

**Parametric Study of Carbon Dioxide Adsorption Behaviour on Manjung Power
Plant Coal Bottom Ash**

by

Mohamad Amalludin Bin Mohd Rashid

16928

Dissertation submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
(CHEMICAL ENGINEERING

MAY 2015

Universiti Teknologi PETRONAS

32610 Bandar Seri Iskandar

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

**Parametric Study of Carbon Dioxide Adsorption Behaviour on Manjung Power
Plant Coal Bottom Ash**

by

Mohamad Amalludin Bin Mohd Rashid
16928

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(Chemical Engineering)

Approved by,

(Dr. Abrar Inayat)

UNIVERSITI TEKONOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK

May 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHAMAD AMALLUDIN BIN MOHD RASHID

ABSTRACT

Coal bottom ash is a promising sorbent for the capture of carbon dioxide as it contains alkaline-Earth metal oxide such as calcium oxide and magnesium oxide. Coal bottom ash is one of the byproduct generated by in coal power plant which currently facing a problem with disposal and lack of usage. The scope of this study is to deepen the understanding of the behavior of coal bottom ash as CO₂ sorbent when subjected to different parameters. In this work, coal bottom ash sorbents are being studied for its ability to capture CO₂ at a different operating temperature and also at different concentration of CO₂. The coal bottom ash sample that is used for this work is obtained from Manjung Coal Power Plant in Perak. The study is divided into two parts, which are characterization study and thermogravimetric analysis study. For the first part of the study, the sample is analysed by using XRD, XRF, and SEM. As for the second part of the experiment, the sample will go through carbonation/decarbonation cycle using TGA. The result from the characterization shows that CBA has 20.6% of CaO and a mere 2.6% of MgO and other various metal oxides. The crystalline structure from XRD proves that it has a slightly similar structure to pure CaO within the sample. The TGA analysis shows that the highest uptake capacity is at 600 °C – 700°C which valued at 37.85% of adsorption percentage and as it goes to 800°C the uptake capacity decreases.

ACKNOWLEDGEMENT

First and foremost, In the name of Allah, the Most Beneficent, the Most Merciful. My first and most gratitude goes to my supervisor, Dr. Abrar Inayat who has been giving supervision, guidance, knowledge, support and time during the process of completing the final year project. I also would like to extend my gratitude to my parents, Mohd Rashid and Zainora Talib that never stop supporting me. A special thanks to chemical engineering department lab technicians that help me with all the equipment and chemicals for this project. Not forgetting also, my family and friends who are there to support me throughout the entire project completion. Last but not least, I would like to thank Universiti Teknologi PETRONAS, which have provided and equipped me with all the facilities to make this project a success.

TABLE OF CONTENTS

CERTIFICATION OF APPROVAL	ii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF ABBREVIATIONS AND NOMENCLATURE	viii
LIST OF FIGURE	ix
LIST OF TABLE	ix
CHAPTER 1 : INTRODUCTION	1
1.1 Background of Study	1
1.2 Problem Statement	2
1.3 Objectives	3
1.4 Scope of Study	3
1.5 Relevancy of the Project	3
CHAPTER 2 : LITERATURE REVIEW	4
2.1 Coal Bottom Ash	4
2.2 Alkaline Earth Metal Oxide – Based Sorbent	10
CHAPTER 3 : METHODOLOGY	15
3.1 Characterization	15
3.2 Thermogravimetric Analysis	16
3.4 - Gantt’s Chart	21
CHAPTER 4 : RESULTS & DISCUSSION	23
4.1 Characterization Analysis	24
4.2 – Thermogravimetric Analysis	28
CHAPTER 5	34
5.1 – Conclusion	34
5.2 – Recommendation for Future Work	35
REFERENCES	36

LIST OF ABBREVIATIONS AND NOMENCLATURE

CBA : Coal Bottom Ash

SWR : Solid waste residue

CaO : Calcium Oxide

CO₂ : Carbon Dioxide

MgO : Magnesium Oxide

CaCO₃: Calcium Carbonate

TGA: Thermogravimetric Analyzer

Wt. % : Weight Percent

w/wt. % : Weight per Weight Percent

°C : Degree Celsius

g : gram

SEM : Scanning Electron Microscope

XRF : X-ray fluorescence

XRD : X-ray diffraction

LIST OF FIGURE

Figure 2.1	Industrial production of fly ash and bottom ash	5
Figure 2.2	Typical Coal Bottom Ash	6
Figure 2.3	Elemental composition for bottom ash, fly ash, shale and volcanic ash	8
Figure 3.1	Thermogravimetric Analyzer Q-Series	17
Figure 3.2	TGA Platinum Pan	17
Figure 3.3	TGA Software Setup Sequence	18
Figure 4.1	Manjung Power Plant Coal Bottom Ash Sample	23
Figure 4.2	SEM images (a) 3000x (90.4 μ m) (b) 1500x (181 μ m) (c) 1500x (181 μ m) (d) 500x (542 μ m)	24
Figure 4.3	X-ray Diffraction of CBA at 2-Theta Scale	27
Figure 4.4	Weight % vs Time at Carbonation T = 500 $^{\circ}$ C	28
Figure 4.5	Weight % vs Time at Carbonation T = 600 $^{\circ}$ C	29
Figure 4.6	Weight % vs Time at Carbonation T = 700 $^{\circ}$ C	29
Figure 4.7	Weight % vs Time at Carbonation T = 800 $^{\circ}$ C	30
Figure 4.8	Adsorption Percentage vs Temperature	32
Figure 4.9	SEM images of CBA 2-Cycle at 1500x (271 μ m)	33

LIST OF TABLE

Table 2.1	Grain size analysis from different power plants in USA	6
Table 2.2	Typical ranges for geotechnical properties of fly ash and bottom ash	7
Table 2.3	Chemical analysis from different power plants in Malaysia	9
Table 2.4	Comparison of chemical contents from dolomite, limestone and coal bottom ash	12
Table 4.1	Chemical composition of the Manjung coal bottom ash of XRF result	25
Table 4.2	Element composition of the Manjung coal bottom ash of XRF result	25
Table 4.3	Weight of CaO left within the sample after experiment	31

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Coal power plant still plays a major role in generating the electricity all around the globe. According to the World Coal Association (2010), in 2006 coal was used in about 41% of global electricity production (Bartoňová & Klika, 2014). As for the country Malaysia, gas is the main fuel source for the electricity generation industry due to the abundance of gas supply all around the Malaysian shore. However, coal starts to gain momentum in the last 10 years as the number of generation fuel from coal rising from 11% in 2002, 26.7% in 2006 and 31% in 2008 (Abdulhameed U. A. and Baharuddin, 2012).

The coal fired power plant generates high amount of solid waste residue (SWR) and some of SWRs are substantially harmful to the environment. Most of the process that generate SWR emit a great amount of CO₂ hence many studies have been done to use SWR directly and indirectly as a sorbent to for CO₂ capture and storage (CCS) (Wee, 2013). The coal fired power plant produces a SWR by-product which in the form of ashes.

The ashes produced can be divided into two, which are fly ash and bottom ash. The bottom ash is the ash that is collected at the bottom of the boiler, as some of the minerals are not burned during the combustion reaction. The industrial ashes contain substantial alkali and earth alkali metals (Ukwattage, 2012). Based on the current technology, the mineral carbonation is seen as a effective option to capture the CO₂ instead of opting for the geological and ocean storage (Wee, 2013).

The coal bottom ashes generated from power plant have become an important economic and environmental objective. Usage of CBA is limited due to its relatively unburned carbon content and different structural properties compared to fly ash. The current uses both of these ashes are in cement and landfill. According to the American Coal Ash Association (ACAA) the recycling rate for concrete product using CBA only 5.28% worldwide. However, with the recent surge from the environmental bodies all around the world to reduce the greenhouse gases released to the atmosphere, many studies have been done to use these ashes as part of the in-situ CCS technology.

The purpose of the project is to study the potential of using coal bottom ash as a sorbent to capture the CO₂. The potential arises as the CBA contains a portion of calcium oxide, CaO, which will react in a carbonation reaction with the CO₂ to produce calcium carbonate, CaCO₃. The study will involve in adjusting the parameters, which could affect the efficiency of the coal bottom ash ability for CO₂ sequestration by using the thermogravimetric analyzer (TGA). Based on this parametric study, we can deepen the understanding on CBA ability capture the CO₂ at different condition. The result of the study will help the industries in reducing their greenhouse gases emission by recycling the unused by-products, which may have gone to waste and create another epidemic of environmental issues.

1.2 Problem Statement

It is widely known that the combustion of fossil fuels all around the world contributes to the build-up of CO₂ in the atmosphere. This will in turn contributes to the greenhouse effect, which will warm up the planet (Florin and Harris, 2008). Based on the climate change report of IPCC, in 2007 the CO₂ concentration was 379 ppm, which was approximately 180 – 300 ppm more than the equilibrium concentration of CO₂ atmosphere for the last 6500 years.

As the amount of coal ashes being produced are also increasing at an alarming rate with lack of usage hence it is a strategic approach to study the functionality of the

coal bottom ashes as a carbon dioxide sorbent. Thus this research will study on the characteristic of the coal bottom ash and investigate the parameters, which will affect the CO₂ capture ability.

1.3 Objectives

The objectives of the research are as follows:

1. To study the characteristic of coal bottom ash.
2. To study the suitability of the coal bottom ash as a CO₂ sorbent.
3. To investigate the parameters which would effect the absorption behaviour of the CO₂

1.4 Scope of Study

The scope of the study is to deepen the understanding on coal bottom ash ability to capture CO₂ at different operating condition. This is important in unlocking the potential of the coal bottom ash to be used as a CO₂ sorbent in many high temperature applications such as biomass gassification. The parameters of which will be studied are the operating temperature and the level of concentration of the CO₂.

1.5 Relevancy of the Project

This project involves the study of parameters, which would affect a carbonation of calcium oxide within the coal bottom ash in a detailed fashion in way I could apply my theoretical knowledge of that I've learned in analytical chemistry to a good use. Furthermore, the knowledge gained from this experiment would help me in deepen the understanding on the current issue of alarming incremental rate of greenhouse gases and ways to solve it using mineral carbonation such as this.

CHAPTER 2

LITERATURE REVIEW

2.1 Coal Bottom Ash

2.1.1 Production of Coal Bottom Ash

Coal bottom ash refers to the heavier particles that fall to the bottom of the furnace during coal combustion. It mainly consists of carbon and other combustible matter in the fine coal. It forms as a result of the combustion of coal within the furnace as a by-product alongside with the fly ash.

The coals are first pulverized to the size of baking flour before it is fed into the boiler. This is to ensure a smooth combustion takes place. During the combustion, the combustible matter in the fine coal is burned, leaving only non-combustible ash behind. 80 – 90% of this ash comes out as a fly ash which come out at the top along with the flue gas (Abdulhameed U. A. & Baharudin, 2012). As for the rest comes out as bottom ash as it is collected at the bottom of the furnace.

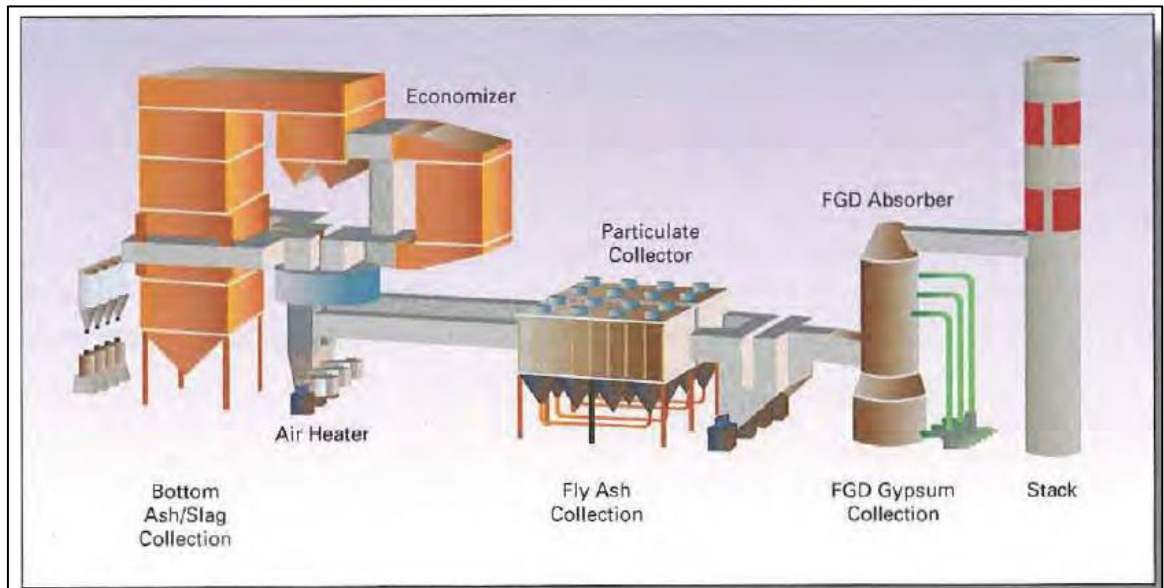


FIGURE 2.1 Industrial Production of Fly Ash and Bottom Ash

The boiler operates at a very high temperature, which is around 1500 – 1700 degrees C hence the ash is softened and melted within the hot zones. The rest of the ashes that do not come out at the top will accumulate on the boiler walls and against steam tubes in the boiler. Eventually as these ashes build up it will drop to the bottom of the boiler where it is removed.

As it is removed from the boiler, the fused bottom ash is still hot. It falls into a water bath or also known as quence tank where it is cooled down before passing through a clinker grinder. This grinder reduces the size of the ashes to smaller particles which approximately around 2 inches. The crushed bottom ash is then removed for storage, disposal or use.

2.1.2 Physical Properties of Coal Bottom Ash

The chemical composition of the coal bottom ash is determined primarily by the chemistry of the source coal and the combustion process ("Coal Ash: Characteristics, Management and Environmental Issues," 2009). Bottom ash is composed of primarily of amorphous or glassy aluminosilicate materials derived from the mineral phases.



FIGURE 1.2 Typical Coal Bottom Ash

As seen in the figure, coal bottom ash has a sandy texture and is generally dull black in appearance. It has a angular particles with very porous surface texture (Muhammad, 2010). The particles of bottom ash ranges from 0.1 mm to 50 mm in diameter. Bottom ash is predominantly sand-sized, usually with 50%– 90% percent passing a 5.475 mm (No.4) sieve and 0% to 10% passing a 0.075 mm (No. 200) sieve. The largest bottom ash particle sizes typically ranging from 19 mm (3/4i in) to 38.1 mm (1.5 in) (Moulton and Lyle, 1973).

It is normally a well-graded material but variations in particle sizes may be observed from the same power plant. However, some bottom ashes, particularly those that are obtained from high-sulfur coals and lower rank coals, are not very porous and are quite dense.

TABLE 2.1 Grain Size Analysis from Different Coal Power Plants in USA

Sieve Size	Bottom Ash		
	Glasgow, WV	New Haven, WV	Moundsville, WV
38 mm	100	99	100
19 mm	100	95	100
9.5 mm	100	87	73
4.75 m	90	77	52
2.36 mm	80	57	32
1.18 mm	72	42	17

0.60 mm	65	29	10
0.30 mm	56	19	5
0.15 mm	35	15	2
0.075 mm	9	4	1

According to the study done by (Abdulhameed U. A. & Baharudin, 2012), it has been stated that categorization given in BS 882: 1992 is based on percentage passing the 600 μ m (No. 30 ASTM) sieve. The main reasoning behind this is because a large number of natural sands divides them at just that size, the grading above and below being approximately uniform.

TABLE 2.1 Typical Ranges For Geotechnical Properties of Fly Ash And Bottom Ash

Property	Fly Ash	Bottom Ash
Specific Gravity	2.1 - 2.9	2.3- 3.0
Bulk Density (Compacted) lbs/ft ³	65 - 110	65 - 110
Optimum Moisture Content, %	10.0 - 35.0	12.0 - 26.0
Hydraulic Conductivity, cm/s	10 ⁴ - 10 ⁶	10 ¹ - 10 ³
Porosity	0.40 - 0.50	0.25- 0.40
Angle of Internal Friction, degrees	25.0 - 40.0	35.0 - 45.0

2.1.3 Chemical Composition of Coal Bottom Ash

The chemical composition of coal bottom ash relies depending on the type of coal that was used. Coal is primarily composed of carbon and hydrogen, but all coal also contains some mineral matter such as clays, shales, quartz and calcite. Furthermore, properties of coal ash are determined by reactions that occur during the high-temperature combustion.

Based on the report by Electric Power Research Institute, it states that the major elemental composition of coal is similar to the composition of a wide variety of rocks in the Earth's crust. As for the major components in the bottom ash are oxides of silicon, aluminum, iron and calcium which comprises approximately 90% of the mineral component within the bottom ash.

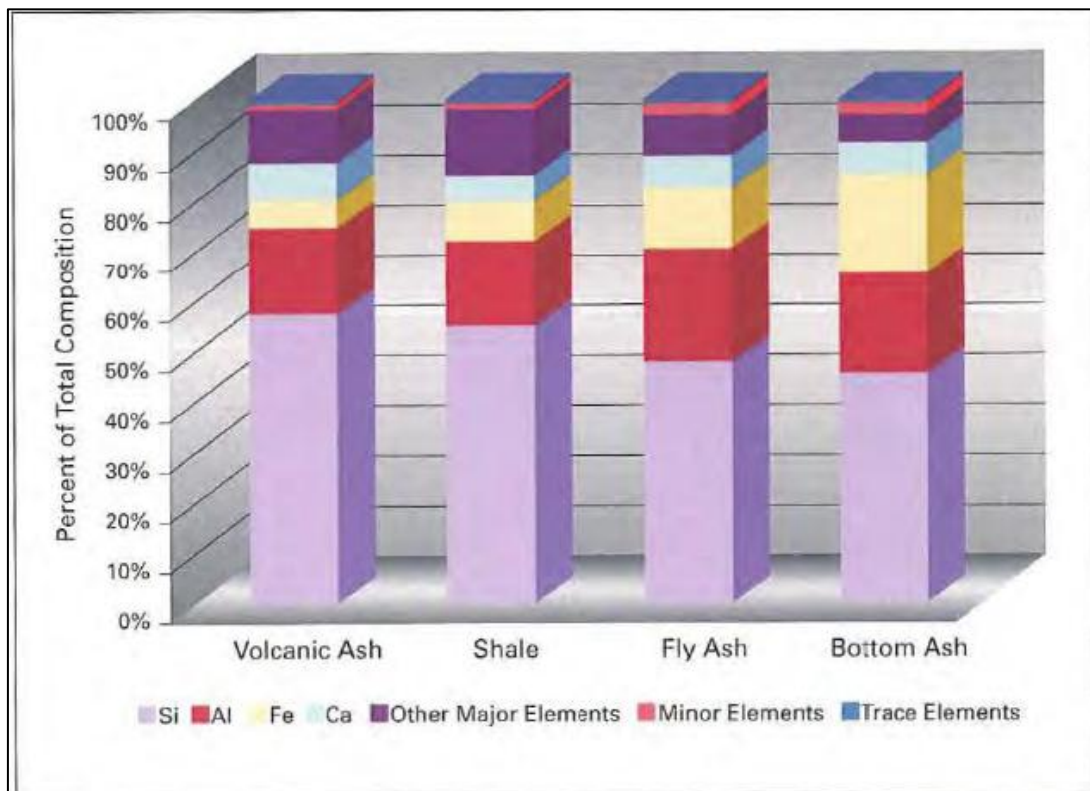


FIGURE 2.3 Elemental Composition For Bottom Ash, Fly Ash, Shale And Volcanic Ash

Based on the figure, we can see that major component of the bottom ash is oxide of silicon which comprises up to 40% of the total composition. The calcium oxide which is the component that we wish to use for the carbon dioxide capture only comprises approximately less than 10%.

There is however a case where the composition of calcium oxide may exceed more than 10% as the coal ash composition depends on the type of the coal that has been used. According to the article by Electric Power Research Institute, subbituminous and lignite coal ashes typically contain relatively high concentration of calcium, with concentration exceeding 15%. Bituminous coal ashes on the other hand generally contain less oxide of calcium.

TABLE 2.3 Chemical Analysis From Different Power Plants In Malaysia

	Bottom Ash Percentages		
	Muhardi et al.,(2010)	Fawzan (2010)	Nagathan et al., (2012)
Chemical contents	Tanjung Bin Power Plant	Jimah Power Plant	Kapar power plant
SiO ₂	42.7	49.4	9.78
Al ₂ O ₃	23	22.3	20.75
Fe ₂ O ₃	17	13.7	37.1
CaO	9.8	9	11.1
K ₂ O	0.96	1	-
TiO ₂	1.64	2.2	-
MgO	1.54	0.87	3.2
P ₂ O ₅	1.04	0.65	-
Na ₂ O	0.29	0.13	-
SO ₃	1.22	0.68	-
BaO	0.19	-	-
MnO	-	0.08	-
ZnO	-	-	1.8

Based on the table, we can observe that the percentage composition of calcium oxide from Malaysian coal power plant is at 9% - 11.1%. A similar chemical analysis on bottom ash was carried out by combustion of bituminous coal and lignite at temperature of 850 C and it has been found that the composition of CaO is within the range of 8.9% - 11.1% (Bartoňová and Klika, 2014).

2.1.4 Current Usage of Coal Bottom Ash

The physical and chemical properties of coal ash make it suitable for many construction and geotechnical uses ("Coal Ash: Characteristics, Management and Environmental Issues," 2009). Furthermore, there is lack of exploitation on the usage of bottom ash compared to the fly ash. Based on the survey done by the ACAA, in 2007, 7.3 million tons of bottom ash and 1.7 million tons of boiler slag were used.

The primary uses of for bottom ash is for structural fills and road base materials. Its use in concrete becomes more significant and important in view of the fact that sources of natural sand as fine aggregates are getting depleted gradually, and it is of prime importance that substitute of sand be explored (Singh and Siddique, 2013). Bottom ash is also used for the production of cement. The main reason why it is beneficial to use ash for production of cement is that it helps in conserving virgin materials such as limestone and reduced the need for disposal sites. Additionally, there is a current study on the usage of bottom ash to design an acoustic absorbing material for highway noise barriers (Arenas, Leiva, Vilches, & Cifuentes, 2013).

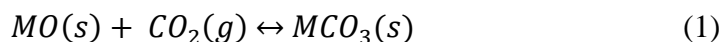
Our study will be on the usage of coal bottom ash to capture the CO₂. Currently there are extensive studies on the usage of fly ash to capture the CO₂ by employing the carbonation reaction between the alkaline materials within the ash with CO₂(Wee, 2013). As for our study, the bottom ash will be used for the dry carbonation process of calcium oxide with the CO₂.

2.2 Alkaline Earth Metal Oxide – Based Sorbent

Alkaline earth metals are defined as the metallic elements that are found in the second group of the periodic table. All of the alkaline earth elements have an oxidation number of +2, making them very reactive. According to the IUPAC, there are six elements, which are under alkaline earth element, which are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra)

The acidic nature of CO₂ facilitates adsorption on the basic sites of some metal oxides, especially those with a low charge / radius ratio, which are more ionic in nature and present more strongly basic sites (Z. Yong and Rodrigues, 2002). The main focus of the study will be only on CaO and MgO. These two types of alkaline metal oxides present in the coal bottom ash. There is however a small portion of BaO presents in the bottom ash based on the study done by Muhardi et al, but the effect it will have on the carbon dioxide capture is expected to be really low as the composition consist of only at 0.19%.

The alkaline earth metal oxides are able to react with the acidic nature of CO₂ to form an alkaline earth metal carbonate through a reaction known as carbonation. Based on the stoichiometry of the equation, 1 mole of metal oxide can chemically adsorb a stoichiometric equivalent of CO₂ to form the metal carbonate. The chemical reaction of any metal oxide is as following:



This reaction releases heat hence it is an exothermic reaction. The metal oxides, M, can be replaced with Be, Mg, Ca, Sr, Ba or Ra.

2.2.1 Calcium Oxide Adsorption Characteristic

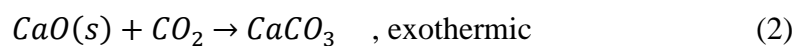
Calcium minerals are the most abundant among alkaline earth metal oxides in nature, commonly found in the form of carbonates such as limestone or dolomite. Based on the table 4, we can clearly observe that the composition of CaO is much higher in limestone compared to coal bottom ash at 46.7% (Sua-iam and Makul, 2013).

TABLE 2.4 Comparison Of Chemical Contents From Dolomite, Limestone And Coal Bottom Ash

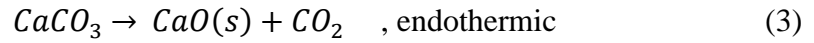
References	Johnsen et al. (2006)	Gritsada et al. (2013)	Muhardi et al. (2010)
Chemical contents	Dolomite	Limestone Powder	Coal Bottom Ash
SiO ₂	0.7	8.97	42.7
Al ₂ O ₃	-	1.02	23
Fe ₂ O ₃	0.1	0.37	17
CaO	32	46.7	9.8
K ₂ O	0.004	0.13	0.96
TiO ₂	0.005	-	1.64
MgO	20.3	2.38	1.54
P ₂ O ₅	-	-	1.04
Na ₂ O	0.003	0.02	0.29
SO ₃	-	0.33	1.22
BaO	-	-	0.19
MnO	-	-	-
ZnO	-	-	-

However, it has to be taken into account the price comparison. In the market price, dolomite and limestone are quite expensive as compared to the coal bottom ash. Furthermore, dolomite and limestone are finite resources (Johnsen et al, 2006). Coal bottom ash on the other hand is a waste product, which is currently has limited usage. Therefore, it is more beneficial to use coal bottom ash rather than dolomite and limestone as it may help in reusing the waste product of coal power plant.

Calcium oxide will react with the CO₂ producing calcium carbonate by the following reaction:



The reversed of this reaction is known as calcination where CaCO_3 may be treated to a very high temperature to yield calcium oxide. The reaction is as follow:

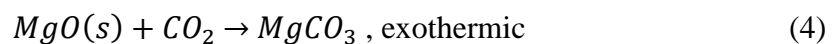


This pair of reaction is very useful as it may be used for the in situ removal of CO_2 in many relatively high temperature applications such as coal gassification process (An et al., 2012). Furthermore, CaO is also capable of scavenging CO_2 to a very low concentration at moderate temperatures (450 – 750 C) and at atmospheric pressure (Florin and Harris, 2008).

Theoretically, the maximum amount of CO_2 that can be adsorbed is 17.8 mmol g^{-1} . This theory is based on the stoichiometric carbonation reaction where 1 mol of calcium oxide reacts with 1 mol of carbon dioxide. However, based on many studies done the real value of the CO_2 captured is much lower than the maximum theoretical value. A study done by Barker, which performs a carbonation on two sizes of CaO sorbent. The micrometer-sized sorbent ($10\mu\text{m}$) reached a capacity of 13.4 mmol g^{-1} where as a nanoparticle-size sorbent (10nm) reached a higher capacity, 16.6 mmol g^{-1} .

2.2.2 Magnesium Oxide Adsorption Charecteristic

Other than calcium oxide, magnesium oxide has also been extensively studied as one of the metal oxide, which could be used to capture CO_2 . The component MgO has around 0.87% - 3.2% of composition within the coal bottom ash based on the study by Muhardiet al. The carbonation of MgO is given by the following equation:



This reaction is an exothermic reaction. Magnesium oxide in comparison with the calcium oxide as a CO₂ sorbent is much better in terms of the lower energy requirement for regeneration (B. Feng et al, 2007). Based on the studies done, CO₂ adsorbed by the magnesium oxides can be recovered by 1 hour of regeneration under vacuum at 973 K. On the other hand, 4 hours of heating needed to be done on calcium oxide.

The CO₂ adsorption capacity is lower for magnesium oxide compared to calcium oxide. Furthermore, as the temperature increases the capacity decreases according to a study done (M. B. Jensen et al, 2005). The typical capacity of magnesium oxide may correspond to less than a half of the capacity of calcium.

CHAPTER 3

METHODOLOGY

This study focusses on the parametric study of the coal bottom ash as CO₂ sorbent. The main reaction that will be observed is the carbonation of the calcium oxide with the carbon dioxide. This study is divided into two parts, which are the characterization study and the adsorption capacities study.

3.1 Characterization

The purpose of the characterization study is to analyze the composition and the suitability of the coal bottom ash as a sorbent. The result of this section will help in confirming the suitability of coal bottom ash as a replacement to other possible sorbent such as dolemite and limestone.

3.1.1 X-ray Diffraction Analysis

X-ray diffraction (XRD) measurement is employed for the identification of the phases of the coal bottom ash sorbent. This analysis is a very important as it will help us in determining the crystalline structure of the coal bottom ashes in detail. Furthermore, it gives us the ability to study the interatomic distance and bond angles. As the coal bottom ash are already in a powder form so it will be placed in the aluminium holder to support the samples in the XRD measurement. The XRD analyses will be conducted on a powder X-ray diffractometer with a Cu K α radiation source.

3.1.2 X-ray Fluorescence Analysis

X-ray Fluorescence (XRF) is used to get the composition of the coal bottom ash. This is one of the most important part in the characterization analysis as it help us determine the chemical composition of the ashes. Our main priority is to measure the amount of CaO presents within the coal bottom ash. Based on this result we can almost predict the adsorption capacity of the sorbent by using a theoretical analysis using the carbonation reaction of CaO with CO₂.

3.1.3 Scanning Electron Microscope Analysis

Scanning Electron Microscope (SEM) analysis is done to get the structural view of the coal bottom ash. Based on this analysis, we can get a clearer view of how the image of the coal bottom ash close at macroscopic level. This will help us in analysing the effect it may have on the carbonation reaction.

3.2 Thermogravimetric Analysis

Thermogravimetric analyzer (TGA) will be used to study the carbonation reaction of calcium oxide within the coal bottom ash with the CO₂. The coal bottom ash will be provided by Mr Shahbaz (Chemical Engineering, University Teknologi PETRONAS). The coal bottom ashes that will be used are first to go through a sieve plate of 25 µm. This is to ensure that the sizes of the particles are uniform throughout the experiment.



FIGURE 3.1 Thermogravimetric Analyzer Q-Series

Around 20 mg of sorbent will be placed within the TGA for the carbonation purpose.

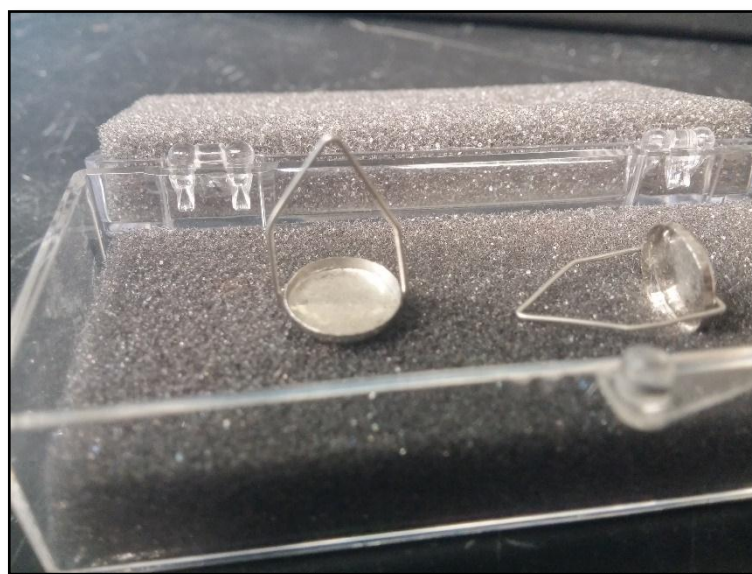


FIGURE 3.2 TGA Platinum Pan

The experimental approach is divided into two parts, which are:

1. Studying the effect of temperature on CO₂ adsorption capacities

Temperature plays a very important role in kinetic of reaction between the CO₂ and the metal oxides within the coal bottom ash specifically calcium oxide. A varying degree of temperature will be set to study this effect. A small sample of coal bottom ash will be inserted inside the TGA and stream of carbon dioxide at a fixed concentration will be flowed in. The experiment will be carried out at different temperatures ranging from 500 °C to 800 °C. The results are then analysed for discussion.

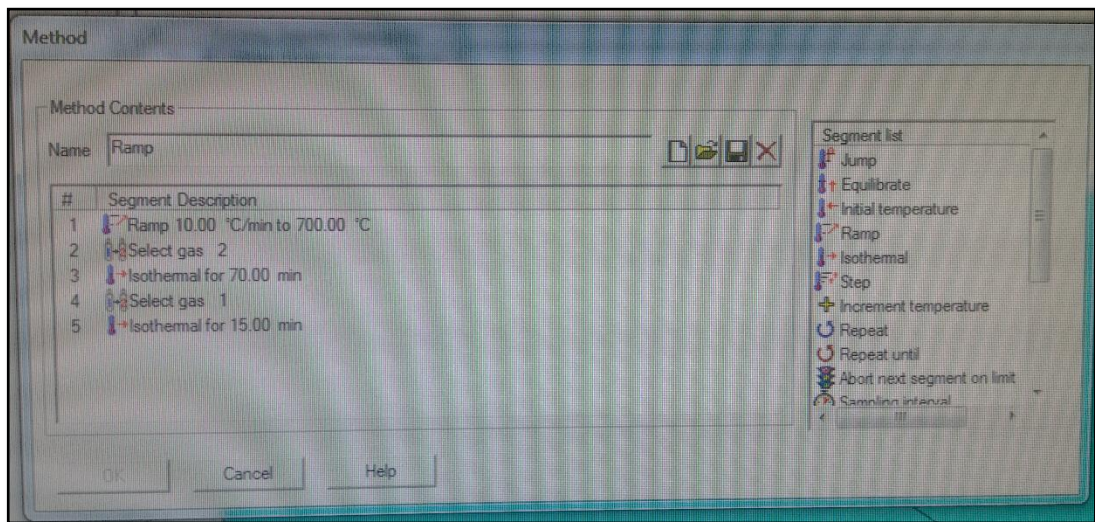


FIGURE 3.3 TGA Software Setup Sequence

Step	Description
1	Ramp 10 °C /min to desired temperature ie – 500 °C (N ₂ as purge gas)
2	Select gas 2 – Switching to CO ₂ gas purge for the carbonation.
3	Isothermal at desired temperature for 200 min.
4	Automated cooling down machine to room temperature before samples are collected.

2. Studying the reversibility of the sorbent

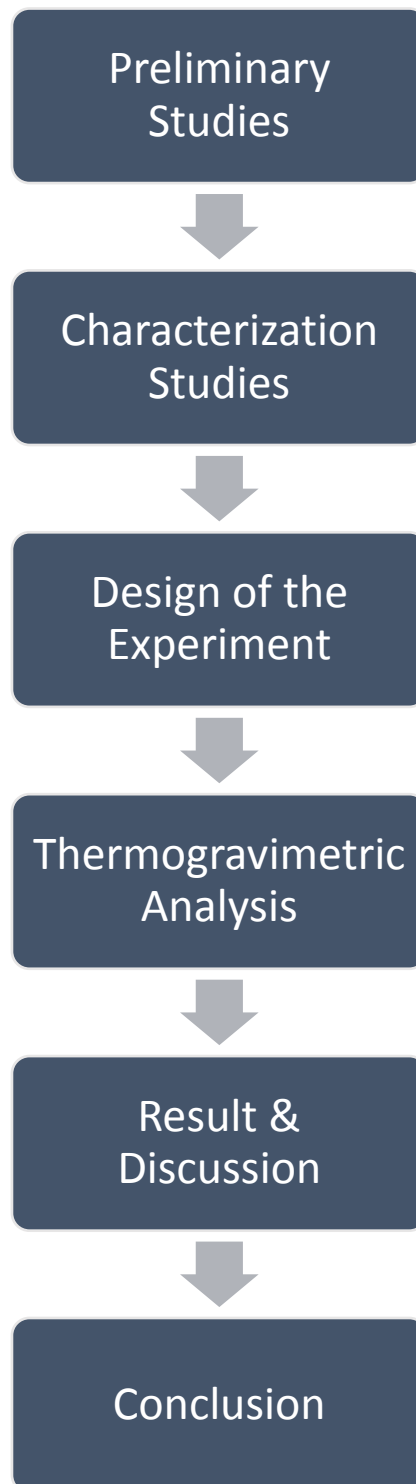
Another aspect to be studied within this project is the reversibility of the sorbent. This is because a good reversibility is needed for sorbent as it can be then used for many times for the process. The samples will be tested under number of cycles of carbonation and decarbonation to study reservesibility of the sample. The samples will be then analysed using BET surface analysis and also XRF to see the changes in the crystalline structure and pore surface which may affect the CO₂ adsorption capacity.

Step	Description
1	Ramp 10 °C /min to 700 °C (N ₂ as purge gas)
2	Select gas 2 – Switching to CO ₂ gas purge for the carbonation.
3	Isothermal at desired temperature for 70 mins
4	Select gas 1 – Switching to N ₂ gas purge for decarbonation
5	Isothermal at desired temperature for 20 min.

Once the sample has been placed on the platinum sample pan it will then be heated to the studied carbonation temperature at a ramp of 10 °C/min. Once the sample had reached the studied carbonation temperature, a flow of CO₂ will be flowed in for the carbonation process. When the carbonation had completed, the temperature will be increased to the decarbonation temperature. The flow of the CO₂ will be then replaced by pure N₂ for decarbonation process. When the decarbonation process had finished, the temperature will be increased or decreased to the studied carbonation temperature again.

A new carbonation/decarbonation cycle began when the temperature is achieved. The carbonation process will be set at 200 min to achieve a relatively high uptake capacity of CO₂, whereas the decarbonation time is set at 30 min to allow the sorbent to be decarbonated completely.

3.3 - Process Flow of the Project



3.4 - Gantt's Chart

FYP 1

No	Detail	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Topic: Parametric Study of coal bottom ash as CO ₂ sorbent	█	█												
2	Preliminary Research Work: Research on literatures related to the topic		█	█	█	█	█								
3	Submission of draft project proposal						█	█							
4	Submission of extended proposal								█	█					
5	Proposal Defense										█				
6	Project Work: Study on research scope and method										█				
7	Project work: Further investigation on the project and do modification if necessary										█	█	█		
8	Submission of interim report													█	█

FYP II

No	Detail	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Characterization Studies: XRF, XRD & SEM														
2	Preparing the TGA equipment for the parametric study - Temperature														
3	Parametric Study on the Reversibility of the sorbent														
4	Analysis of the sample result : XRF & SEM														
5	Submission of the Progress Report														
6	Pre-Sedex														
7	Submission of Draft Final Report														
8	Submission of Dissertation (soft bound)														
9	Submission of Technical Paper														
10	Oral Presentation														
11	Submission of Project Dissertation (hard-bound)														

CHAPTER 4

RESULTS & DISCUSSION

The result for his study is divided into two parts, which are the characterization of the coal bottom ash properties and also the parametric study of the coal bottom ash itself subjected to the thermogravimetric analyzer.



FIGURE 4.1 Manjung Power Plant Coal Bottom Ash Sample

4.1 Characterization Analysis

4.1.1 Scanning Electron Microscopy Analysis

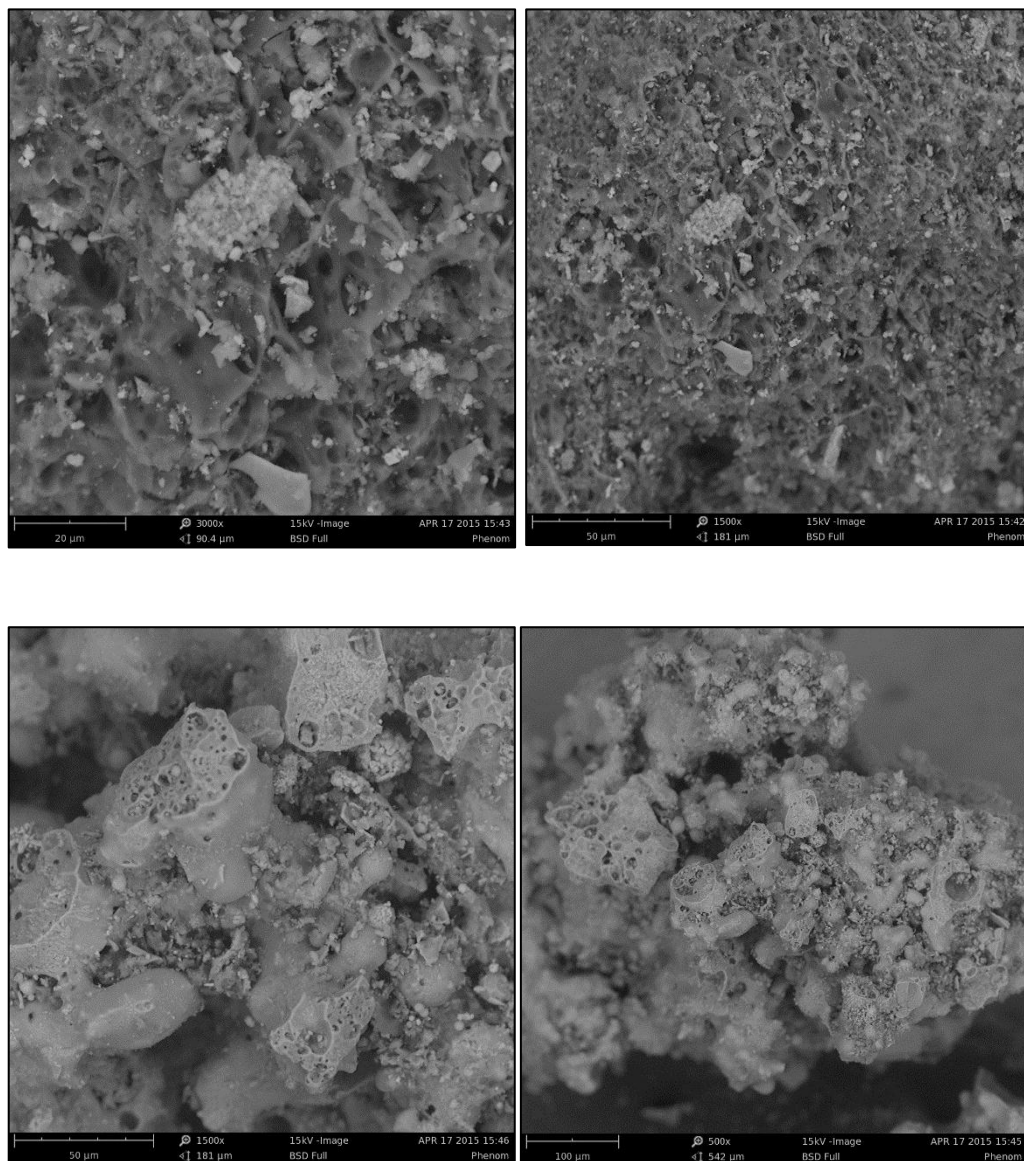


Figure 4.2 SEM images (a) 3000x (90.4μm) (b) 1500x (181μm) (c) 1500x(181μm) (d) 500x (542μm)

The images here show that the particle has very porous and large surface area. These then suggest that the pore volume of CBA is high which is an essential characteristic for an adsorbent. As a higher surface area can give more room for reaction mechanism to take place and thus increase the uptake capacity

4.1.2 X-ray Fluorescence Analysis

TABLE 4.1 Chemical Composition Of The Manjung Coal Bottom Ash Of XRF Result

Chemical Compound	Concentration (%)	Stat. Error (%)
SiO ₂	31.2	0.67
Fe ₂ O ₃	27.2	0.187
CaO	20.6	0.397
Al ₂ O ₃	8.88	1.47
SO ₃	3.05	1.4
MgO	2.6	3.03
P ₂ O ₅	1.71	2.53
TiO ₂	1.47	1.71
K ₂ O	1.33	1.51
Cl	0.487	3.06
SrO	0.344	0.744
Na ₂ O	0.34	23.2
BaO	0.296	6.44
MnO	0.261	2.41
Others	0.232	51.242

TABLE 4.2 Element Composition Of The Manjung Coal Botom Ash Of XRF Result

Element	Concentration (%)	Stat. Error (%)
Fe	35.4	0.187
Ca	24.3	0.395
Si	22	0.657
Al	6.67	0.146
Mg	2.18	2.96
S	1.89	1.4
K	1.79	1.5
Ti	1.62	1.66
P	1.24	2.44
Cl	0.712	3.2
Ba	0.624	6.62
Sr	0.583	0.747
Na	0.371	18.2
Mn	0.357	2.47
Others	0.263	57.418

The result shows that the coal bottom ash obtained from the Manjung Power plant has a high CaO composition, which is at 20.6% whereas when compared with the coal bottom ash obtained from Kapar Power plant which is averaged at 11.1%. The significant increase of this result is due to the coal used for the power plant. The initial composition of the coal used has high element of Ca which comes in the form of metal oxide.

Furthermore, the composition of MgO is also low at 2.6%. Therefore, during the thermogravimetric analysis later the carbonation process mainly due to the CaO as opposed to the carbonation of MgO.

As for the elemental result the highest composition is iron, which corresponds to the existence of iron oxide in the sample. However, even though iron is the highest element in the sample, Fe₂O₃ is lower compared to SiO. This suggests that iron exist in elemental state and also in metal state in the sample compared to SiO where most of the Si are in metal oxide state.

4.1.3 X-ray Diffraction Analysis

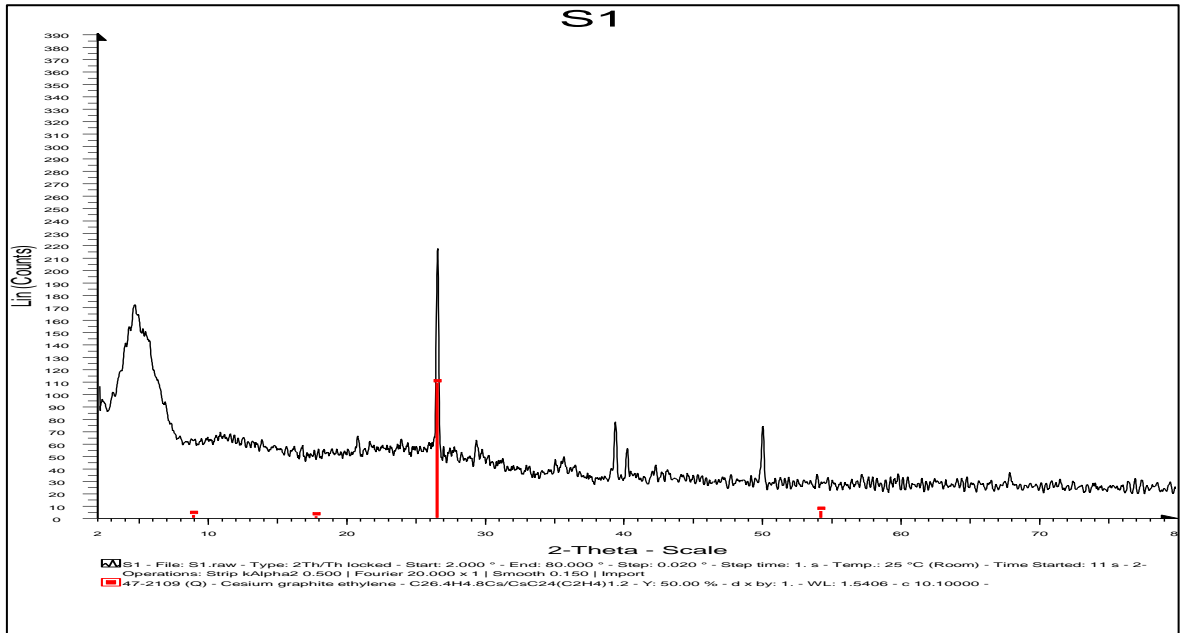


FIGURE 4.3 X-Ray Diffraction Of CBA At 2-Theta Scale

Based on Figure 9, it shows that CBA has a crystal structure of cesium graphite ethylene with highest peak at 26 at 2-theta. Another 2 peaks are also observed occurring at 39 and 50. These two peaks correspond to pure CaO crystal structure. The reason the peak at 26 is the dominant peak may be due to the fact that the amount of CaO in the CBA is only 20% with the rest of the sample having a different crystalline structure.

4.2 Thermogravimetric Analysis

4.2.1 Effect of Carbonation Temperature

Each test had been done using the same ramp and approximately the same amount of weigh which is 20mg. The only variable adjusted for this test is the carbonation temperature, which was tested at 500 °C, 600 °C, 700 °C and 800 °C.

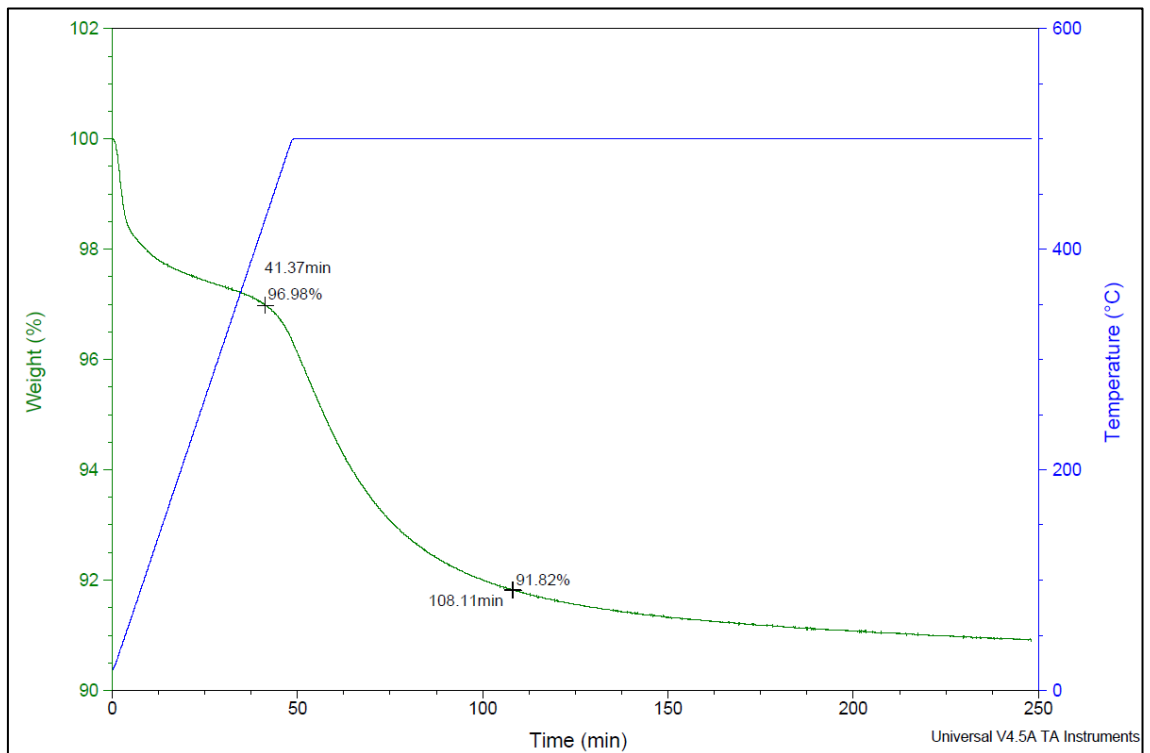


FIGURE 4.4 Weight % Vs Time At Carbonation T = 500 °C

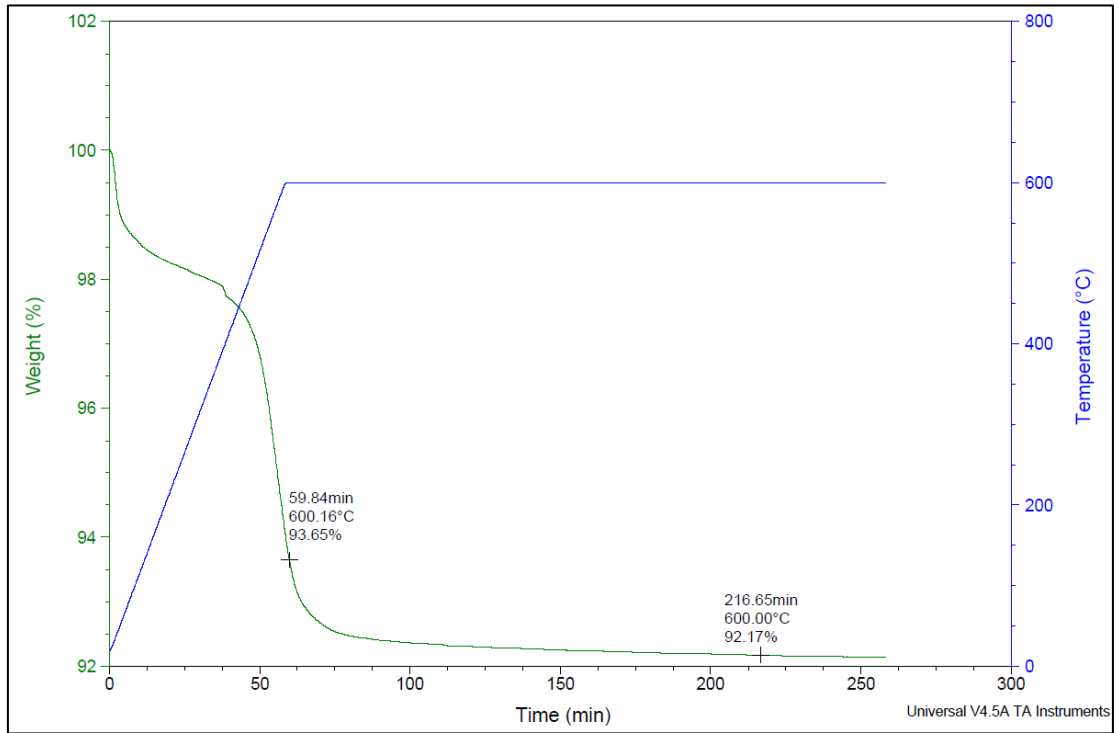


FIGURE 4.5 Weigh % Vs Time At Carbonation T = 600 °C

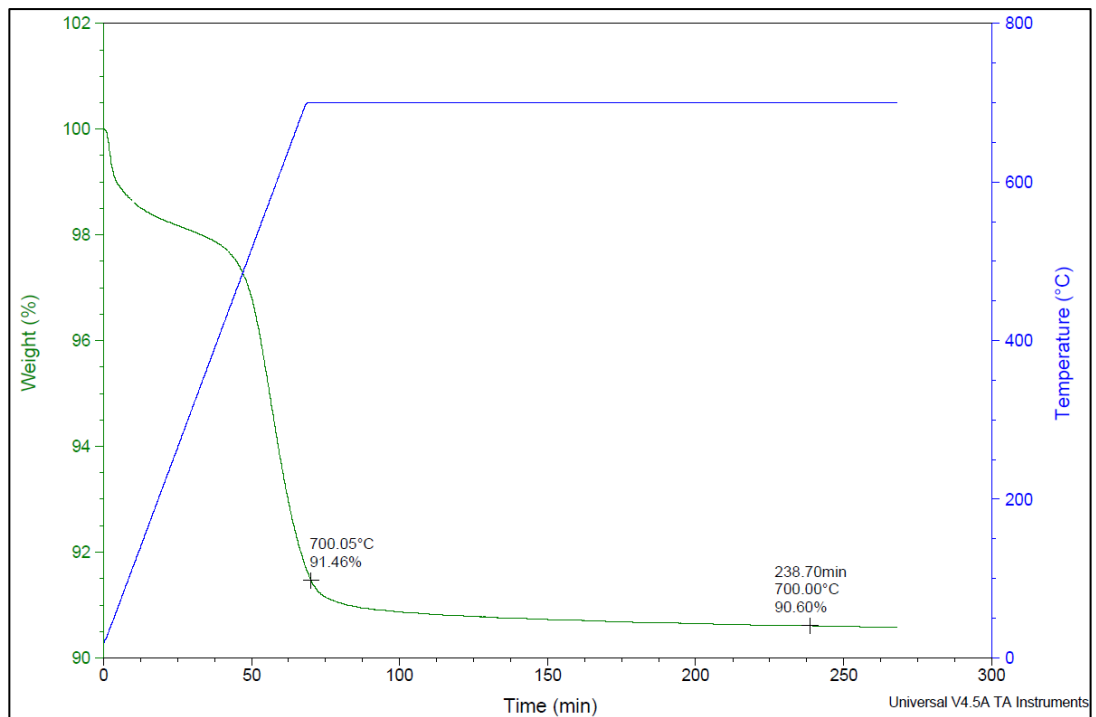


FIGURE 4.6 Weigh % Vs Time At Carbonation T = 700 °C

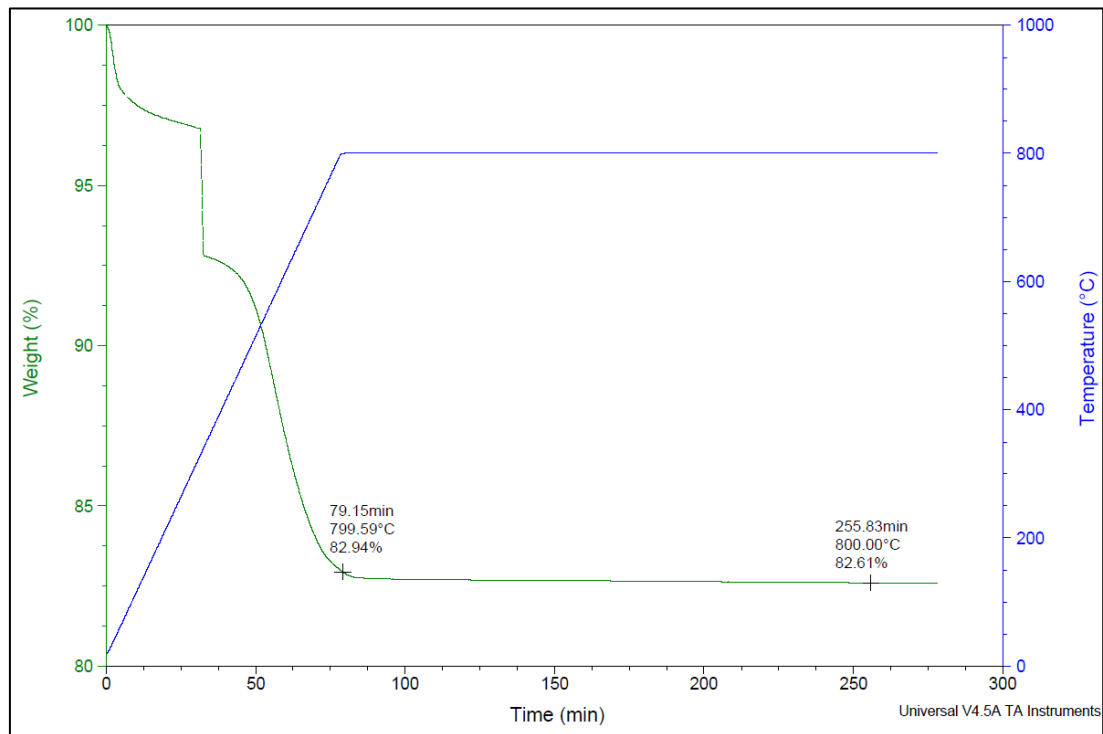


FIGURE 4.7 Weigh % Vs Time At Carbonation T = 800 °C

Based on the experiments carried out at these four different carbonation temperature, it has been noted that the weight loss tends to be decreasing as the carbonation temperature increases. Initially the sample was going through decomposition process where the heat energy decompose the sample as the temperature increases which explains the sudden drop in the weight of the sample.

However when the temperature reaches the desired carbonation temperature, the weight loss suddenly stop increasing and going through at much smaller rate. It has been noted that at 500°C had a drop of weight approximately around 6.44% where as at 800 °C only had 0.33%. This may be due to the fact that carbonation is taking place and slowing down the decomposition rate as the metal carbonate is forming on the surface of the sample. The trend shows that as the temperature increases the weight loss decreases as the carbonation process begins.

Despite the graph shown, the real picture in order to look at the reactivity is done by calculating the amount of CaO left in the sample rather than the weight loss of CBA

as CaO is only a portion of what is in the CBA. The weight changes may be caused by the chemical bonds of the component in the CBA breaking and releasing O₂ back to gaseous phase leaving only the metal behind.

CO₂ Adsorption Analysis

The sample that had went through carbonation are then sent to XRF laboratory to analyse on how much of CaO is presence in the sample. By using this method, we found out the adsorption percentage at temperatures that had been tested using TGA.

Refering back to the carbonation equation of calcium oxide, the ratio of mol needed for this reaction with CO₂ is 1:1 therefore we the percentage of adsorption calculation is as follow.

$$\begin{aligned} \text{Initial weight of CaO in the sample} &= 0.21 \times 20\text{mg} \\ &= 4.2\text{mg} \end{aligned}$$

TABLE 4.3 Weight Of Cao Left Within The Sample After Experiment

Temperature (°C)	Final Weight of CaO (mg)
500	2.97
600	2.7
700	2.61
800	2.952

$$\text{Percentage of Adsorption} = \frac{\text{Initial Weight of CaO} - \text{Final Weight of CaO}}{\text{Initial Weight of CaO}}$$

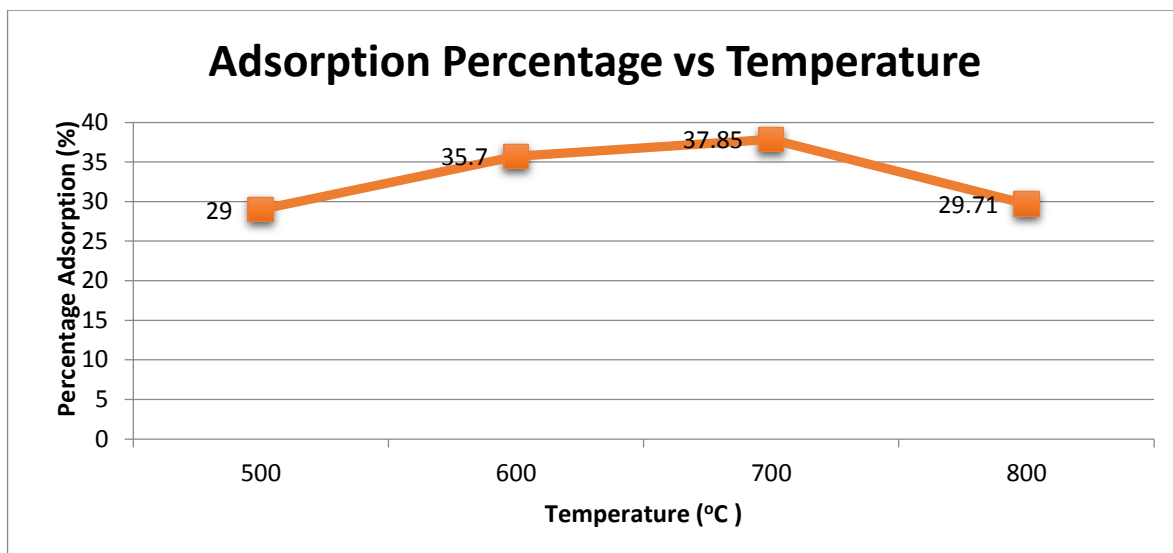


FIGURE 4.8 Adsorption Percentage Vs Temperature

The result shows that the percentage of adsorption by the CaO is highest at 700°C which valued at 37.85% whereas the lowest is at 500°C. The trend shows that the percentage decreases as the temperature hits 800°C which is concurring to our previous result on the reactivity based on the weight loss.

The low rate of carbonation of CO₂ at low temperature may be due to the reactions are kinetically controlled. As the temperature increases at higher temperature around 600°C-700°C, the adsorption percentage increases. This suggests that the reaction mechanism may be changing from kinetic control to diffusion or that the reaction is being controlled by mass diffusion and kinetic.

Reversibility Analysis

In this analysis, it is to provide an insight on how does the CBA perform after a series of carbonation/decarbonation reaction. After the experiment, the samples are then sent to SEM imaging to see the changes that had taken place on the surface of the CBA.

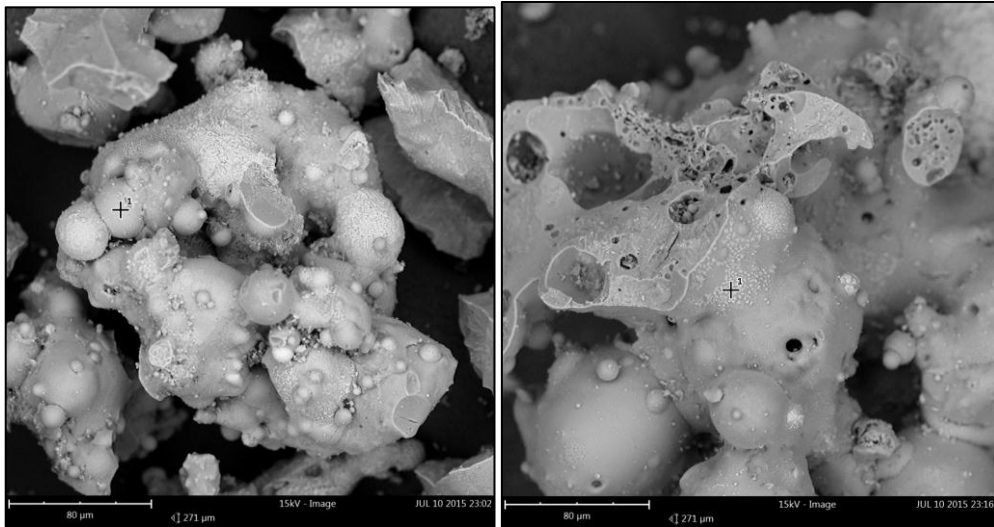


FIGURE 4.9 Sem Images Of Cba 2-Cycle At 1500x (271 μ m)

Referring to Figure 4.9, it shows that the porosity of the sample decreases and the pores are also decreasing based on the figure. This may be resulted due to sintering effect by the formation of metal carbonate on top of the existing metal oxide. This would have affect the carbonation/decarbonation of CaO especially as the sample goes through multiple cycle it will cause the pore structure to collapse and blockage of the pore due to the formation of carbonate.

However, based on this imaging, the main factor of the deterioration of the adsorption behaviour may not be analyzed perfectly as it is not clear on which is the dominant factor: sintering effect or the closure of pores and decrease in surface area. From the figure 15, it is concluded that after going 2 –Cycle of carbonation/decarbonation the pore seems to be closed and reduce which reduced the surface area for further adsorption.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study has a clear and distinct objective in which to study the characteristic of the coal bottom ash from Manjung Power Plant. The result shows a positive point as the sample contains 20.6% of CaO, which mean it has a high percentage of CaO that can be used for carbonation process with CO₂. The SEM image also shows that it has a high surface area and pore volume, which is good for a sorbent to have.

Despite the sample having low CaO content compared to other samples like dolomite or even a pure CaO from other pre- secursors, the prices of CBA is cheap compared to other adsorbent. Therefore, it term of the suitability it shows a promising for industrial uses in the future and also may be used for futher studies to increase the effieency of the uptake capacity.

As for the TGA analysis, it has shows that as the temperature increases the adsorption uptake increases and as it gets to 800°C it decreases back. This is similar to the weight vs temperature graph, which also shows the same trend. From here we conclude that the highest uptake of CO₂ is at the range of 600°C – 700°C.

In conclusion, all the objectives have been met and CBA obtained from Manjung Power Plant shows a promising alternative as CO₂ adsorbent for the future to come as further study needed for it to be used for widescale and in much more effiecient way.

5.2 Recommendation for Future Work

As for future work, it is recommended to find a way to combine the coal bottom ash with Ni–Mg–Al, where it would make the coal bottom ash not just as a sorbent but also as a catalyst for biomass process specifically. The biomass process produces high amount of CO₂ therefore, by utilizing a combined coal bottom ash and Ni–Mg–Al it would then favor the process as it helps in getting rid of the CO₂ and also increases the efficiency of the biomass process in generating H₂.

Furthermore, the study on the reversibility analysis also could have been done for more than 2-cycles and preferably at around 30 cycles. This is to ensure a substantial amount of results are obtained for the analysis rather than short cycle. Different parameters also could be studied given if the TGA equipment can purge 2 gases at the same time. This will then in turn help to study a mixed gas with different concentration of CO₂ would behave in this type of parametric study as it would be a closer approach to real life situation.

Another interesting aspect, which could be done to the coal bottom ash, is to turn it into an activated carbon component. This is also a good idea to enhance the CBA potential as it may help increase the surface area and also the uptake capacity tremendously.

REFERENCES

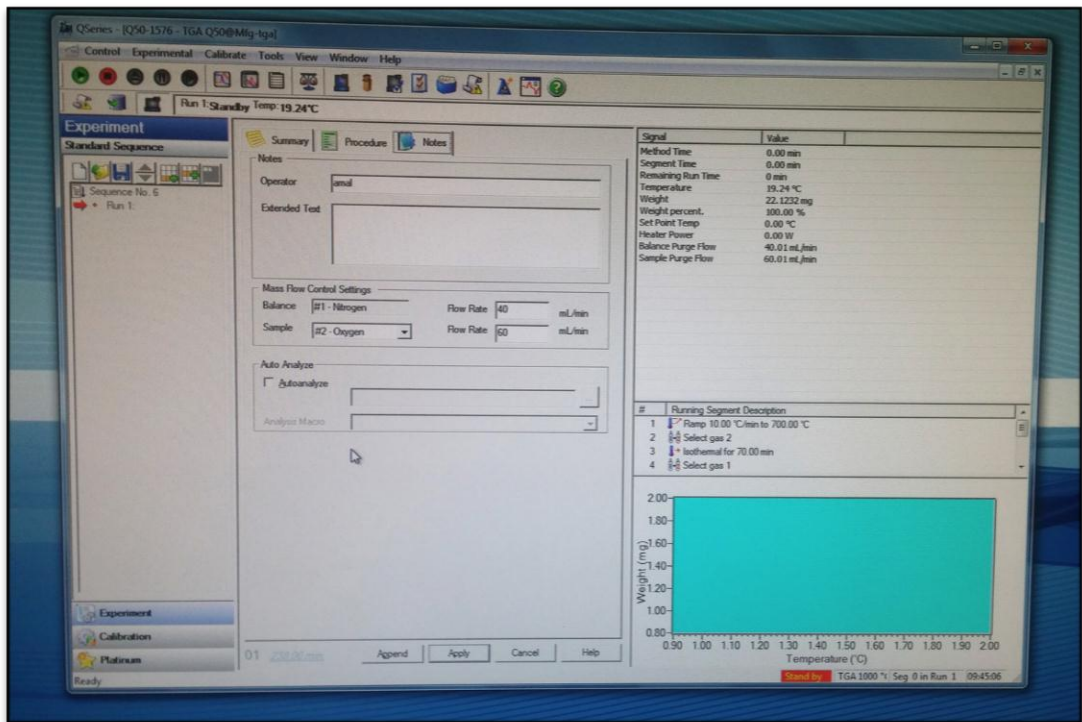
- Abdulhameed Umar Abubakar, and Baharudin, K. S., 2012. Potential use of Malaysian Thermal Power Plants Coal Bottom Ash In Construction. *International Journal of Sustainable Construction Engineering & Technology*, **3(2)**.
- An, H., Song, T., Shen, L., Qin, C., Yin, J., and Feng, B., 2012. Coal gasification with in situ CO₂ capture by the synthetic CaO sorbent in a 1 kWth dual fluidised-bed reactor. *International Journal of Hydrogen Energy*, **37(19)**, 14195-14204.
- Arenas, C., Leiva, C., Vilches, L. F., and Cifuentes, H., 2013. Use of co-combustion bottom ash to design an acoustic absorbing material for highway noise barriers. *Waste Management*, **33(11)**, 2316-2321.
- Florin, N. H., and Harris, A. T. , 2008. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. *Chemical Engineering Science*, **63(2)**, 287-316.
- Lee, J., Han, S.-J., & Wee, J.-H., 2014. Synthesis of dry sorbents for carbon dioxide capture using coal fly ash and its performance. *Applied Energy*, **131(0)**, 40-47.
- Moulton, and Lyle., 1973. Bottom Ash and Boiler Slag. *International Ash utilization symposium*.
- Muhammad, M. S., 2010. *Strength characteristics of Compacted Residual Soil-Bottom Ash mixture*. Universiti Teknologi Malaysia.
- Singh, M., and Siddique, R. ,2013. Effect of coal bottom ash as partial replacement of sand on properties of concrete. *Resources, Conservation and Recycling*, **72(0)**, 20-32.
- Sun, Y., Parikh, V., and Zhang, L. ,2012. Sequestration of carbon dioxide by indirect mineralization using Victorian brown coal fly ash. *Journal of Hazardous Materials*, **209–210(0)**, 458-466.
- Wee, J.-H. (2013). A review on carbon dioxide capture and storage technology using coal fly ash. *Applied Energy*, **106(0)**, 143-151.
- An, H., Song, T., Shen, L., Qin, C., Yin, J., & Feng, B. ,2012. Coal gasification with in situ CO₂ capture by the synthetic CaO sorbent in a 1 kWth dual fluidised-bed reactor. *International Journal of Hydrogen Energy*, **37(19)**, 14195-14204.
- Arenas, C., Leiva, C., Vilches, L. F., and Cifuentes, H. ,2013. Use of co-combustion bottom ash to design an acoustic absorbing material for highway noise barriers. *Waste Management*, **33(11)**, 2316-2321.

- B. Feng, H. An, and Tan, E. 2007. *Energy Fuels*, **21**, 426.
- Bartoňová, L., and Klika, Z., 2014. Effect of CaO on retention of S, Cl, Br, As, Mn, V, Cr, Ni, Cu, Zn, W and Pb in bottom ashes from fluidized-bed coal combustion power station. *Journal of Environmental Sciences*, **26(7)**, 1429-1436.
- Coal Ash: Characteristics, Management and Environmental Issues., 2009: Electrical Power Research Institute.
- Florin, N. H., and Harris, A. T., 2008. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. *Chemical Engineering Science*, **63(2)**, 287-316.
- Johnsen, K., Ryu, H. J., Grace, J. R., and Lim, C. J. , 2006. Sorption-enhanced steam reforming of methane in a fluidized bed reactor with dolomite as -acceptor. *Chemical Engineering Science*, **61(4)**, 1195-1202.
- M. B. Jensen, G. M. Pettersson, O. Swan g, and Olsbye, U., 2005.
- Sua-iam, G., and Makul, N., 2013. Utilization of limestone powder to improve the properties of self-compacting concrete incorporating high volumes of untreated rice husk ash as fine aggregate. *Construction and Building Materials*, **38(0)**, 455-464.
- Ukwattage, N. L., Ranjith, P. G., Yellishetty, M., Bui, H. H., and Xu, , 2012 . A laboratory-scale study of the aqueous mineral carbonation of coal fly ash for CO₂ sequestration. *Journal of Cleaner Production*(0).
- Z. Yong, V. M., and Rodrigues, A. E. ,2002. *Separation Purification Technology*, **26**.

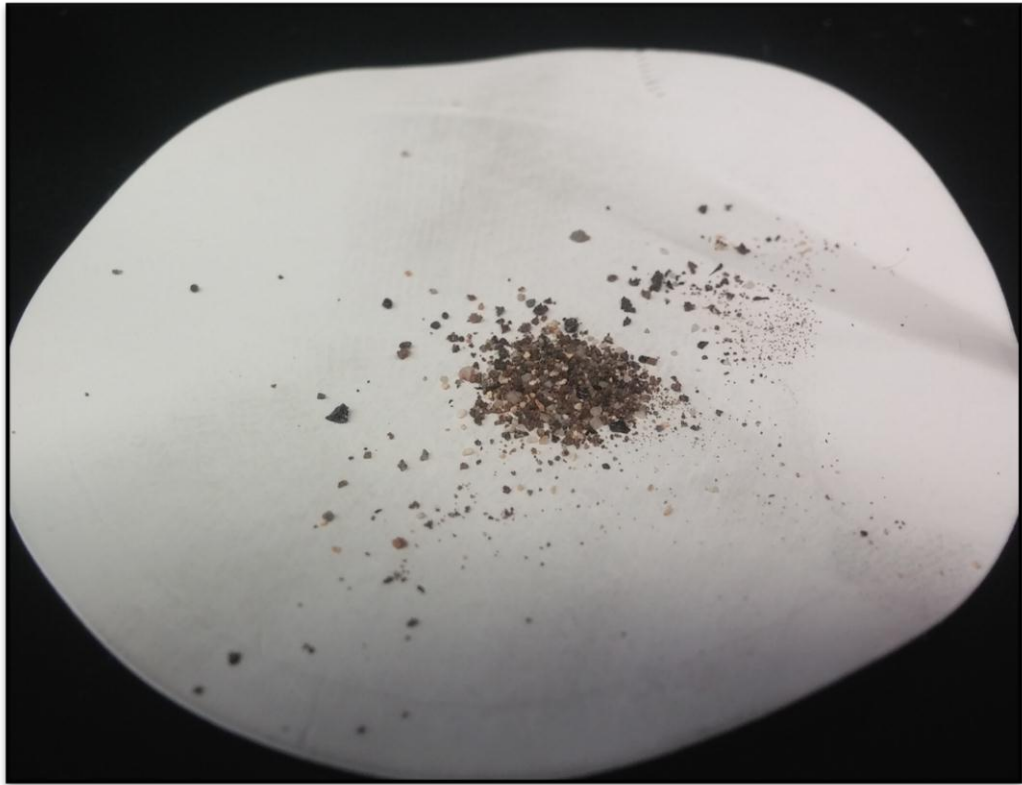
APPENDICES



APPENDIX 1.1 Thermogravimetric Analyzer Q50 Series Used For Carbonation Process



APPENDIX 1.2 Software Setup For The TGA Q50 Carbonation Process



Appendix 1.3 Sample of CBA after carbonation using TGA at 600oC