

### **EKC 499 FINAL YEAR PROJECT**

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# INDIRECT CARBONATION OF COAL FLY ASH FOR CARBON DIOXIDE CAPTURED VIA MECHANOCHEMICAL REACTION

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# INDIRECT CARBONATION OF COAL FLY ASH FOR CARBON DIOXIDE CAPTURED VIA MECHANOCHEMICAL REACTION

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### LIST OF SYMBOLS

	Symbol	Unit
С	Concentration	mol/L
Ca <sup>2+</sup>	Calcium ion	-
CaO	Calcium oxide	-
CO <sub>3</sub> <sup>2-</sup>	Carbonate ion	-
$Mg^{2+}$	Magnesium ion	-
M <sub>CO2</sub>	Mass of carbon dioxide	g
M <sub>CFA</sub>	Mass of coal fly ash	g
Т	Temperature	°C

### LIST OF ABBREVIATIONS

ATAB	Abu terbang arang batu
CFA	Coal fly ash
CO <sub>2</sub>	Carbon dioxide
EBT	Eriochrome black T
EDTA	Ediaminetetraacetic acid
EDX	Energy-dispersive x-ray
FA	Fly ash
FTIR	Fourier-transform infrared
KCL	Potassium chloride
KHCO <sub>3</sub>	Potassium hydrogen carbonate
L/S	Liquid-to-solid
MSWI	Municipal solid waste incinerator
rpm	Rotation per minute
SEM	Scanning electron microscope
TNB	Tenaga nasional berhad

## PENGKARBONAN TIDAK LANGSUNG ABU UNTUK MENYERAP KARBON DIOKSIDA DENGAN TINDAK BALAS MEKANIKAL KIMIA

#### ABSTRAK

Pembuangan bahan mineral yang dihasilkan di Malaysia mempunyai potensi untuk penyerapan mineral karbon dioksida (CO<sub>2</sub>). Salah satunya abu terbang arang batu (ATAB). Mengurangkan CO<sub>2</sub> daripada melarikan diri ke persekitaran, proses karbonasi (pengkarbonan tidak langsung) digunakan untuk menangkap CO<sub>2</sub>. Pengkarbonan tidak langsung menjalani pengekstrakan kalsium, diikuti dengan proses pengkarbonasi menggunakan mesin bola penggilingan. Proses pengekstrakan, pengaruh masa penggilingan, kelajuan putaran penggilingan dan nisbah pepejal-cecair telah diterokai. Meningkatkan masa penggilingan dari 10 hingga 180 minit dan kelajuan putaran dari 100 hingga 400 rpm meningkatkan jumlah kalsium yang diekstrak. Proses pengkarbonasi, kalium hidrogen karbonat (KHCO3) digunakan sebagai agen karbonasi di mana kepekatannya berubah-ubah. Kepekatan 2.5 hingga 5.5 mol/L, menunjukkan peningkatan jumlah kalsium yang diekstrak. Ekstrak CO<sub>2</sub> dari ATAB juga meningkat disebabkan pengaktifan zat mineral terutamanya kalsium. Kapasiti CO<sub>2</sub> tertinggi dan kalsium yang diekstrak dicapai pada 0.2310 g CO<sub>2</sub>/g ATAB dan 0.210 g Ca<sup>2+</sup>/g ATAB. Kaedah operasi yang sama, pengkarbonasi diulang menggunakan gelombang mikro (buka kapal). Mesin bola penggilingan menunjukkan kecekapan karbonasi yang lebih tinggi berbanding gelombang mikro. Kesan positif yang ditunjukkan oleh mesin bola penggilingan di mana jumlah kalsium yang diekstrak dan keupayaan untuk menangkap CO<sub>2</sub> lebih tinggi berbanding gelombang mikro. ATAB dicirikan menggunakan mikroskop elektron pengimbasan (SEM).

## INDIRECT CARBONATION OF COAL FLY ASH FOR CARBON DIOXIDE CAPTURED VIA MECHANOCHEMICAL REACTION

#### ABSTRACT

Many mineral wastes that produced in Malaysia have the potential candidates for  $CO_2$  mineral sequestration. One of them is by using coal fly ash. Therefore, to reduce  $CO_2$  from escaping towards the surroundings, carbonation (namely indirect carbonation) process is used to capture CO<sub>2</sub>. Indirect carbonation undergoes calcium extraction, followed by carbonation process using planetary ball mill. In extraction process, the influence of milling time, milling rotational speed and solid-liquid-ratio were explored. Increasing the milling time from 10 to 180 minutes and rotational speed from 100 to 400 rpm subtly increases the amount of calcium extracted. In carbonation process, KHCO<sub>3</sub> was used as a carbonating agent in this study where the concentration was varied. At concentration from 2.5 to 5.5 mol/L, shows increasing of amount calcium being extracted. Addition to it, CO<sub>2</sub> capacity of coal fly ash also increased due to the activation extraction of mineral particles especially calcium. The highest CO<sub>2</sub> capacity and calcium extracted achieved were at 0.2310 g CO<sub>2</sub>/g CFA and 0.210 g Ca<sup>2+</sup>/g CFA. Using similar operating conditions, the carbonation was repeated using open vessel microwave. Planetary ball mill demonstrates higher carbonation efficiency compared to microwave. It gave positive impact shown by planetary ball mill where the amount of calcium extracted and the ability to sequestrate  $CO_2$  is higher as compared to microwave. Lastly, CFA were characterized using scanning electron microscopy (SEM) and FTIR spectrometer.

#### **CHAPTER ONE**

#### **INTRODUCTION**

#### **1.1** Ash Carbonation for Carbon Dioxide Storage

Carbon dioxide (CO<sub>2</sub>) is the biggest contributor towards global warming through human activity, mainly by burning of fossil fuels. In 2015, 82.2 % of CO<sub>2</sub> released in the USA are from human activities. Fossil fuels usage have become the world's primary source of energy and greenhouse gas emissions based on history made (EPA, 2015). Global warming causes greenhouse effect, where almost 100 % of the observed temperature is increasing over the last 5 years due to the increase concentrations of greenhouse gas in the atmosphere. Due to that, it will eventually contributes two major effects which are increasing temperature on the earth by about 3 °C to 5 °C by the year 2100 and rising of the sea level by at least 25 metres by the year 2100 (Rendek et al., 2006). Therefore, CO<sub>2</sub> released must be captured and stored using a proper technology method. Carbon capture technologies are available in the market, however it is very expensive and contribute almost 70-80 % of total cost of a complete carbon capture system including capture, transport and storage (Leung et al., 2014). There are three main carbon capture systems, which are post-combustion, oxyfuel combustion and precombustion.

Mineral carbonation is commonly applied for capturing  $CO_2$ . It is actually a reaction of  $CO_2$  with metal oxides materials to form insoluble carbonates where calcium and magnesium act as the major metals. Suitable materials consists of silicate rocks, serpentine and olivine materials for example alkaline industrial residues like fly ash or slag from steel production (IPCC, 2014). Between these residues, fly ash is the suitable material for carbonation to occur. This is because it has high content of calcium oxides and fast kinetics dissolution where it requires shorter time for a substance to break down into individual ions needed (Tamilselvi Dananjayan *et al.*, 2016). Mineral carbonation can be achieved using two different routes, direct and indirect mineral carbonation (Zhang *et al.*, 2017). Indirect mineral carbonation consists of two major steps, where the extraction of calcium and magnesium takes place and continue with carbonation of calcium and magnesium ions rich with CO<sub>2</sub> stored in a basic environment (Zhang *et al.*, 2017). In addition, mineral carbonation can be divided into dry (gas-solid), wet (gas-liquid) processes according to the phase in which the carbonation occurs (Olajire, 2013).

#### **1.2 Problem Statement**

Direct minerals carbonation is the simplest route where the solid residues are carbonated in a single step either in an aqueous or gaseous phase (Bobicki *et al.*, 2012). Unfortunately for direct gaseous route, the reaction rates of this process is too slow and low carbonation ratio limitations (Voormeij and Simandl, 2004). Whereas for direct aqueous route, the reaction is too fast because most of the alkaline components are reactive ions and tend to consume a lot of energy due to pre-treatment process (Jo *et al.*, 2012). Therefore, indirect aqueous route has been preferred due to its high capacity of  $CO_2$  storage and high purity of precipitated calcium carbonates. Calcium oxides and magnesium oxides can be converted to a high amount of carbonates. For the alkaline industrial waste, coal fly ash is favourable as a source of calcium and magnesium, where the content of free calcium oxide reaches 12 %, highest among all the waste studied (Jaschik, 2016). For ash carbonation process, there are various parameters that can be manipulated in order to achieve high content of  $CO_2$  being absorbed. Previous studies, most of them were manipulating the reaction temperature, stirrer speed, ash-to-water ratio (Jaschik, 2016). Besides those parameters used, there are certain parameters that are possible to be counted. There are extracting agent concentration, rotational speed, milling time and solid-liquid ratio on calcium extraction efficiency (Wee, 2013). These parameters can be relatively correct by observing the amount of  $CO_2$ being captured and also the amount of calcium ions being extracted.

There are several experimentation methods that can used for carbonation process. The conventional method that is commonly used is microwave where this method is uniformly heated. Besides that, this method uses less energy consuming as compared to other conventional heating method (Uliasz-Bocheńczyk *et al.*, 2009). However, based on previous studies, this method is hardly interact with the material used. Other possible method that can be used is mechanochemical reaction which is planetary ball mill. In planetary ball mill, mechanochemical refers to the conversion of kinetic to thermal energy occurred from the collision between steel balls and the body of ball mill. The advantage of this method is that the extraction of the particles can be achieved at the highest level due to the nanoparticle size produced (Ahmaruzzaman, 2010). Based on previous studies, using planetary ball mill is efficient and faster than other conventional methods (Li *et al.*, 2016). Although it consumes a lot of energy, however this method is very suitable for multi-phase materials where solid and liquid reaction takes place (Li *et al.*, 2016). This method is rarely used because it produces high pressure.

However, comparison between these two methods can be achieved in the aspect of carbonation efficiency.

#### **1.3** Research Objective

The objectives of this research are:-

- i. To identify the amount of calcium extracted at different operating parameters via mechanochemical activation reaction.
- To identify the CO<sub>2</sub> storage capacity of coal fly ash using indirect aqueous carbonation.
- iii. To compare the performance of carbonation efficiency of two different experimentation methods, planetary ball mill and conventional heating.

#### **1.4** Scope of Study

In this research study, the sample used was coal fly ash where it captured and stored CO<sub>2</sub> from carbonates. By observation, the coal fly ash physically was already at its finest particle and uniform size which leads to a good contact and reaction. For indirect carbonation, the coal fly ash was extracted at different operating parameters using planetary ball mill and then undergoes reaction with carbonates to capture and store CO<sub>2</sub>. Extraction process occurred at varying rotational speed (100-400 rpm), milling time (10-180 min) and solid-liquid ratio (0.5-3 g/100 mL). Optimum parameters were achieved for coal fly ash extraction, the experiment was proceeded for carbonation process with carbonates where it occurred at varying agent concentration (2.5-5.5 mol/L). The best operating parameters were used for subsequent experiments. Carbonation efficiency of coal fly ash was achieved by comparing two different methods, planetary ball mill and open vessel microwave using the previous optimum parameters part.

#### **CHAPTER TWO**

#### LITERATURE REVIEW

#### 2.1 Mineral Carbonation for CO<sub>2</sub> Sequestration

Concentration of CO<sub>2</sub> being released to the surroundings can be reduced by  $CO_2$  sequestration method. In other meaning, carbon dioxide is separated by capturing and storing it. There are several technologies or method that can be used for carbon capture storage, such as geological storage, ocean storage and others. Based on Shukla et al. (2010) study, he stated that geological storage is very economical in terms of storage cost and technique. However, Tsang et al. (2008) study stated that this method is high risk. Co-workers must be careful with technical issues evaluation where they must be really specified with the understanding of migration in subsurface formations and the development of technology regarding monitoring the storage must be safe and effective. In addition with Harvey et al. (2013) study, he stated that geological storage did not provide high capacity for the CO<sub>2</sub> to be captured and stored. Therefore, the amount of CO<sub>2</sub> being released is huge and will not give a positive impact towards the environment. Moving to ocean storage, Voormeij and Simandl (2004), stated that injecting CO<sub>2</sub> on ocean bottom is safe because the CO<sub>2</sub> is transformed to a liquid phase and store it by dissolution. Since the liquid CO<sub>2</sub> is less dense than water, the droplets will rise and dissolved in the seawater. Even though the deeper the  $CO_2$ being injected, the more effective it is however Ormerod (2002) stated that injection deeper requires more advanced technologies. More technologies are used, more money that need to be spent and also maintenance. Good side of using ocean storage is that it has high capacity for the  $CO_2$  being stored in a long term perspective, study from Adams and Caldeira (2008).

Other alternative sequestration route is mineral carbonation, where carbonation of minerals take place. CO<sub>2</sub> is chemically stored in solid carbonates. Based on Goldberg P (2001) study, mineral carbonation consists of some fundamental advantages as compared to other sequestration route. The major advantage is it has the highest capacity among all the sequestration route because of its availability of having large feedstock. Table 2.1 shows the  $CO_2$  storage capacity for each of the current technologies used for CO<sub>2</sub> sequestration. Feedstock or raw material used can be easily get from natural rocks that are rich in alkaline silicates. Based on Kunzler et al. (2011) study, all identified locations in the world have a full access of natural mineral resources. In other meaning, the distance between the carbonation plant and the natural mineral resources are close. All identified locations are located at China, South Africa, Russia, Northern Europe, USA, Australia and others. However, based on Lackner (2002) study, stated that natural mineral carbonation is extremely slow in terms of kinetics due to low concentration of CO<sub>2</sub>, about 0.03-0.06 % only. That is why, W (1990) proposed an accelerated carbonation involves utilize alkaline waste residues. Another support from Bobicki et al. (2012), where it stated that alkaline waste residues are highly reactive and pre-treatment is not required to achieve high carbonate conversions. Huijgen et al. (2007), where this study also stated that alkaline waste residues contain a high amount of calcium and magnesium metals and high degree of alkalinity.

Technology	CO <sub>2</sub> Storage Capacity <sup>a</sup>	References
	(Gt)	
Geological	1,800	Shukla et al. (2010);
Storage		Harvey <i>et al.</i> (2013)
Ocean Storage	10,000	Adams and Caldeira (2008)
Mineral	>10,000	Lackner (2002)
Carbonation		
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#### Table 2.1 CO<sub>2</sub> storage capacity for each technologies

a: maximum estimated capacity

#### 2.2 Alkaline Waste Residues for Carbonation

Examples of industrial alkaline solid wastes are from steelmaking slag, paper mill waste, ashes waste, cement wastes and others. All these alkaline waste consists of high content of calcium and magnesium oxides where it is ideal for CO<sub>2</sub> sequestration to occur. Several studies of Sandvik et al. (2011) stated that using coal fly ash, especially at 20-150 µm particle size had the best carbonation efficiency (71.84 kg CO<sub>2</sub>/t FA). Study from Wang et al. (2010) stated that fly ash do not require any comminution and been produced in high volumes, close with the point sources of CO<sub>2</sub> emissions even though the carbon sequestration capacity is low as compared to other wastes. Based on Montes-Hernandez et al. (2009) study focused on coal fly ash, stated that all coal-fired power plants in the world are generating almost 12,000 million metric tonnes of CO<sub>2</sub> and 600 million metric tonnes of fly ash annually. Add on to that, only 16 % of fly ash had been utilized for further use and others are sent to the landfills for decompose. Uliasz-Bocheńczyk et al. (2009) studies resulted a carbonate conversion of 82 % using coal fly ash and sequestrated 26 kg CO<sub>2</sub>/t ash at 30 °C while Montes-Hernandez et al. (2009) studies resulted a maximum carbon sequestration of 7.85 g CO<sub>2</sub>/100 g ash at ambient temperature. This study demonstrated that 1 ton of fly ash contains 4.1 wt. % of free lime which is calcium oxide and can uptake  $CO_2$  up to 26 kg. Table 2.2 shows the maximum amount of  $CO_2$  that can be stored within all the alkaline wastes availabilities. Among all the alkaline waster residues, Fang *et al.* (1999) has concluded that coal fly ash has the largest portion of  $CO_2$  emissions for carbon capture storage.

Table 2.2 Alkaline waste corresponds towards CO<sub>2</sub> storage capacity

Alkaline Waste	Max CO <sub>2</sub> Storage Capacity	References
	(kg CO <sub>2</sub> /kg waste)	
Steelmaking	0.19 kg CO <sub>2</sub> /kg slag	Huijgen et al. (2005)
Slags		
Red Mud	0.0153 kg CO2/kg red mud	Yadav et al. (2010)
MSWI Bottom	24 kg CO <sub>2</sub> /ton kg bottom ash	Rendek et al. (2006)
Ash		
Coal Fly Ash	$26 \text{ kg CO}_2$ /ton kg coal fly ash	Montes-Hernandez et al.
		(2009)
Alkaline Paper	218 kg CO <sub>2</sub> /ton kg APMW	Pérez-López et al. (2008)
Mill Waste		

#### 2.3 Coal Fly Ash Reaction during Carbonation

Based on Criado *et al.* (2005) study, it stated that during carbonation, coal fly ash is being activated in terms of alkalinity for capturing and storing CO<sub>2</sub>. Another study from Lackner, *et al.* (1995) shown that during carbonation, the components exist in coal fly ash is calcium and magnesium, where there are rich in alkali. These components consist of minerals where olivine, serpentine and wollastonite are used to sequester CO<sub>2</sub> via the formation of carbonate minerals. In general, coal fly ash consists of silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), lime (CaO) and

iron oxide (Fe<sub>2</sub>O<sub>3</sub>). A study from Back. M *et al.* (2008) stated that kinetic tests had been done towards coal fly ash that contained 11.5 wt. % of CaO, where this substance is being extracted to produce high capacity of Ca<sup>2+</sup> ions. This ion will undergoes carbonation and produce carbonate minerals. All alkali elements that existed in coal fly ash have a huge role in increasing the carbonation of CO<sub>2</sub>. Study from Stumm. W *et al.* (1996), where extraction test is used to obtain high content of CaO of 34 wt. % from 7 wt. % which is before extraction occurs. However in the similar study also stated that 34 wt. % of CaO being extracted is the maximum amount. This is because the possibility of equilibrium between calcium minerals and extraction solution to occur is high. Based on Jo *et al.* (2012), study shows the chemical reaction of coal fly ash carbonation mechanisms as shown below:

**Reaction A:** 
$$CaO + H_2O \rightarrow Ca(OH)_2$$
 (2.1)

**Reaction B:** 
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3(s) + H_2O$$
 (2.2)

Chemical reaction A is the reaction between limes with the presence of water as the solvent to produce calcium hydroxide. During this reaction, all the CaO are being extracted and only  $Ca^{2+}$  activated alkali ions will further use for carbonation reaction. The reaction is then continued for carbonation. Chemical reaction B is the reaction of all  $Ca^{2+}$  activated alkali ions with the presence of  $CO_2$  to produce precipitate calcium carbonates. Based on Huijgen *et al.* (2005) study, the precipitate calcium carbonates are produced from another reaction where carbonate ions take place as shown below:

**Reaction C:**  $CO_2 + H_2O \rightarrow CO3^{2-} + 2H^+$  (2.3)

**Reaction D:** 
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$$
 (2.4)

In chemical reaction C,  $CO_2$  is dissolved in water and produce carbonate ions. Carbonate ions are then reacted with  $Ca^{2+}$  ions and produce precipitate calcium carbonate as shown in chemical reaction D. Based on similar study, the precipitate calcium carbonates produced are usually consists of more than 90 wt. % of carbonates. In the other way meaning,  $CO_2$  is sequestrated in a high uptake capacity.

#### 2.4 Carbonation Routes

#### 2.4.1 Direct Dry Carbonation Route

Routes for carbonation can be categorized into two parts, direct and indirect carbonation. Figure 2.4 illustrates the basic concept of reaction occurred in direct and indirect carbonation. To be more specific, in general direct carbonation occurred when the substance or the alkaline metal oxide is reacted with either gaseous or aqueous  $CO_2$  in a single step (Sipila, 2007). In single step, extraction of calcium and magnesium ions are absence and there is only carbonation process that exists. Reaction with the presence of CO<sub>2</sub> gaseous is called direct gas-solid carbonation while for aqueous CO<sub>2</sub> is called direct aqueous carbonation (Sipila, 2007). Based on Pan (2012) and Olajire (2013) studies, stated that direct gas-solid carbonation is the simplest reaction or approach to mineral carbonation. However, dry route appeared as a very slow process and reaction kinetics are very slow for Ca/Mg-silicates. Maximum capacity for it to capture  $CO_2$  was found to be 26.3 g of  $CO_2/kg$  of coal fly ash at 10 bar for 1 hour. This shows that this dry route carbonation are still insignificant, even if the pressure is elevated. But not for Mazzella et al. (2016), where the total amount of 140.6 g/kg coal fly ash was sequestrated at 25 °C and 45 °C. This is because in this direct gas-solid carbonation process, the kinetic of the process is strongly influenced by the reaction temperature. If the pressure is low, the capable of captured  $CO_2$  is high. Based on González (2014) study, it stated that more than 70 wt. % of CO<sub>2</sub> was captured at condition of 25 °C and 5 bar. Further dry route reaction at 45 °C and 5 bar, the amount of  $CO_2$  is increasing. This shows that temperature plays an important role in carbonation process. Another study from Dacosta and co-worker (2014), where they investigated a direct gas-solid for  $CO_2$  capture and storage. The flue gas passed through the bed of finely ground (2.5–60  $\mu$ m) silicate rocks which are mostly olivine, serpentine and etc. The amount of CO<sub>2</sub> absorbed is higher than 18 % but however it couldn't last long due to the absence of moisture/water. They stated that with the present of moisture, it is sufficient enough to convert the metal oxides such as silicates oxides, magnesite silicates and others into a high reactive hydroxides. Based on Huijgen (2005), they conclude that direct gas-solid carbonation route cannot be developed in becoming an industrial viable process. However, improvements can be made by considering the multi-step carbonation route.

#### 2.4.2 Direct Aqueous Carbonation Route

In a wet or aqueous carbonation, the minerals are mixed in a liquid medium which acts as a solvent. Based on history study from Schramke (1992), it carried out this direct aqueous carbonation of coal fly ash using water as the solvent. Rate of mineral carbonation can be increased, by having a direct aqueous mineral carbonation. This route is similar with dry route, where it uses only single step. The difference is that this wet route presence of aqueous suspension. Commonly solvent used is water, where based on Huijgen *et al.* (2007), he stated that the presence of water is known to accelerate carbonation reaction. Based on Sipila (2016) he stated that direct aqueous mineral carbonation has already achieved a high carbonation degrees and rate but however the process is too expensive to be applied in a larger scale of industry. Study done by Kwak and co-workers (2011), in investigating reaction of direct aqueous carbonation of finely ground olivine (1 g) mixed with water. The reaction was kept at 80 °C, maintained at 20 bar for 20 hours. Final CO<sub>2</sub> storage capacity has increased to 67 %. However, the drawback was it required 7 days. Besides that, Hujigen and co-workers (2006) had studied the direct aqueous mineral carbonation of finely ground wollastonite was suspended by water. They came out of an idea where the carbonation reaction occurred in two steps: where extraction or calcium leaching and then carbonation. It gave a positive impact where capacity had increased to 75 % after 15 minutes at 200 °C. Table 2.4 below shows the carbonation yield for direct dry and direct aqueous carbonation methods.

Ash	Carbonation Method	Carbonation Yield (g	References
		CO <sub>2</sub> /g FA)	
Fly Ash	Direct dry method	0.207	Sanna (2014)
Fly Ash	Direct aqueous	0.230	Bobicki et al.
	method		(2012)
Fly Ash	Indirect aqueous	0.111	Pan et al. (2016)
	method		

Table 2.4 Carbonation yield of carbonation method

#### 2.4.3 Indirect Carbonation

When the process of carbonation is divided into two steps, it is classified as indirect carbonation. In other way meaning, the reactive metals which contain calcium and magnesium are first extracted in one step and then followed by carbonation step to form carbonates. Based on Soong et al. (2006) study, a multistage carbonation process can overcome the slow reaction kinetics obtained from only a single step carbonation. Multistage consists of two steps where extraction at atmospheric pressure and carbonation at temperature and pressure of >500 °C and >20 bar take place. Study from He et al. (2013) stated that by doing extraction as the first step, high calcium coal fly ash is achieved. Moreover, 35-40 % of calcium is extracted within an hour. Calcium extraction performance can be achieved higher when the extracting agent concentration is increasing from 0.5 to 3 mol/L. As for carbonation step, Allen (2010) and Sanna (2014) studies stated that the conversion of  $Ca^{2+}$  into precipitate calcium carbonate is very low, at only 41-47 % when the mixture is carbonated by CO<sub>2</sub>. In addition, this studies also included its substitution of using KHCO<sub>3</sub> as the source of  $CO_3^{2-}$ . This resulting to a higher carbonation efficiency by 90-93 %.



Figure 2.4 Basic concepts of direct and indirect carbonation method (Siti

Norhana et al., 2017)

#### 2.5 High Energy Milling via Size Reduction

One of the ways to increase the rate of mineralization is by introducing mechanical activation as the pre-treatment method to improve the kinetics of dissolution of minerals contain in the coal fly ash for example silicon oxides (SiO<sub>2</sub>), aluminium oxides (Al<sub>2</sub>O<sub>3</sub>) and calcium oxides (CaO). Based on De Gisi *et al.* (2017) study, mechanical milling or ball milling contributes to CO<sub>2</sub> sequestration under certain carbonation conditions. Li and Hitch (2017), has stated that the conversion of mechanically-active minerals such as olivine for CO<sub>2</sub> sequestration is increasing from 22.5 % to 31.5 %. Tkáčová *et al.* (1993), study stated that ball milling uses a high mechanical energy such as grinding to enhance the reaction. Further grinding into nanoparticles will leads to a larger surface area

and size reduction occurred. As related with Rigopoulos *et al.* (2015), it stated that extraction of wanted minerals like oxides content can be achieved at high amount if the particles are reduced into smaller particles. Another study from Rigopoulos *et al.* (2015) where it stated that  $CO_2$  sequestration using a mechanical activation which is ball mill increase the efficiency where during ball milling process, the particles leads to the formation of more smaller, finer and uniform in terms of specific surface area and pore volume.

Many structural parameters had been done to achieve high carbonation efficiency and CO<sub>2</sub> uptake capacity (Haug et al., 2010);(Turianicová, 2013). There are milling time, rotational speed, extracting agent concentration and solidliquid ratio. O'Connor (2001) study stated that as the milling time increasing, larger surface area and formation of nanoparticles occurred. On top of that, longer time for the sample to be fully extracted. Nanomaterials that produced using ball mill technique has shown significantly higher CO<sub>2</sub> storage capacity. To be more specific it has been increased from 56.3  $\mu$ mol g<sup>-1</sup> to 222.1  $\mu$ mol g<sup>-1</sup> in the milled sample used. Another study from Kliev (2006), stated that fully extraction of minerals occurred when the milling time increases, reaching 1.08 % after 60 minutes of mechanical activation. This leads to the amount of sequestrated  $CO_2$ weighed of 0.82 g. Based on Kleiv (2009), indirect carbonation is the best route to maximize the mechanical activation carbonation where two steps are used. First step is extraction and followed by carbonation. Based on Mutter (2010) study, it stated that at the maximum rotational speed, 500 rpm of the ball mill, more than 65 % of the mixture is finer as the product. Add on to it, possibility of all calcium or magnesium oxides been fully extracted or at its equilibrium is high. Therefore more Ca<sup>2+</sup> or Mg<sup>2+</sup> will be converted into calcium carbonate and achieved high  $CO_2$  uptake capacity. Another study from Fathi and Zahrani (2008) regarding the rotational speed of ball mill, stated that at 250 rpm to 300 rpm the crystalline size had decreased from 49  $\mu$ m to 43  $\mu$ m. Size reduction for this method are mostly by introducing mechanical activation towards the minerals used.

#### 2.6 Mechanical Activation of Minerals

Based on Summers et al, (2005) study, it stated that mechanical activation of minerals really helped in inducing changes of surface compositions and crystal structures of minerals, where it enhances the rate of dissolutions. The rate of dissolutions are actually based on the material conditions itself (Atashin et al., 2015). This study, Li and Hitch (2015) stated that mostly all the minerals are mechanically activated under wet conditions. Moreover, Haug (2009) study also investigated the carbonation efficiency of different conditions where it uses 100 % dry, 100 % wet and 10 % wet samples only. Addition of the same study, where at 100 % dry, the minerals contain low crystallinity and only achieve efficiency of 16 %. Besides that, another study from Musa and Morrison (2009) where it shows that at 100 % wet sample or coal fly ash, the pH value or the alkalinity of the dissolved minerals are higher. This leads to a higher concentrate minerals occurs in the sample. In conjunction with that, some studies stated that 100 % wet sample gives the worse result because it produces low rate constants (Saldi, et al, 2009). Another study from Alexander, et al, (2007) stated that the suitable conditions for maximizing the dissolution kinetics is at only 10 % of wet milling. However, based on Erdem and Ergün (2009) study, energy consumption for this method (mechanical activation) is must higher than economically feasible, where it reaches to 2300 kWh/ton. Table 2.6 below shows the energy consumption during milling. Certain studies from O'Connor, et al, (2004), Huijgen and Comans (2005) stated a positive impacts of mechanical activation where it actually increases the rate constants and gain potential within the grinding technology.

Sample	Energy	Consumption	References
Conditions	(kWh/ton)		
100 % dry	700 kWh/ton		Haug et al. (2011)
condition			
10 % wet	800 kWh/ton		Alexander, et al. (2007)
condition			
100 % wet	6400 kWh/ton	l	Gerdemann, et al. (2006)
condition			

Table 2.6 Energy consumption during milling

#### 2.7 Method of Ball Milling for Mechanochemical Synthesis

In order to achieve high extraction and high amount of  $CO_2$  captured, suitable ball milling method must be used. Based on Dreizin (2017) study, he stated that there are three main mill types that can be used for mechanochemical synthesis. There are planetary ball mill, attritor mill and shaker mill. A study from Suryanarayana (2001), where it stated that all the methods must be sufficient enough to transfer energy from the milling tools to the powder in order to avoid deformation of the powder or ash particles. Table 2.7 below shows the advantages and disadvantages of different ball milling method.

Table 2.7 Advantages and disadvantages of ball milling method

Method	Advantages	Disadvantages	References
Planetary	Large batch size and	-	Umbrajkar
Mills	variable milling speed		(2005)
Shaker	High collision energy	Small capacity for	Toozandehjani et
Mills		process to occur	al. (2017)
Attritor	Existence of cooling	Difficult towards high	Ward (2005);
Mills	jacket and a continuous	pressure and unable to	Chen (2005)
	process	process small	
		quantities.	

#### **CHAPTER THREE**

#### **MATERIALS AND METHODS**

#### 3.1 Materials and Chemicals

Coal fly ash was used as a sample for this experiment. To undergo carbonation reaction, potassium hydrogen carbonates (KHCO<sub>3</sub>) was used for the existence of CO<sub>2</sub>. In addition, Ediaminetetraacetic Acid (EDTA), Eriochrome Black T (EBT) and potassium chloride (KCl) were used for titration process. These process was used to determine the amount of CO<sub>2</sub> being absorbed during carbonation. Table 3.1 below shows the list of chemicals used throughout this experiment.

Chemicals	Purity	Supplier	
Coal Fly Ash	-	TNB Janakuasa Manjung,	
		Perak, Malaysia	
KHCO <sub>3</sub>	>99%	R&M Chemicals	
EDTA	98%	Ajax Chemicals	
EBT	65%	Sigma Chemicals	
KCL	99.5%	R&M Chemicals	

Table 3.1 List of chemicals used in carbonation

#### 3.2 Equipment

For calcium extraction and carbonation process, planetary ball mill (Retsch 100, Germany) was used as the major equipment while open vessel microwave synthesizer (CEM Mars 6, USA) were used only for comparison of method based on efficiency of CO<sub>2</sub> sequestration. Lastly for characterization analysis, FTIR (Thermo Scientific Nicolet iS10, USA) and SEM (Hitachi TM 3000, Japan) was used for structural and elemental analysis of coal fly ash where the compositions were identified and traced. Table 3.2 below shows the list of equipment followed by the usage of each equipment's.

Table 3.2 List of equipment used in	n carbonation	and the usage
-------------------------------------	---------------	---------------

Equipment	Usage	Supplier
Planetary ball	Extraction and carbonation	Retsch 100, Germany
mill		
Open vessel	Extraction and carbonation	CEM Mars 6, USA
microwave		
FTIR	Characterization of coal fly ash	Thermo Scientific
		Nicolet iS10, USA
SEM	Characterization of coal fly ash	Hitachi TM 3000, Japan

#### 3.3 Project Management Plan

Figure 3.1 below shows the overall flow diagram in completing the experiment.



Figure 3.1 Schematic flow of the experiment

#### **3.4** Experimental Procedure

#### 3.4.1 Preparation of Coal Fly Ash

Coal fly ash was obtained from a coal-fired power plant, Tenaga Nasional Berhad Janakuasa Manjung located in Perak, Malaysia. Distilled water was added together with the sample using L/S ratio of 20 mL/g. For each run, 5 g of sample and 100 ml of distilled water were prepared and mixed.

#### 3.4.2 Extraction of Coal Fly Ash with Water

Extraction process was investigated using planetary ball mill (Retsch 100, Germany) equipment. The coal fly ash-slurry was put in the ball mill together with the grinding balls. This extraction process was operated at varied operating parameters. In this process, (10-180 min) milling time, (100-400 rpm) rotational speed and (0.5-3 g/100 mL) solid-liquid ratio were studied. By varying all these parameters, the optimum conditions for calcium extraction could be found. Coal fly ash was extracted to produce active calcium ions, Ca<sup>2+</sup> and further reacted for carbonation process. Amount of calcium extracted was calculated using formula as follows:-

$$Ca^{2+} \text{ extracted} = \frac{Mca2+(g)}{Mcoal \ fly \ ash(g)}$$
(3.1)

#### 3.4.3 Indirect Aqueous Carbonation

Under indirect carbonation using planetary ball mill, there were two stages occurred. First was extraction process, followed by carbonation. In this carbonation process, KHCO<sub>3</sub> was added to the extracted calcium alkaline residue,  $Ca^{2+}$  ions as the source of CO<sub>2</sub> which contains  $CO_3^{2-}$  ions. The prepared solution undergoes carbonation at only one varied parameter which was the KHCO<sub>3</sub>

concentration which acts as a source of  $CO_2$ . The basic principle of carbonation process was introducing  $CO_3^{2-}$  into the extracted calcium. Using the same and optimum operating parameters achieved from extraction and carbonation using ball mill, the experiment was then repeated using an opened vessel microwave synthesizer (CEM Mars 6, USA) at reaction temperature of 75°C and power of 300 W, only for comparison purpose.

Comparison between different two carbonation methods also were studied which were direct aqueous carbonation and indirect aqueous carbonation using planetary ball mill. Under direct aqueous carbonation, extraction and carbonation processes were run simultaneously. The extraction of CFA with water were mixed together with the addition of KHCO<sub>3</sub>. This direct aqueous carbonation process was run for 30 minutes.

#### 3.4.4 Analysis for Carbonation Efficiency

Concentration of  $CO_2$  being absorbed was determined using titration method with standard disodium EDTA solution. Metallochromic indicator (EBT) was used to indicate the exact moment when all metal ions (Ca<sup>2+</sup>) in the solution were sequestrated by a chelating agent (EDTA). 0.2 g of the indicator was added to the sample via carbonation in the previous section. Then, the sample was titrated with 0.2 M EDTA solution. Reddish purple colour was occurred and turn to blue accordingly. The volume was recorded. From the volume taken, CO<sub>2</sub> concentration was calculated using stoichiometry method. CO<sub>2</sub> capacity was obtained using formula as follows:-

$$CO_2 capacity = \frac{Mco2(g)}{Mcoal fly ash(g)}$$
(3.2)

### 3.4.5 Coal Fly Ash Characterization

Samples of coal fly ash were characterized by several methods to identify the affects towards carbonation performance. The samples were analysed using FTIR spectrometer (Thermo Scientific Nicolet iS10, USA) and SEM (Hitachi TM 3000, Japan) which identify the surface chemistry characteristics and surface morphology of coal fly ash.

#### **CHAPTER FOUR**

#### **RESULTS AND DISCUSSION**

This experiment were divided into three sections, where the first section shows the amount of  $Ca^{2+}$  being extracted at different operating parameters. Furthermore, the second section shows the comparison between different carbonation and equipment methods in terms of  $CO_2$  capacity as well as carbonation efficiency. Last but not least, the last section consists of characterization of coal fly ash sample.

#### 4.1 Calcium Extraction with Water

#### 4.1.1 Effect of Milling Time

Figure 4.1 shows the influence of milling time towards the amount of calcium extracted from CFA. It can be shown that, increasing of milling time from 120 minutes until 180 minutes resulted in an increase amount of calcium being extracted from 0.051 g Ca<sup>2+</sup>/g CFA to 0.210 g Ca<sup>2+</sup>/g CFA. The calcium extraction increases rapidly in the beginning, however it nearly levels off within two hours. These extraction trend were quite similar with He *et al.* (2013) and Eloneva (2008) studies using the same raw material, where this extraction process consists of two different stages, namely fast and slow extraction stage. Under the fast calcium extraction stage, all the extracted calcium experienced good contact with liquid phase. This is because, primarily most of the calcium-containing species were located on the solid particle surfaces layer. As the extraction runs at 180 to 200 minutes, the amount of calcium being extracted gradually decreases from 0.210 g