THE DETERMINATION OF HEAVY METALS IN COAL ASH

SUSIE ANAK SANJAN

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Department of Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak
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DECLARATION

No portion of work referred to in this dissertation has been submitted in support of an application for another degree or qualification of this or any other university or institution of higher learning.

Susie Anak Sanjan

Resource Chemistry Program (2005-2008)

Department of Chemistry

Faculty of Resource Science and Technology

University Malaysia Sarawak

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The Determination of Heavy Metals in Coal Ash

Susie Anak Sanjan

Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak

ABSTRACT

Heavy metal is chemical element that cannot be destroyed. Coal is one of the sources used to generate energy and electricity. A coal fired power plant is an energy conversion center that burns fossil fuels to produce electricity. The combustion of coal will produce residue known as ash. The large amount of ashes production will cause the contamination of the environment. This study was carried out to determine the heavy metals in coal ash by using Flame Atomic Absorption Spectrophotometer (FAAS) instrument. The coal ash samples were collected from eight location of coal ash ponds at Sejingkat Power Corporation Sdn Bhd located at the sejingkat. The concentration of heavy metals such as Pb, Zn, Ni, Cd and Mn were analyzed quantitatively. The highest concentration of heavy metal founds in all location of coal ash pond was Pb, followed by Zn, Ni and Cd in descending order. Therefore, Mn shows the lowest concentration.

Key words: Heavy metals, coal, coal ash

ABSTRAK

Logam berat merupakan unit kimia yang tidak boleh dimusnah. Arang batu merupakan sumber bagi menjana tenaga elektrik. Kilang arang batu bahan bakar merupakan pusat penukaran tenaga bahan api kepada tenaga elektrik. Pembakaran arang batu akan menghasilkan keledak atau sisa arang yang juga dikenali sebagai abu. Penghasilan abu arang batu dalam kuantiti yang banyak akan menyebabkan pencemaran ke atas alam sekitar. Kajian ini dilakukan untuk menentukan logam berat di dalam abu arang dengan menggunakan Spektroskopi Serapan Atom Nyala (FAAS). Sampel abu arang batu diambil dari lapan kawasan yang berbeza di kolam abu arang di Sejingkat Power Corporation Sdn, Bhd. Yang terletak di sejingkat. Kandungan logam berat seperti Pb, Zn, Ni, Cd dan Mn telah dianalisis secara kuantitatif. Kandungan logam berat yang paling tinggi dijumpai ialah Pb, diikuti dengan Zn, Ni dan Cd. Kandungan logam berat yang paling rendah dijumpai ialah Mn.

Kata Kunci: Logam berat, arang batu, abu arang batu

CHAPTER ONE

INTRODUCTION

Heavy metals are chemical elements that can have toxic or poisonous effects even when present at low concentrations (SenGupta, 2002). Contamination of the environment by heavy metals is a great health concern.

The demand for energy is increasing day by day. Coal is one of the sources used to generate energy and electricity. When coal is burnt, it produces residues known as ash (Fay and Golomb, 2002). The generation of huge amount of ash caused by the combustion of coal ash in thermal power plant is one of the major sources of environmental pollution. Previous research related to coal ash has shown that it can be hazardous to human health and the environment (Mandal and Sengupta, 2006). It has the potential chance to contaminate the soil and groundwater of the surrounding areas with the toxic trace elements present in it.

Coal ash is produced at the Sejingkat Power Corporation Sdn Bhd. Thermal Power Plant located by the Sarawak River nearby Kampung Goebilt at Muara Tebas. The objective of this study was to determine heavy metals in coal ash. Literature search has not yielded any study on heavy metals in the coal ash produced at this power plant. The ash sample was taken from the ash pond to be analyzed.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metal

2.1.1 What is Heavy Metal?

Heavy metals are elements having atomic weights between 63.546 and 200.590 refer to chemical elements that have metal or both metal and non-metal characteristics (Wild, 1996). Heavy metals remain in the environment as they cannot be destroyed or degraded. Some examples of heavy metals are copper (Cu), zinc (Zn), arsenic (As), mercury (Hg), aluminium (Al), cadmium (Cd), and lead (Pb). Some of heavy metals is useful in trace amounts in living organisms. In excessive levels they can be harmful to the organism (Nriagu, 1992).

Basically, heavy metal has a specific gravity greater than 4.0 and densities above 5 g/cm^3 (Wild, 1996). Non-essential heavy metal, when present in some media, they can find their ways into human body systems, can accumulate in surface soils, surface ground water, street dust, rain water and plant materials and, hence, find their way into the human body (Odero *et al.*, 2000).

2.1.2 Environmental Effect of Heavy Metal

Heavy metal is dangerous because it tends to increase its concentration in a biological organism over time, compared to the chemical concentration in the environment. At low concentrations, heavy metal can give toxic or poisonous effect. The threshold toxic concentrations differ for each heavy metal and are governed primarily by the chemistry of each heavy metal in question and related physiological effects (SenGupta, 2002).

Heavy metal may enter the food chain from soils and result in health hazards (Mashi *et al.,* 2005). There are 38 elements constituting heavy metal. 12 out of then 38 elements Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sn and Zn are considered as those whose concentration in the environment is easily influenced by human activities (Mashi *et al.,* 2005).

Cadmium, chromium, mercury, lead, arsenic, and antimony are example of non-essential heavy metals. These heavy metals are particularly of concern to health (Odero *et al.,* 2000). In soil, air, and water, some heavy metal like arsenic and selenium are often exist in different oxidation states. The reactivities, ionic charges, and solubilities of these types of metals in water vary widely. For their short and long term toxic effects, the maximum permissible concentration of these heavy metal in drinking water as well as in municipal and industrial discharges are closely regulated through legislation.

With the exception of three most toxic heavy metals i.e. cadmium, mercury, and lead, heavy metals are required as necessary ingredients for living cell. Mining, metallurgical, electroplating are the example of industries that have increased the production and amount heavy metal in the life cycles of living organism.

The mobility of heavy metals in the environment is increased by to the lowering of pH in rain and surface waters and the increased use of surfactant (SenGupta, 2002). Therefore, heavy metal can be considered as pollution agents which can harm to human health and the environment in short or long term periods (Odero *et al.*, 2000).

2.2 Heavy Metal in Coal

Coal can be defined as the most abundant and predominant product of plant residue coalification (SenGupta, 2002). Coal which is a combustible sedimentary rock is brown to black in colour. It is composed mainly of consolidated and chemically altered plant remains which are solid hydrocarbon fuel formed by ancient decomposition of woody substance under conditions of heat and pressure (ACAA,2003).

Coal is source of energy. It is found buried deeply in the ground or under the seabed and also close to the surface. Its characteristics are affected by several factors according to the biological origin and geological history. The characteristics and chemical compositions of coal such as the moisture content, amount of minerals (ash) sulfur, nitrogen, and oxygen are highly variable (Fay and Golomb, 2002). Trace elements in coal can be divided according to their properties whether they are primarily associated with the organic fraction of coal, with the mineral fraction or with both.

As, Cd, Hg, Pb and Zn are elements are concentrate in the organic fraction of coal. While elements such as Cr, Cu, and Se are present in both the mineral and organic matter but they tend to be inorganically related where Boron and Berylium were found to be largely combined with the organic fraction of coal (Chadwick *et al.,* 1989). The trace elements are enriched from 4 to 10 times during coal combustion (Fernandez-Turiel *et al.*, 1994).

Coal is one of the most impure fuels that can be used to generate electric energy. Coal is a major source of energy for electric power generation. The basic coal structure can be regarded as a three-dimensional polymeric network which consists of hypothetic monomeric ‘’ basic unit’’ that have a mean molecular weight of about 400, connected by relatively weak linkages (Chadwick *et al.,*1989). Chemical structure of coal determines their hydrogenation mechanism. Coal chemical reactions and coal constitution, show that coal has a macromolecular character (Wender *et al.,*1981).

2.3 Mobilization of Trace Elements by Coal Utilization

The used of coal in large quantities caused the occurrence of its mobilization (Chadwick *et al.,* 1989). The yearly world production of coal in 1978 was estimated to be 2.974×10^9 tonnes (Quenton, 1980).). In a year, a single large power plant of more than 2000 MW will burn about 10^7 tonnes of coal (Wiersma and Crockett, 1978). Physicochemical alterations to trace elements will occur during the coal combustion process. The alterations enhaced their toxicity. Ash that is removed in a wet condition may have considerably higher elemental enrichment (Chadwick *et al.*,1989).

In modern electric power plants, coal combustion takes place in furnaces that are operated at temperature of 1600°C. A portion of non-combustible mineral matter will be retained in the furnace during the coal combustion process as either slag or bottom ash. Other residues will leave as fly ash and volatilized minerals. The proportion of bottom ash, slag and fly ash produced will be different with coal ash content, plant design and the particulate collection device employed (Bolton *et al.,* 1973).

2.3.1 Coal Fired Power Plant

A coal fired power plant is an energy conversion center that burns fossil fuels to produce electricity. Coal power production is a quite simple process. Generally, chunks of coal in the majority of coal fired power plants are crushed into fine powder and are fed into a combustion unit where it is burned. In a fossil fuel power plant, the chemical energy inherent in the fossil fuel is converted first to raise the enthalpy of combustion gases. Chemical energy that is stored in coal is converted successively into thermal energy, mechanical energy and at last converted into electrical energy. Basically the electrical energy is generated based on heat from the burning coal that is used to generate steam that is used to spin one or more turbines to generate electricity (Fay and Golomb, 2002). About 23% of the electricity consumed worldwide is generated by coal-fired power plants (EIA,2002). When coal is burnt, it produces side mineral matter like bottom ash and fly ash with the flue gases and volatilized minerals (Chadwick *et al.,* 1989).

2.3.2 Behavior of Trace elements within power plants

Mass-balance studies involve the comprehensive examination into the behavior of trace elements in power plants. Mass-balance studies show that a consistent and selective partitioning of trace elements between the various exit streams is produced by coal combustion in power plant, permitting the categorization of elements into three groups which are Group I, Group II and Group III.

Al, Ba, Ca, Ce, Cs, Fe, K, Mg, Mn and Th are the elements in Group I, that partition equally between bottom ash and fly ash and are not concentrated in the outlet fly ash.

In Group II, As, Cd, Cu, Pb, Sb, Se and Zn are the heavy metal that concentrate in the inlet fly ash compared to the bottom ash and the outlet fly ash compared to the inlet fly ash.

While for Group III, Br, Hg and I are three elements that are present in the gas stage and depleted in all of ashes. Cr, Ni, U and V are the some of heavy metal that exhibit intermediate behavior between Group I and Group II (Chadwick *et al.,* 1989).

2.4 Coal Ash

2.4.1 What is Coal Ash?

Coal ash is the residue that is produced during coal combustion. It is refers to any solid material or residue, for instance fly ash, bottom ash or boiler slag which is produced primarily from the combustion of coal. It is the incombustible inorganic matter in coal. Mineralogical analysis show that coal combustion residues could be divided into three major matrices which are a glass like mullite, magnetic spinal and quartz (Twardowska and Szczepanska, 2002).

Silica, alumina and iron oxide are the major constituent of coal the combustion residual. The concentration of silica, alumina and iron oxide are influenced by the predominant phase constituents, which are quartz (SiO_2), alumino silicates (gehlenite,

$Ca_2Al_2SiO_7$) and hematite (Fe_2O_3) (Asokan, 2003; Janos et al., 2002). Coal ash is often complicated by high concentration of metal. Combustion of coal in thermal power plants generates a lot of ashes, which are disposed off in large ponds in the vicinity of the thermal power plant (Schwab *et al.*, 1991).

Chemical, mineralogical, physical, radioactive and morphological properties of coal combustion residues in general vary. This is because they are influenced by coal source or quality, combustion process, degree of weathering, age of the ash and particle size (Adriano *et al.*,1980; Asokan, 2000; McCarthy and Dhar, 1999).

Essential micro and micronutrients that contained in coal ash are beneficial for plant growth and improved physicochemical properties of soil (Chaudhuri *et al.*, 2003). Coal ash ranges from coarse sand to clay (Asokan *et al.*, 1999). The source, topography of disposal site and location from where the ash is collected may influence the texture and the particle size distribution of coal ash (Asokan, 2000; Rajasekhar, 1995; Sivapullaiah *et al.*, 1998; Skarzynska *et al.*, 1989).

Limestone, iron, aluminum, silica sand and clay are the substances that are found in coal ash. In the trace quantities, coal ash consists of the oxidized forms of the naturally occurring elements. The coal can be bituminous, sub-bituminous, lignite or mixture of these coals (ACAA, 2003). There are other mineral phases present in coal combustion residues such as Albite ($Ka_lSi_3O_8$), Mullite ($Al_6Si_2O_{l3}$), Esperite (CaPb)$ZnSiO_4$, Tenorite (CuO) and Nepoutite $(NiMg)_3Si_2O_{15}(OH)_4$ (Kolay and Singh, 2001; Saxena *et al.* 1998).

The binding properties, sorption characteristics of the final products or processes may be influenced by the microstructure of coal ash. From the observation of coal ash particles by using electron microscopy it is seen that the particles of coal ash vary in shape and size. This coal ash particles form hollow shaped, cenospheres in nature and are spherical (Asokan, 2003; Fisher *et al.*, 1978; Kolay and Singh, 2001; Murarka *et al.*, 1993; Norton *et al.*, 1986).

2.4.2 Types of coal ash

Bottom ash and fly ash are two types of residue that are produced from the coal-fired thermal power plants. Bottom ash collected from the bottom of the boiler is the coarse-grained fraction (Baba, 2002). Bottom ash is agglomerated ash particles formed in pulverized coal furnaces. Bottom ashes are too large to be carried in the flue gases and impinge on the furnace walls or fall through open gates to an ash hopper at the bottom of the furnace.

Basically, the colours of the bottom ashes are grey to black. It has a porous surface structure and relatively angular. In industry, bottom ash is used as a feed stock for cement manufacturing, as an aggregate or in construction in lieu of other constituents like sand and gravel (ACAA,2003). Wet disposal is the method that been used to dispose the bottom ash in a slurry form to nearby waste disposal sites, also known as ash pond (Baba, 2002).

Ash ponds are a surface impoundment used to dispose of ash primarily from the combustion of coal. Coal ashes are stored for disposal as a slurry or sludge. A large ash pond is referred to as an impoundment, ash reservoir, or surface impoundment (ACAA,2003).

Coal-fired power plants produce large amounts of fly ash. Coal fly ash is a product of burning finely ground coal in a boiler to produce electricity. Electrostatic precipitators or baghouses and secondary wet scrubbers, the air pollution control equipment, are used to remove coal fly ash from the plant exhaust gases (ACAA, 2003).

Fly ash refers finely divided mineral residue resulting from the combustion of coal in electric generating plants. Fly ash contains of fine sized particles, ranging from 0.5 to 200 µm (Baba, 2002). Fly ash can vary in colour from tan to gray to black. The colours are depending on the amount of unburned carbon in the ash. The lighter colour of the fly ash indicates the lower carbon content (ACAA, 2003).

Generally fly ash is a pozzolan. Pozzolan is basically siliceous and aluminous materials that will finely separated form and in the presence of moisture, chemically react with calcium oxide at normal temperature to form a compound processing cementitious properties. Several fly ashes exhibit self-hardening properties in the presence of moisture (ACAA, 2003).

Fly ash which consists of heavy metal like silica, aluminium, oxides of iron, calcium, magnesium, arsenic, chromium, lead, zinc, nickel and others toxic metals are used partially in industry such as cement making, concrete mixing, and ceramics (Scotti *et al.*, 1999). Cr, Ni, Cu, Pb, Cd, Zn are the major heavy metals found in fly ash (Mester *et al.*, 1999).

2.4.3 Enrichment of Trace Element in Fly Ash

Physicochemical properties of the elements, their chemical form in the coal, processes of coal combustion and mechanisms of emission control devices are the factors that influence the enrichment of trace in fly ash (Kaakinen *et al.*, 1975; Phung *et al.*, 1979; Fulekar *et al.*, 1983).

The enrichment factor is the term that states the extent of trace element in fly ash. This is the ratio of the concentration of element (X) to refractory element, in the fly ash, divided by the corresponding abundance ratios in the crustal rocks (Mason, 1960).

$$EF = \frac{([X]/[Al])\ \text{Fly ash}}{([X]/[Al])\ \text{crust}}$$

Many volatile elements like Zn, Pb, Sb, Se, Ni, Br, Cd, Cu, Hg, and I have larger EF in the suspended fly ash particles. When the EF for urban aerosols is higher, it indicated that the coal combustion is not responsible for their presence in urban particulates. In urban, if the major source of certain enriched element is coal combustion, the account must be taken of the relatively low EF reported for many elements in suspended fly ash particles. The greater settling velocities of larger fly ash particles would be expected lead to a fractionation with time, resulting in increased EFs for volatile elements (Chadwick *et al.*,1989).

2.5 Environmental Effect of Coal Ash

The coal based thermal power plants all over the world are cited to be one of the major sources of pollution affecting the general aesthetics of environment in terms of land use, health hazards and air, soil and water in particular and thus leads to environmental hazards. The production of ash is one of the major environmental problems related to the use of coal as fuel in the thermal power plant (Mandal and Sengupta, 2006).

Coal combustion product which is ash is often complicated by high concentration of metal (Schwab *et al.,* 1991). Arsenic contamination, having serious environmental pollution has been directly related to trace element production from the combustion of coal (Chadwick *et al.,* 1989).

Zn, Cd, Pb, Mo, Ni, As, Se and B are the trace elements in coal combustion residue which are an important concern for land disposal due to their environmental significance. The ultimate impact of each trace element will depend upon its state in Coal Combustion Residues (CCRs) and toxicity, mobility and availability in the ecosystem (Keefer, 1993; Spears, 2002).The leaching of heavy metals to surface and underground water source is one of the major concerns with coal combustion residues disposal. The leaching of heavy metal may contaminate the ground water quality around the ash disposal area (Anderson *et al.,* 1993; Sandhu *et al.,* 1992).

Fly ash can cause the degradation of the environment. It reduces the pH and permeability of water and clogs natural drainage, making it turbid. Fly ash poses a serious difficulty for its disposal (Gupta *et al.,* 2005).

2.5.1 Atmospheric Emission of Trace Element

The magnitudes of atmospheric trace element deposition from power plants have been assessed (Chadwick *et al.,* 1989). The investigation on surface soils area of industrial areas in Poland, showed that the surface area contained increased U and Th concentrations (Jaworowski and Grzybowska, 1977).

Heavy metals are released into the surrounding environment by two different pathways through coal combustion in plants.

- One of the pathways is atmospheric emissions via stack, including elements which are volatilized and those which are condensed and enriched with fine particles that escape from the particulate controls (Fernandez-Turiel *et al.*, 1994).

- The second pathway is leaching of combustion wastes which are fly ash and slags formerly these are ponded or landfilled (Fernandez-Turiel *et al.*, 1994).

2.5.2 Solid Waste

Fly ash, bottom ash, and slag are the examples of solid waste produces during the combustion of coal in power plants. The most important waste material in modern pulverized coal power plant is fly ash (Chadwick *et al.,* 1989). Various forms of fly ash emission control tools are in use. 70 to 90 % are the range of ash retention (UNGA, 1980). The solid waste is transported to the disposal site by the use of conveyor belts. The solid waste is damped using nozzle on the conveyer belts to prevent spreading of ash by wind

(Baba and Kaya, 2003). During coal combustion the wastes are enriched from 4 to 10 times for some of these trace elements (Fernandez-Turiel *et al.*, 1994).Therefore, the production of energy in coal-fired power plants mobilizes an important variety and quantity of trace elements (Sabbioni and G6etz, 1983).