DESIGN AND DEVELOPMENT OF A CARBONATOR FOR CARBON DIOXIDE CAPTURE USING LOCALLY PRODUCED LIME

By

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DECLARATION

I declare that the work in this thesis entitled "Design and Development of a Carbonator for Carbon Dioxide Capture Using Locally Produced Lime" has been carried out by me in the Department of Chemical Engineering, Ahmadu Bello University Zaria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or another Institution.

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CERTIFICATION

This thesis entitled "Design and Development of a Carbonator for Carbon Dioxide Capture Using Locally Produced Lime" by YUNUSA, Hussaini Mohammed meet the regulation governing the award of Masters of Science Degree in Chemical Engineering of the Ahmadu Bello University, and it is approved for its contribution to knowledge and literacy Presentation.

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DEDICATION

This project work is dedicated to the most beloved, our noble Prophet, Prophet Muhammad (S.A.W).

ACKNOWLEDGEMENT

My deepest and greatest gratitude goes to Almighty Allah for His love and kindness in making this thesis a huge success. May His peace be upon the last prophet, Muhammad (S.A.W), his entire family and those that follow his footsteps until the Last Day.

My profound appreciation goes to my lovely parent, AlhajiYunusa and HajiyaZainaba, my wife and my son, brothers and sisters for their sacrifice and prayer in the course of my academic pursuit.

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To all, I say a big thank you.

ABSTRACT

The work seeks to address environmental issue through the design and development of a carbonator for CO_2 capture. A fixed bed carbonator with height 1.7 m and diameter 0.9 m for CO_2 capture was successfully designed and fabricated at a flow rate 7.9g/hr of carbon dioxide using 2kV household electric generator as a source of flue gas. The flue gas was analyzed using NHA-506EN NANHUA Instrument gas analyzer and the average composition of the flue gas after allowing the generator to ranfor 30min was found to be 7.78% CO, 2.50% CO_2, 46ppm NOx, and 392ppm HC. The material of construction used was mild steel and the fabrication was based on the specifications obtained from Aspes Plus version 11.1 software. Hydrated lime $Ca(OH)_2$ powder was made into pellets of different sizes: 0.8, 1.2, 1.5 and 2cm and packed differently at a height of 0.4m in the carbonator. Flue gas at 150^oC was passed through the bed of hydrated lime at 1atm. The average readings obtained from the outlet of the carbonator (top) were found to be 7.71%CO, 0.06% CO_2, 46ppm NOx and 390ppm HC. These results showed that there was decrease in carbon dioxide concentration as time pass by. For the 0.8cm pellet size and packing height of 0.4 m, there was 97.6% carbon dioxide capture which compares favorably with literature values. The product (used lime) was taken for chemical analysis: XRF analysis gave 56.46%CaO, 1.52% SiO_2, 3.44% Fe_2O_3; X-ray diffraction (XRD) showed that the used lime is crystalline and scanning electron microscopy (SEM) presented irregular, heterogeneous and coarse particles. It was found that fixed bed reactor with 0.8cm pelletized lime was more effective for CO_2 capture.

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LIST OF ABBREVIATIONS

A_p	Surface Area of Particle
$Ca(OH)_2$	Calcium Hydroxide
$CaSiO_3$	Wollastonite
CCS	Carbon Capture and Storage
CERT	Centre for Energy Research and Training
CDIAC	Carbon Dioxide Information Analysis Centre
ChED	Chemical Engineering Department
EIA	Energy Information Administration
EOR	Enhanced Oil Recovery
EPA	Environmental Protection Agency
GHG	Greenhouse Gases
HL	Hydrated Lime
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
IPCC	Intergovernmental Panel on Climate Change
MEA	Monoethanolamine
Mg_2SiO_4	Olivine

$Mg_3Si_2O_5(OH)_4$	Serpentine
NARICT	National Research Institute for Chemical Technology
OECD	Organisation for Economic Co-operation and Development
PC	Pulverized Coal
ppm	Part per million
PS	Pellet Size
SEM	Scanning Electron Microscope
USAID	United States Agency for International Development
V_p	Volume of particle
XRD	X-ray diffraction

CHAPTER ONE

INTRODUCTION

1.1 Preamble

Carbon dioxide (CO_2) is a naturally occurring gas which plants use to live and grow. Over millions of years, plants and algae have been buried to produce oil and natural gas deposits, effectively 'locking away' the CO_2 they were using. When fossil fuels are burned to produce electricity, the carbon within them is released back into the carbon cycle as CO_2. This is now being emitted at such a rapid rate that the Earth's natural carbon cycle cannot accommodate. Rising concentration of CO_2 in the atmosphere is causing climate change; this involves global warming, increases in extreme weather events, ocean acidification and sea level rise. Reducing the rate of CO_2 emissions is, consequently, a priority (Research Council UK, 2008).

Fossil fuels, namely coal, natural gas, and oil, are currently the dominant sources of energy used for electricity generation worldwide. Nearly 70% of the world's electricity is derived from a fossil fuel source with coal accounting for 41% of the world's electricity generation (IEA, 2010). While coal utilization comprises a significant fraction of total electricity generation, it is also responsible for 43% of the world's carbon dioxide emissions (International Energy Agency, 2010). With increasing concern over carbon dioxide emissions, current efforts are focused on processes that can economically and efficiently reduce carbon dioxide emissions to the atmosphere.

There are various technologies for capturing CO_2 from a mixture of gases. These technologies are classified into four main groups: post-combustion, pre-combustion, oxyfuel combustion and industrial separation. Of course, the only large scale and

proven commercially available technology to separate CO_2 from combustion gases is based on amine absorption systems (Rao and Rubin, 2002).

Calcium-based sorbents have been extensively used for removal of acid gases. The most recent technologies have focused on CO_2 removal using either calcium oxide or calcium hydroxide, which can simultaneously reduce the concentrations of additional acid gases. This research work focuses on post combustion capture using calcium hydroxide ($Ca(OH)_2$) as sorbent.

1.2 Problem Statement

Anthropogenic carbon dioxide (CO_2) emissions are contributing to global climate change. Works on CO_2 capture using locally sourced hydrated lime is limited. There is therefore need to design and develop carbonator to test the effectiveness of locally sourced hydrated lime.

1.3 Justification

The following are the justifications for this research work

i) Fabricated pilot plant carbonator can serve as study aids for students of chemical engineering and related fields.

ii) Design and construction data will be provided for Nigerian based sorbent for carbon dioxide capture.

iii) Availability of locally produced lime

1.4 Aim and Objectives

1.4.1 Research aim

The aim of this research is to design and fabricate a carbonator for carbon dioxide capture from generator emission using locally produced lime.

1.4.2 Research objective

i) To design a carbonator to capture CO_2.

ii) To fabricate the carbonator.

iii) To test run the carbonator.

iv) To analyse the used lime.

1.5 Research Scope

The work will be limited to the use of lime produced from Jakura limestone to capture carbon dioxide emitted from household generator.

CHAPTER TWO

LITERATURE SURVEY

2.1 Global Climate Change

Global climate change is one of the most prominent environmental and energy policy issues of our age. Although scientific and economic uncertainties remain, there is little doubt that human beings are altering the Earth's climate (Crowley, 2000). Through the burning of fossil fuels, certain industrial processes, and various land use practices, we are contributing greatly to the accumulation of so-called greenhouse gases (GHGs) in the atmosphere, which trap heat and block outward radiation. By far the most prevalent of these GHGs is CO_2. About 96% of these carbon emissions resulted from using fossil fuels for energy. For these reasons, climate change discussions have been focused on the reduction of CO_2 (EPA, 2002).

Currently, about 60% of the emitted carbon is held in the atmosphere. The other 40% is converted into so-called 'carbon sinks' such as oceans, forests and rocks. Over geological times naturally occurring rock weathering is an important carbon sink. Carbonate rocks form the world's biggest carbon reservoir as was shown in Table 1 (Liu *et al.*, 2000).

Table 2.1: Distribution of Carbon on earth (Dunsmore 1992).

Source	**Amount (10^{15} kg)**	**Relative amount (%)**
Calcium carbonate	*35,000*	46.64
Ca-Mg-carbonate	25,000	33.31
Total carbonates	60,000	79.99
Sedimentary carbon(e.g. graphite)	15,000	19.99
Fossil fuels	4	0.0053
Other geological carbon	15,004	19.99
Total carbon in lithosphere	*75,004*	99.94
Oceanic HCO^-_3 and CO^{2-}_3	42	0.056
Dead surficial carbon(e.g humus)	3	0.0040
Atmospheric CO_2	0.72	0.00095
All life	0.56	0.00074
Total non-geological carbon	46.28	0.06

Since the industrial revolution, anthropogenic (man-made) emissions of CO_2 have increased

significantly. It is this dramatic increase in atmospheric CO_2 that is the main cause of global warming. According to the carbon cycle, increasing atmospheric concentration of CO_2 has the knock-on effect of increasing the amount of dissolved CO_2 in the oceans. This dissolved CO_2 then reacts with the ocean water to produce carbonic acid, decreasing the pH. The threat of ocean acidificationis vastlyunderestimated (Research Council UK, 2008).

Itaffects all sea lifeand ecosystems,which in turn wouldhave an impact onhuman systems.There are not big emptyspaces undergroundto store CO_2. Just likeoil and gas, CO_2 canbe stored betweenthe grains of therock, within the pore spaces. It does notseem obvious tothe naked eye, butthere is a lot of spacebetween the smallgrains of sandstone(Research Council UK, 2008).

Concentrations of atmospheric CO_2 have been increasing from approximately 280 ppmv in the pre-industrial era to 389.47 ppmv, as measured in April 2009 as shown in

Figure 2.1. The detrimental effects of increasing CO_2 levels on global climate have been well documented, and it is clear that there is a need to reduce CO_2 levels. According to the United Nations Intergovernmental Panel on Climate Change (IPCC) report (IPCC , 2007), climate change has been proven to be unequivocally linked to human activity from observations of increases in global average air and ocean temperatures, rising global average sea levels and widespread melting of sea-ice in the Arctic.

To begin to understand Nigeria's contribution to global climate change, the country's carbon dioxide emissions must first be observed. Figure 2.2 provides good representation of CO_2 emissions in Nigeria. The total amount of **CO_2** emissions in Nigeria is approximately 22,700 metric tons of carbon. As regards to gas flaring, the **CO_2** emitted by this occurrence increases rapidly around 1970 and then decreases to minimal levels around the year 1990. Shortly after 1995, the levels of flaring induced **CO_2** levels once again increase. The levels of flaring also seem to have a strong influence on overall levels of **CO_2** being emitted by Nigeria. When flaring spikes, so does the overall **CO_2** levels. When flaring decreases, the levels of **CO_2** follow. Levels of **CO_2** emitted from liquids also provide for some fluctuations on the graph, **CO_2** emitted from liquids increases around 1975, and then peaks around the year 1995. After this peak,**CO_2** levels emitted from liquids declines, with some fluctuations (Carbon Dioxide Information Analysis Centre, 2013).

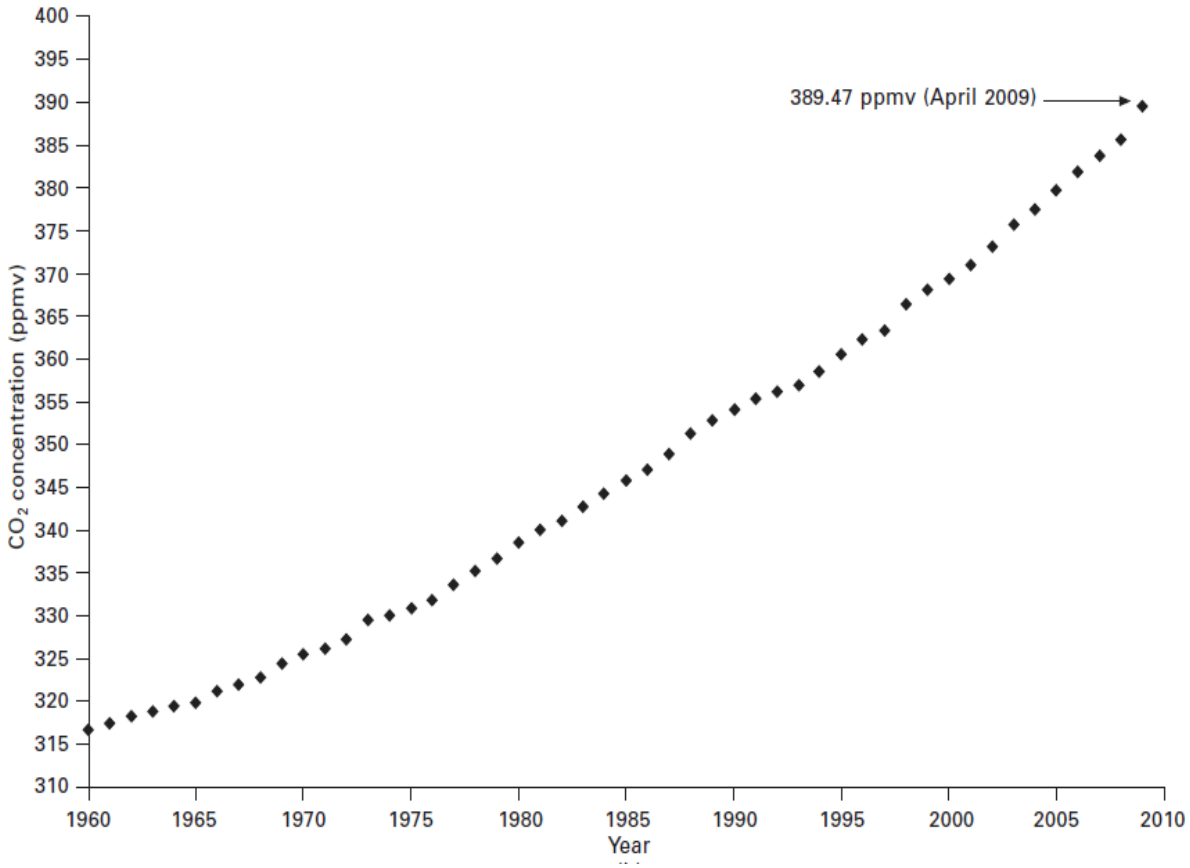


Figure 2.1: Average annual atmospheric CO_2 concentrations based on direct measurements at Mauna Loa Observatory from 1960–2009 (Maroto-Valer, 2010).

Nigeria began emitting significant levels of **CO_2** around the year 1972. Nigeria's highest emission levels occurred just before 2010, but seem to be increasing. Although significant levels of **CO_2** emissions did not start until around 1972, levels of**CO_2** started to increase gradually after 1958. This can most likely be accredited to the beginning of oil production in Nigeria. However, Nigeria holds the largest area of natural gas reserves in Africa. In 2007, the Nigerian National Petroleum Corporation calculated that approximately 40 percent of the country's gas production was flared, resulting in about 45 million tons of **CO_2** emissions, one of the principal greenhouse gases that causes global climate change (CDIAC, 2013). Gas flaring is a process in which excess gas from drilling associated with natural gas or oil is burned off,

releasing**CO_2** into the atmosphere. With proper infrastructure, it is possible to harness flaring, thus converting it into usable energy which would indefinitely reduce **CO_2** emissions in Nigeria (CDIAC, 2013).

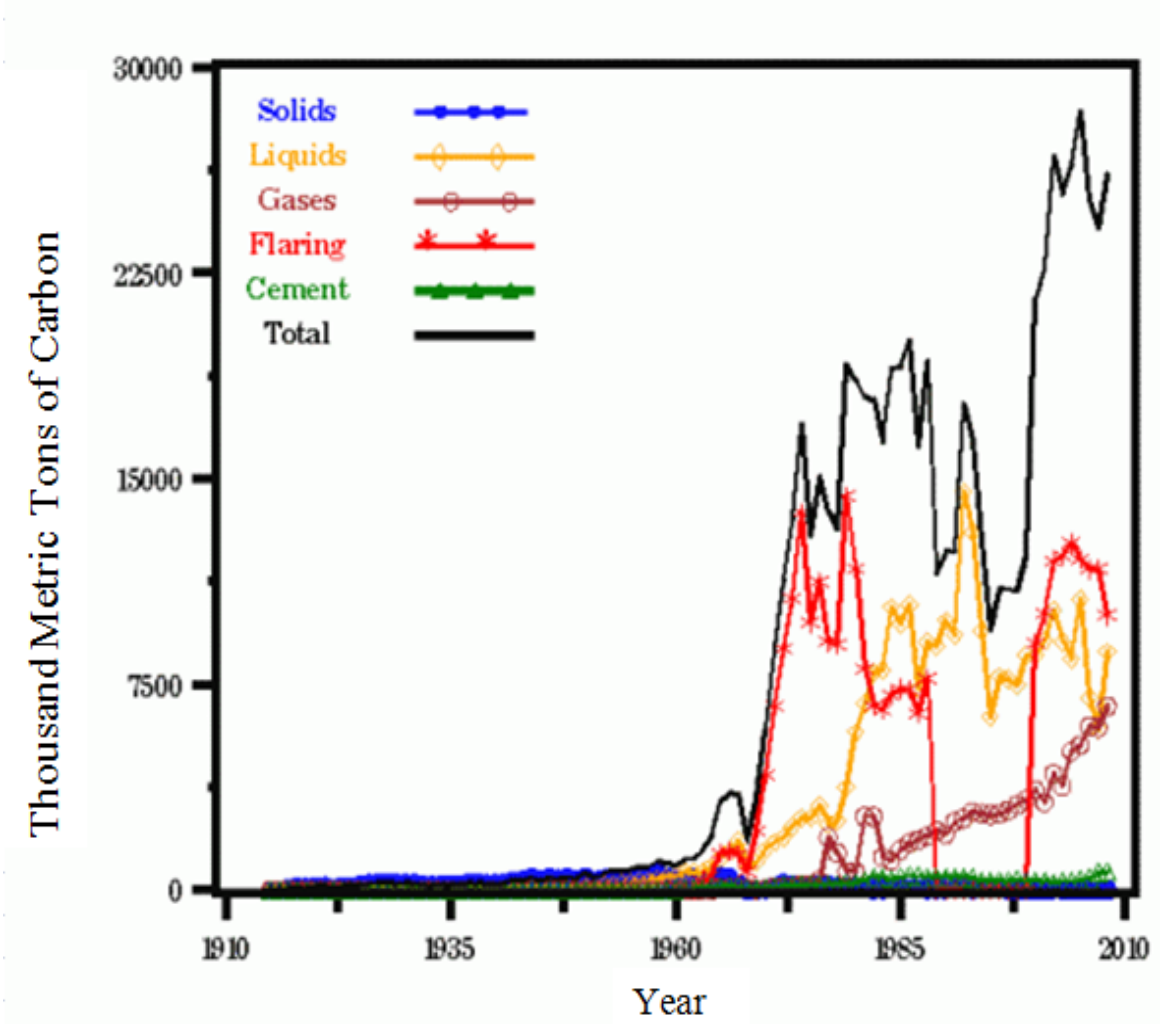


Figure 2.2: Carbon emissions per capita for Nigeria (metric tons of carbon) (Carbon Dioxide Information Analysis Centre, 2013)

Globally, the Intergovernmental Panel on Climate Change (IPCC) concludes a significant reduction of worldwide greenhouse-gas (GHG) emissions is required in order to stabilise the global average temperature increase at 2.0°C to 2.4°C above pre-industrial levels. Equivalent CO_2 emissions need to be cut by at least 50% by 2050 compared to the year 2000 (IPCC, 2007). The IEA regularly analyses pathways for

reducing energy-related CO_2 emissions. Compared to a business-as-usual Baseline Scenario, carbon capture and storage (CCS) from power generation could contribute in 2050 to 10% of the required global reduction in energy-related CO_2 emissions (IEA, 2009). Apart from CCS in power generation, CCS from industrial and upstream applications is expected to provide a similar emission reduction. CCS is thus a potential key contributor to CO_2 emission mitigation, in addition to other important aims such as improving energy efficiency and increasing renewable power generation.

CCS has been applied commercially in the oil and gas industry for several decades. This includes technologies along the CCS value chain such as solvent-based separation of CO_2 from gas streams, transportation of CO_2 by pipeline and storage of CO_2 in aquifers. CO_2 is also used for enhanced oil recovery (EOR).

CO_2 capture and storage (CCS) is a technically feasible strategy to reduce anthropogenic CO_2 emissions from large point sources, and particularly fossil fuel-fired power plants, by up to 90 % (IPCC, 2005). One of the key features of this technology is that it allows for the continued use of fossil fuels, including coal which is relatively cheap and abundant, while simultaneously reducing CO_2 emissions to the atmosphere. Overall, CCS consists of three main steps: separating and capturing CO_2 from other exhaust gases; compressing the CO_2 to supercritical conditions in order to transport it to its storage location and final isolation from the atmosphere by a variety of methods as illustrated in Figure 2.3.

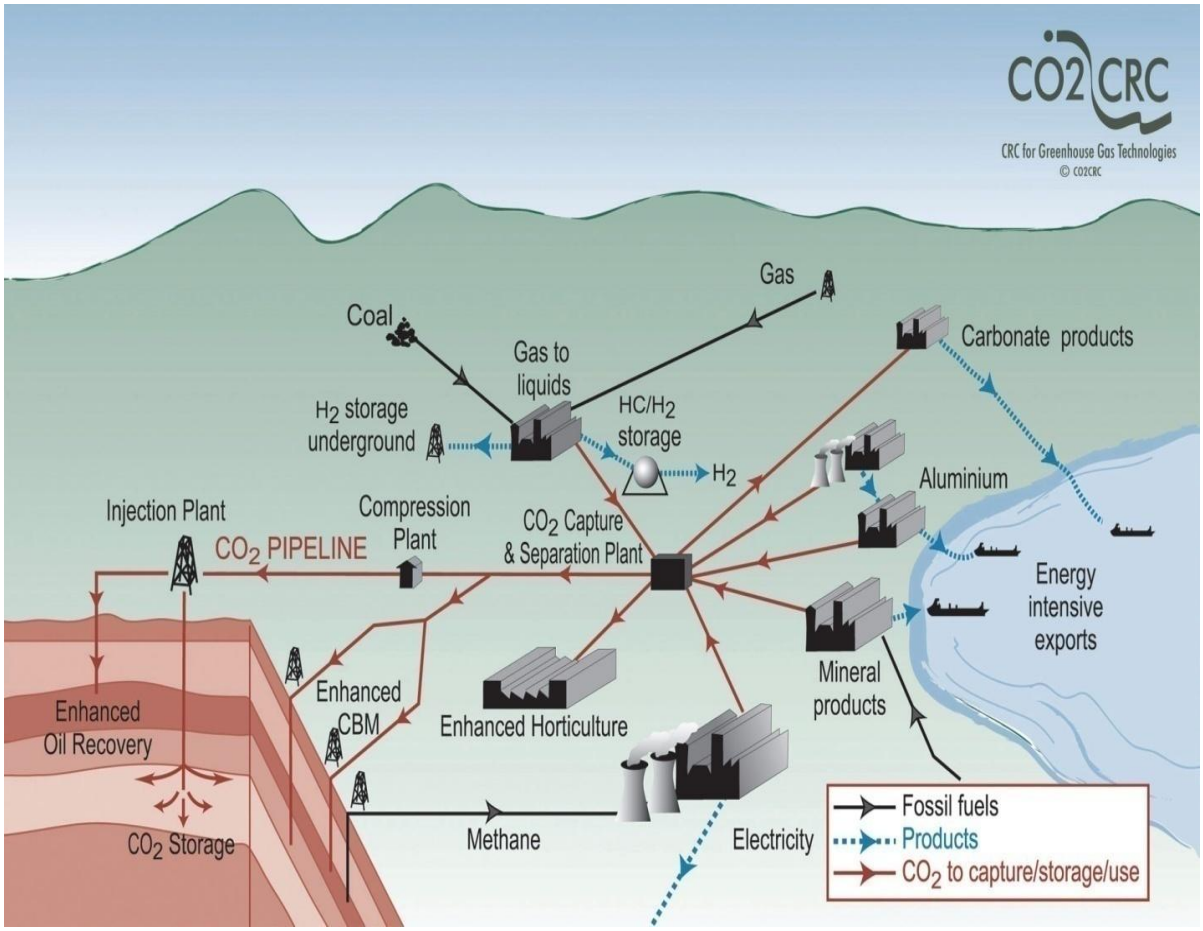


Figure 2.3: Schematic diagram of various CCS alternatives (CO_2CRC, 2007).

CCS is however still an emerging technology in the power sector, where it has not yet been demonstrated at large scale. Applying CCS to full-size power plants requires scale-up of commercially available CO_2 capture processes. Consequently, current cost and performance information related to CCS from power generation is limited to estimates from engineering studies and pilot projects. This is different to established power technologies for which cost and performance data of commercial units are well known and regularly summarized (OECD, 2010).

2.2 Overview of CO_2 Capture Technologies

A variety of technologies for separating (capturing) CO_2 from a mixture of gases are commercially available and widely used today, typically as a purification step in an

industrial process. Figure 2.4 illustrates the variety of technical approaches available. The choice of technology depends on the requirements for product purity and on the conditions of the gas stream being treated (such as its temperature, pressure, and CO_2 concentration). Common applications for CO_2 capture systems include the removal of CO_2 impurities in natural gas treatment and the production of hydrogen, ammonia, and other industrial chemicals. In a few cases it is used in the manufacture of other chemicals (Metz *et al*., 2005).

2.2.1 Post-combustion processes

As the name implies, these systems capture CO_2 from the flue gases produced after fossil fuels or other carbonaceous materials (such as biomass) are burned. Combustion-based power plants provide most of the world's electricity today. In a modern coal-fired power plant, pulverized coal (PC) is mixed with air and burned in a furnace or boiler. The heat released by combustion generates steam, which drives a turbine-generator as can be seen in Figure 2.5. The hot combustion gases exiting the boiler consist mainly of nitrogen (from air) plus smaller concentrations of water vapor and CO_2 formed from the hydrogen and carbon in the fuel.

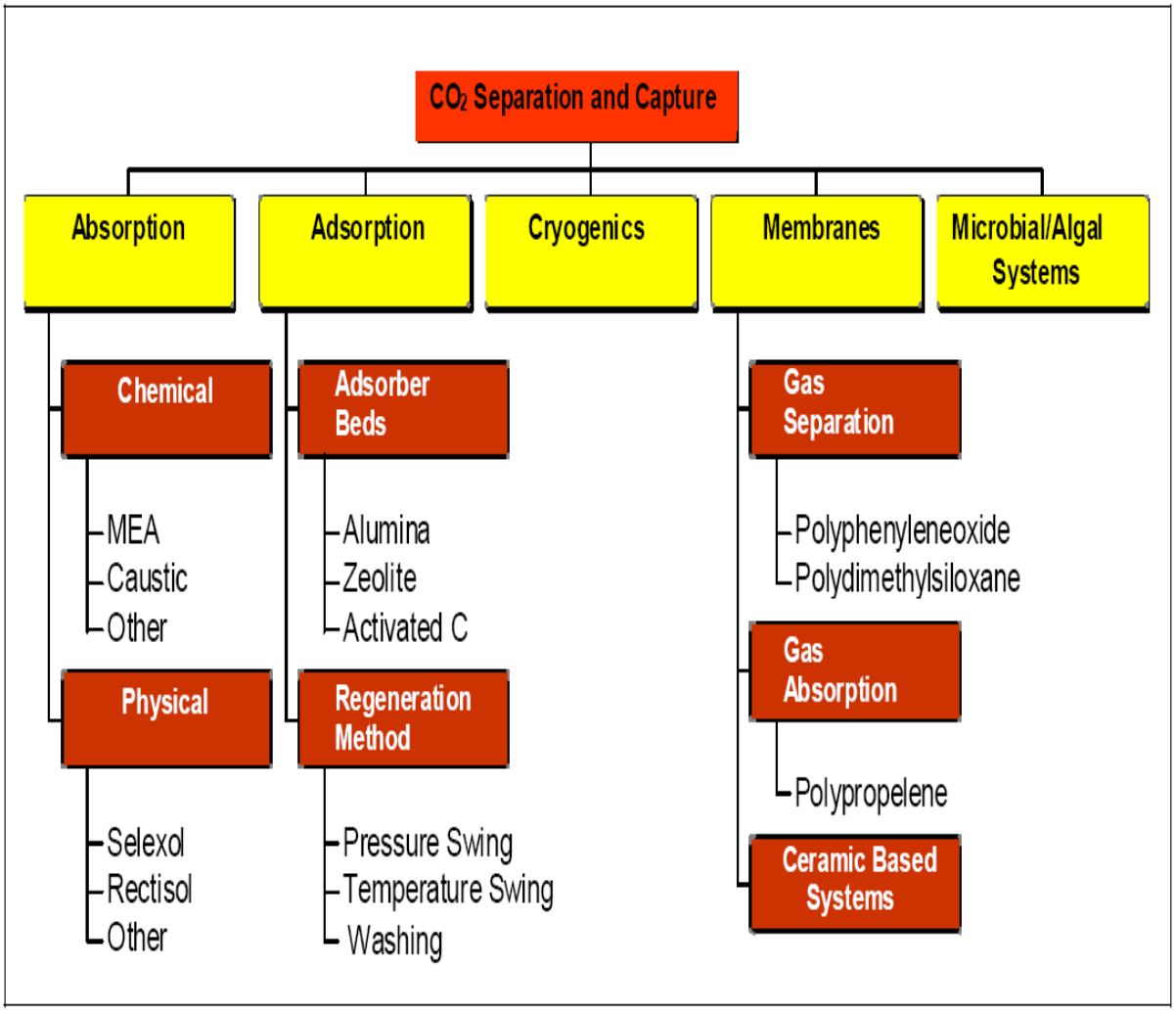


Figure 2.4: Technical Options for CO_2 Capture (Rao and Rubin, 2002)

Additional products formed during combustion from impurities in coal include sulfur dioxide, nitrogen oxides, and particulate matter (fly ash). These regulated air pollutants, as well as other trace species such as mercury, must be removed to meet applicable emission standards. Post-combustion CO_2 capture systems have been in use commercially for many decades, mainly in industrial processes for purifying gas streams other than combustion products. The use of amines to capture CO_2 was first patented 80 years ago and since then has been used to meet CO_2 product specifications in industries ranging from natural gas production to the food and beverage industry (Rochelle, 2009).

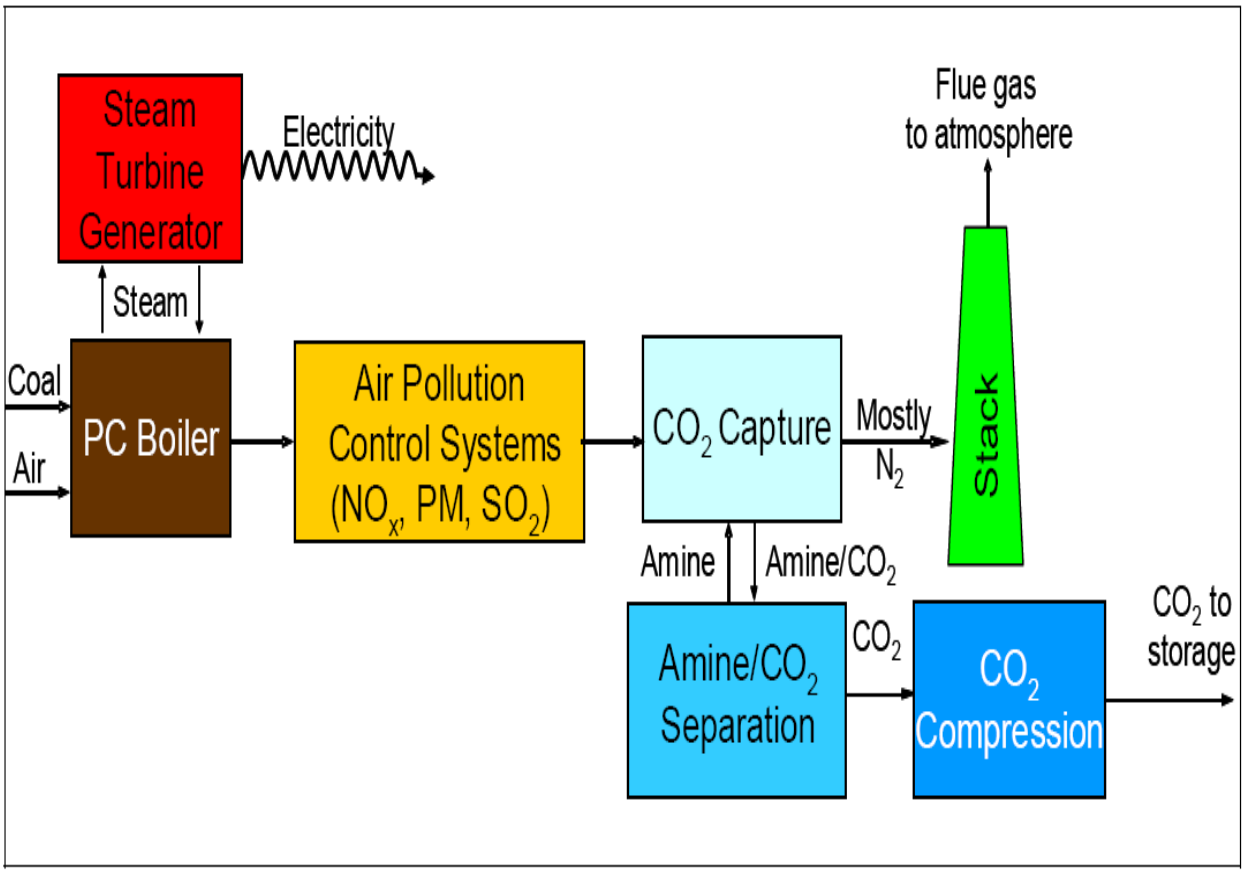


Figure 2.5: Schematic of a Coal-Fired Power Plant with Post-Combustion CO_2 Capture Using an Amine Scrubber System (Rubin, 2008).

There are various types of post combustion CO_2 capture. Some are discussed below:

Amine-based capture processes

Amines are currently used to remove CO_2 from gas streams in several areas of the oil and gas industry, and have been for over sixty years (Spooner and Engel, 2011). These class of solvents called amines (more properly, alkanolamines) are a family of organic compounds that are derivatives of alkanols (commonly called the alcohols group) that contain an "amino" (NH_2) group in their chemical structures. Because of this complexity, there are multiple classifications of amines, each of which has different characteristics relevant to CO_2 capture (Kohl *et al.*, 1997). For example, MEA reacts

strongly with acid gases like CO_2 and has a fast reaction time and an ability to remove high percentages of CO_2, even at the low CO_2 concentrations found in flue gas streams. Other properties of MEA, however, are undesirable, such as its high corrosivity and regeneration energy requirement. Various research groups are involved in synthesizing and testing a variety of amine mixtures and "designer" amines to achieve a more desirable set of overall properties for use in CO_2 capture systems.

The use of amines to capture CO_2 was first patented over eighty years ago. Since then amine-based systems have been used to meet CO_2 product specifications in industries ranging from natural gas production to the food and beverage industry. A number of vendors currently offer commercial amine-based processes, including the Fluor Daniel Econamine FG Plus process, the Mitsubishi Heavy Industries KM-CDR process, the Lummus Kerr-McGee process, the Aker Clean Carbon Just Catch process, the Cansolv CO_2 capture system and the HTC Purenergy Process. The hundreds of commercial aqueous amine systems currently in operation typically vent the captured CO_2 to the atmosphere. Fig. 2.7 shows the amine based capture unit installed more recently at a natural gas treatment plant in Oklahoma, USA. That unit is part of an integrated CCS system that includes CO_2 capture, pipeline transport and sequestration in a depleted gas formation.

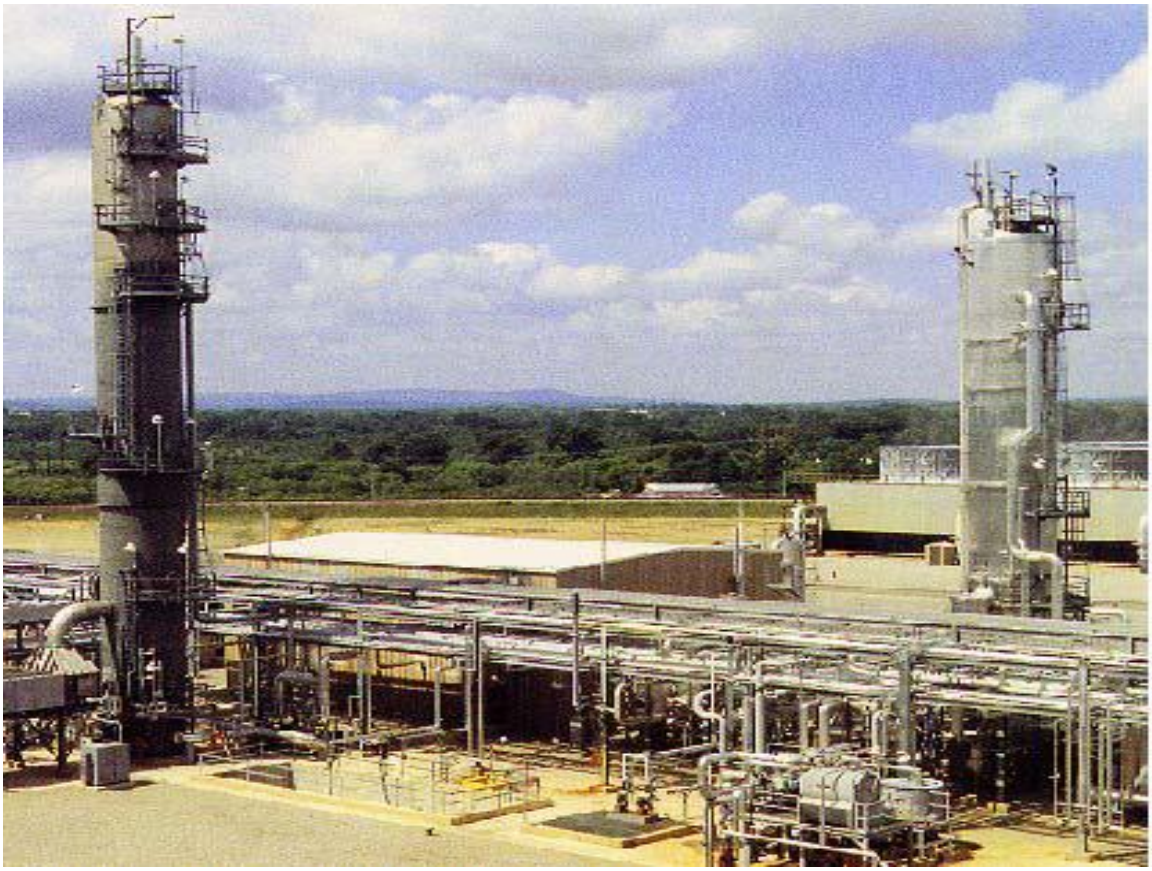


Plate 2.1: Amine-Based Post-Combustion CO_2 Capture Systems Treating a Portion of the Flue Gas from a Coal-Fired Power Plant in Oklahoma, USA (Fogler, 2010).

Challenges of carbon capture using amine

i) Low pressure gas increases difficulty of transferring CO_2 from the gas into amine

ii) Oxygen content of the gas can cause amine degradation and acid formation

iii) CO_2 degradation of primary (and secondary) amines

iv) High energy consumption

v) Very large facilities

b. Liquid solvent-based approaches

Liquid solvents (typically a mixture of a base and water) selectively absorb CO_2 through direct contact between the chemical solvent and the flue gas stream. Regeneration of the solvent and release of CO_2 then takes place in a separate vessel (the regenerator) through a change of process conditions, such as a swing in temperature or pressure. In general, the aim of solvent research is to identify or create new solvents or solvent mixtures that have more desirable characteristics than currently available solvents. Such properties include increases in CO_2 capture capacity, reaction rates, thermal stability, and oxidative stability, along with decreases in regeneration energy, corrosivity, viscosity, volatility, and chemical reactivity with flue gas impurities. All of these attributes tend to lower the cost of CO_2 capture compared to current solvents. Unfortunately, most real solvents exhibit a combination of desirable and undesirable properties. Laboratory- and bench-scale research thus seeks new solvents that yield a more optimal blend of properties.

c. Solid sorbent-based approaches

Solid sorbents capture (adsorb) CO_2 on their surfaces, as shown in Figure 2.8. The capture mechanism can be either a chemical or physical surface interaction. Solid sorbents that rely on chemical mechanisms are similar to liquid solvents. They include amines supported on the surface of other materials (called supported amines), as well as carbonates such as calcium carbonate (limestone) and sodium carbonate (soda ash). Sorbents that rely on physical surface interactions include materials such as activated carbon, zeolites, and metal organic frameworks (MOFs).

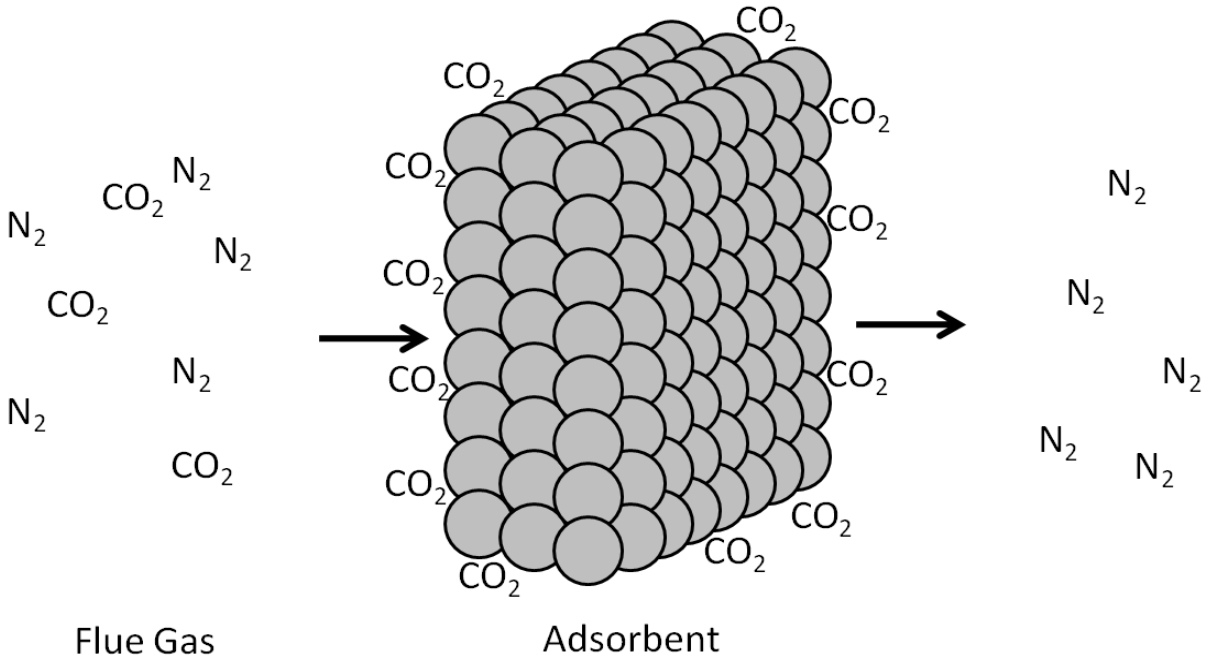


Figure 2.6: Schematic of CO_2 Adsorption on the Surfaces of a Solid Sorbent

(Fogler, 2010)

d. Membrane-based approaches

Membranes are porous materials that can be used to selectively separate CO_2 from other components of a gas stream. They effectively act as a filter, allowing only CO_2 to pass through the material. The driving force for this separation process is a pressure differential across a membrane, which can be created either by compressing the gas on one side of the material or by creating a vacuum on the opposite side. Membranes have been used for gas purification in a number of industrial applications since the 1980s. Two important physical parameters of a membrane are its selectivity and permeability (Kotowicz*et al*, 2010). Selectivity reflects the extent to which a membrane allows some molecules to be transported across the material, but not others. For post-combustion CO_2 capture, the selectivity to CO_2 over N_2 (the main constituent of flue gas) determines the purity of the captured CO_2 stream. The permeability of a membrane

reflects the amount of a given substance that can be transported for a given pressure differences. This determines the membrane surface area needed to separate and capture a given amount of CO_2.

2.2.2 Pre-combustion processes

To remove carbon from fuel prior to combustion, it must first be converted to a form amenable to capture. For coal-fueled plants, this is accomplished by reacting coal with steam and oxygen at high temperature and pressure, a process called partial oxidation, or gasification. The result is a gaseous fuel consisting mainly of carbon monoxide and hydrogen—a mixture known as synthesis gas, or syngas—which can be burned to generate electricity in a combined cycle power plants. This approach is known as integrated gasification combined cycle (IGCC) power generation. After particulate impurities are removed from the syngas, a two-stage "shift reactor" converts the carbon monoxide to CO_2 via a reaction with steam (H_2O). The result is a mixture of CO_2 and hydrogen. A chemical solvent, such as the widely used commercial product Selexol (which employs a glycol-based solvent), then captures the CO_2, leaving a stream of nearly pure hydrogen that is burned in a combined cycle power plant to generate electricity as depicted in Figure 2.9.

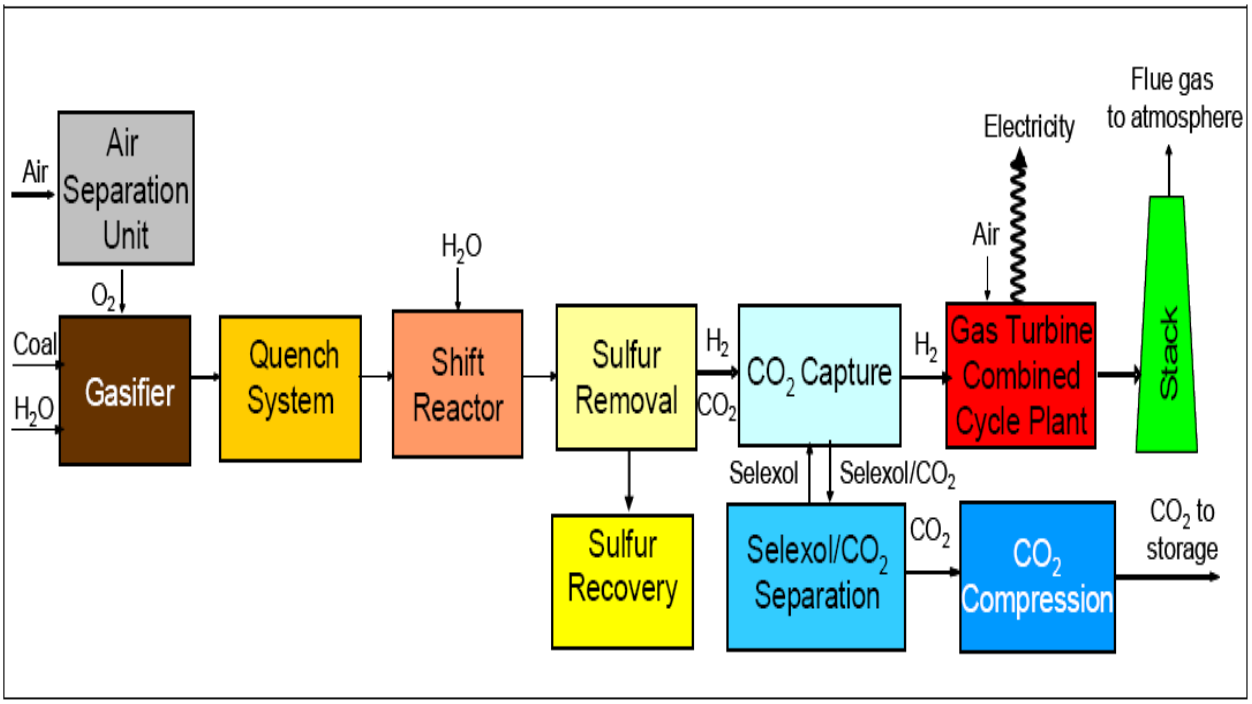


Figure 2.7: Schematic of an Integrated Gasification Combined Cycle (IGCC) Coal Power Plant with Pre-Combustion CO_2 Capture Using a Water-Gas Shift Reactor and a Selexol CO_2 Separation System (Rubin, 2008).

The use of membrane for Pre-combustion CO_2 capture is discussed below:

a) Pre-combustion CO_2 capture using a membrane to separate CO_2

Membrane technology has been used commercially for gas purification and CO_2 removal in the production of hydrogen, but it has not been used specifically for pre-combustion CO_2 capture in IGCC plants or related industrial processes that require a high CO_2 recovery rate with high CO_2 purity. Applications to IGCC are of interest since the mixture of CO_2 and H_2 following the shift reactor is already at high pressure, unlike post-combustion applications, which require additional energy to create a pressure differential across the membrane.

Figure 2.10 shows a schematic of a membrane separation process for CO_2 capture in an IGCC application, where CO_2 is preferentially separated from hydrogen in the gas stream following the water-gas shift and sulfur removal steps. To date, membrane technology has been used commercially for gas purification and CO_2 removal in the production of hydrogen, but it has not been used specifically for pre-combustion CO_2 capture in IGCC plants or related industrial processes that require a high CO_2 recovery rate with high CO_2 purity.

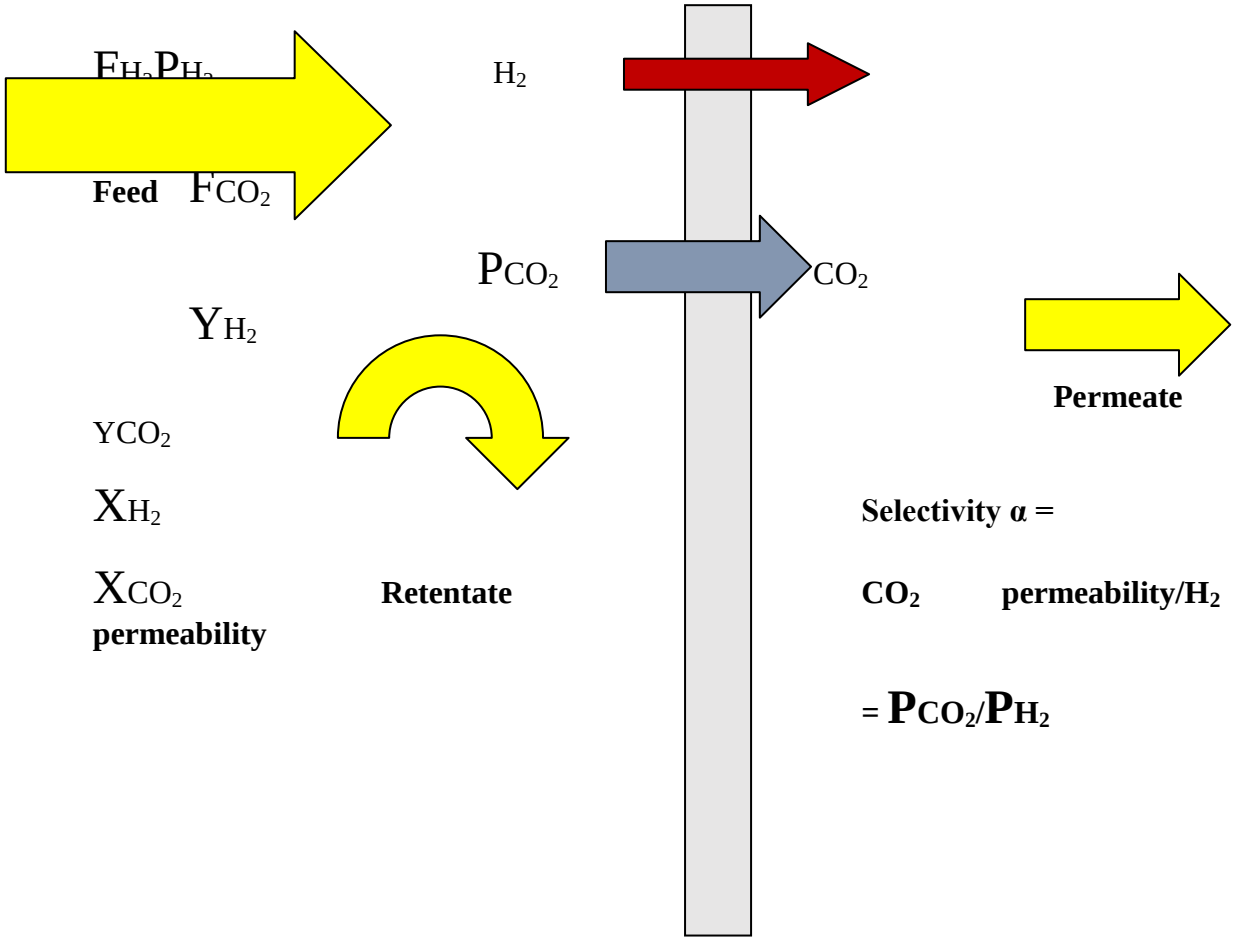


Figure 2.8: Schematic of Pre-Combustion CO_2 Capture Using a Membrane to Separate CO_2 and H_2 in the Gas Stream of an IGCC Power Plant (DOE, 2010)

2.2.3 Oxy-combustion systems

Oxy-combustion (or oxyfuel) systems are being developed as an alternative to post-combustion CO_2 capture for conventional coal-fired power plants. Here, pure oxygen rather than air is used for combustion. This eliminates the large amount of nitrogen in the flue-gas stream. After the particulate matter (fly ash) is removed, the flue gas consists only of water vapor and CO_2, plus smaller amounts of pollutants such as sulfur dioxide (SO_2) and nitrogen oxides (NOx). The water vapor is easily removed by cooling and compressing the flue gas. Additional removal of air pollutants leaves a nearly pure CO_2 stream that can be sent directly to storage as depicted in Figure 2.11.

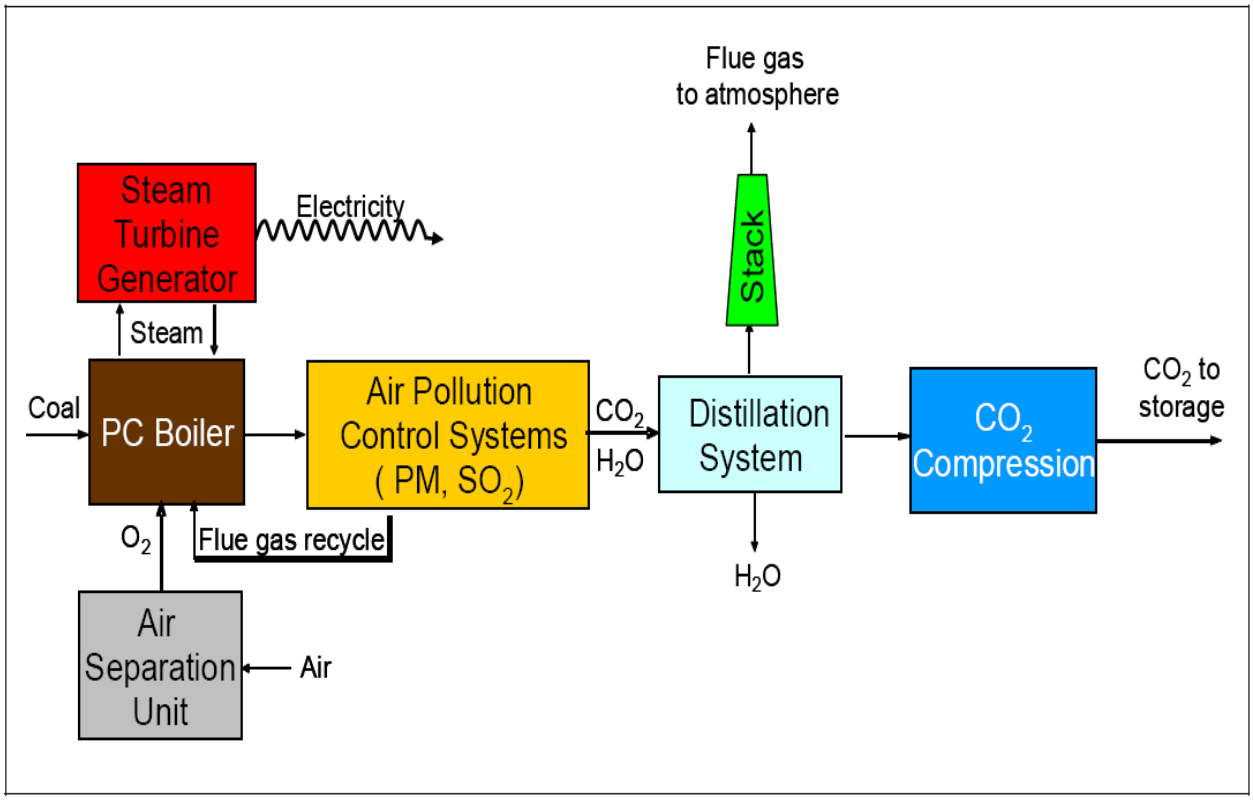


Figure 2.9: Schematic of a Coal-Fired Power Plant Using Oxy-Combustion (Rubin, 2008).

2.3 Mineral Carbonation Mechanism and Processes

2.3.1 Carbonation mechanism

Carbonation is a strongly exothermic reaction and calcium carbonate ($CaCO_3$) is formed by the reaction between cementitious materials and CO_2 through eight steps, as shown in Figure 2.11 (Fernández-Bertos*et al,* 2004). In general, carbonation is a diffusion-controlling reaction in which the outside surface of the solid is firstly carbonated by the diffusion of CO_2 into the inner region of the solid and the carbonated area then becomes larger and larger, as shown in Figure 2.12 (Shafique*et al,* 1998).

2.3.2 Calcium and magnesium (and iron) sources for mineral carbonation

There are several different elements that can be carbonated, but alkaline earth metals; calcium and magnesium, have proven to be the most suitable due to their abundance and insolubility in nature. Iron has also been suggested for carbonation, but as it is a valuable mineral resource sought after for other purposes, it is less suitable for large-scale carbonation implementations (Huijgen and Comans, 2003). In addition to the abundant magnesium and calcium containing minerals, there are also industrial solid residues that contain large amounts of Mg, Ca and even Fe. Tables 2.2 and 2.3 show various materials investigated for carbonation.

Table 2.2: Mineral types investigated for carbonation in research papers and reports (Sipilä *et al.,* 2007).

MINERAL	**FORMULA/COMPOSITION**
Feldspar	$CaAl_2Si_2O_8$
Ilmenite	$FeTiO_3$
Listwanite	Carbonated serpentanite
Magnetite	Fe_3O4
Olivine	$(Mg, Fe)_2SiO_4$
Pyroxne	$CaMgSi_2O_6$ + (Fe, Al)
Tale	$Mg_3Si_4O_{10}(OH)_2$
Wollastenite	$CaSiO_3$

Carbonation is an exothermic reaction and calcium carbonate is formed by the reaction between cementious materials and CO_2 through eight steps as shown in Figure 2.13 (Fernandez-Bertos*et al.*, 2004).

Table 2.3 Materials (synthetic) investigated for carbonation in research papers and reports (Sipilä *et al*, 2007).

MATERIAL	**FORMULA/COMPOSITION**
Brucite	$Mg(OH)_2$
Calcium silicate	$CaSiO_3$, Ca_2SiO_4
Caustic lime	CaO
Enstate	$MgSiO_3$
Forsterite	$MgSiO_4$
Hydromagnesite	$(MgCO_3)_4 .Mg(OH)_2 . 4H_2O$
Limestone	$CaCO_3$
Magnesia	MgO
Magnesite	$MgCO_3$
Merwinite	$Ca_3Mg(SiO4)_2$
Nesquehonite	$MgCO_3 . 3H_2O$
Slaked lime	$Ca(OH)_2$

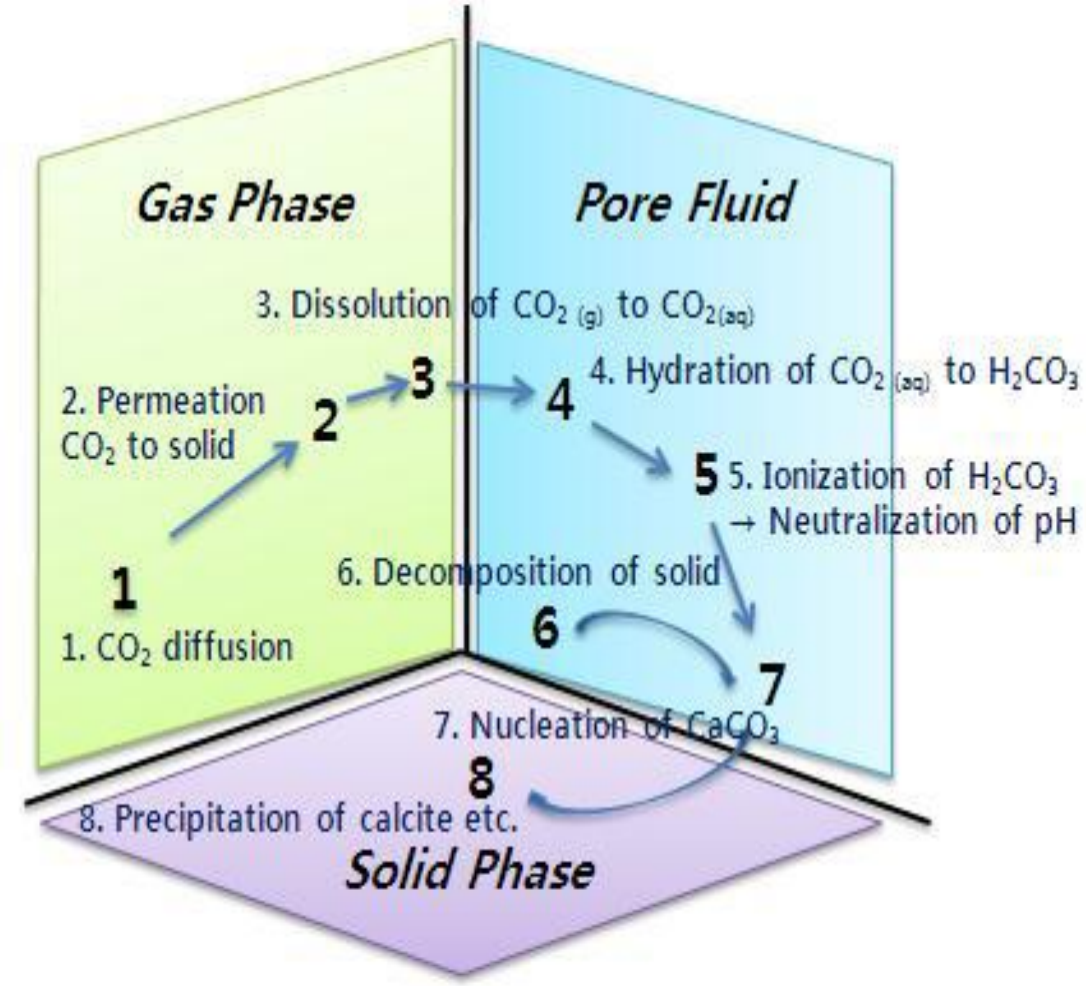


Figure 2.10: Schematic of accelerated carbonation in eight steps (modified from Marie (Maries, 1985).

2.3.3 Carbonation processes

The various processes are discussed below:

a) Natural carbonation

Natural carbonation occurs by the reaction between atmospheric CO_2 and alkaline materials, which is called "weathering". It is well known that the "weathering" depends on the initial chemical composition, the characteristic of minerals in alkaline materials and the amount of CO_2 uptake. Natural carbonation generally progresses very slowly over a long time (Costa *et al.,* 2007).

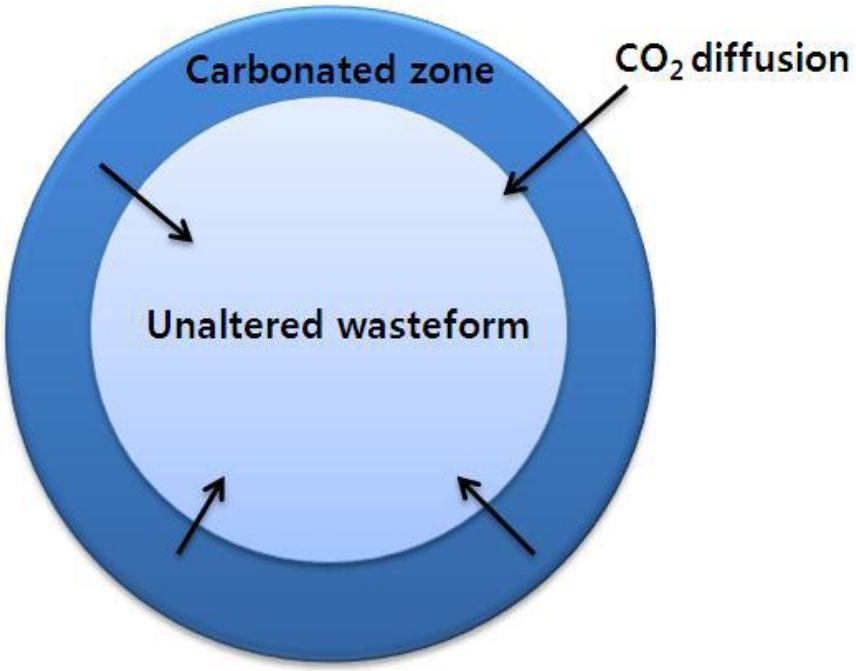


Figure 2.11:Schematic of carbonation showing a diffusion-controlling reaction.

b) Accelerated carbonation

The new technology of carbonation is widely used in many industries as an alternative method to natural carbonation which proceeds very slowly in nature. In accelerated carbonation, CO_2 in a high purity is artificially injected into solid wastes to make the reaction much faster than that by atmospheric CO_2, and the reaction can be finalized within a few minutes or hours. This technology is applied to the treatment of solid wastes in which toxic metals are stabilized by carbonated materials, so that the treated solid wastes can be reutilized in other fields (Costa *et al.*, 2007).

c) Mineral carbonation applying the accelerated carbonation

Mineral carbonation is one of technologies utilizing CO_2, and is used to form carbonated materials by the reaction between CO_2 and Ca or Mg-bound compounds such as wollastonite ($CaSiO_3$), olivine (Mg_2SiO_4), and serpentine ($Mg_3Si_2O_5(OH)_4$)

(Elonevaet *al.*, 2004). This technology can be also considered as an accelerated carbonation in terms of making the reaction shorter using high purity CO_2. One of advantages of this technology compared to other CO_2 storage technologies is that CO_2 is stably stored in final products such as $CaCO_3$ and $MgCO_3$. However, this technology needs a process to pressurize Ca or Mg silicates which do not actively react with CO_2 under normal temperature and pressure and also needs mining development and fragmenting processes. In addition, the carbonation depends on the textural characteristics such as grain size, specific surface area and porosity of Ca or Mg in the sample under normal temperature and pressure. Most of the carbonation rates are under about 550 kg of CO_2 which is the highest value among those reported (Santos *et al.*, 2009). Therefore, this is currently more of a research level field rather than a real industry application due to its low economical efficiency compared to ground, underground, and marine storage (IPCC, 2005). Equations (1)-(6) present a direct carbonation route (Huijgen*et al.*, 2003). The equations (1) and (2) are processes in which wollastonite ($CaSiO_3$) and olivine (Mg_2SiO_4) directly react with CO_2, and the equations (3)-(6) are to increase reaction efficiency by converting those minerals into CaO, $Ca(OH)_2$, MgO, and $Mg(OH)_2$. The carbonation of CaO and $Ca(OH)_2$ are as fast and are completed within a few minutes, whereas the carbonation of $Mg(OH)_2$ under dry conditions is very slow for sequestrating CO_2.

$CaSiO_3(s) + CO_2(g) + 2H_2O(l) \rightarrow CaCO_3(s) + H_4SiO_4(aq) \quad \Delta H = -75kJ/mol\ CO_2$.....…...2.1

$2Mg_2O_4(s) + CO_2(g) + 2H_2O(l) \rightarrow Mg_3Si_2O_5(OH)_4(s) + MgCO_3(s) \quad \Delta H=-157kJ/mol\ CO_2$..2.2

$Mg(OH)_2(s) + CO_2(g) \rightarrow MgCO_3(s) + H_2O(l/g)$ $\Delta H = -81kJ/mol$ CO_2…….....…..2.3

$MgO(s) + CO_2 \rightarrow MgCO_3(s)$ $\Delta H = -118kJ/mol$ CO_2…….…….…….2.4

$Ca(OH)_2$ (s) + $CO_2(g) \rightarrow CaCO_3(s) + H_2O(l/g) \rightarrow$ $\Delta H = -113kJ/mol$ CO_2….……..…2.5

$CaO(s) + CO_2$ (g) $\rightarrow CaCO_3(s)$ $\Delta H = -178kJ/mol$ CO_2……...…..… 2.6

By upgrading a waste product into a product of high commercial value, expensive CO_2 sequestration processes could become economically feasible. One such approach has been investigated by researchers who studied the use of waste cement for the development of high-purity $CaCO_3$ by CO_2 carbonisation in accordance with the process scheme shown in Figure 2.13. The feasibility of producing $CaCO_3$ from waste cement by first extracting calcium from pulverized waste cement in a water slurry at high CO_2 pressure (several MPa), followed by the precipitation of $CaCO_3$ from the extracted solution at lower CO_2 pressures, producing high purity $CaCO_3$ (up to 98% was achieved) from waste cement at relatively high reaction rates (Sipilä*et al.*, 2007).

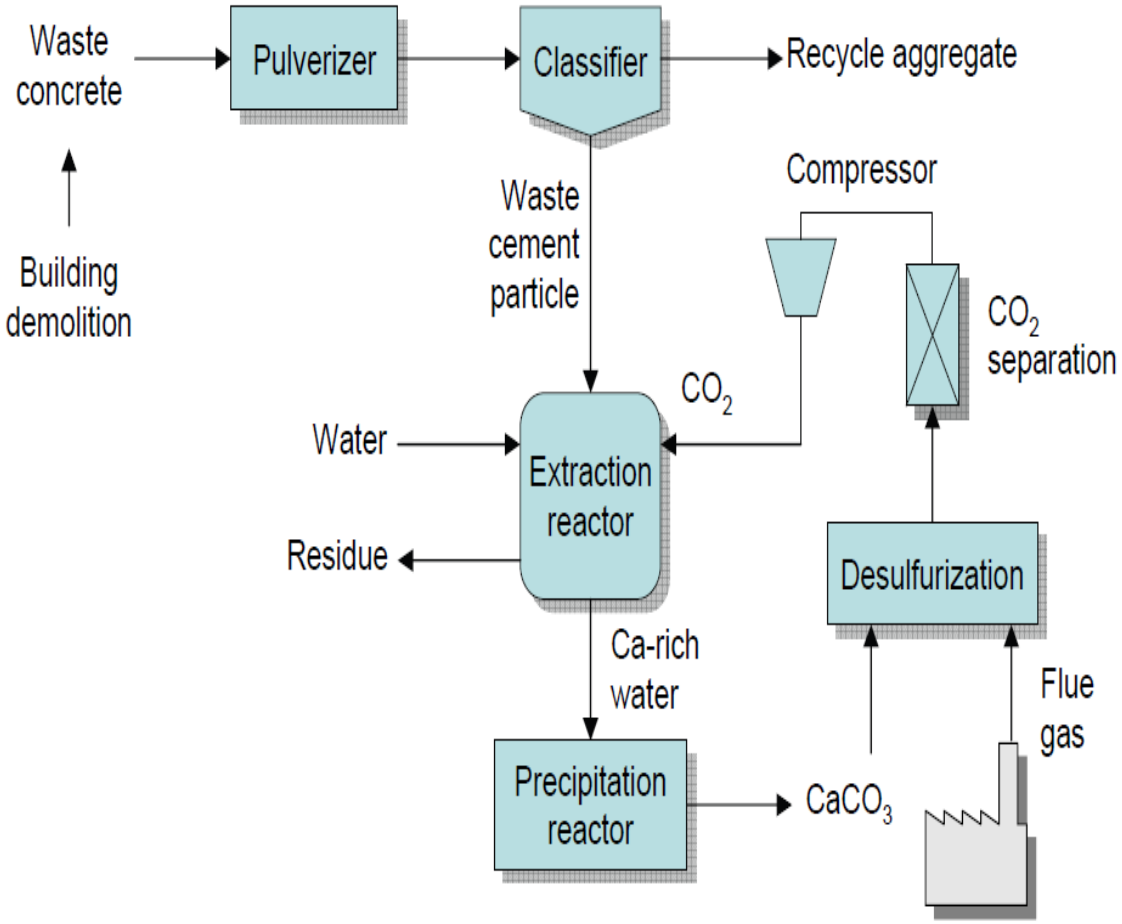


Figure 2.12: Schematic illustration of a $CaCO_3$ production process from waste cement (Sipilä*et al.*, 2007)

The carbonation set-up of Figure 2.14 consists of a close loop in which a mixture of air and carbon dioxide was introduced at a certain relative rumidity (RH). A sample holder containing a lime sample was also introduced into the loop through a set of valves. Due to the carbonation reaction, an amount of CO_2 molecules were immobilized reducing the concentration of carbon dioxide in the circulating gas mixture. The CO_2 concentration in the gas was measured using an IR absorption device. A pump was used to circulate the gas while also temperature and RH were measured. As the IR absorption device to measure the carbon dioxide concentration should be

protected from internal condensation, a water absorber or cooler was considered. As such features could also act as ‘‘sinks’’ for carbon dioxide that could lead to a wrong estimate of the amount of carbon dioxide taken up by the carbonation, experimental conditions have been designed to avoid condensation while measuring RH into the system (Van Balen, 2005)

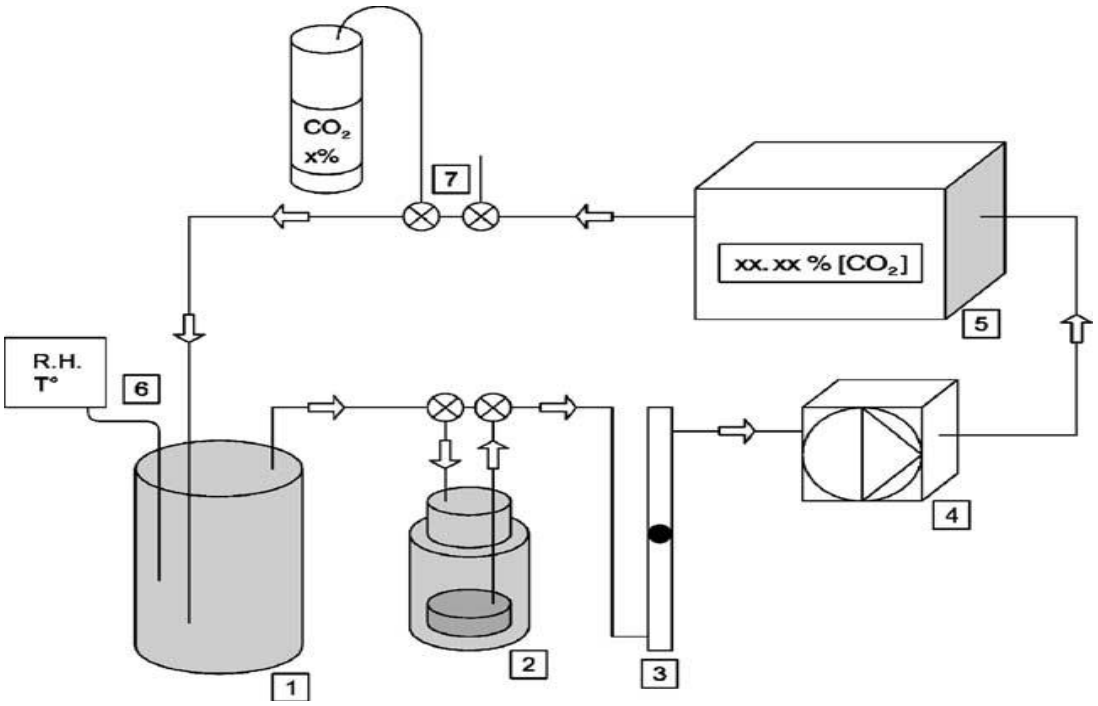


Figure 2.13: Schematic representation of the experimental set-up. (Van Balen, 2005)

The components are as follows:

1. A buffer gas volume, a water flow through the double walls linked with a thermal bath is keeping the buffer at a constant temperature.

2. Sample holder, the sample holder can be connected through two valves that deviate the airflow through the sample holder when measurements start.

3. Flow meter with a valve to set the flow speed (Cole Palmer, flow set at approximately 1.5 l/min).

4. Hermetically sealed pump.

5. ABB Advance Optima Easyline IR (CO_2) measuring device (0–100%).

6. RotronicHygroflex device to measure RH and temperature from a measuring cell in one (second in the direction of the flow) of the buffer volumes.

7. Valves to control the direction of the flow, allowing to ‘‘fill’’ the set-up with a humidified standard gas (20% or 50% (CO_2) according to the start concentration wanted) before the sample holder (with the sample) is connected to the loop. (Van Balen, 2005).

Due to the set-up, gas compression and expansion are occurring between the pump and the flow meter/controller so that condensation of water may occur in the tubing when the set-up is not properly dried between each test. Local condensation in the tubes however protected the IR (CO_2) measuring device against internal condensation.

The samples of lime putty (varying between 0.09 and 1 g, most weighing approximately 0.35 g) were spread thinly over a plastic sample cup to avoid as much as possible diffusion resistance in the mass of the sample. The cup with the sample was then introduced in the sample holder. Thanks to this procedure, an accurate mass of lime could be introduced in the experimental set-up and the mass of the sample after the experiment could be measured. The carbonated samples were stored in a closed reservoir to prevent further carbonation until they were subjected to TA to verify the amount of lime that had carbonated. TA was performed on a Mettler Toledo TGA/SDTA 851e.

Raw data collected from the set-up include time (s) and (CO_2) (%), and at distinct moments RH (%) and temperature (^{O}C) are manually introduced in a spreadsheet. Typically, data from the ABB Advance Optima Easyline IR (CO_2) are automatically collected every 100 s. Carbon dioxide concentration (CO_2) (%) was given with two decimals; RH (%) with one decimal and time is given in units of seconds.

From the above research work, the uptake of carbon dioxide due to the carbonation reaction of $Ca(OH)_2$ in ambient temperature of approximately 20^{o}C has been studied. Different types of lime have been used and the CO_2 concentration has been varied to identify the influence of different variables on the kinetics of the reaction. A closed loop system has been developed and validated that allows measurement of the carbonation progress directly from monitoring CO_2 uptake. Thermal analysis (TA) was used to verify the degree of carbonation that reached up to 83%. Factor analysis on the data set has demonstrated that reaction speed is not dependent upon the CO_2 concentration within the limits tested. Carbonation speed depends on the specific surface of the lime. The results of this study contribute to research carried out on lime mortar carbonation models and on the carbonation process in general (Van Balen, 2005).

2.4 Process Selection

Carbonator being a reactor can be actualized by fixed bed process or fluidized bed process.

2.4.1 Fluidized bed reactor

In a fluidized-bed reactor, fluid is introduced at many points and at a sufficiently high velocity that the upward flow through a bed of particles causes the particles to lift and

fall back in a recirculating pattern. The result is an expanded “fluidized-bed” of particles+ fluid holdup, behaving somewhat like a vigorously boiling liquid. The fluid completesits passage through the bed of particles by disengaging at the upper “surface”.

The fluidized-bed reactor was originally developed for catalytic “cracking” in petroleum processing to enable continuous operation in a situation in which rapid fouling of catalyst particles occurs. It may also be used for noncatalytic reactions in which the particulate material is a reactant (Missen*et al.,* 1999).

2.4.2 Fixed Bed Reactor

Many process industries are based on solid catalysts and the main catalytic process in being done in the fixed-bed reactors. The solid catalyst is in the form of pellets, packed in as a fixed bed inside the reactor. The gas is introduced in the reactor and is passed through the catalyst bed. Due to direct contact of gas with catalyst, a series of reactions takes place. Since the reaction takes place only on the surface of the catalyst so the reaction is limited by the available surface area. This problem can be overcome by allowing more than one "bed" in the reactor for the gas to pass over, under, and/or through. The catalysts in fixed-bed reactors do not need to be as resilient, as they do not travel in the bed.

Comparing merits of Fixed Bed Reactor and Fluidized Bed Reactor.

1. In passing through fixed beds, gases approximate plug flow. It is quite different with bubbling fluidized beds where the flow is complex and not well known, but certainly far from plug flow, and with considerable bypassing. This behaviour is unsatisfactory from the standpoint of effective contacting and requires much more catalyst for high gas conversion, and greatly depresses the amount of intermediate which can be formed

in series reactions. Hence, if efficient contacting in a reactor is of primary importance, then the fixed bed is favoured.

2. Effective temperature control of large fixed beds can be difficult because such systems are characterized by low heat conductivity. Thus in highly exothermic reactions hot spots or moving hot fronts are likely to develop which may ruin the catalyst. In contrast with this, the rapid mixing of solids in fluidized beds allows easily and reliably controlled, practically isothermal, operations. So if operations are to be restricted within a narrow temperature range, either because of the explosive nature of the reaction or because of product distribution considerations, then the fluidized bed is favoured.

3.Fixed beds cannot use very small sizes of catalyst because of plugging and high-pressure drop, whereas fluidized beds are well able to use small-size particles. Thus for very fast reactions in which pore and film diffusion may influence the rate, the fluidized bed with its vigorous gas-solid contacting and small particles will allow a much more effective use of the catalyst.

4. If the catalyst has to be treated (regenerated) frequently because it deactivates rapidly, then the liquid-like fluidized state allows it to be pumped easily from unit to unit. This feature of fluidized contacting offers overwhelming advantages over fixed bed operations for such solids (Levenspiel, 1999)

Fixed bed reactor was selected because of its lower capital cost and ease of operation.

2.5 Review of Related Studies

Figure 2.6 presents the assessment of mass and heat flow balances for the proposed post combustion fluidized bed system for CO_2 capture using lime carbonation/calcination cycle. A typical coal with a lower heating value of 25 MJ/kg has been selected as fuel. The sulphur content and its effect on CO_2 capture was neglected in order to simplify the study. A mass flow of 94 kg/s of CO_2 exit from the power island. The heat balance takes into account the heat generated in the calcination process and particle and gas flows through the calciner. The lime flow in the calciner was calculated assuming a CO_2 retention efficiency of 0.3. At the exit of the calciner, particles were removed from the flue gases. The calciner unit used to regeSSnerate the limestone is heated with a mixture of natural gas and oxygen. In the calciner heat balance, a working temperature of 850 °C was assumed. Products formed in the calciner will pass through a heat exchanger unit.

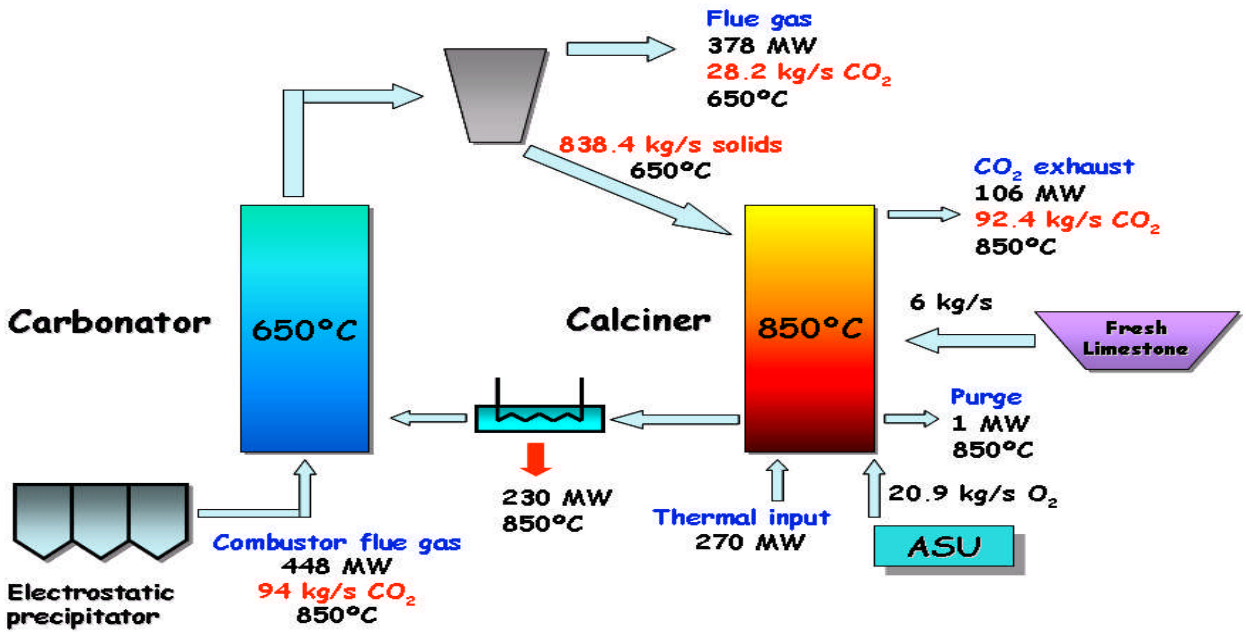


Figure 2.14: Post combustion fluidized bed system for CO_2 capture (Shimizu *et al.*, 1999)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials/Equipment

Table 3.1 showed list of materials and equipment that were used in the course of this research and the methodology.

Table 3.1: Materials/Equipment and their sources

S/No	Materials/Equipment	Source
1	*Gas analyzer* (NHA-506EN NANHUA)	NITT, Zaria
2	Thermometer	Chemical Engineering Department(ChED), Zaria
3	Household electric generator (2kVA)	ChED, Zaria
4	Hydrated lime	NARICT, Zaria
5	Weighing balance	ChED, Zaria
6	Measuring cylinder	ChED, Zaria
7	Measuring tape	CERT, Zaria
8	Beakers	ChED, Zaria
9	Hand gloves	CERT, Zaria
10	Water	ChED, Zaria
11	Weighing balance	ChED, Zaria
12	Arc welding machine	Engineering skills, Zaria
13	Carbonator	Fabricated

3.2 Methodology

3.2.1 Flue gas analysis

A four litre gallon fuel was fed into the tank of a household electric generator. The generator was turned on and allowed to run for about 30 minutes for it to stabilsed. Gas analyzer was connected to sockets and also allowed to be in "ready mode". Flue emission point from generator exhaust was connected to gas analyzer. Gas composition was read directly off the gas analyzer at various time intervals as depicted in Figure 3.1

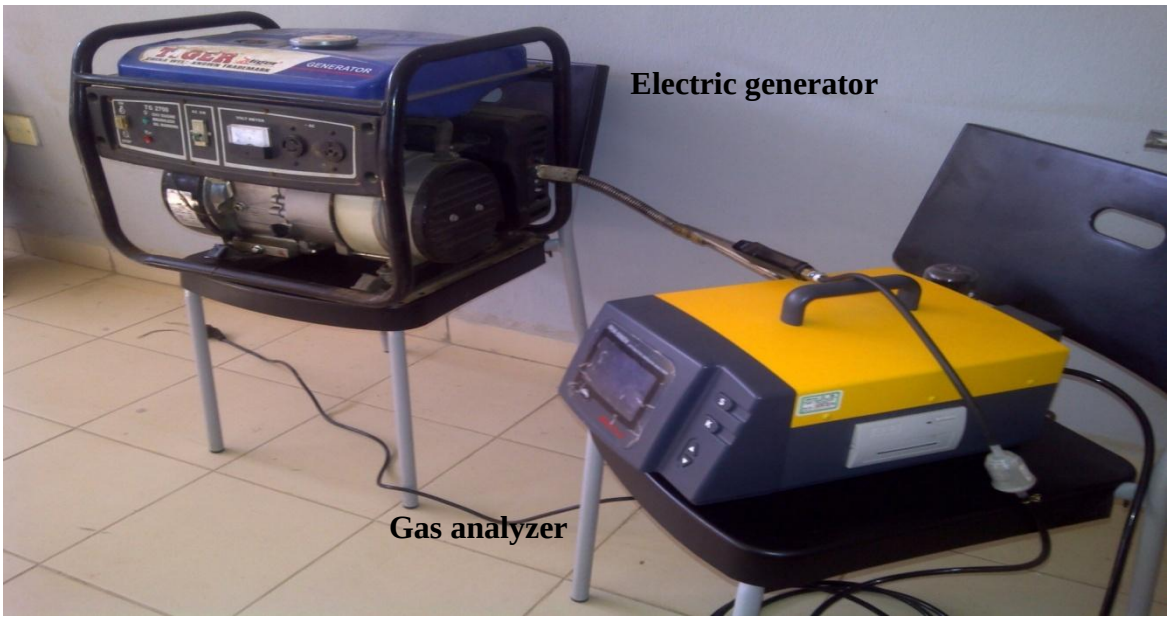


Plate 3.1: Set up for Flue gas Analysis

The generator does not have a steady reading due to working mechanism of generator and environmental condition such as flow of air which is dependent on wind current. The result was used in Aspen plus component specification as shown in Figure 3.2.

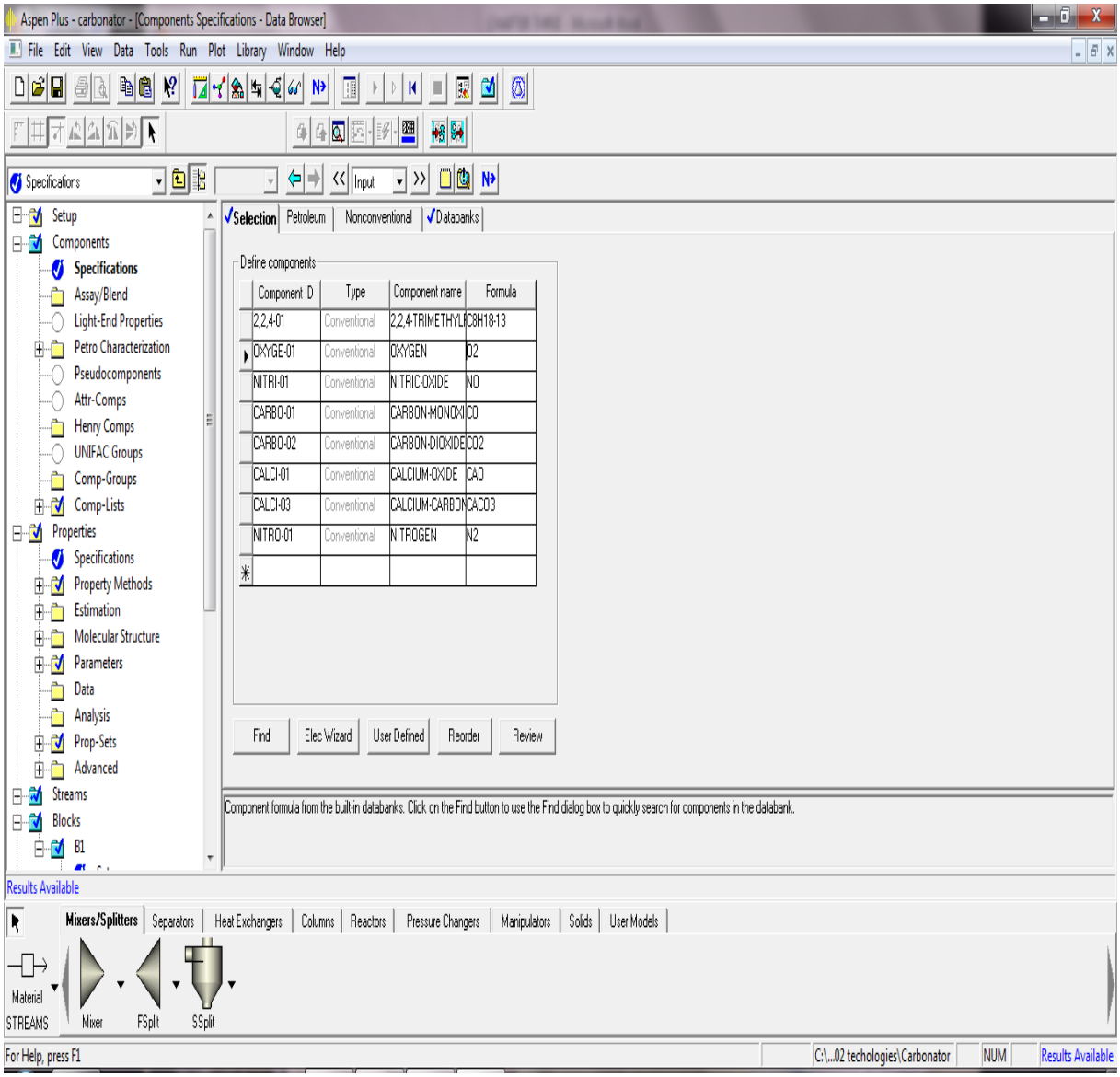


Figure 3.1: Component Specification showing reactants and products

3.2.2 Carbonator design using Aspen Plus software

Aspen Plus software was used for the design and simulation. The reactor from simulator library that best suit the carbonator was selected, inlet and outlet streams were attached to the reactor and all the input stream parameters and reactor properties were specified as shown in Figure 3.3.

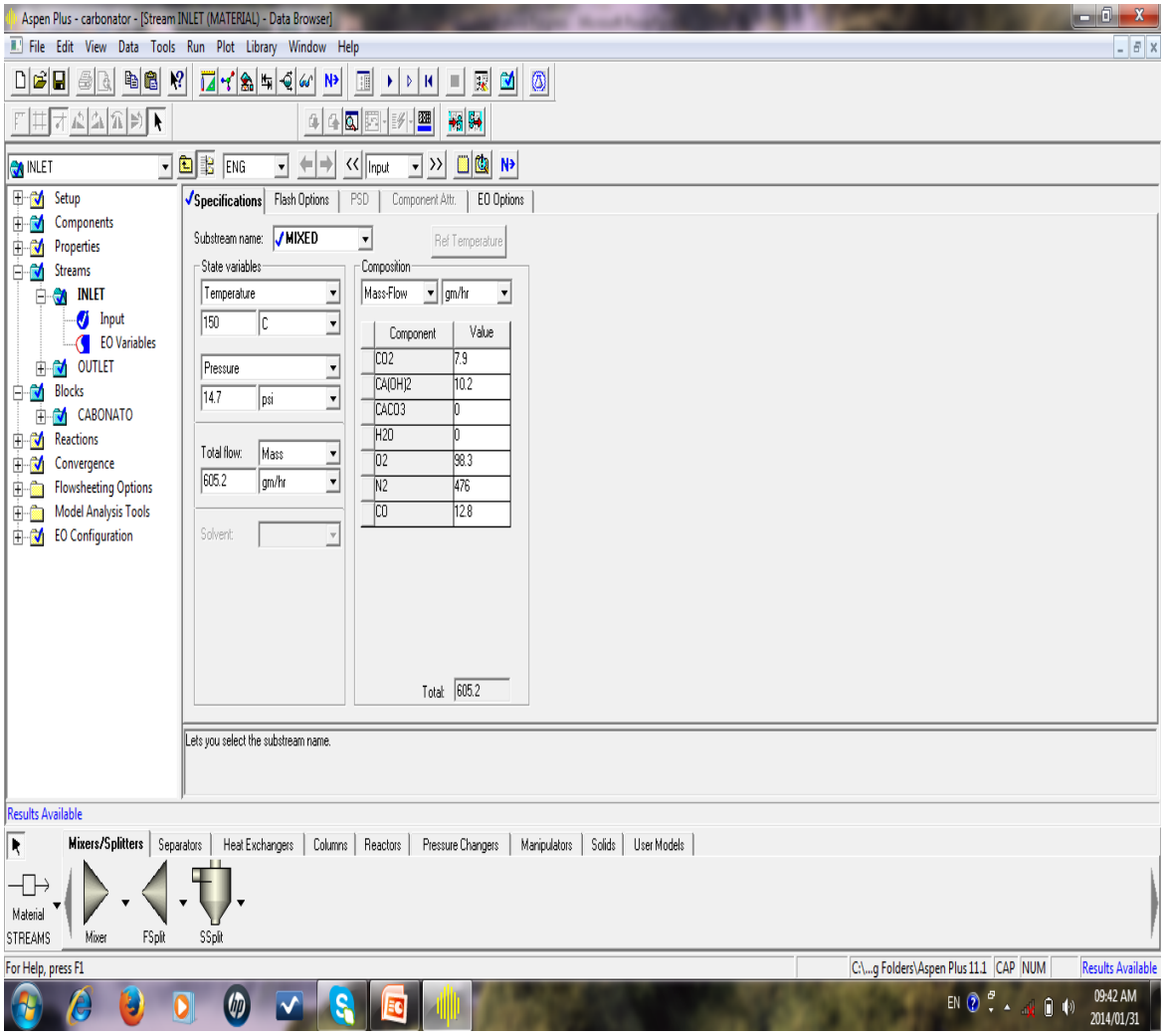


Figure 3.2: Aspen Plus Input Specification showing temperature, pressure and flow rates

The stoicheometry and the kinetics parameters were specified: the activation energy and reaction order is depicted in Figure 3.4

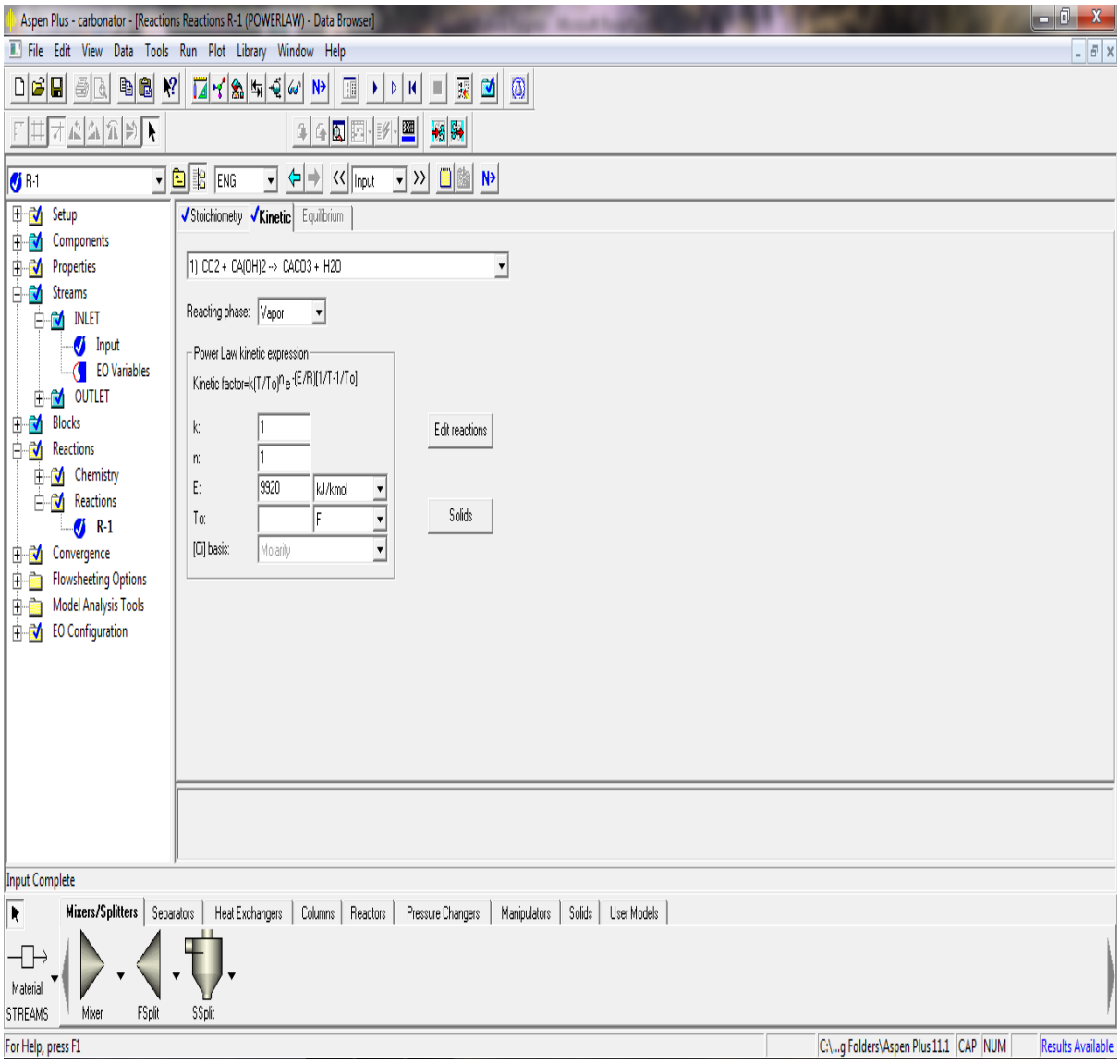


Figure 3.3: Aspen Plus Reaction Specification depicting kinetic parameters

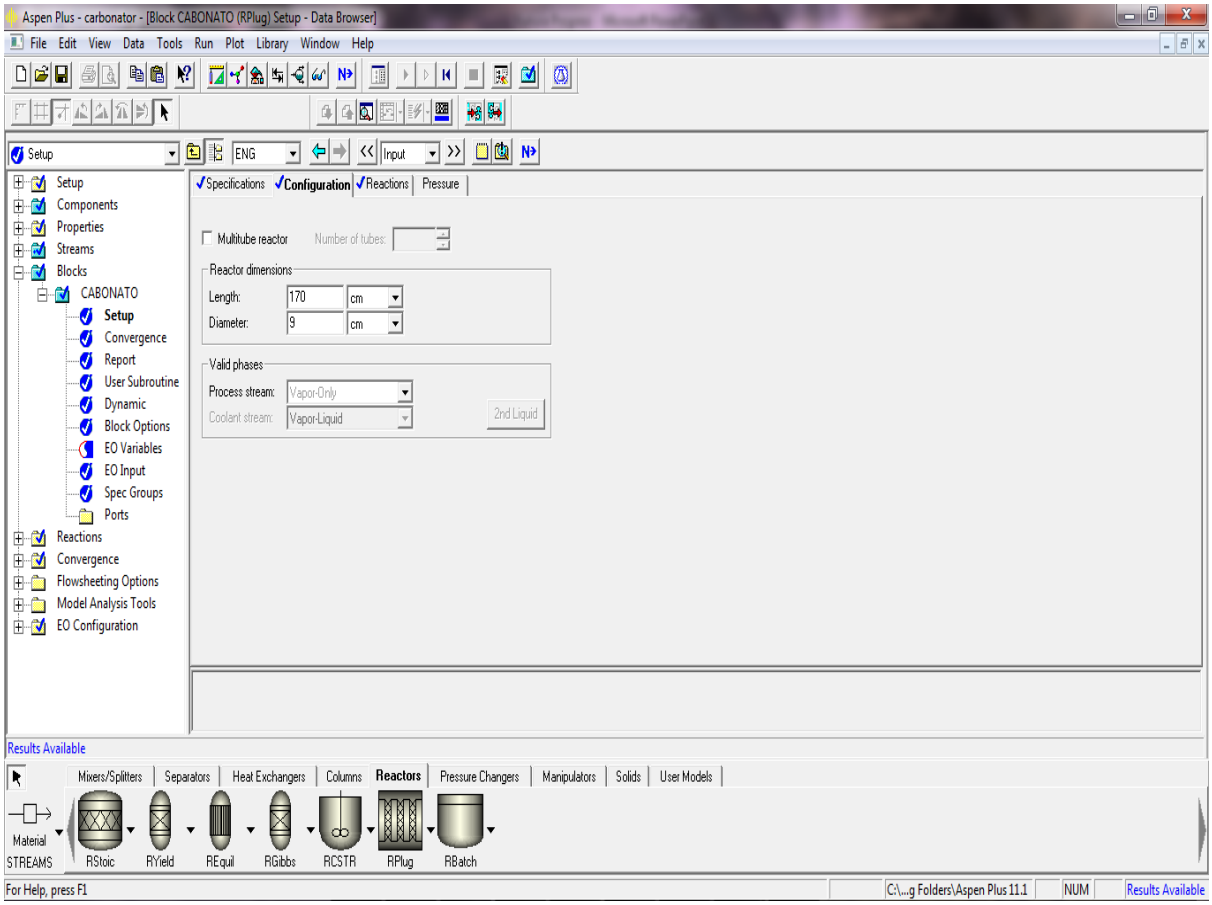


Figure 3.4: Design Results from Aspen Plus showing carbonator configuration

3.2.3 Material selection

The materials that were most suitable for the operating conditions of the carbonator were selected. Then market survey was carried out on the availability and cost of the materials.Best alternative material selection for unavailable materials was done. Best fabrication bid from several based on cost and quality of work was considered.

3.2.4 Construction of carbonator

The materials for construction were procured. Mild steel was used for the fabrication. Work was given close monitoring to have work done according to specifications. The construction was done by Engineering skills, Samaru, Zaria.

3.2.5 Pelletization of hydrated lime (HL)

$Ca(OH)_2$, (HL) powders (originated from Jakura limestone from Kogi State) was used as the starting materials for the pelletization process. HL powder was provided by National research Institute for Chemical Technology, Basawa, Zaria (NARICT). The pellets were prepared in batch mode. 250g of hydrated lime was thoroughly mixed with 100g of water to form semi solid paste. The paste was passed through syringe of diameters 0.8cm, 1.2cm, 1.5cm and 2.0cm to form pellet sizes of 0.8cm, 1.2cm, 1.5cm and 2.0cm respectively. The pellets were then air dried in an indoor environment.

3.2.6 Test running of carbonator

The required batch dosage of $Ca(OH)_2$ was charged into the carbonator i.e. carbonator column was packed with 0.8cm pellet size at 40cm carbonator height. The generator was turned on and allowed to stabilize for 30min where generator flue gas emission point was connected to gas inlet point of carbonator as shown in Plate 3.2. Flue gas through the carbonator was analyzed for time 2, 4, 6, 8, 10, 12, 14 and 16 min. The same procedure was carried out for pellet sizes of 1.2 cm, 1.5 cm and 2.0 cm respectively. The gas analyzer was connected to gas outlet point of carbonator. Readings were taken and recorded of gas composition on gas analyzer at time interval over the batch time. Figure 3.5 shows results of streams from Aspen plus software.



Plate 3.2: Experimental setup for test running of carbonator packed with various pellet sizes at NARICT, Zaria

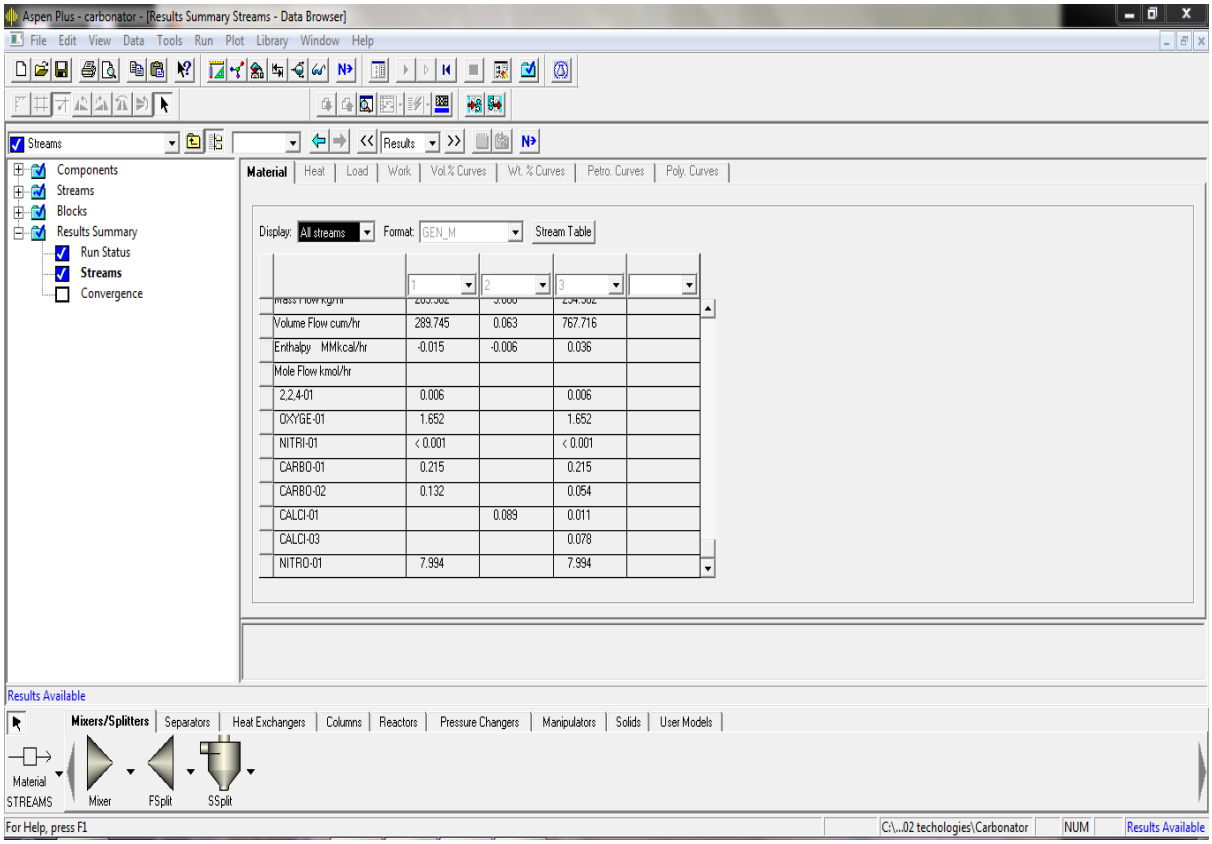


Figure 3.5: Result of streams of inlet and outlet streams of Aspen Plus software

Table 3.2: Design and Operating Parameters for Carbonator

Parameters	**Values**
Flow rates of CO_2	7.9g/hr
Temperature of flue gas	150^{o}C
Pressure	14.1psi
Carbonator length	1.7 m
Carbonator diameter	0.9 m

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Chemical Composition Analysis for Hydrated Lime

20g of hydrated lime sample was taken to Multi-User Science Research Laboratory, Ahmadu Bello University, Zaria. The result is as shown in Table 4.1. From the XRF result shown, it can be seen that major component present is calcium oxide which has about 94.593wt%, and the trace amount of impurities like magnesium oxide has only 0.225wt%. The magnesia content and impurities like silica, alumina, and iron are a function of the limestone from which the lime is made.

4.2 XRF Analysis of Hydrated Lime

The results of the chemical analysis indicated that the composition of CaO is 56.46%, Fe_2O_3 3.44%, ZnO 1.38% and SiO_2 1.52%. Used lime with high calcium oxide (CaO) content, with less than 2% MgO can be use for paper manufacturing (Agnello, 2003). Also the metallurgical industries use lime as a flux in the production of pig-iron and nonferrous metals, the used lime can also be use for this because of less than 2% SiO_2 and Al_2O_3 content, low sulphur and phosphorus content. This used lime is recommended for these purposes (Neville., 1992).

Table 4.1: Chemical Composition analysis for hydrated lime

Elements	**Concentration (wt %)**
MgO	0.225
Al_2O_3	0.663
SiO_2	3.318
P_2O_5	0.089
SO_3	0.072
Cl	0.033
K_2O	0.110
CaO	94.593
TiO_2	0.046
Mn_2O_3	0.002
Fe_2O_3	0.148
SrO	0.701

20g of hydrated lime was analyzed with an XRD Analyzer at Nigerian Geological Survey Agency, Kaduna. Result is shown in Figure 4.1. From the XRD pattern shown, the peaks show that HL is pure crystalline in nature.

Table 4.2: Chemical Composition analysis for used lime

OXIDE%	**Used Lime**
Al_2O_3	0.82
SO_3	0.02
CaO	56.46
TiO_2	0.32
V_2O_5	0.01
MgO	0.063
Fe_2O_3	3.44
ZnO	1.38
Y_2O_3	0.54
SiO_2	1.52
In_2O_3	0.74
BaO	0.1
Lu_2O_3	0.05
$H2O^+$	34.34

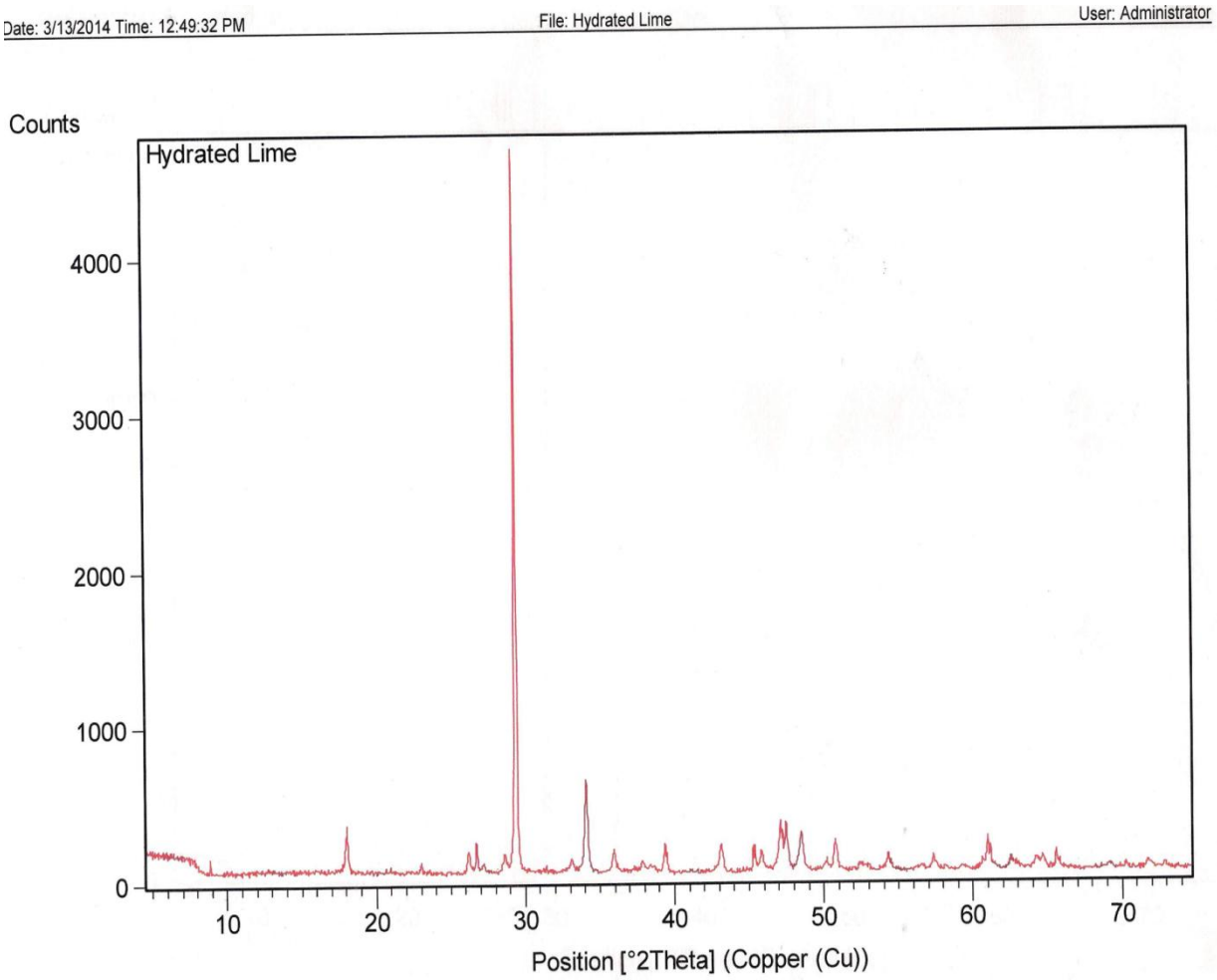


Figure 4.1: XRD Analysis of Hydrated Lime

20g of used lime was analyzed with an XRD Analyzer at Nigerian Geological Survey Agency, Kaduna. Result is shown in Figure 4.2. From the XRD pattern shown, It can be seen that there is no much difference with the hydrated lime used for the work because is showing almost the same peak and the peaks show that used lime is also pure crystalline. Also the XRD analysis of the used lime revealed the presence of only calcite polymorph. Metastable crystalline phases of calcium carbonate such as aragonite, vaterite and amorphous calcium carbonate were not identified.

were not identified.

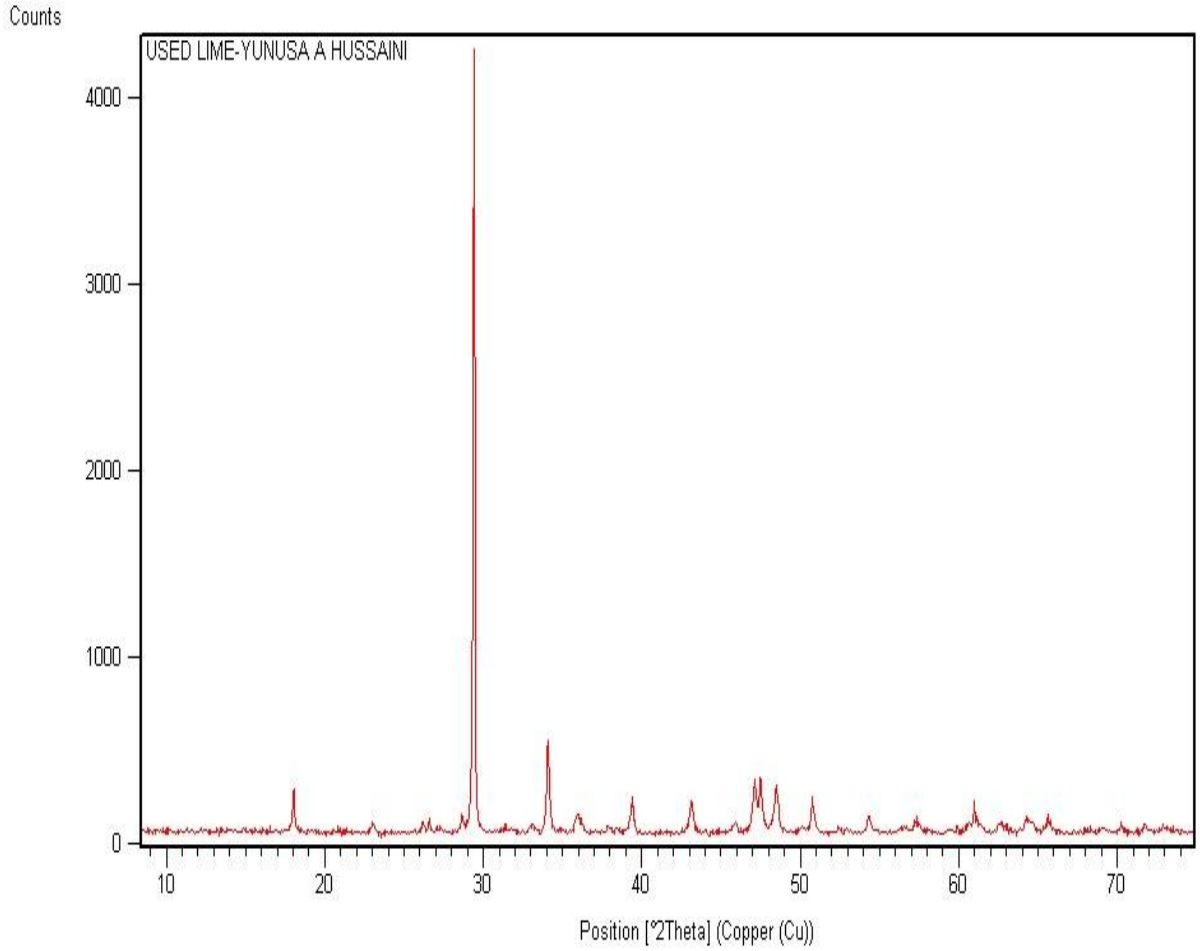


Figure 4.2: XRD Analysis of used Lime

4.3 SEM analysis of hydrated lime

The morphology of the hydrated lime was investigated by SEM as shown in Plate 4.1 at 30000× magnification. It was observed that the hydrated lime presented irregular, heterogeneous and coarse particles. The smaller size of the particles and aggregates could provide higher specific surface areas. The size of the particle should directly respond to the surface area.

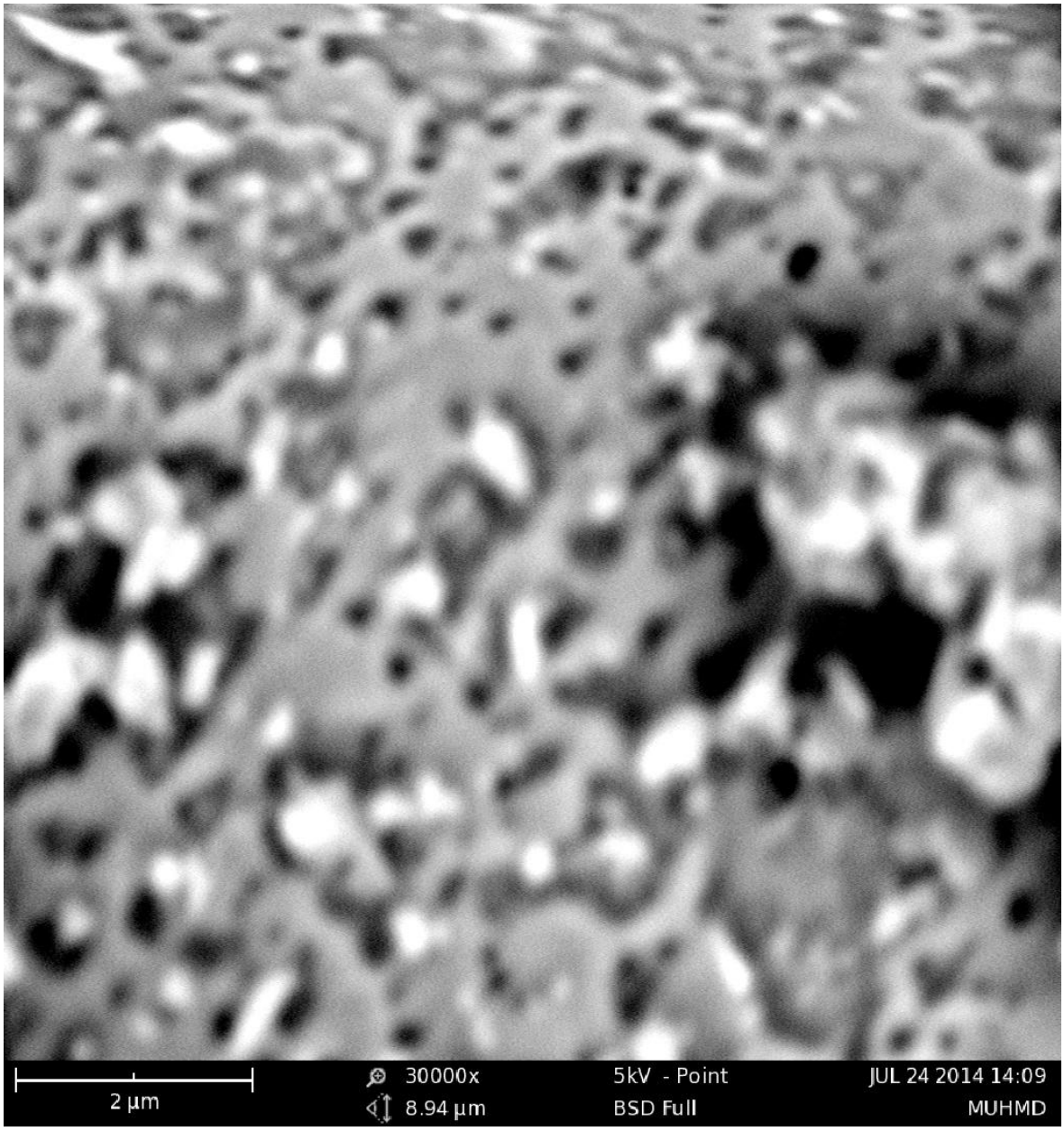


Plate 4.1: SEM image of a hydrated lime at 30000× magnification.

Plate 4.2 shows the scanning electron microscopy of used lime at a magnification of 30000x. A considerable difference has been recorded in the morphology of the used

lime formed after the carbonation reaction. According to the SEM images, the used lime typically comprises whitish shape of particles showing that it is calcium carbonate. The micrometer-sized rhombohedral calcite crystals, precipitated at the used lime surface, also play a role in creating an impermeable layer hindering the diffusion of the CO_2 along the sample thickness where calcium hydroxide crystals were still present. In other words, there were various sizes and shapes of particles.

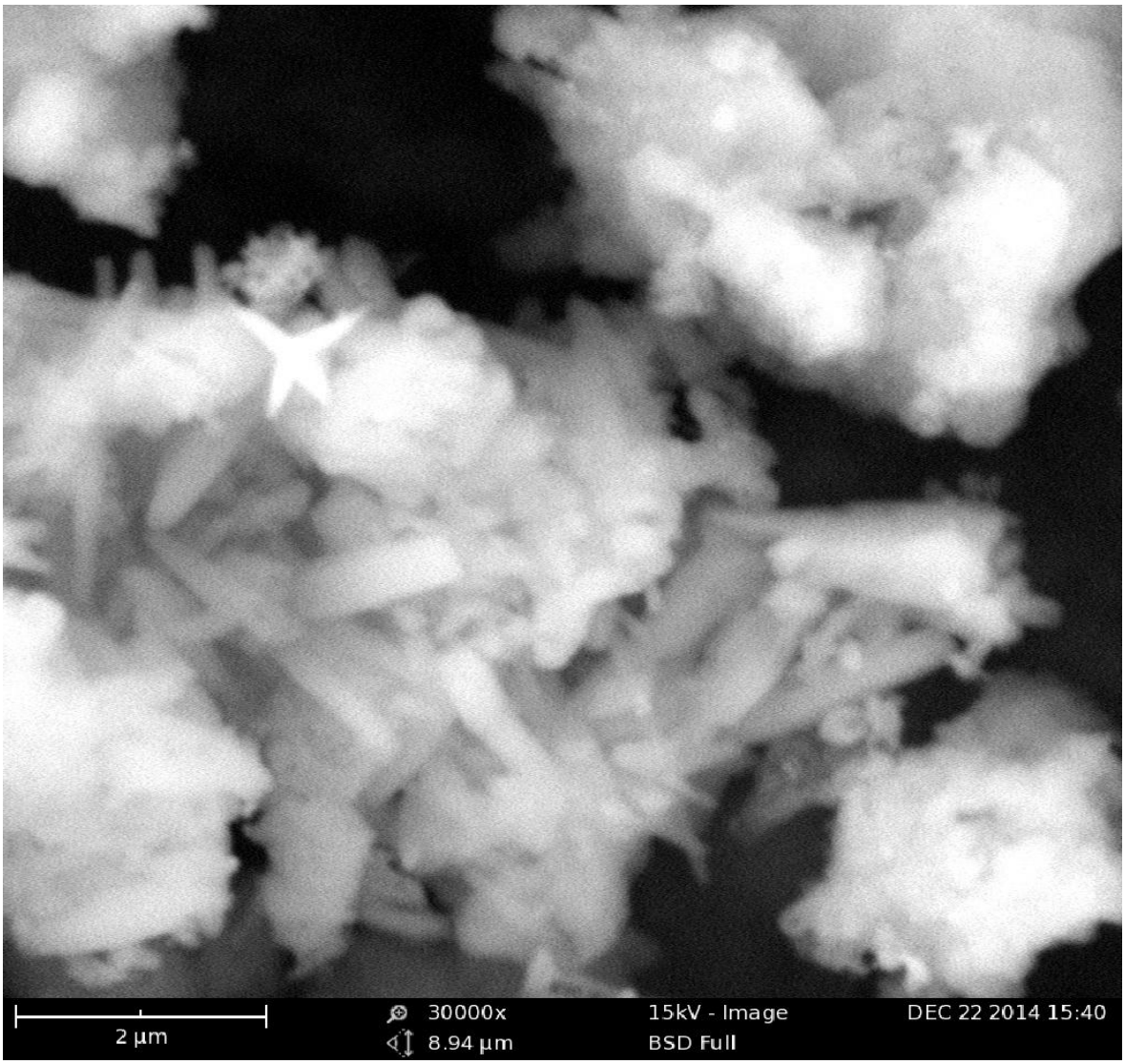


Plate 4.2: SEM image of a used hydrated lime at 30000x magnification

4.4 Hydrated Lime Pellets Produced



Plate 4.3: Hydrated Lime Pellets Produced

4.5 Flue Gas Analysis

Flue gas was analyzed by connecting flue gas analyzer to generator exhaust. Readings on analyzer was taken at time 2-16 min with 2 min interval. Graph of components between the time intervals is presented in Figure 4.6. The figure shows that HC and NO have negligible concentration whereas CO has higher concentration than CO_2. CO_2 is been investigated in this research work.

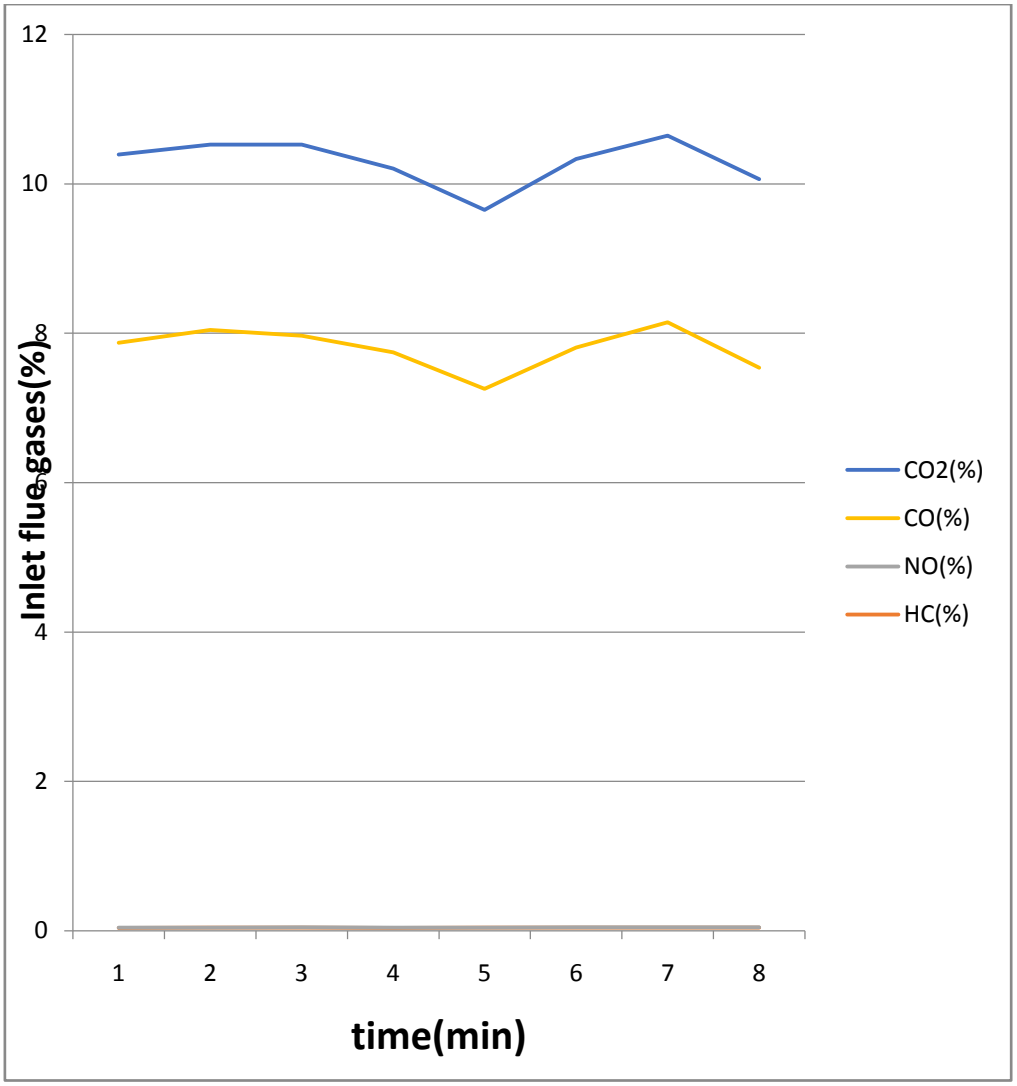


Figure 4.3: Flue gas composition from generator exhaust at various time

4.5.1 Working Drawing

Using the design parameter, working drawing was done using AutoCAD software.

The projected view of the carbonator is presented in Figure 4.7 with the required specifications obtained from Aspen Plus software. In addition, Figure 4.8 shows the isometric view of the carbonator.

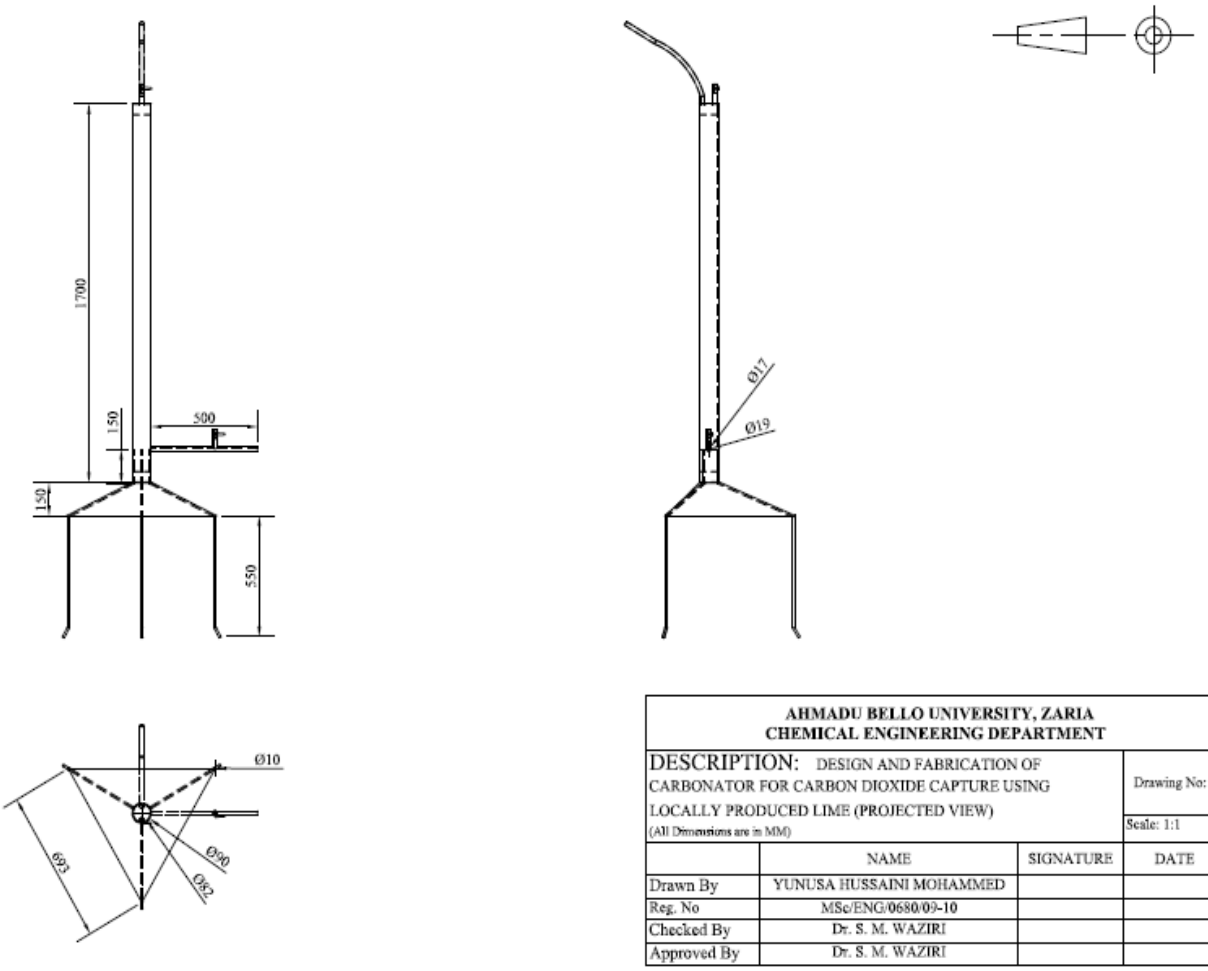


Figure 4.4: Projected View of Carbonator

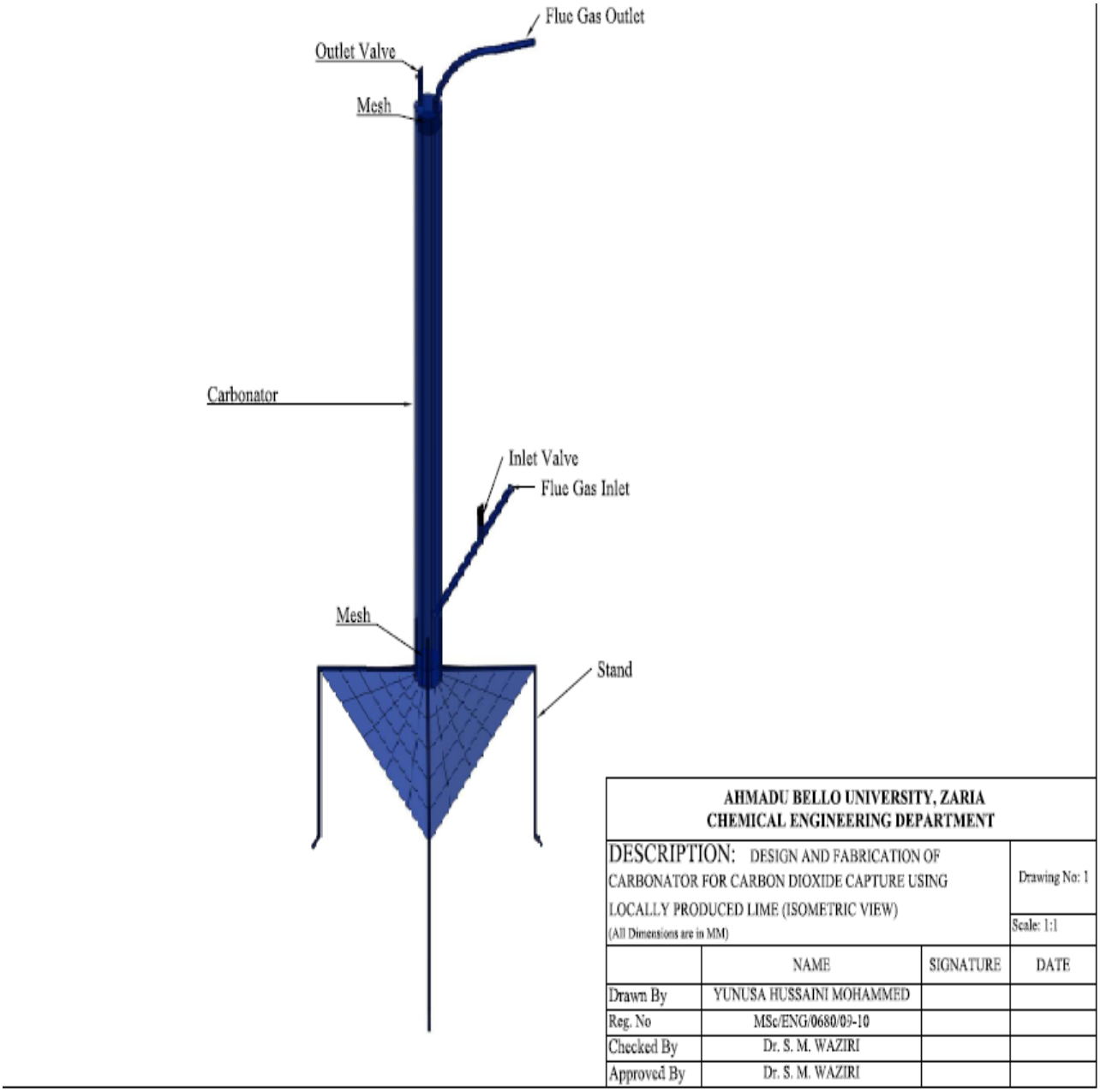


Figure 4.5: Isometric View of Carbonator

4.5.2 CONSTRUCTION

The working drawing was taken to Engineering Skills Samara, Zaria for construction. Constructed carbonator is shown in Plate 4.4 with all the inlet and outlet streams shown. Hacksaw was used to cuts the metals according to the specifications; an electrode was used for the welding process using a welding machine. Mesh was used to support the bed where the HL was supported.

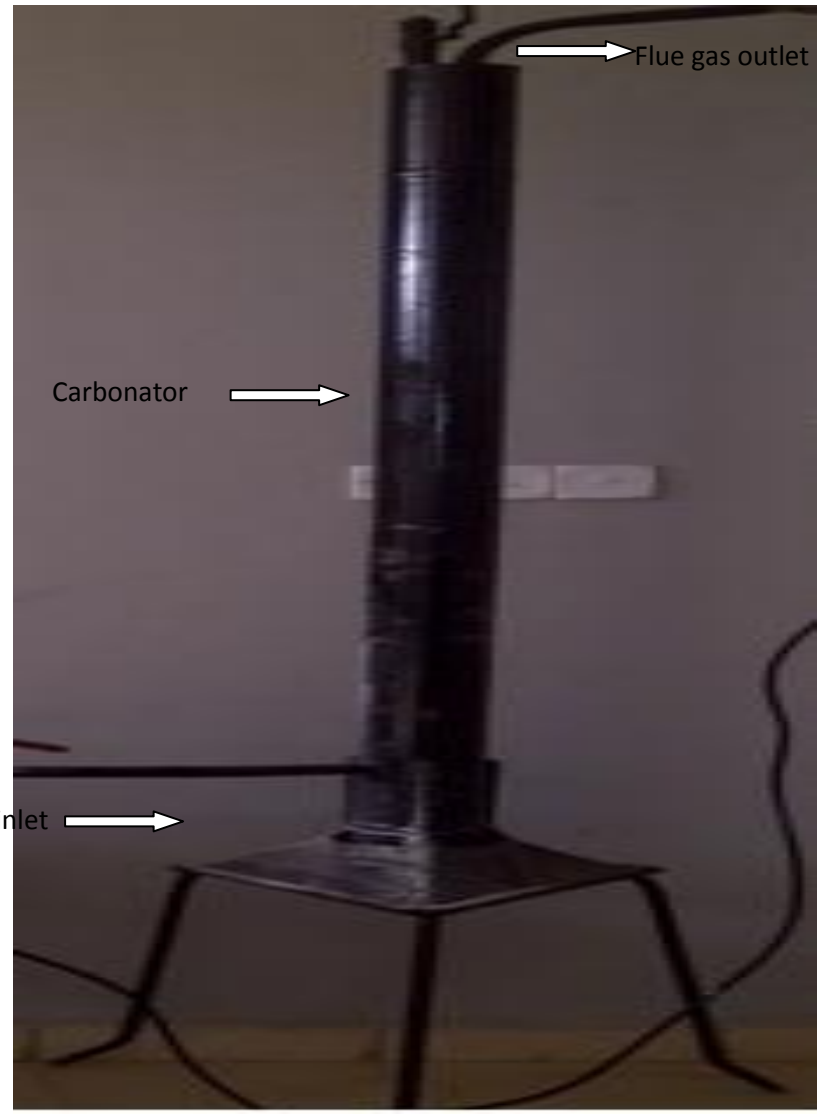


Plate 4.4: Fabricated Carbonator

Figure 4.6 shows the $\%CO_2$ depletion with time for various pellet sizes, as it can be observed from the graph, for the 0.8cm pellets size, the maximum range of $\%CO_2$ removal is from 2min to 7min. For the 1.2cm, the maximum range of $\%CO_2$ removal can be seen from 2min to 6min. For the 1.5cm, the maximum range of $\%CO_2$ removal can be seen from 2min to 7min. Likewise for the 2.0cm, the maximum range of $\%CO_2$ removal can be seen from 2min to 6min. Gas analyzer was used to verify the degree of carbonation. And for the the 0.8 cm pellet size, there is 97.6% carbon dioxide removal which is in agreement with the work of Van Balen (2005) where he studied the uptake of carbon dioxide due the carbonation reaction of $Ca(OH)_2$ in an ambient temperature of 20^oC. He developed and validated closed loop system that allows measurement of the carbonation progress directly from monitoring CO_2 uptake. Thermal analysis (TA) was used to verify the degree of carbonation that reached up to 83%.

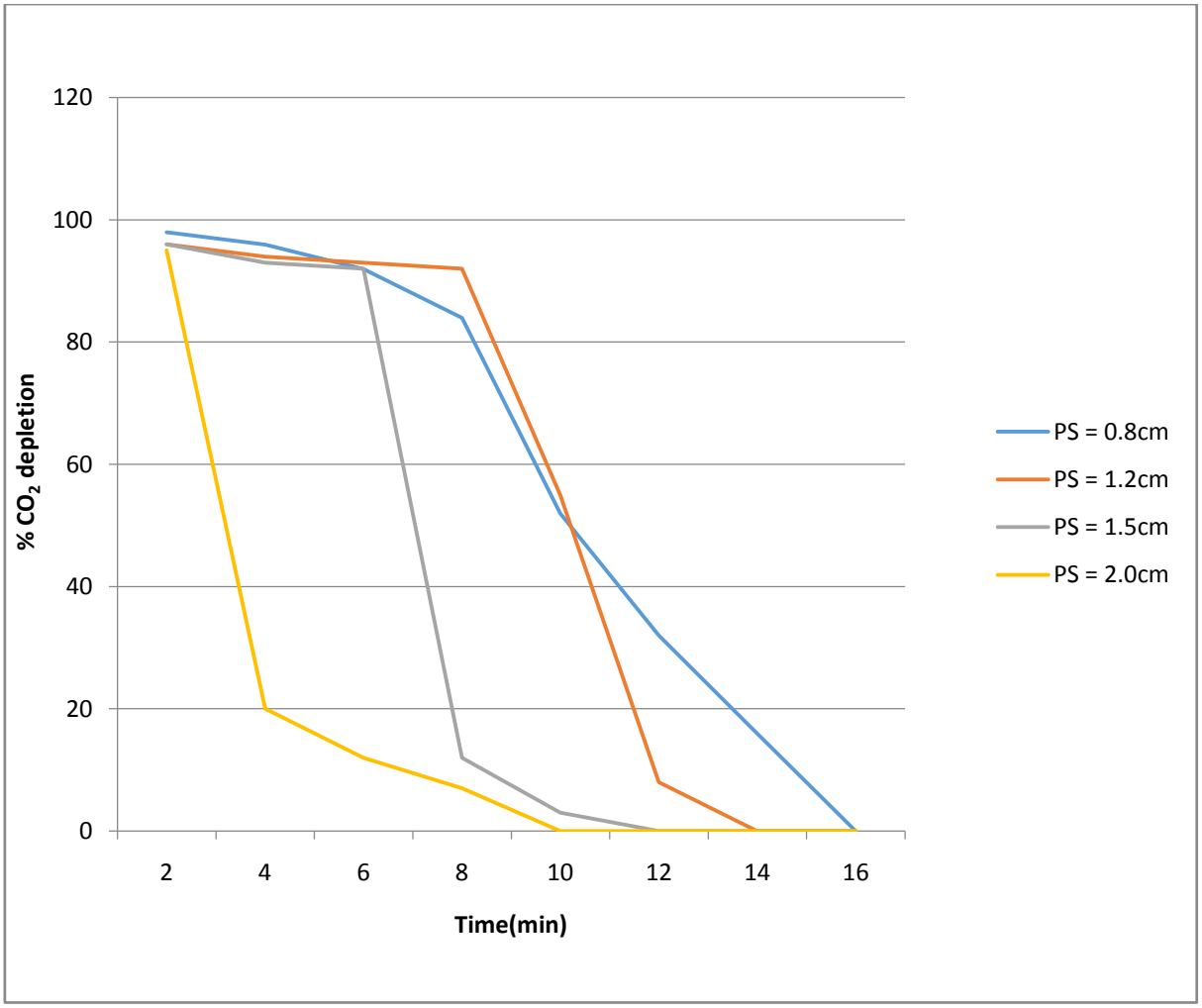


Figure 4.6: Percentage CO_2 depletion with time for various pellet sizes

Figure 4.7 shows the relationship between bed used up time and pellet size. From the figure, it is interesting to note that the larger pellet size (2.0cm) got used up faster. This could be as a result of the smaller surface area which the larger pellet size has ($5030cm^2$) as shown in Table 4.3. Carbonation is a surface reaction; the carbonated layer hinders the diffusion of CO_2 gas to the uncarbonated part which leads to incomplete carbonation. Therefore, the bed got used up faster at 12min. And for the smaller pellet size (0.8cm) which has a surface area of 7537cm, there is enough surface area for carbonation reaction which gives it longer time before the bed got used up in 16min.

The kinetics of carbonation reaction of $Ca(OH)_2$ with CO_2 in humid N_2 has been studied at 60-90^0 C by using a differential reactor. $Ca(OH)_2$ reacted with CO_2 to form $CaCO_3$ when the relative humidity exceeded 0.08. The reaction ceased before 1 h, and $Ca(OH)_2$ was incompletely converted. The reaction rate and final conversion of $Ca(OH)_2$ were significantly affected by relative humidity, were slightly dependent on temperature, and were zeroth order with respect to gas phase CO_2 concentration. The carbonation of $Ca(OH)_2$ was well described by the asymptotic equation which is obtained by assuming chemical reaction control and considering the surface coverage by product. The rate-controlling step might be the dissolution of $Ca(OH)_2$ at the water-adsorbed surface. The reaction behavior of $Ca(OH)_2$ with CO_2 was similar to that with SO_2. The model derived for the reaction with CO_2 may be applied to that with SO_2 with proper modifications. The results of this study are useful to the design and efficient operation of the processes using hydrated lime to remove SO_2 from the flue gas, in which both SO_2 and CO_2 are present (Shih et al, 1999).

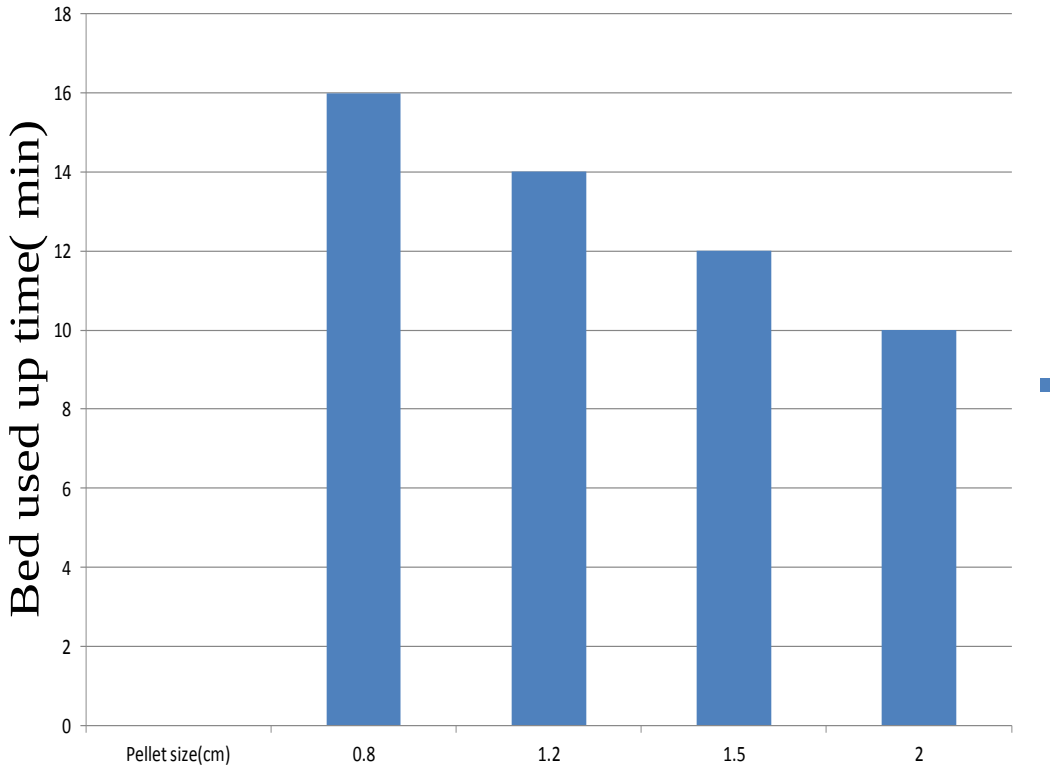


Figure 4.7: Bed used up time vs Pellet size

Table 4.2 and 4.3 show some fixed bed characteristics which are required in determining bed performance. The number of pellets per bed, overall surface area, sphericity and porosity were all calculated as shown in appendix A. As it can be observed from Table 4.3, for the 0.8 cm pellet size, it has an overall surface area of 7537 cm^2 which gives the CO_2 more area to be trapped because carbonation is a surface reaction. Unlike the larger pellet size (2.0 cm^2), the overall surface area is small, therefore less CO^2 diffuses to the surface of the adsorbent.

Table 4.3 Characteristics of Fixed Bed Reactor

Pellet size, cm	Sphericity	Porosity	Number of pellets/bed	Overall surface area, cm^2
0.8	*1.44*	*0.3415*	4187	7537
1.2	1.19	0.3416	1232	6123
1.5	1.04	0.3417	635	5600
2.0	0.87	0.3420	267	5030

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

After the experimental work and analysis of the results, the following conclusions were made:

1. A carbonator was designed and fabricated.

2. Fixed bed reactor of diameter x height, 0.90 m x 1.70 m respectively was found effective in removing 7.9 g/hr of CO_2 from a household generator.

3. For bed height 40cm and 0.8 cm pellet size, percentage CO_2 removal of 97.6% was achieved.

4. The X-ray fluorescence analysis shows that the used lime has the properties of calcium carbonate with 56.46% CaO, 0.82 Al_2O_3, 1.52% SiO_2 and 0.063% MnO. For the SEM analysis result, the used lime presented whitish, micrometer-sized rhombohedral calcite crystals particle.

5.2 RECOMMENDATIONS

1. Work should be carried out on fluidized bed for carbonator to compare performance with fixed bed.

2. Other local raw materials should be considered for bed parking.

3. A reactivation system for deactivated pellet should be designed and fabricated.

4. Small size carbonator should be fabricated.

REFERENCES

Agnello, V.M. (2003). *A review of the dolomite and limestone industry in South Africa***.**Department of Minerals and Energy, Mineral Economics, South Africa.Pages 2-10.

Costa, G.; Baciocchi, R.; Polettini, A.; Pomi, R.; Hills, C.D.; Carey, P.J. (2007).*Current status and perspectives of accelerated carbonation processes on municipal waste combustion residue*.Environ. Monit. Assess, 135, 55-75.

Crowley T.J. (2000*)*.Causes of climate change over the past 1000 years. *Science*289:270–77. DOI: 10.1126/science.289.5477.270

Dunsmore, H. E. (1992). *A geological perspective on global warming and the possibility of carbon dioxide removal as calcium carbonate mineral.* Energy Conversion and Management.Volume 33.Pages 565–572.DOI: 10.1016/0196-8904(92)90057-4

Eloneva, S. (2004).Mineral Carbonate Process Modeling and Carbonate Product Stability. Helsinki University of Technology: Greater Helsinki, Finland. Retrieved on 13 December, 2014 from www.oalib.com/references/8691093

Fernández-Bertos, M.; Simons, S.J.R.; Hills, C.D.; Carey, P.J. (2004).A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2.J. Hazar. Mater. 112. Pages 193-205.

Fogler P. (2010). Carbon Capture: A Technology Assessment, Energy and Natural Resources.*Congressional Research Service,*7-5700, R41325.Pages 13, 14, 15, 29, 38 and 53.

Huijgen, W.J.J., Comans, R.N.J., (2003). Carbon Dioxide Sequestration by Mineral Carbonation. Literature Review, ECN-C-03-016, Energy Research Centre of The Netherlands, Petten, The Netherlands. Retrieved on August 9, 2013 from *www.sciencedirect.com/science/.../S0883292711003118*

Kohl A. L. and Nielsen, R. B. (1997).Gas Purification. 5th ed. (Houston, TX: Gulf Publishing Company.

Kotowicz, J. Chmielniak, T. andJanusz-Szymańska, K. (2010). *The Influence of Membrane CO_2 Separation on the Efficiency of a Coal-fired Power Plant. Energy*. Volume 35, pages 841-850. 10.

Levenspiel O. (1999). *Chemical Reaction Engineering*.3rd Edition. John Wiley & Sons Inc., United States of America. Page 427.

Liu, H.; Katagiri, S.; Kaneko, U. & Okazaki, K. (2000).Sulfationbehavior of limestone under high CO_2 concentration in O_2/CO_2 coal combustion. Fuel 79/8, pp. 945-953.

Maries, A. (1985). The activation of portland cement by carbon dioxide. In Proceedings of Conference in Cement and Concrete Science, Oxford, UK.

Maroto-Valer M., (2010).Developments and innovation in carbon dioxide (CO2) capture and storage technology.Woodhead Publishing Limited. Washington, DC. Volume 1, Page 4.

Metz, B., Davidson, O., de Coninck, H., Loos M., Meyer, L., Eds.; (2005).Special Reporton Carbon Dioxide Capture and Storage, IntergovernmentalPanel on Climate Change.Cambridge UniversityPress: New York. Retrieved on September 17, 2012 fromwww.aidic.it*/icheap9/webpapers/77Mofarahi.pdf*

Missen, R.W. Mims, C. A. Saville, B. A. (1999). *Introduction to chemical reaction engineering and kinetics*.Hermitage Publishing Services.University of Toronto, Toronto.Page 290.

Neville A.M (1992*). Lime and other Alternative cement.* Hill Book Company. New York 4th Edition.Pages 120-121.

Rao A. B, and Rubin, E. S.(2002). A Technical, Economic and Environmental Assessment of Amine-Based CO_2 Capture Technology for Power Plant Greenhouse Gas Control.Environmental Science & Technology.volume 36, no. 20 pages 4467-4475.

Rochelle, G. (2009). Amine Scrubbing for CO_2 Capture.*Science*. Volume 325, pages 1652-1654.

Rubin, E. S. (2008), "CO_2 Capture and Transport," *Elements*, vol. 4, pp. 311-317.

Santos, A., Ajbary, M., Morales-Flórez, V., Kherbeche, A., Pinero, M., Esquivias, L., (2009).

Larnite powders and larnite/silica aerogel composites as effective agents for CO_2

sequestration by carbonation. J. Hazard. Mater. 168, 1397–1403.

Shafique, B. S.; Walton, J.; Gutierrez, N.; Smith, R.; Tarquin, A (1998). Influence of carbonation on leaching of cementitious waste forms. J. Environ. Volume 22, pages 463-467.

Sipilä J., Teir S., and Zevenhoven R. (2008).*Carbon dioxide sequestration by mineral carbonation*.Laboratory of Energy Engineering and Environmental Protection (eny.tkk.fi), Espoo, Finland.Pages 6 and 26.

Shih S. M., Ho C.S., Song Y.S., Lin J.P. (1999). Industrial & Engineering Chemistry Research 04/1999; 38(4).

Shimizu T.; Hirama T.; Hosoda H.; Kitano K.; Inagaki M.; Tejima K., (1999), A twin fluid-bed reactor for removal of CO2 from combustion processes, *Trans. IChemE,* 77, pages 62–68.

Spooner, B. and D. Engel, (2011)."Carbon Capture Using Amine-Based Technology", *Carbon Dioxide Sequestration and Related Technologies,* Scrivener Publishing, Salem, MA.

Van Balen, K. (2005). Carbonation reaction of lime, kinetics at ambient temperature.Department of Civil Engineering and Raymond LemaireInternationalCentre for Conservation, Engineering Faculty, KULeuven, 3001 Louvain, Belgium.*Cement Concrete Res*. 35 647–657.

Carbon Dioxide Information Analysis Center (CDIAC). (2013) Retrieved from http://cdiac.ornl.gov/trends/emis/ngr.html on May 16, 2012.

CO_2CRC, (2007), *CO2CRC image library - diagrams (general),* The Cooperative Research Centre for Greenhouse Gas Technologies, Retieved on April 2, 2013 from http://www.co2crc.com.au/imagelibrary/diagrams_g.html

US Department of Energy.DOE/NETL (2010). Carbon dioxide capture R&D annual technology update, draft. Pittsburgh: National Energy Technology Laboratory. Retrived on December 12, 2012.

U.S. Greenhouse Gas Inventory Report.(2002). Inventory of U.S. greenhouse gas emissions and Sinks.1990–2000.Rep. EPA 430-R-02– 003, Off.Atmos.

Programs, Washington,DC.Retrieved on June 17, 2012 from www.epa.gov/.../ghgemis.

United State Environmental Protection Agency. (n.d). Nonroad Compression-Ignition Engines -- Exhaust Emission Standards.Washington, D.C. Retrieved on 18 September, 2012 from epa.gov/oms/standards/nonroad/nonroadci.htm

Energy Inf. Adm. (2001). *Annual energy review 2000*. Rep. DOE/EIA-03842001, US.Retrieved on 2 April, 2013 from https://e-reports-ext.llnl.gov/pdf/243846.pdf.

Environmental Protection Agency (2002).Global Climate Change Policy Book. Retrieved on 13th April, 2013 from http://yosemite.epa.gov/oar/globalwarming.nsf/UniqueKeyLookup/SHSU5BNMAJ/$File/bush_gccp_021402.pdf

Intergovernmental Panel on Climate Change.Carbon Dioxide Capture and Storage.Cambridge University Press: Cambridge, UK, 2005.

Intergovernmental panel on climate change (IPCC): Climate change 2007. Synthesis report, Geneva, Switzerland; 2007.

International Energy Agency (2009)"Technology Roadmap: Carbon Capture and Storage," Retrieved from http://www.iea.org/papers/2009/CCS_Roadmap.pdf.

Organisation for Economic Co-operation and Development.(2010), Projected Cost of Generating Electricity.Paris, France.

Nigeria and Climate Change (2013). Retrieved January 2, 2014 from http://cdiac.ornl.gov/trends/emis/ngr.html

Research Council UK (2008).Carbon capture and storage. Triple science support program. Retrieved on September 3rd 2013 from www.geos.ed.ac.uk/sccs/public

APPENDIX

A1 Determination of mass of sample in carbonator

Bulk density = $\frac{massofsample}{volumeofcylinder}$

Mass of empty cylinder = 0.4kg

Mass of sample = 1.7kg

Mass of cylinder + sample = 2.1 kg

Volume of cylinder = $0.002m^3$

Bulk density = $\frac{1.7kg}{0.002m^3}$

Bulk density = $850kg/m^3$

Height of sample in carbonator = 40cm

Diameter of carbonator = 9cm

Volume of carbonator = $\pi r^2 h$

= $2.54*10^{-3}m^3$

Therefore:

Mass of sample in the carbonator was obtained from

Density = $\frac{mass}{volume}$

Mass = density* volume

Mass of sample in carbonator = 2.16kg

A2 Characterization of the Fixed Bed Reactor Porosity

The internal pores of the individual grains are disregarded in porosity calculation.

The average porosity (∈) of a fixed granular bed (FGB) is a statistical characteristics of bed which is required for thermal and hydraulic analysis of contact and adsorption vessels.

$$\in = 1- \left(\frac{\rho_b}{\rho_s}\right)$$

Where:

ρ_b= bulk density

ρ_s = density of grains in the solid form

Average porosity of grains of different shapes

$$\in = \frac{A}{\left(\frac{D}{d}\right)^n} + B$$

Where A, B and n are constant dependent on the shape of the grains.

For cylinders:

A= 0.9198

B = 0.3414

n = 2

$$\in = \frac{A}{\left(\frac{D}{d}\right)^n} + B$$

$$\in = \frac{0.9198}{\left(\frac{40}{0.4}\right)^2} + 0.3414$$

$\in = 0.3415$

$$\in = \frac{A}{\left(\frac{D}{d}\right)^n} + B$$

$$\in = \frac{0.9198}{\left(\frac{40}{0.6}\right)^2} + 0.3414$$

$\in = 0.3416$

$$\in = \frac{A}{\left(\frac{D}{d}\right)^n} + B$$

$$\in = \frac{0.9198}{\left(\frac{40}{0.75}\right)^2} + 0.3414$$

$\in = 0.3417$

$$\in = \frac{A}{\left(\frac{D}{d}\right)^n} + B$$

$$\in = \frac{0.9198}{\left(\frac{40}{1}\right)^2} + 0.3414$$

$\in = 0.3420$

A3 Sphericity

Volume of particle = V_p

Surface Area of particle = A_p

Surface Area of sphere of same volume ($V_s = V_p$) = A_s

Sphericity = A_s/A_p

Lower sphericity ==> larger surface area

Surface area of cylinder, $A_p = \pi D^2/2 + \pi D^2 H/2$

Volume of cylinder, $V_p = \frac{\pi D^2 H}{4}$

Surface area of sphere, $A_s = \pi D^2$

Volume of sphere, $V_s = \frac{\pi D^3}{6}$

For 2cm size, cylinder D = 2cm and H = 2cm

$A_p = 18.84 cm^2 Vp = 6.28 cm^3$

$V_s = 6.28 = \frac{\pi D^3}{6}$, $D = \sqrt[3]{12}$

$A_s = \pi(\sqrt[3]{12})^2 = 16.46\ cm^2$

Sphericity = 16.46/18.84 = 0.87

For 1.5cm size, cylinder D = 1.5cm and H = 1.5cm

$A_p = 8.825 cm^2 V_p = 2.64 cm^3$

$V_s = 2.64 = \frac{\pi D^3}{6}$, $D = \sqrt[3]{5}$

$A_s = \pi(\sqrt[3]{5})^2 = 9.18 cm^2$

Sphericity = 9.18/8.825 = 1.04

For 1.2cm size, cylinder D = 1.2cm and H = 1.2cm

$A_p = 4.972 cm^2 V_p = 1.36 cm^3$

$V_s = 1.36 = \frac{\pi D^3}{6}$, $D = \sqrt[3]{2.6}$

$A_s = \pi(\sqrt[3]{2.6})^2 = 5.94cm^2$

Sphericity = 5.94/4.972 = 1.19

For 0.8cm size, cylinder D = 0.8cm and H = 0.8cm

$A_p = 1.8cm^2 V_p = 0.4cm^3$

$V_s = 0.4 = \frac{\pi D^3}{6}$, $D = \sqrt[3]{0.77}$

$A_s = \pi(\sqrt[3]{0.77})^2 = 2.6\ cm^2$

Sphericity = 2.6/1.8 = 1.44

A4 Calculation of Overall Surface Area for Reaction

$$N_P = \frac{V_R\ 1-\varepsilon}{V_P}$$

Overall surface area = Np x Ap

$VR = \frac{\pi D^2 H}{4}$

$= \frac{\pi 9^2 40}{4} = 2543cm^3$

For pellet size 2cm

$Vp = 6.28cm^3$, $\varepsilon = 0.3420$, Ap =

$Np = \frac{2543(1-0.3420)}{6.28}$

= 267

Overall surface area = 267 x 18.84

$= 5030.3cm^2$

For pellet size 1.5cm

Vp = 2.64cm^3, ε = 0.3417

Np = $\frac{2543(1-0.3417)}{2.64}$

= 635

Overall surface area = 635 x 8.82

= 5600.7cm^3

For pellet size 1.2cm

Vp = 1.36cm^3, ε = 0.3416

Np = $\frac{2543(1-0.3416)}{1.36}$

= 1232

Overall surface area = 1232 x 4.97

= 6123cm^2

For pellet size 0.8cm

Vp = 0.4cm^3, ε = 0.3415

Np = $\frac{2543(1-0.3415)}{0.4}$

= 4187

Overall surface area = 4187 x 1.8

= 7536.6cm^2