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Extraction of Metal Oxides from Coal Bottom Ash by Carbon Reduction and Chemical Leaching

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Abstract

Coal Bottom Ash (CBA) is an inevitable waste product that accumulates up to a significant volume each year. These vast volumes pose a problem in the disposal of the coal which conventionally is loaded onto ash dumps located landfill. There are several papers that have studied the chemical and physical properties of CBA, and it was found that CBA is composed of Silica (SiO_2), Ferric Oxide (Fe_2O_3), Alumina (Al_2O_3), Calcium Oxide (CaO), Potassium Oxide (K_2O), Sodium Oxide (Na_2O), Magnesium Oxide (MgO), Titanium Oxide (TiO_2), Phosphorous Pentoxide (P_2O_5), and Sulfur Trioxide (SO_3). The objective of this research is to establish the ideal extraction and purification methods for metal oxides. Extraction of the metal oxides will be conducted by means of carbon reduction and chemical leaching, and after which, the metal oxides will be separated. It is expected that metal oxides can be successfully extracted from the CBA, and hence promoting sustainability, and the potential of the metal oxides to be used in many different industries.

Selection and peer-review under responsibility of the scientific committee of the 6th International Conference on Recent Advances in Materials, Minerals & Environment (RAMM) 2018.

Keywords: Metal Oxides, Extraction, Coal bottom ash.

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1. Introduction

As Malaysia’s economy develops, the industrialization growth that takes place in the country today grow rapidly. This also means that the human population is also on the rise and has outstretched the city. As a result, there is an increase in the electricity demand for energy. In order to meet the growing demand for electricity, Malaysia plans to have a new electricity generation capacity of 6 Gigawatts between 2015 and 2020 [1]. Based on the research, the number of coal used in power plants to generate electricity keeps growing exponentially from the year 2005 to 2030, which will consequent in it becoming the primary source of fuel in power plants in Malaysia in order to meet increasing electricity demand. It is expected that in the year 2030, coal will become the major fuel source contributing to 49% of the total generation fuel followed by natural gas, 44%, hydropower, 5.7% and oil, 1.0% [2]. The electricity production and its share in 2005, 2010, and 2030 are tabulated in Table 1.

Table 1: Electricity Production and its share in 2005, 2010 and 2030 [2].

Fuel by Type	**Electricity Production (GWh)**			**Share of Electricity Production (%)**		
	2005	2010	2030	2005	2010	2030
Coal	23,134	49,675	154,686	26.5	41.6	49.0
Oil	2,489	2,855	3,107	2.9	2.4	1.0
Natural Gas	55,899	55,700	139,025	64.0	46.6	44.0
Hydro	5,784	11,245	18,166	6.6	9.4	5.7
Total	87,306	119,475	315,984	100	100	100

The table shows that the electricity production will be greatly increase in 2030, and depend heavily on the coal and natural gas as fuel sources. Natural gas is the major fuel source used to generate electricity in 2005 with 64%, but the number dropped significantly in 2010 due to the rise in prices of natural gas and the coal started increasing from 26.5% to 41.6%.

Besides, many countries are also using coal to generate electricity since coal is cheaper than other fuel sources like petroleum and natural gas. According to research, world electricity production in 2012 around 40.4% is come from coal [3]. Therefore, coal plays an important role in electricity generation worldwide. It is desirable as a leading fuel source due to its ample availability.

1.1. The usage of coal for energy generation and the waste produced

Coal plays an important role in electricity generation worldwide, hand in hand with fossil energy resource in the world. In Malaysia, the biggest thermal power plant also uses coal as its major fuel source. Comparing to other types of fossil fuel thermal power plant such as petroleum and natural gas to generate electricity, coal fired power plant is considered the most economical thermal power plant since coal price is more affordable and cheaper than other fuel sources [4].

After coal is combusted in the dry bottom furnace, two types of coal ashes are produced [5]. Type One is about 20 percent of the unburned coal ash, which is coal bottom ash with predominantly sand size and can be collected by water filled hopper at the bottom of the boiler. Type Two is about 80 percent of the unburned fly ash and is collected by electrostatic precipitator or bag house and some is entrained in the flue gas. Fly ash is much lighter than bottom ash as is shown in Fig. 1.

However, the use of coal in electricity generation has led to increasing coal waste that brings forth environmental issues and human health effects, such as air pollution, respiratory diseases and groundwater contamination when heavy metals leach into groundwater [6]. In order to reduce impacts of coal bottom ash to the environmental and human health, extraction methods can be used to solve the problem by extracting metal oxides from bottom ash to reduce the heavy metal elements contained. In other words, it is advisable to extract heavy metals from bottom ash and develop methods for greater adoption and production of high value metals. After extracting the heavy metal from the coal bottom ash, the content of heavy metals in coal bottom ash is reduced and it could be safe for usage in the construction industry [7].

Heavy metals oxides exist naturally in bottom ash. Since they have high melting points, the heavy metals cannot volatilize and cause incomplete combustion in the furnace. Another reason that heavy metals still exist in bottom ash is because the time of ash particles remain in the furnace is short during combustion process [8]. However, the heavy metals in coal ash could melt and become fluid, and then react with oxygen. After cooling down, the fluids will turn into crystalline solids or spherical particles [9].

Fig. 1. Fly Ash and Bottom Ash

2. Coal bottom ash chemical composition

Based on previous researches, bottom ash chemical components are mainly made up of heavy metal elements such as Aluminum Oxide, Calcium Oxide, Iron (III) Oxide, and Silicon Dioxide; along with trace elements such Zinc, Barium, Lead, Titanium, Manganese, Phosphorus, and also Carbon. Table 2 below shows the chemical component of coal bottom ash results from different coal fired power plant in Malaysia [10]. The main chemical compounds in three coal fired power plants are Silicon Dioxide, Alumina Oxide and Iron (III) Oxide with the percentage compositions in the range of 9.78 to 49.4%, 20.75 to 23% and 17 to 37.1% respectively. Only a small percentage of Sodium Oxide, Potassium Oxide, Magnesium Oxide, and other chemical compounds are present in coal bottom ash collected with traces of Zinc Oxide, and Barium Oxide.

Table 2. Chemical compounds of coal bottom ash [10].

Chemical contents	**Coal bottom ash percentages**		
	Muhardi et al., (2010)	Fawzan (2010)	Naganathan et al., (2012)
	Tanjung Bin Power Plant	Jimah Power Plant	Kapar power Plant
$\mathbf{SiO_2}$	42.7	49.4	9.78
$\mathbf{Al_2O_3}$	23.0	22.3	20.75
$\mathbf{Fe_2O_3}$	17.0	13.7	37.1
CaO	9.80	9.00	11.1
$\mathbf{K_2O}$	0.96	1.00	-
$\mathbf{TiO_2}$	1.64	2.20	-
MgO	1.54	0.87	3.2
$\mathbf{P_2O_5}$	1.04	0.65	-
$\mathbf{Na_2O}$	0.29	0.13	-
$\mathbf{SO_3}$	1.22	0.68	-
BaO	0.19	-	-
MnO	-	0.08	-
ZnO	-	-	1.8

3. Method of extraction

Previous researches show that there are many methods of extraction that can be used to recover heavy metals from coal ash [11]. The method of extraction depends on the reactivity of the metal itself. The more reactive the metals are to form a positive ion, the more energy it needs to lose or reduce the electrons, and hence, the more difficult it is to extract the metals from its compound. The methods that can be used to extract metals from coal ash are chemical leaching, biotechnological leaching processes, carbon reduction, magnetic separation, and electrolysis. However, these methods have their own strengths and shortcomings.

Magnetic separation as shown in Fig. 2 is to extracted heavy metals from coal bottom ash by using magnetic force. A vertical ring magnetic separator is used for iron removal [12]. The iron oxides cannot be fully extracted by this method, because the iron contained in coal ash is mostly trivalent iron with weak ferromagnetic property [13].

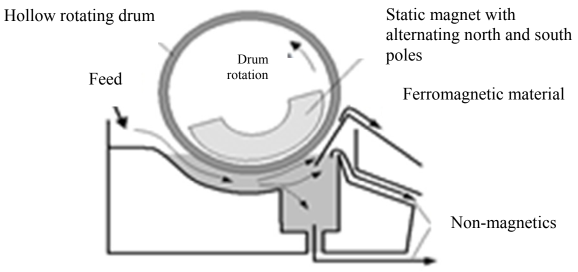


Fig. 2. Magnetic separation method to separate ferromagnetic material [12].

Chemical leaching is the process of separation of heavy metals from coal bottom ash by dissolving metals into liquid form, as can be seen in Fig. 3 [14]. In other words, metal oxides bound in coal bottom ash are turned into metal ions that are released into the acid solution. For example, immobilized metals will become mobilized after the chemical leaching treatment. In addition, acid is used most often in chemical leaching process to dissolve heavy metals contained in coal bottom ash. However, chemical leaching method is considered uneconomical since this method requires the usage of strong acids and expensive acid proof equipment [15].

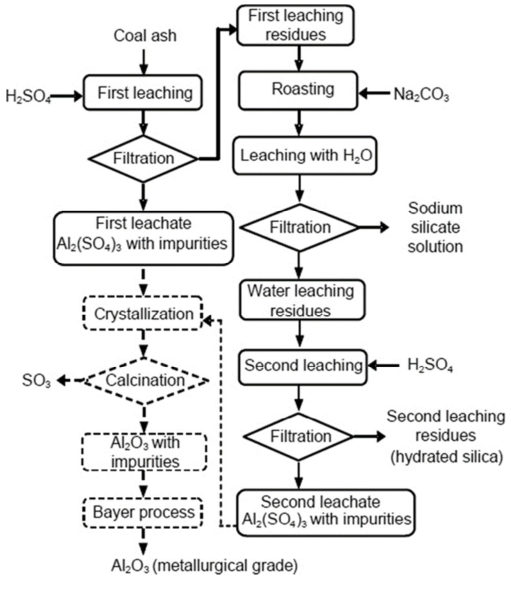


Fig. 3. Process of chemical leaching method [14].

Electrolysis in Fig. 4 is a process that uses electricity to extract or separate the heavy metals in coal bottom ash [16]. In other words, electrolysis involves decomposed ionic substances into simpler substances using electricity energy. In electrolysis, the current is flow through the electrolyte solution and splits up. The electrolyte solution contains positive and negative ions. During the electrolysis process, negative ions are attracted to the positive electrode and lose electrons called oxidation. Positive ions move to the negative electrode and gain electrons called reduction [17].

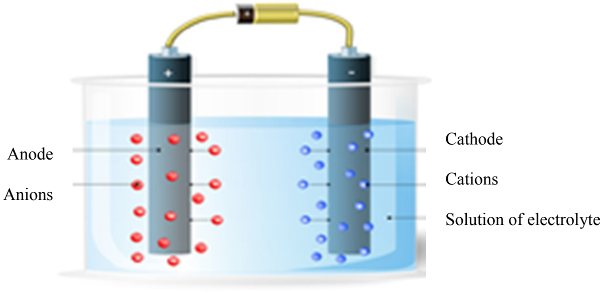


Fig. 4. Electrolysis method [16].

Bioleaching is the extraction of heavy metals from coal bottom ash by using microorganisms [18]. To extract the metals by microorganisms, it needs a highly acidic condition for growing during the extraction process. Furthermore, microorganisms will also produce acid by themselves which result in huge amounts of acids need to be handled properly, as shown in Fig. 5. Technically, bioleaching could provide a satisfying and environment friendly solution for extract heavy metals from coal bottom ash, this process is operated under mild conditions. However, until now, no suitable microorganism is found that can combine efficient extraction of heavy metals with environment friendly operating conditions [15].

Fig. 5. Bioleaching method [18].

In order to provide an economically viable process and suitable method for extraction of metal from coal bottom ash, carbon thermal reduction method is used to do a further investigation on it. Carbon thermal reduction method as per Fig. 6, is to remove the oxygen from the metal oxide that less reactive than the carbon and leave metal in the reaction container. The chemical compositions of coal bottom ash that cannot be extracted by carbon reduction due to their high reactivity, such as potassium, sodium, magnesium and aluminum oxide.

The other less reactivity metals contain in coal bottom ash can be extracted by this method, but those metal oxides percentage is very low and only iron (III) oxide has a high percentage. Moreover, based on the previous research shown that the Iron (III) Oxide is an economic metal that mostly recovery from coal ash [19]. Lastly, the concentration of unburned carbon in coal bottom ash is lower compared to fly ash [5]. Hence, carbon is often to add into coal bottom ash to let the metal oxides fully reduce with carbon.

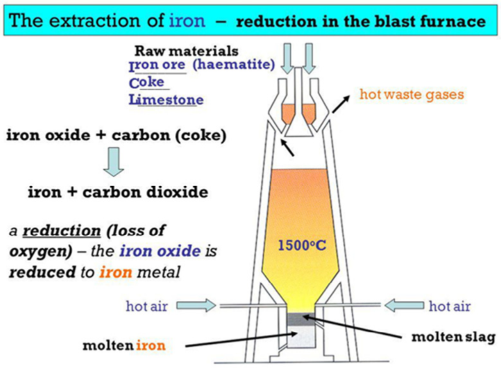


Fig. 6. Extraction of iron by carbon reduction [19].

4. Experimental Method

4.1. Carbon Reduction Method

The extraction of metal from bottom ash by carbon reduction method was studied with different temperature of tube furnace and different reduction time of coal bottom ash and it was separated by using the mechanical shaker. Only fine bottom ash will be used in experiment, while coarse bottom ash will not be used at all because some of the less reactive metal oxides may be surrounded by high reactive metal oxides which would prevent the carbon reduction to occur. The fine bottom ash is then mixed thoroughly with the carbon powder (80:20 respectively). The mixed sample was then placed into the oven with temperature 110 ± 5□ and left for 24 hours to ensure that the sample is free from any moisture. An alumina boat placed on the pan and the sample is added into the alumina boat. The dried sample was then placed into a tube furnace and burned at 800, 900, 1000 and 1100°C. Argon gas flow is connected straight into the tube furnace and controlled by flow meter. Gas bubbler is used to remove excess gas from tube furnace [22]. The coal bottom ash was determine using X-ray Florescence (XRF) testing.

4.2. Chemical Leaching Method

Chemical leaching is the process of separating heavy metals from coal bottom ash by dissolving metals into liquid form. The metal oxides bound in coal bottom ash are turned into metal ions that are released into acid solution. In addition, acid is used most often in chemical leaching process to dissolve heavy metals contained in coal bottom ash. The material that are used are Glacial Acetic Acid, Nitric Acid and Ammonia Nitrate [21]. Single step extraction procedure (SSEP) was developed to optimize the leaching time to achieve the best leaching of the elements. In all experiments, a solid-liquid ratio of 5.0 g ash / 500 mL extract was used and the contents were stirred in a magnetic stirrer at 500 rpm. Take 10 mL samples for a period of 4 hours. Each sample was centrifuged at 10,000 rpm for 10 minutes and the next step was filtered with a 0.2 μm PTFE filter and the major and minor metals were analysed using ICP-AES.

The concentration of trace metals in SSEP samples was obtained using ICP-AES (French ULTIMA 2000). Before analysis, samples were diluted with 2% HNO3 solution. For the water-soluble step, the dilution factor is kept 1:10. 1:20 for the acid-soluble step. The other two steps are 1:50 calibration standard samples and samples the same. Analysis should use 1.0M ammonium nitrate and 0.11M acetic acid solution (AS) for ion exchange (IE). Table 3 shows the steps phase for leaching with different leaching solution.

Table 3. Steps phase for leaching with different leaching solution

STEPS	PHASE FOR LEACHING	LEACHING SOLUTION
1	Water Soluble (WS)	Ultrapure Water
2	Ion Exchangeable (IE)	1.0M Ammonium Nitrate
3	Acid Soluble (AS)	0.11m Acetic Acid
4	Reducible (RD)	0.158M Dithionite, 0.3M Citrate And 1.0M Bicarbonate

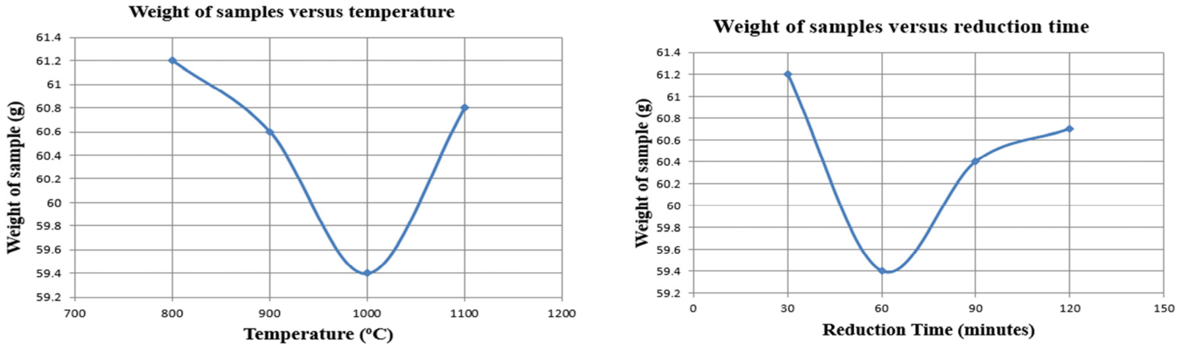
5. Results

5.1. Carbon Reduction Method

From Fig. 7, it can be clearly seen that the weight of sample decreased with the increment of the reaction temperature from 800□ to 1000□. When the temperature is increased further to 1100□, the weight of sample increased, showing that too high of a temperature promotes oxidation for metals and carbon. The weight of the sample is reduced due to the removal of oxygen from less reactive metal oxides such as Manganese (II) Oxide, Zinc Oxid**e** and Iron (III) Oxide to form carbon **d**ioxide during the reduction process. Therefore, it is shown that the sample weight reached the minimum temperature at 1000□, which means that this is the optimum temperature for the reduction of metal oxide by Carbon. This could be due to the fact that lesser reactive metal oxide loses oxygen and become metal and carbon gains oxygen from the metal oxide become carbon dioxide during the thermal reduction process. However, the sample weight loss in optimized conditions could mean that other less reactive metal oxides also could be extracted at the same time, and not only iron (III) oxide [21].

As can be seen from Fig. 7, the sample weight only decreased in the initial stage of 1 hour. With the increment of time, the sample weight began to increase after 1 hour. Therefore, based on the results of this experiment shows that the sample weight reached the minimum time at 1 hour which means this is the optimum time for the reduction of metal oxide by Carbon.

The temperature of tube furnace was maintained at approximately 800, 900, 1000 and 1100□. The temperature to extract metal cannot be too high, because it will result the titanium dioxide reduction at the same time which would affect the slag and the formation of small metal nugget separation from coal bottom ash. Besides, increment of the time to extract the metal from coal bottom ash is rarely helpful, because when the reaction between carbon and metal oxide proceeds in the tube furnace for a certain time, the reducing agent begins to be consumed and the metal oxide is also gradually decreased, and hence, the contact between carbon and metal oxide in coal bottom ash will become weak. The optimized reduction conditions were selected based on the obtained result showed the most efficiency temperature and reduction time to reduce the sample weight. The small metal nuggets are formed and separated from molten metal due to difference density of metal.



(a) (b)

Fig. 7. Effect of carbon thermal reduction on sample weight after combustion a) versus temperature, b) versus Reduction time

5.2. Chemical Leaching Method

Fig. 8 shows the graph representing the comparison of result for two methods that were conducted which are water soluble method and ion exchangeable method. Ion exchangeable method was deemed as a more suitable method for extraction metal in chemical leaching perspective.

This is determined from the results where the concentration of aluminum for the water soluble method is 4,165 mg/kg and ion exchangeable method is 237,000 mg/kg respectively. For Zinc however, the concentration achieved for the water soluble method is 6.4 mg/kg and the ion exchangeable method is 10.25 mg/kg. The concentration of iron for the water soluble method is 163.45 mg/kg and the ion exchangeable method is 16,905 mg/kg respectively.

Referring to the Fig. 8, Aluminum was found to be higher in concentration when compared to the two other element metals, which are zinc and iron. This result shows that the efficiency of the both methods is higher for the extraction for aluminum compared to zinc and iron. Results also show that the concentration of iron is higher than zinc, proving that these methods are more efficient for the extraction of iron when compared to zinc.

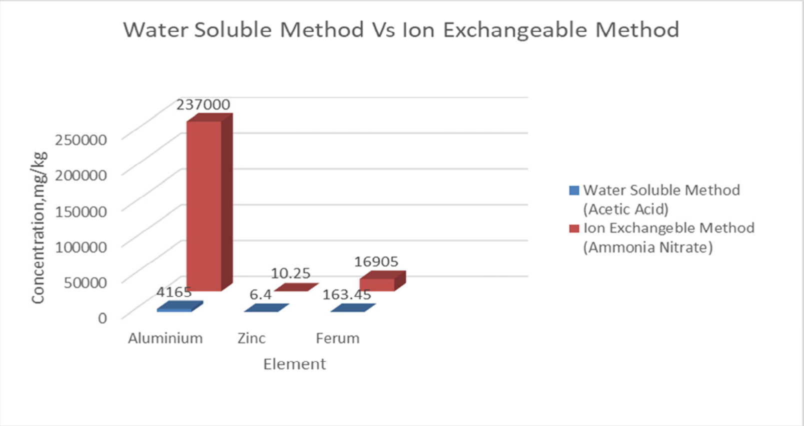


Fig. 8. Water soluble method versus ion exchangeable method

6. Conclusion

The results showed that both carbon reduction and chemical leaching method has the potential in extraction or purification of metal oxides from coal bottom ash waste. For the carbon reduction method, the optimized temperature for extraction was 1000 °C where at this temperature give the optimum time for the reduction of metal oxide by carbon. While for chemical leaching method, it was more suitable for extraction of aluminium as compared to zinc and iron. Thus, it is expected that metal oxides can be successfully extracted from the CBA, and hence promoting sustainability, and the potential of the metal oxides to be used in many different industries.

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