °C. Above 50 °C, the capture started to reduce again. This could be because the carbonation reaction of $Ca(OH)_2$ depended on the amount of water on the sorbent surface, relative humidity (RH) and temperature. González et al. (2014) and Ukwattage et al. (2015) showed that with increase in temperature, CO_2 solubility in water reduces (equation (11)) (carbonic acid) but calcium leaching increases in the water layer (equation (12)). Since CO_2 dissolution reduced above 50 °C in the present study, carbonation reaction above that temperature reduced. This observation is analogous to those made by Ukwattage et al. (2015) and other studies (Shin et al., 1999; Pontiga et al., 2013; Yang et al., 2003; Beruto and Botter, 2000), who noted that water catalyzes the carbonation reaction and below a critical relative humidity (RH) there could not be appreciable carbonation reaction. Shin et al. (1991) suggested that RH has a more dominant effect on carbonation reaction than that by temperature. All samples for hydrated cases had the same moisture/water content (liquid to lime ratio: 0.65) at the start of the test; but with increase in temperature, the RH in the reaction environment reduces. Although an increase in temperature had a positive effect on CO_2 capture, above 50 °C, the reduction in RH exerted a more dominant effect and capture started to reduce. This observation is in agreement with those of Shih et al. (1999). Girard et al. (2008), who concluded that above 50 °C, evaporation of water from surface of droplets is significantly higher and independent of the RH. It is thus apparent that nano-droplets from the sorbent surface evaporated rapidly with an increase in temperature above 50 °C, which reduced, the carbonation reaction significantly. Interestingly, conversion of $Ca(OH)_2$ to $CaCO_3$ by carbonation reactions produced additional water layer that catalyzed the ongoing carbonic reaction (Pontiga et al., 2013).

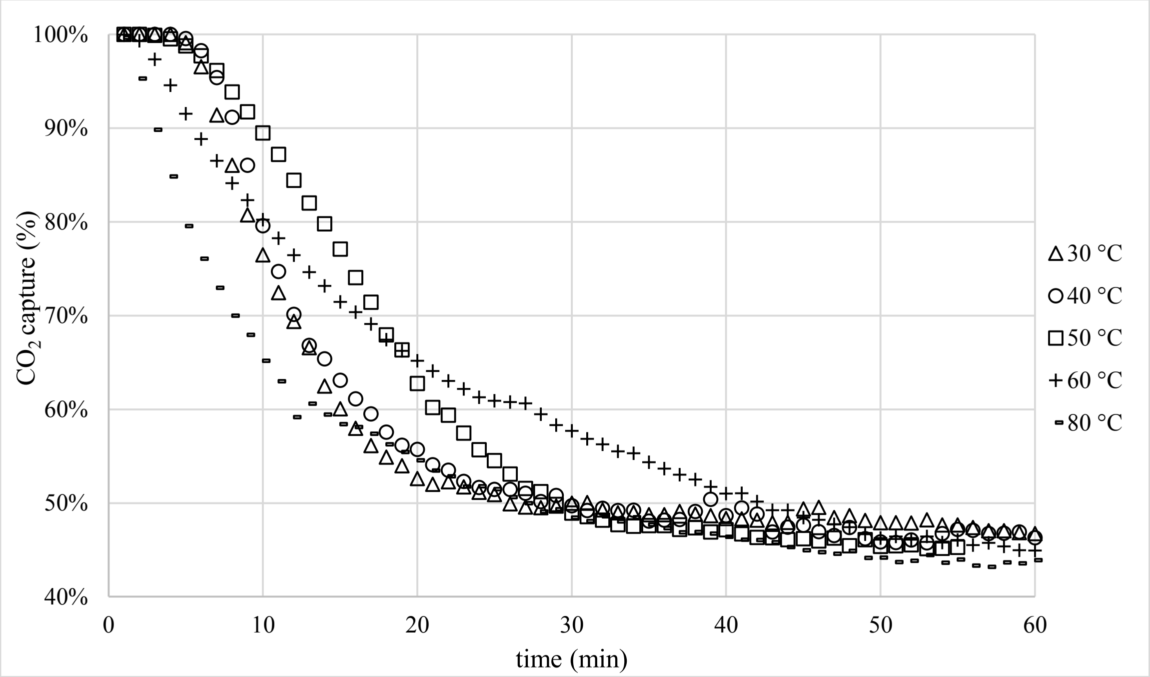

Figure 20: CO_2 captured by 50 g of hydrated fly ash

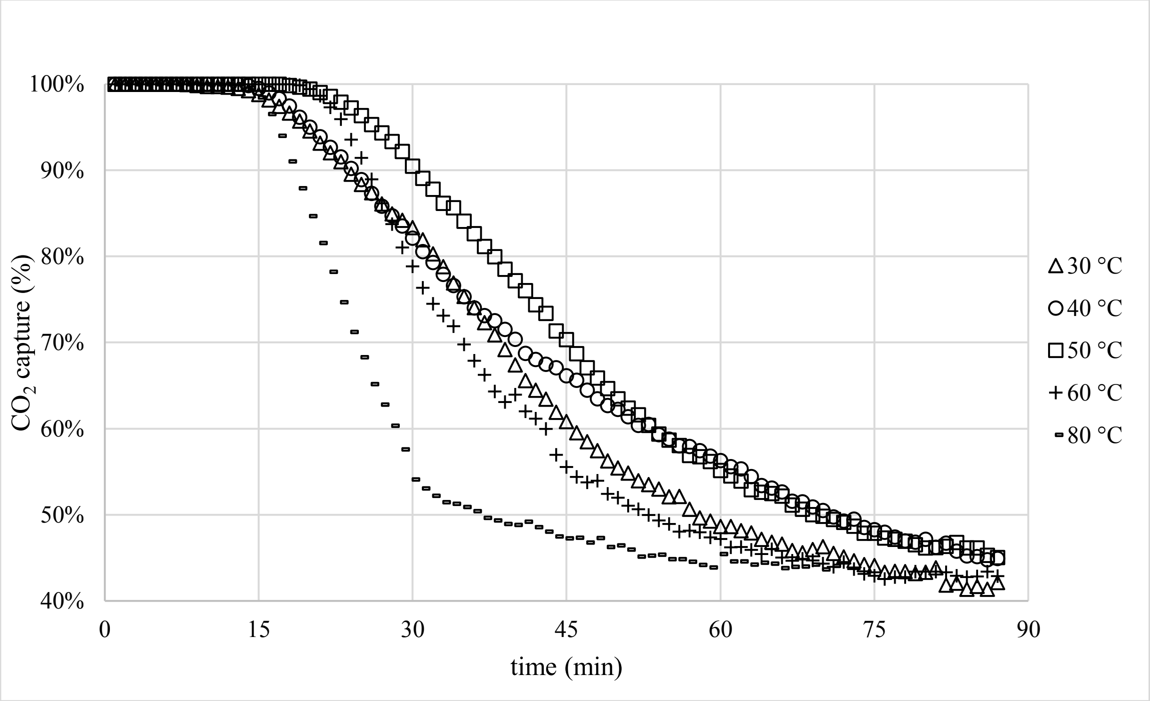

Figure 21: CO_2 captured by 30 g of hydrated quicklime

Comparing results from dry experiments with those from hydrated cases, one notes that surface carbonation reaction of $Ca(OH)_2$ on hydrated particles helped capture significantly higher amount of CO_2 than that by CaO in dry fly ash or quicklime. Interestingly, in rapid reaction stage, even 30 g of hydrated quicklime (at 50 °C) showed significantly higher capture (Figure 21) than 50 g of dry quicklime samples at any temperature (Figure 17). The addition of water or hydration of the sample extended the first stage reaction, even at low temperature. This observation had also been noted by Manovic and Anthony (2010). They suggested that steam enhanced the carbonation via solid state diffusion in the product layer. During carbonation reaction, release of H_2O due to decomposition of $Ca(OH)_2$ increased the humidity and the reaction surface area eventually favoring the capture (Wu et al., 2007; Shih et al., 1999). In addition to this, $Ca(OH)_2$ has higher specific surface area than CaO which enhanced surface carbonation reaction (Kalinkin et al., 2005). In this study, where temperature is considerably lower than that of Manovic and Anthony (2010), water enhanced the first stage reaction and catalyzed the carbonation reaction even at much lower temperature as observed by Beruto and Botter (2000).

Figure 22 shows the amount of CO_2 captured by unit mass of hydrated samples at different temperatures during the rapid reaction stage. It can be seen that with increase in temperature, CO_2 capture increased and it again reduced, as above 50 °C dissolution of CO_2 in water reduces.

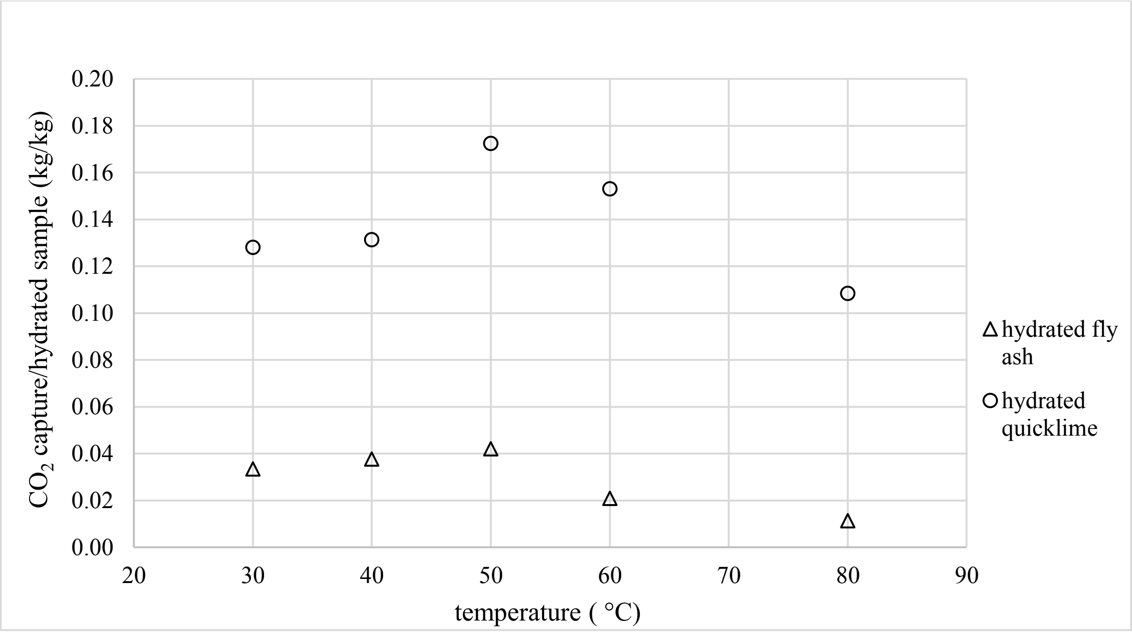

Figure 22: Mass of CO_2 captured per unit hydrated sample during fast reaction stage

It is observed for most experiments that transition from an initial fast kinetically controlled stage to a slower diffusion controlled stage took place rapidly, and the start of this transition typically happened at when CO_2 capture reached around 95%. Comparison of CO_2 capture in this kinetically controlled regime for dry and hydrated fly ash at different temperature is shown in Figure 23. A unit mass of dry and hydrated fly ash sample captured around 0.04 unit of CO_2 at 700 °C and 50 °C respectively. The partial pressure of CO_2 was maintained at 31 kPa during the experiments. At all the other temperatures, as showed in Figure 23, a unit hydrated fly ash sample showed significantly higher capture than that of dry fly ash sample; this shows the improvement through hydration.

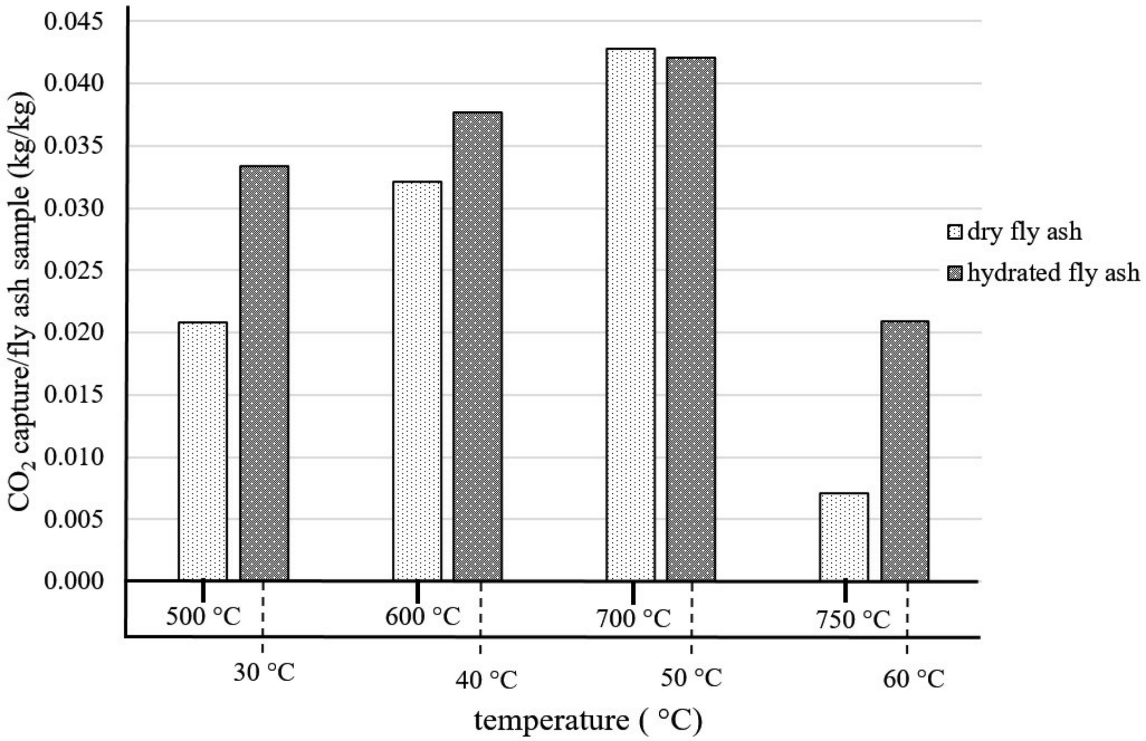

Figure 23: CO_2 captured by of dry and hydrated fly ash during initial rapid carbonation stage

The similar result of improvement through hydration on CO_2 capture in fast reaction regime was also clearly apparent for quicklime as shown in Figure 24. Other studies also noted that carbonation of hydrated fly ash ($Ca(OH)_2$) was much faster than that of dry fly ash (CaO) (Manovic and Anthony, 2010; Wang et al., 2008).

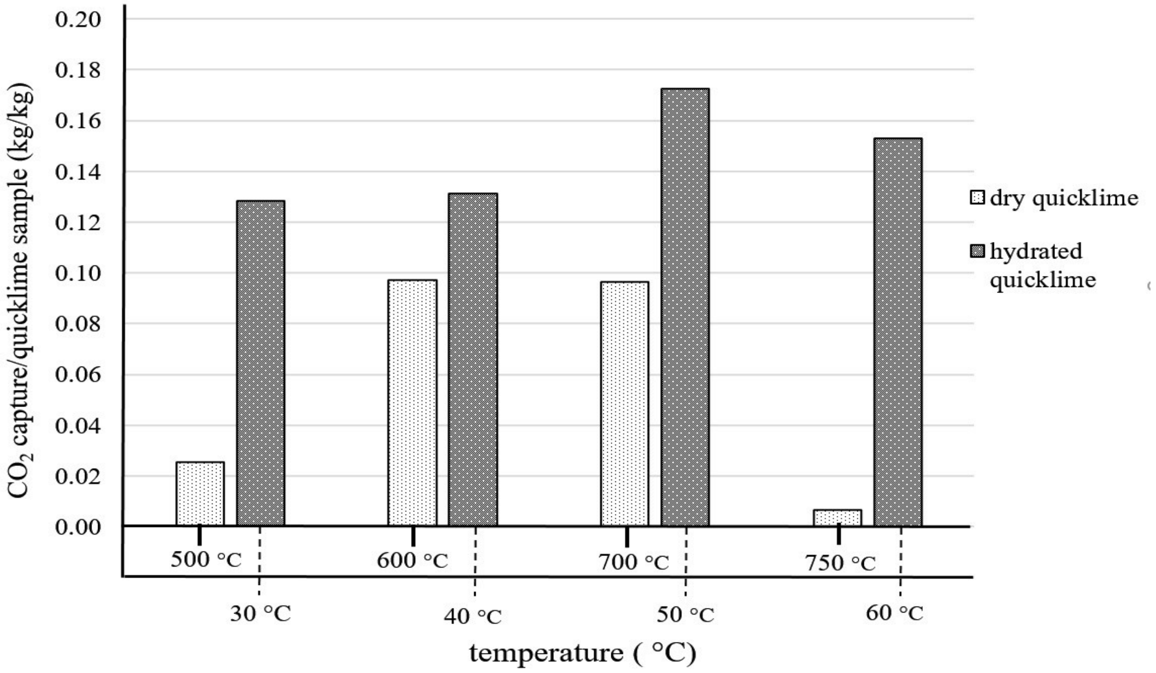

Figure 24: CO_2 captured by of dry and hydrated quicklime during initial rapid carbonation stage

4.2 EFFECT OF PARTIAL PRESSURE OF CO_2

4.2.1 Dry Test

The sharp drop in the amount of CO_2 capture after the short initial period was the transition of the reaction from a rapid kinetic regime to a slow CO_2 diffusion regime. This stage occurred early for high CO_2 partial pressure followed by the next lower CO_2 partial-pressure. Figure 25 shows that time required to reach a steady stage capture where carbonation reaction was controlled by diffusion of gas into the pores, was around 30 minutes at CO_2 partial pressure of 17 kPa whereas, at the highest CO_2 partial pressure (37 kPa) it was 8 minutes. This could be because the carbonation speed and the rate of development of $CaCO_3$ layer on particle surface increased with the increase in CO_2 partial pressure during the kinetically controlled stage. However, the latter stage, being diffusion controlled, the effect of partial pressure of CO_2 on capture was negligible this observation was also made by Bhatia and Perlmutter (1983); Sun et al. (2007).

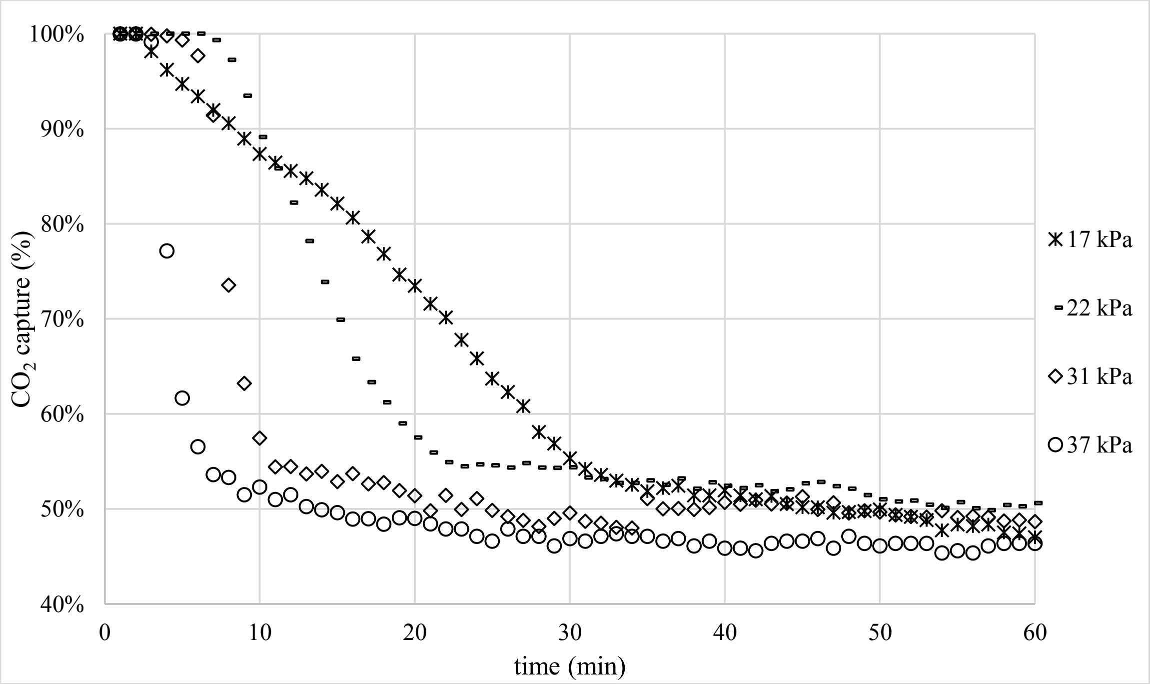

Figure 25: CO_2 captured by 50 g of dry fly ash at 700 °C

At a given initial time period, higher CO_2 capture was noted for dry quicklime (Figure 26) compared to that for dry fly ash (Figure 25). For example, at the 20th minute, dry fly ash captured between 51-75%, while dry quicklime captured between 85-98% of CO_2. This was due to the higher amount (>90%) of CaO in the former compared to only 37.25% in latter. However, the characteristics of capture in both samples at different partial pressure are similar.

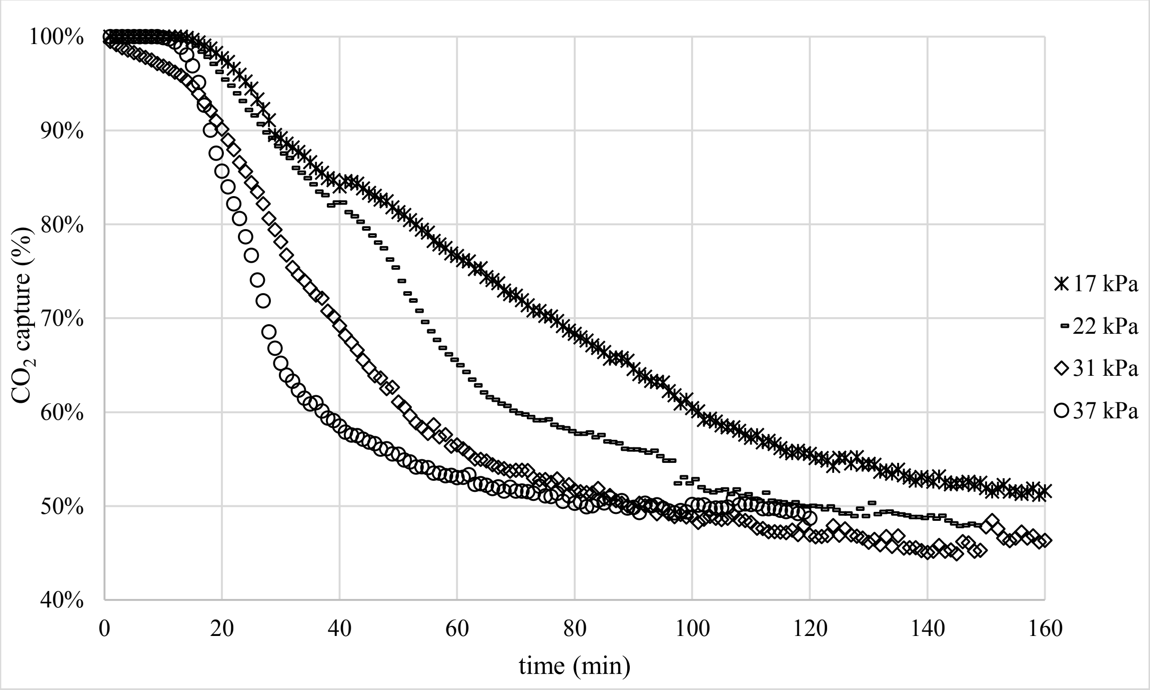

Figure 26: CO_2 captured by 50g of dry quicklime at 700 °C

Figure 27 shows the amount of CO_2 captured at 700 °C per unit mass of fly ash or quicklime sample at different CO_2 partial pressure during the first reaction stage, which is a kinetically controlled regime. As noted by Bhatia and Perlmutter (1983) and Sun et al. (2007), an increase in mass of CO_2 capture per sample mass with increase in CO_2 concentration due to higher surface carbonation rates, and inter particle diffusion rates was observed. However, CO_2 captured in diffusion-controlled regime (slow reaction stage) was independent of CO_2 partial pressure (Figure 26).

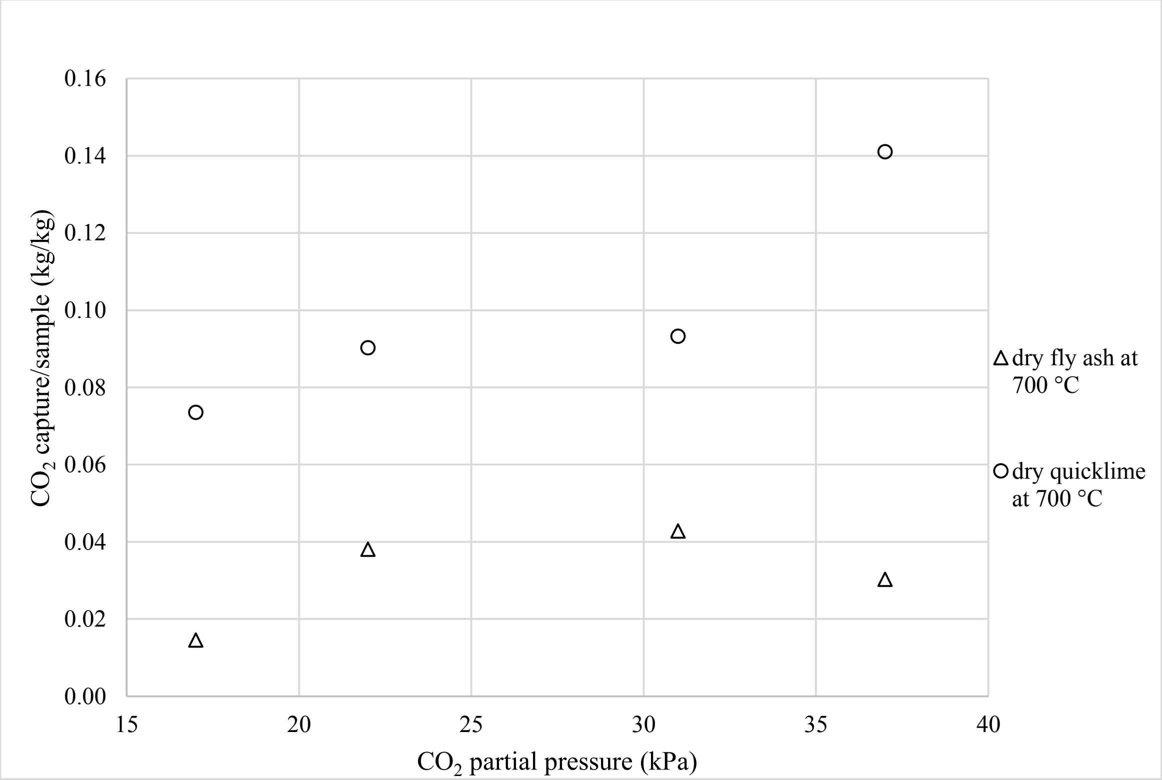

Figure 27: CO_2 captured by dry fly ash and quicklime during rapid reaction stage

4.2.2 Hydrated Test

The effect of CO_2 partial pressures on CO_2 capture by hydrated fly ash and by hydrated quicklime at 50 °C is shown in Figure 28 and Figure 29 respectively. It is apparent that at the start, carbonation reaction took place on the surface of the sorbent, under kinetically controlled regime, and once a $CaCO_3$ layer builds up on the sorbent surface the reaction is controlled by diffusion of CO_2 into the pores. The speed of surface carbonation (kinetically controlled) was higher for higher CO_2 partial pressure, and this trend continued till the transition of reaction stage. This characteristic was similar to that of dry test cases (Figure 25 and Figure 26). In the diffusion-controlled regime, no effect of CO_2 partial pressure was observed as it was governed by diffusion rate of CO_2. This observation was similar to those made by others Bhatia and Perlmutter (1983) and Shimzu et al. (1999). The reasons for higher capture by hydrated samples in comparison with dry samples have been discussed earlier.

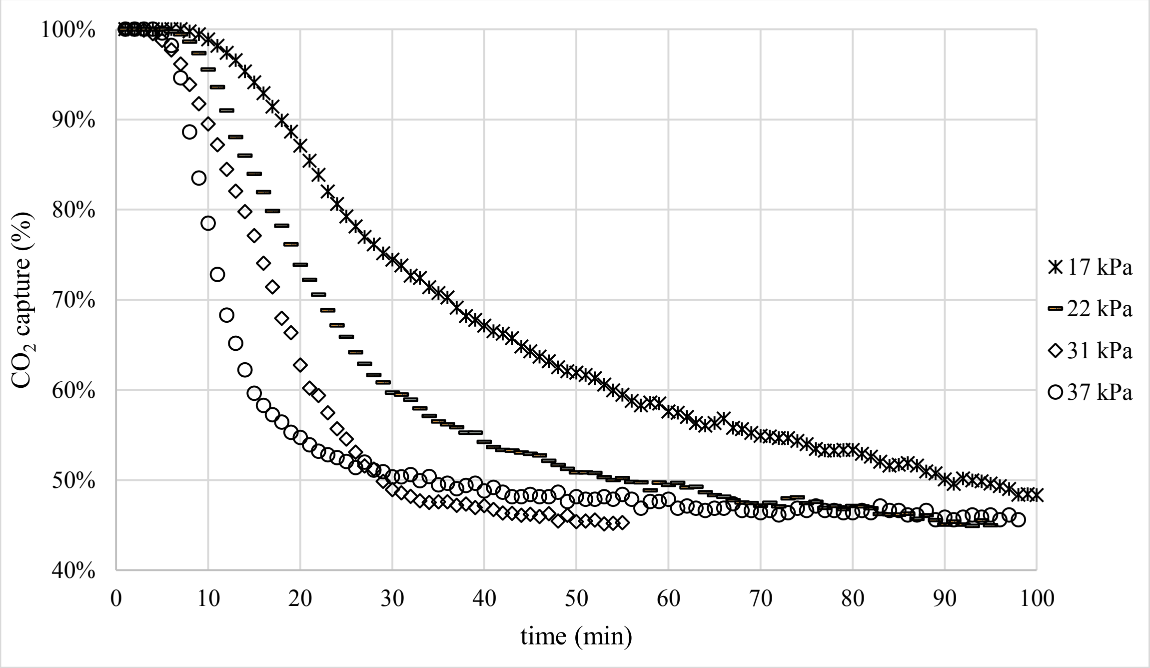

Figure 28: CO_2 captured by hydrated fly ash at 50 °C

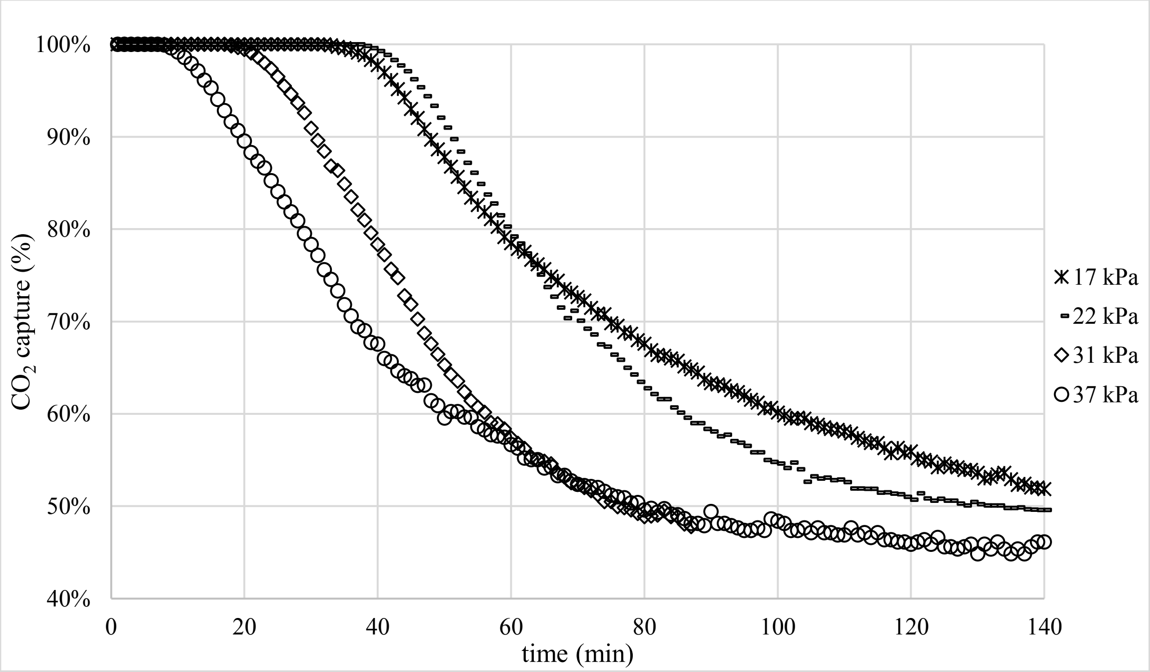

Figure 29: CO_2 captured by hydrated quicklime at 50 °C

The variation of CO_2 captured per unit mass of hydrated sample with CO_2 partial pressure during the initial fast reaction stage at 50 °C is shown in Figure 30. There was a negligible effect of CO_2 partial pressure on CO_2 capture for the hydrated fly ash. Sun et al. (2007) also made similar observation for hydrated fly ash. However, hydrated quicklime showed a steep increase in CO_2 capture with increase in partial pressure from 17 kPa to 22 kPa (Figure 30), but above 30 kPa there was steady reduction till 37 kPa. This could be because of the carbonation of hydrated quicklime, being an exothermic reaction, released heat that increased reaction temperature and above a certain temperature, the capture started to reduce. This is evident from Figure 21, where increase in temperature above 60 °C, at 30% CO_2 concentration, showed significant reduction in capture in the rapid reaction stage.

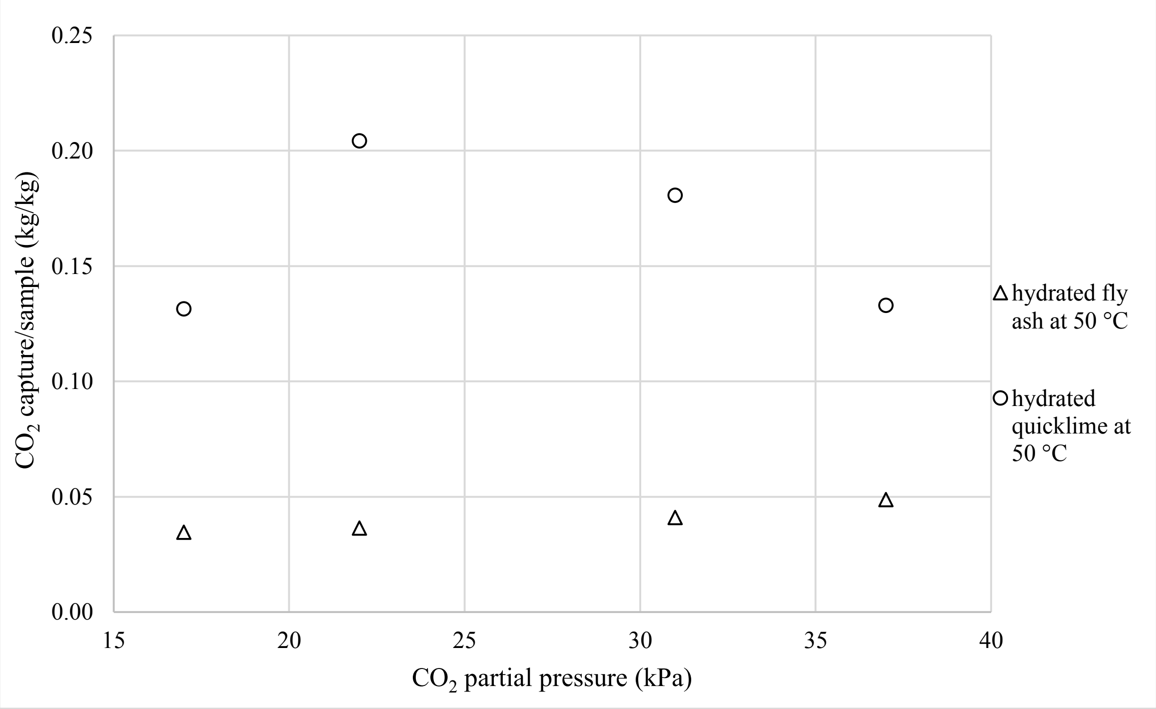

Figure 30: CO_2 captured by hydrated fly ash and quicklime during fast reaction stage

The change in the temperature inside the reactor due to exothermic carbonation reaction, at 50 °C in hydrated quicklime, at different CO_2 partial pressure is shown in Figure 31. At the start of the experiments, there was a sudden increase in the temperature in all cases of the kinetically controlled regime. The duration of increase in temperature was longer at lower partial pressure than that at higher partial pressure, which is analogous to the duration of rapid reaction stage in those experiments. The rapid reaction stage is followed by a slower CO_2 diffusion regime where the temperature again fell back to the set reactor temperature. In this regime, there was no noticeable increase in the temperature observed due to the slow carbonation reaction and CO_2 diffusion in to pores. Figure 31 shows that at CO_2 partial pressures 17 kPa and 37 kPa, the increase in temperature was around 5 °C and 15 °C respectively. The reduction in amount of CO_2 captured in rapid reaction stage above 30 kPa partial pressure (Figure 30) could be because of this sudden increase in local temperature at the reaction site.

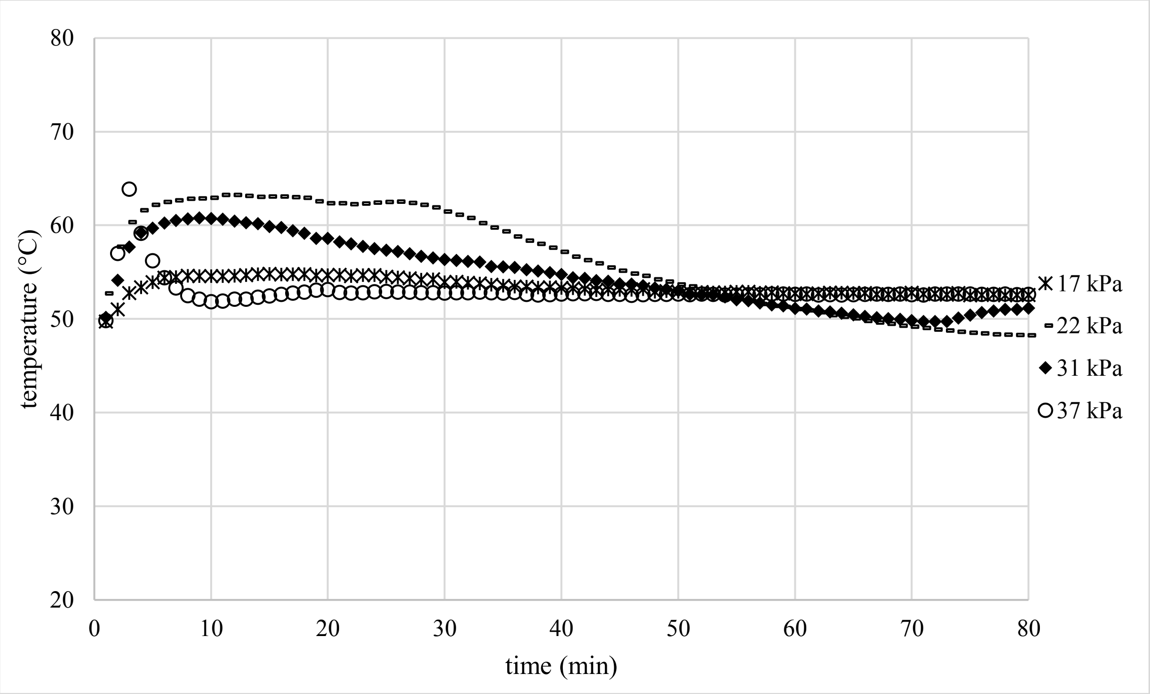

Figure 31: Change in reaction temperature during carbonation reaction of lime at reactor temperature of 50 °C

4.3 EFFECT OF PARTICLE SIZE

Circulating fluidized bed boilers produces two types of ash; fly ash and bed ash. The ratio of fly ash and bottom ash depends on a number of factors, and this ratio could be as high as 50:50 for high ash coal. Bottom ash is coarse and typically in 200- 2000 micron range while the fly ash is much finer in the range of 20- 200 micron. In Point Aconi plant both sizes were, however, relatively small. The average size of fly ash as shown in Figure 13 is very small (20- 50 micron) while that of bed ash was about 300 micron. So, it is necessary to examine if the coarser bottom ash from a CFB boiler with limestone addition could make any contribution to the CO_2 capture.

The effect of particle size on the carbonation reaction of bottom ash and dry lime at 700 °C and at 31 kPa CO_2 partial is shown in Figure 32 and Figure 33 respectively. It can be seen in Figure 32 that there was no notable difference in CO_2 capture by bottom ash of any particle size observed.

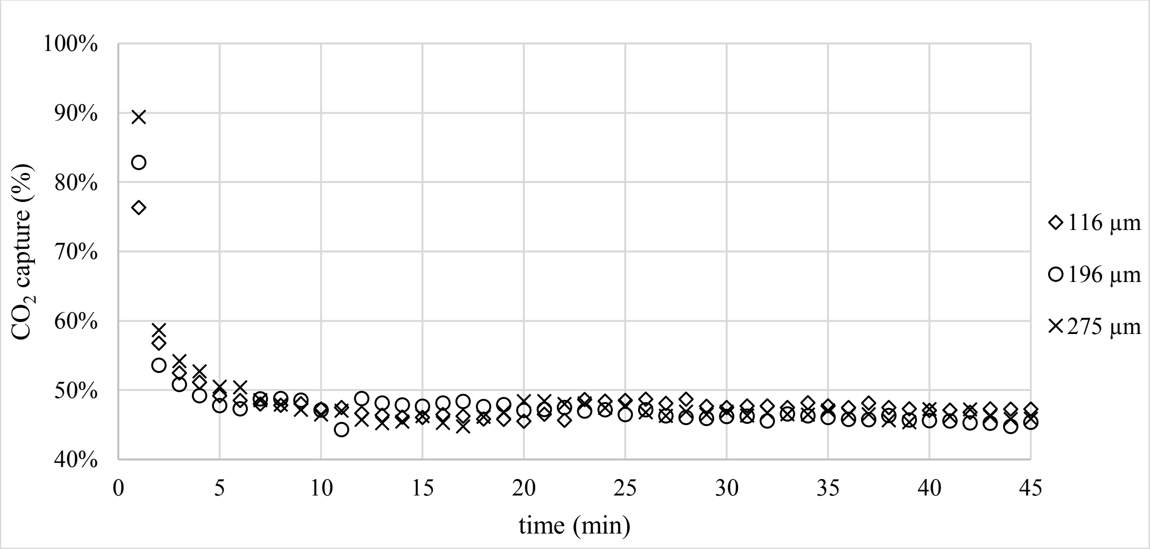

Figure 32: CO_2 captured by dry bottom ash at 700 °C

There was not much capture in the initial stage of reaction as was observed for much finer fly ash, and all the particle sizes carbonated under diffusion controlled regime soon after the start of the experiment. After 5 minutes, CO_2 captured by bottom ash reduced to around 50% (Figure 32), whereas dry fly ash captured nearly 98% of the CO_2 supplied for similar experiments (Figure 16).

The CO_2 captured by dry lime for similar condition and particle sizes is shown in Figure 33. It can be seen that at 19th minute (in the fast reaction stage), CO_2 captured by 116µm, 196µm and 275µm lime particles was 100%, 98% and 95% respectively. This could be due to smaller particles have higher pore surface area than larger particles. Similar results have been observed by Samari, (2014), and, for the same reason, the transition from rapid kinetically controlled regime to slow diffusion controlled regime occurred early for larger particles than smaller particles.

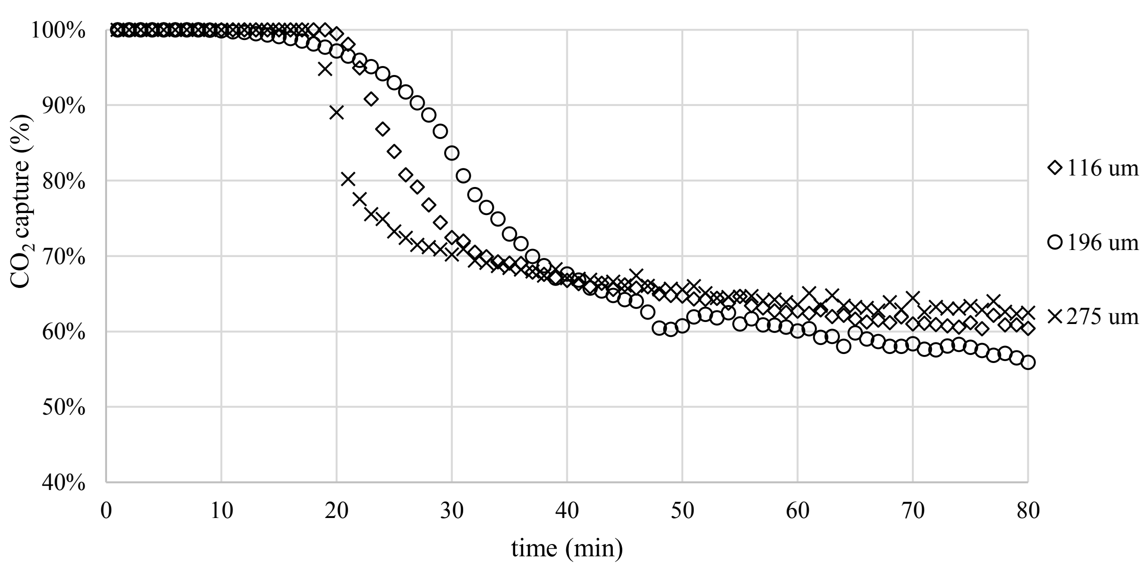

Figure 33: CO_2 captured by dry quicklime at 700 °C

A comparison of mass of CO_2 captured per unit mass of dry lime or bottom ash during the kinetically controlled regime is shown in Figure 34. Dry lime captured significantly higher amount of CO_2 than bottom ash due to its higher lime content. In case of dry lime, particles smaller than 200 µm captured more than 0.15 kg CO_2 per unit lime compared to around 0.13 kg CO_2 captured by particles larger than 275 µm. Interestingly, there was no major difference in the mass of CO_2 captured by bottom ash of any particle size; all the bottom ash samples captured around 0.015 kg CO_2 per unit sample. This showed that the amount of CO_2 captured by bottom ash during first 1-2 minutes was nearly same for any particle size at 700 °C.

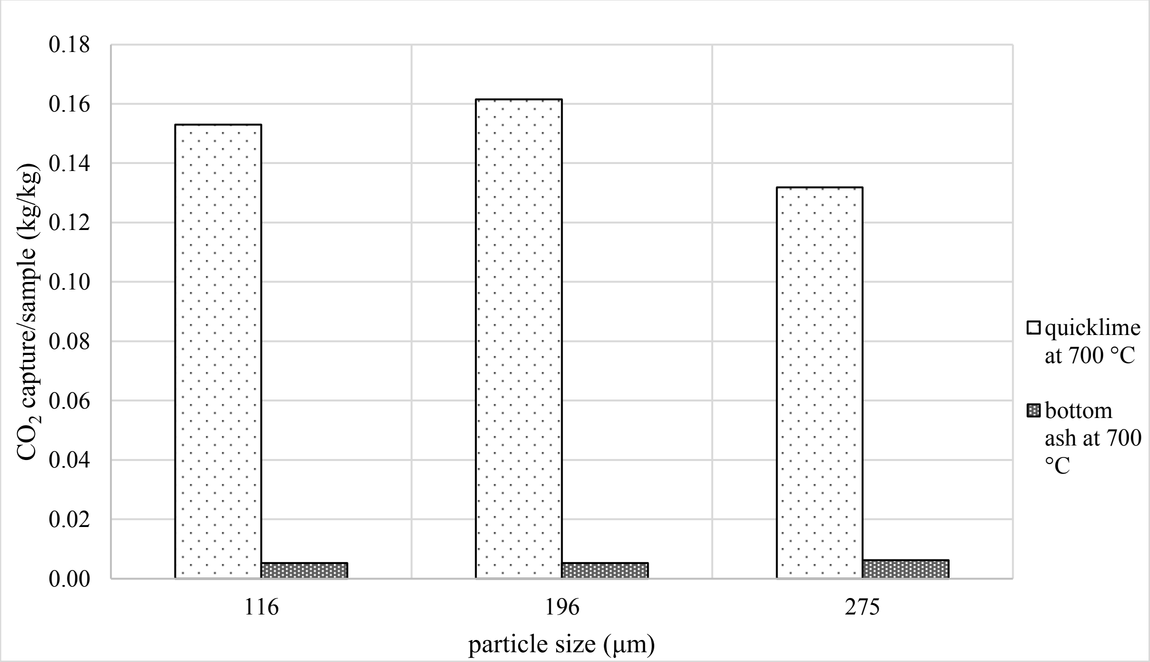

Figure 34: CO_2 captured per unit sample at 700 °C during initial rapid reaction stage

4.4 POTENTIAL APPLICATION IN POINT ACONI BOILER

The following table gives the overall performance of the Point Aconi CFB boiler that runs on a mixture of coal and petcoke. It shows that if all unreacted CaO in the fly ash can be utilized the maximum reduction in CO_2 emission of the plant would be 20.2 million tons per year. This translates into 1.4% of the total emission from the plant. The percentage figure does not appear to be very attractive but if one compares the energy and auxiliary power consumption of this option with other options like amine scrubbing one will find it to be exceptionally attractive. Additional feature is that though the amount of capture and sequestration is small the carbon capture remains in most stable form without any possibility of being released to the atmosphere.

Another futuristic option is recycling of fly ash in the boiler to capture additional SO_2 and burning of unburnt carbon. This potential could theoretically provide a closed loop solution of CFB boiler however small it might be.

Table 4: CO_2 capture potential at Point Aconi power plant

MWe	197
Steam flow rate, TPH	527
Steam temperature, °C	540
Steam pressure, bar	128
Mass of CO_2 produced, kg/s	50.2
Heat input, MWt	485

Fuel feed rate, kg/s	16.83
Limestone feed rate, kg/s	1.55
Amount of fly ash produced, kg/s	2.38
CaO fraction in fly ash	0.38
Maximum CO_2 absorbed, kg/s	0.70
Yearly reduction in CO_2, mT/yr	20.21
Reduction in CO_2	1.40%

CHAPTER 5: RECOMMENDATION FOR FUTURE WORK

1. Further research on the engineering feasibility and economic analysis of this method should be conducted and compared with the other carbon mitigation methods to evaluate the commercial potential.
2. Carbonated CFB fly ash would have significantly less free lime compared to fresh fly ash. So, the application of this ash in building and construction materials such as brick, cement and concrete could be investigated.
3. A study on increasing the effectiveness of carbon dioxide capture rate of CFB ash by addition of additives, such as ammonia, would be helpful.
4. This study investigated carbonation of un-treated fly ash at atmospheric pressure. So, carbonation reaction of CFB fly ash in pressurised dry, and aqueous conditions could possibly show a better option.
5. This thesis represents CFB ash carbonation in small scale reactor; a work on design and operation of a pilot scale plant for continuous CO_2 capture by CFB fly ash would be interesting to study.

CHAPTER 6: CONCLUSION

Investigation into the carbonation of untreated CFB ash in dry and hydrated conditions to capture CO_2 from CFB power plants showed that carbonation reaction in CFB ash and lime is feasible and they follow the pattern: rapid initial conversion of the sorbent, followed by a very slow reaction.

Carbon dioxide capture in the initial fast-reaction regime increased with temperature, but above a certain temperature (700 °C for dry cases and 50 °C for hydrated cases) the capture rate reduced. Increase in temperature from 600 °C to 700 °C in dry fly ash, and, 40 °C to 50 °C in hydrated fly ash, extended the rapid reaction stage by 1 minute in both the cases. Hydrated fly ash showed similar or even higher capture rate than dry fly ash at significantly lower temperature (30-80 °C).

The rapid initial CO_2 capture by fly ash was kinetically controlled and its duration varied inversely with the partial pressure of CO_2. At the highest partial pressure of 37 kPa, the time required to reach the slow diffusion state of capture by hydrated fly ash at 50 °C was around 30 minutes, whereas it was approximately 90 minutes at the lowest partial pressure of 17 kPa. At these partial pressures (37 kPa and 17 kPa), the time required by dry fly ash at 700 °C was 30 minutes and 8 minutes respectively.

No significant effect of particle size for the bottom ash (116 μm to 196 μm) on the capture was observed and the CO_2 capture dropped below 60% just after 1 minute of start of the tests. Similar experiments with the dry fly ash took 10 minutes to drop to the same level.

From above, it could be concluded that CO_2 sequestration by untreated hydrated fly ash could be an option for CO_2 capture from CFB power plants.

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