HEAVY METAL LEACHING FROM DIFFERENT FLY ASHES USES DIFFERENT LEACHING METHODS

Mr. Kittitat Leelarungroj

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บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
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By	Mr. Kittitat Leelarungroj
Field of Study	Hazardous Substance and Environmental Management
Thesis Advisor	Dao Suwansang janjaroen, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

--Dean of the Graduate School

(Associate Professor Sunait Chutintaranond, Ph.D.)

THESIS COMMITTEE

--Chairman

(Assistant Professor Chantra Tongcumpou, Ph.D.)

--Thesis Advisor

(Dao Suwansang janjaroen, Ph.D.)

--Examiner

(Penradee Chanpiwat, Ph.D.)

--Examiner

(Seelawut Damrongsiri, Ph.D.)

--External Examiner

(Assistant Professor Cheema Soralump, Ph.D.)

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ABBREVIATION

°C	- Degree Celsius
AAS	- Atomic Absorption Spectrometry
ASTM	- The American Standard of Testing and Materials
BA	- Bottom ash
BCFA	- Bituminous coal fly ash
BS	- Boiler slag
Ca/S	- Calcium to sulfur ratio
CCPs	- Coal Combustion Products
cm	- Centimeter
DI	- Deionized
DMA	- Dimethyl arsenate
DOC	- Dissolve Organic Carbon
d_{32} or SMD	- Sauter Mean Diameter
ESP	- Electrostatic Precipitator
FA	- Fly ash
FGD	- Flue gas desulfurization
g	- Gram
h	- Hour
IC	- Ion chromatography
ICP-OES	- Inductive Couple Plasma-Optical Emission Spectrometry
ICP-QMS	- Inductive Couple Plasma-Quadrupole Mass Spectrometry
ID	- Internal diameter
LCFA	- Lignite coal fly ash

LCs	- Leaching concentrations
LOI	- Loss on ignition
L/S	- Liquid to solid ratio
MCLs	- Maximum concentration limits
mg/kg	- Milligram per kilogram
mg/L	- Milligram per liter
min	- Minute
mm	- Millimeter
MMA	- Monomethyl arsenate
mL	- Milliliter
MSWI	- Municipal Solid Waste Incinerator
OD	- Outer diameter
ppm	- Part per million
RCRA	- The Resource Conservation and Recovery Act
rpm	- Round per minute
SAR	- Synthetic acid rain
SEM	- Scanning Electron Microscope
SS	- Sewage sludge
T-BCFA	- Treated-bituminous coal fly ash
TCLP	- Toxicity Characteristic Leaching Procedure
US	- Ultrasound
USEPA	- United States Environmental Protection Agency
w/w	- Weight by weight
XRD	- X-Ray Diffractrometer
XRF	- X-Ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 State of the problem

In order to respond the future energy demand, all energy resources need to be applied. The coal is one of the most important electricity producing fuels. Millions tons of coal fly ash are produced as by-product from thermal power stations every year. Coal combustion products (CCPs) include fly ash (FA), bottom ash (BA), boiler slag (BS) and flue gas desulfurization residue (FGD) (Punshon et al., 2003). Fly ash is fine particulate inorganic matter which is accumulated heavy metals collected from electrostatic precipitators (Wu & Ting, 2006). The researchers find the new resources instead of coal such as husk, bagasse and municipal solid waste ash from manufacturing industries because coal is a nonrenewable resource and produce greenhouse gas as the cause of climate change (Chai et al., 2009; Neupane & Donahoe, 2013). However, fly ashes generally contain hazardous ions of heavy metals especially As (V), Cr (VI), Pb and Zn. These elements are potential risks which affect environment and human health (Chai et al., 2009; Su & Wang, 2011). For elements in fly ash, Cd, Cu, Mo, Sb, V and Zn are remarkably enriched on the surface, whereas Ba, Co, Cr, Mn, Ni and Pb tend to be spread between the surface and the matrix. The elements accumulating in the cores of fly ash particles are not directly exposed to leaching but the releasing depends on dissolution rates of the surface layers (Izquierdo & Querol, 2012). In addition, dissolution behavior of elements from leaching in the environment relates to particle size, solid/liquid ratio, time, surface area, pH and initial concentrations of elements. In the past, the management of coal fly ash is disposing into landfills, lagoons and disposal mounds, it may leak and affect soil, groundwater and environment. At the present, a small amount of coal ash is used in cement and construction industry (Wang et al., 2008). For example in the U.S., the reuse of fly ash in highway applications can solve landfill problems and increase the strength of material but it is costly and consumed more time to stabilize the road (Cetin et al., 2012). The process for generating the electricity by burning coal is shown in Figure 1.1.

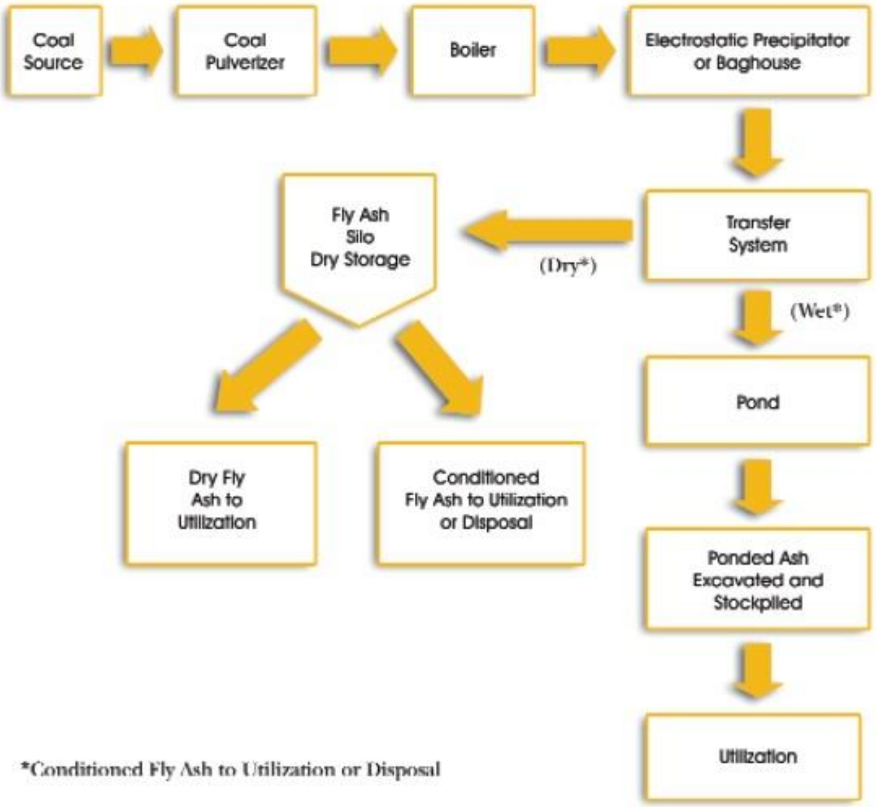


Figure 1.1 Method of fly ash transfer (Application & Association, 1999)

Toxicity Characteristic Leaching Procedure (EPA, 1992) and Jar Leaching (Scott et al., 2003) are generally used to determine the leaching of heavy metals in the high acidic condition and leaching trends, respectively. Moreover, Column Leaching according to US EPA method 1314 is used to investigate the leaching behavior of heavy metals by using synthetic acid rain (Neupane & Donahoe, 2013; Yılmaz, 2015). The method used to analysis pseudo-total of trace elements is microwave assisted digestions according to US EPA method 3051 part A. The results from jar and column leaching test are used to compare with industrial effluent standard as shown in Table

1.1. For TCLP, the result is used to compare with the resource conservation and recovery act (RCRA) for hazardous waste (D-List) according to Table 1.2.

In this study, lignite coal fly ash samples from Maemoh power plant, bituminous coal fly ash from the GHECO-ONE and BLCP power plants were investigated the effect of ash chemical composition on leachability using TCLP, jar leaching, column leaching experiments and microwave assisted digestion. Municipal solid waste fly ash collected from SCG power plant was investigated the effect of size analysis on the leachability using sieve analysis for separating size of fly ash and TCLP as the leaching test. Moreover, the researcher expected that the results from analysis can suggest the application of fly ashes in cement or construction materials which can improve the quality and increase the resistance into concrete. Arsenic, chromium, lead and zinc are the generally hazardous elements in fly ash to be investigated and analyzed by leaching test.

Table 1.1 Industrial effluent standards

Heavy metals	Concentration
1. Zinc (Zn)	Not more than 5.0 mg/l
2. Chromium (VI)	Not more than 0.25 mg/l
3. Chromium (III)	Not more than 0.75 mg/l
4. Copper (Cu)	Not more than 2.0 mg/l
5. Cadmium (Cd)	Not more than 0.03 mg/l
6. Barium (Ba)	Not more than 1.0 mg/l
7. Lead (Pb)	Not more than 0.2 mg/l
8. Nickel (Ni)	Not more than 1.0 mg/l
9. Manganese (Mn)	Not more than 5.0 mg/l

Table 1.1 Industrial effluent standards (continue)

Heavy metals	**Concentration**
10. Arsenic (As)	Not more than 0.25 mg/l
11. Selenium (Se)	Not more than 0.02 mg/l
12. Mercury (Hg)	Not more than 0.005 mg/l

Table 1.2 Maximum metal concentration of hazardous waste for toxicity characteristics (D-List)

Contaminant	**TCLP Maximum (ppm)**
Arsenic	5.000
Barium	100.000
Cadmium	1.000
Chromium	5.000
Lead	5.000
Mercury	0.200
Selenium	1.000
Silver	5.000

This list was used to determine the characteristic of hazardous wastes from TCLP method (EPA 2007). This standard aims to determine hazardous waste if the heavy metals concentration was higher than this standard.

1.2 Hypothesis

1. Size of fly ash particles will affect heavy metal leachability.
2. Fly ash chemical compositions play an important role in heavy metal leachability.

1.3 Objectives

1. To study the effect of physical properties of fly ash on leachability
    - Using municipal solid waste ash from SCG industry
2. To study the effect of fly ash composition on leachability
    - Using lignite coal fly ash from Maemoh power plant, bituminous coal fly ash from GHECO-ONE power plant and treated-bituminous coal fly ash from BLCP powerplant.

1.4 Scope of Study

- The fly ash samples were collected from electricity generation using municipal solid waste at SCG industry and coal from Maemoh, GHECO-ONE and BLCP power plant.
- DI water, acetic acid, nitric acid and synthetic acid rain were used as leachants for leaching tests.
- Physical and chemical properties of fly ashes were analyzed by SEM, XRF and microwave assisted digestion method.
- The methods used to analyze the leaching of heavy metals are TCLP, water-based leaching test, microwave assisted digestion and column leaching test.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Fly ash

The electricity production by burning coal generates by-products including bottom ash (around 20%) and fly ash (around 80%). Fly ash is a fine powdered material from electricity generation in thermal power plants. It is used as the cementitious and pozzolanic ingredient in portland cement concrete. Fly ash is normally captured by electrostatic precipitation. Fly ash is enriched with alumina, silica and ferric oxide as the major components, while magnesium oxide (MgO), sodium oxide (Na_2O), potassium oxide (K_2O) and sulfur trioxide (SO_3) are minor. Moreover, fly ash contains trace elements (As, B, Cr, Pb, Se and Zn) on the surface and within the particle (Punshon et al., 2003). The size of fly ash is in the range between 1-150 microns. Normally, the properties of fly ash are different depending on combustion temperature, moisture content, and coal types. In geology, coals used to generate electricity can be divided into four types.

2.1.1 Types of coal

2.1.1.1 Lignite: Lignite is brownish black, high moisture (>45%) and high in sulfur.. Lignite is like soil more than a rock, and decomposes when exposed to the weather. Lignite is also called brown coal, and considered the lowest grade of coals used in power generation.

2.1.1.2 Sub-bituminous: This coal is also called black lignite and contains (20-30)% moisture. Sub-bituminous is bright, lustered, and used for generating electricity and space heating.

2.1.1.3 Bituminous: Bituminous coal is the black, soft, smooth, and dense. This coal is the most common coal which has a moisture content less than sub-bituminous (<20%). Bituminous is used for generating electricity, and is the main fuel for iron industries.

2.1.1.4 Anthracite: Anthracite is the highest grade of coals. It is hard, black and lustrous. Anthracite is low in sulfur and moisture (<15%) and high in carbon.. Anthracite is like metallic and produce higher energy than the others (Speight, 1994).

Table 2.1 shows the chemical composition and moisture content of each fly ash (Chindaprasirt & Jaturapitakkul, 2006)

Types of coal	Chemical composition (percentage by mass)					
	C	H	O	N	S	Moisture
Lignite	60 – 75	5 – 6	20 – 30	1	1	50 – 70
Sub-bituminous	75 – 80	5 – 6	15 – 20	1	1	25 – 30
Bituminous	80 – 90	4 – 6	10 – 15	1	5	5 – 10
Anthracite	90 – 98	2 – 3	2 – 3	1	1	2 – 5

As shown in Table 2.1, the main components of coals are carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S). For moisture content, lignite has the highest moisture content, and anthracite has the lowest. The carbon content shows the amount of heat which can generate during the combustion process of coal. The grade of coal is considered from the high carbon content. Thus, anthracite has highest quality. On the other handlignite has lowest quality of all (Chindaprasirt & Jaturapitakkul, 2006).

Besides elemental chemical compositions, fly ashes can be categorized by pH. The pH of ash-water is likely controlled by ratio of concentration Ca/S in fly ash.

The fly ash can be separated in three main groups based on Ca/S ratio and pH of ash:

- Strongly alkaline ashes: The dissolution of free-lime controls leaching, with pH in the range 11-13 (Heasman et al., 1997) ,and large amounts of calcium in leachate (Ca/S>>1).
- Mildly alkaline ashes: The dissolution of anhydrite controls leaching with low Ca and Ca/S ratio (pH 8-9) (Querol et al., 2001).
- Acidic fly ash: The amounts of CaO and MgO are depleted which is related to sulphate content. So fly ash maintains the acidic components concentrating on the fly ash surface (Swaine, 1990).

2.1.2 Classification

In the United States, American Standards of Testing and Materials (ASTM) separates fly ash into class F and C. The properties of each class of fly ash are shown in Table 2.2 (Testing & Materials, 1980).

2.1.2.1 Class F: Fly ash is generated from burning anthracite or bituminous coal. This class has pozzolanic properties and the main components are silica, alumina and ferric oxide (around 70%).

2.1.2.2 Class C: Fly ash is generated from lignite or sub-bituminous coal burning. This class has pozzolanic, some cementitious properties. The main components are silica, alumina and ferric oxide (around 50%).

Table 2.2 shows the chemical properties, moisture content and loss on ignition (LOI) of each class of fly ash followed by ASTM C618

Properties	Class of fly ash	
	F	C
SiO_2+Al_2O_3+Fe_2O_3, min, %	70.0	50.0
SO_3, max, %	5.0	5.0
Moisture content, max, %	3.0	3.0
Loss on ignition, max, %	6.0	6.0

2.2 Leaching process

Leaching is the process which components of solid are released into liquid phase by the effect of solvent. Leachant is the liquid which is used in leaching test to dissolve heavy metals from fly ash. Leachate is the aqueous effluent which contains hazardous substances that may cause environmental impact.

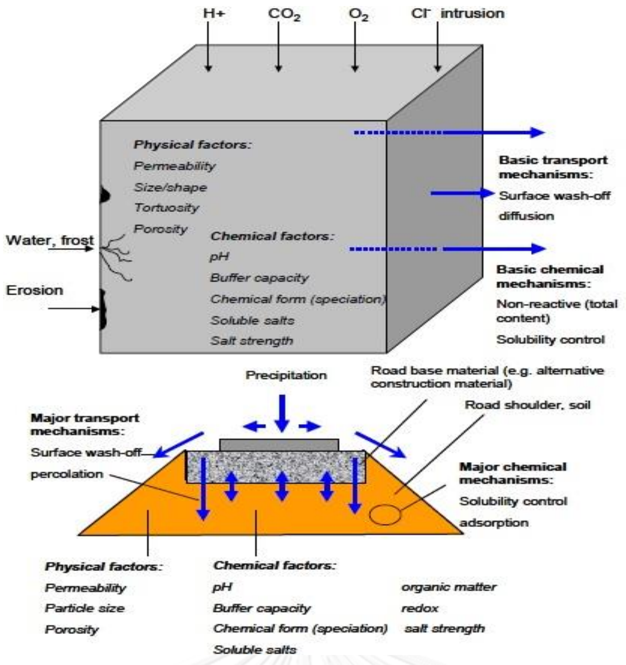


Figure 2.1 Material-specific and external factors (chemical and physical) influencing the release of contaminants from monolithic (concrete, blocks, bricks) and granular material (sand, gravel)

2.3 Factors controlling release of contaminants (H.A. van der Sloot & Dijkstra, 2004)

In terms of release behavior, the processes that cause the releasing of contaminants from materials to liquid phase are (Figure 2.1):

2.3.1 Chemical process

2.3.1.1 Basic chemical mechanisms

The basic chemical mechanisms control the releasing of contaminants in materials:

- Solubility process

Solubility is the property of solute (solid, liquid or gas) to dissolve in solvent (solid, liquid or gas). The factors which affect the solubility are chemical and physical properties of solute and solvent, temperature, pressure and pH of solvent.

- Adsorption process

Adsorption is the process which atoms, ions or molecules of gas, liquid or dissolved solid react on the surface of materials. This process produces the layer of adsorbate on the surface of adsorbent.

2.3.1.2 pH

The pH of material and environment are significant for determining the releasing of contaminants. The pH is usable for sorts of materials such as monolith, granular, cements, soil, sediments, fly ash, etc. This influences to dissolution process (minerals or elements), solubility and sorption processes. The relationship curve between pH value and concentration of leachate of each group of contaminants (salts, cations, and anions) is shown in Fig 2.1. According to Fig 2.2, heavy metals leached from each construction material (wood, brick and concrete) at different pH. Figure 2.3 shows the potential leachability of different construction materials at various pH.

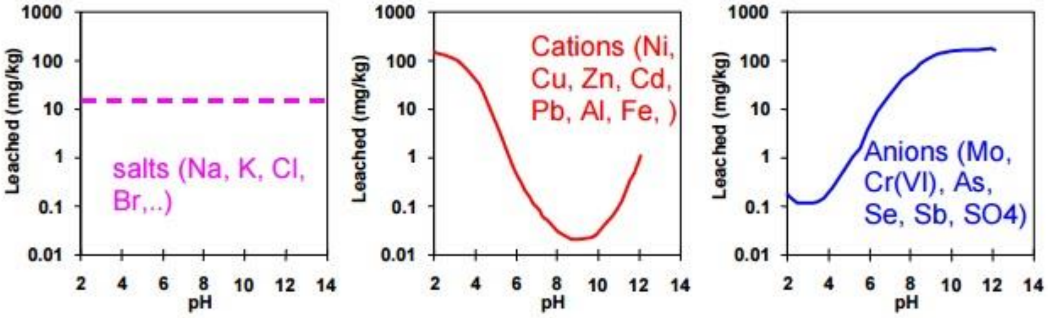


Figure 2.2 General leaching behavior of contaminants as a function of pH

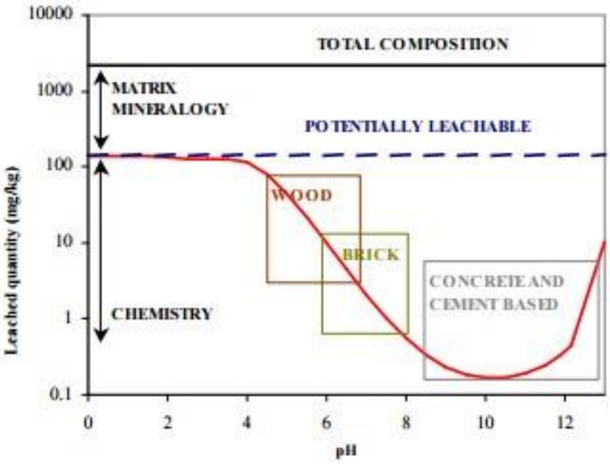


Figure 2.3 The pH dependent leaching of construction materials

2.3.1.3 Chemical form of contaminants in the material

The chemical form of contaminants determines its characteristic leaching behavior includes redox form (reduced and oxidized form). Heavy metals can form a complexation with natural water, soils and natural materials. Complex forms of heavy metals are normally highly soluble.

2.3.1.4 Total composition of the material

The geochemical mechanisms and physical factors associate with the releasing of other elements in materials.

2.3.1.5 Redox

The chemical forms of contaminants are influenced by reduction and oxidation state of the material. Oxidation reaction usually increases the potential of leached amounts of heavy metals in materials while reduction reaction has opposite effect.

2.3.1.6 Acid-base buffering

The acid-base buffering capacity was used to determine the fluctuation of pH under influence of external factors.

2.3.1.7 Organic matter and dissolved organic carbon (DOC)

Solid and dissolve organic carbon (or dissolve organic matter) is complex molecules that have a high affinity to prevent heavy metal releasing. DOC can increase potential of leaching. DOC is the one of large amounts in organic environments (soils, sediments and fly ash).

2.3.1.8 Composition of water phase and ionic strength

Ionic strength (such as salt strength) of solution in the material associates with the solubility of components. The high ionic strength generally enhances the leaching of contaminants. For other components such as chloride (Cl^-) or carbonates (CO_3^{2-}), metal complexation may occur, which subsequently decreases metal leachability.

2.3.1.9 Temperature

The increasing temperature can lead to the higher solubility. Moreover, an increase in temperature can increase the chemical reaction rates and diffusion transport.

2.3.1.10 Time

Time is the one factor which is significant in contaminant release. In general, the time associates with rate of reactions (kinetic rates) or processes, the changing of environmental conditions or properties of materials, and the time scale of materials which apply in many applications (construction buildings).

2.3.2 Physical factors

2.3.2.1 Basic transport mechanisms

Diffusion is the movement of atoms or molecules from high concentration (or high chemical potential) to low concentration (or low chemical potential) area.

Mass transfer is the movement of mass from one phase, fraction or component to another. Mass transfer associates in many processes absorption, adsorption, evaporation, precipitation and leaching.

2.3.2.2 Granular/monolithic

Granular or monolithic materials are important because of the different transport of water in two types of material. The release behavior of water in granular materials is percolation and diffusion for monolithic materials. For diffusion process, the releasing of water doesn’t depend on the types of material only, but the time-dependent diffusion is important as well.

2.3.2.3 Particle size

The particle size associates with the distance of contaminants which flows from the center of the particle to the liquid phase for granular materials. The flow and reaction is fast for small particle size. The diffusion process tends to influence the transport of contaminants in the rough grain particle size.

2.3.2.4 Porosity

For monolithic and granular materials, the pore space or porosity (pore space to total volume ratio) is a factor that influences the transport of contaminants to liquid phase. At high porosity, the transport of liquid is easily and highly released in media or materials.

2.3.2.5 Permeability

The permeability determines the movement of liquid flow into the materials ,or the contaminants will be released overtime. In general, the transport of liquid will flow around materials with a low permeability.

2.3.2.6 Size and shape

Size and shape (geometry) is a factor which is related to surface area of materials, and is important for diffusion process. Diffusion process will be faster for materials with a high surface area per weight unit.

2.3.2.7 Erosion

Erosion process can increase effect of releasing contaminants due to two factors:

- Erosion can increase surface area of materials
- The new fresh surface is exposed to acid rain leading to a higher contaminants concentrations and higher release.

2.3.3 External factors

External factors are significant for contaminant release. These factors are liquid flow rate (monolithic materials) and an occurrence of special flow path (granular materials).

2.3.4 Organic substances from construction materials

There are many processes which are important for leaching of organic substances from materials include:

- Diffusion
- Dissolve organic carbon (DOC)
- pH, redox and ionic strength
- Volatilization process
- Degradation process

2.3.5 Chemical reaction of fly ash (Brouwers & Eijk, 2003)

$$SiO_2 + 2OH^- \Leftrightarrow SiO_3^{2-} + H_2O \tag{1}$$

$$Al_2O_3 + 2OH^- \Leftrightarrow 2AlO_2^- + H_2O \tag{2}$$

$$CaO + H_2O \Leftrightarrow Ca^{2+} + 2OH^- \tag{3}$$

$$Na_2O + H_2O \Leftrightarrow 2Na^+ + 2OH^- \tag{4}$$

$$Fe_2O_3 + 3H_2O \Leftrightarrow 2Fe^{3+} + 6OH^- \tag{5}$$

$$TiO_2 + OH^- \Leftrightarrow HTiO_3^- \tag{6}$$

2.3.5.1 Metal hydroxide precipitation

The precipitation of metal hydroxide normally depends on two factors: concentration of metals and pH of water. This technique is primarily used for removing heavy metals or contaminants from waste water. According to figures 2.4, 2.5 and 2.6, it shows theoretical solubility of metals hydroxide (Cr, Pb, and Zn) and the bold line area is solid form (precipitation) (Ayres et al., 1994).

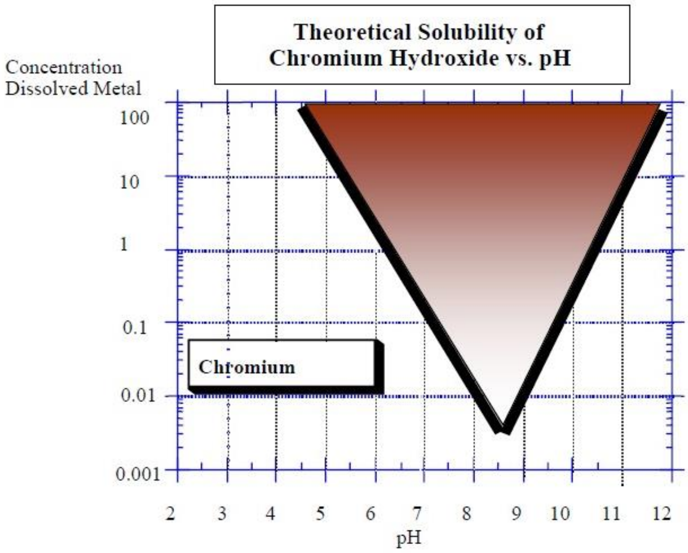


Figure 2.4 Theoretical Solubility of Chromium Hydroxide

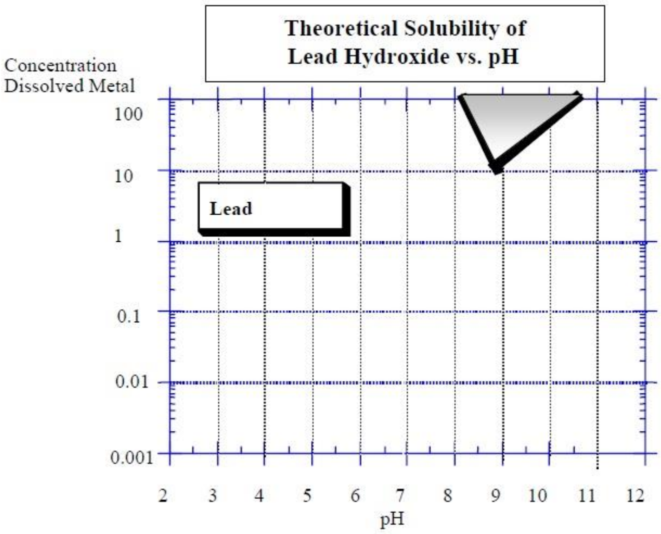


Figure 2.5 Theoretical Solubility of Lead Hydroxide

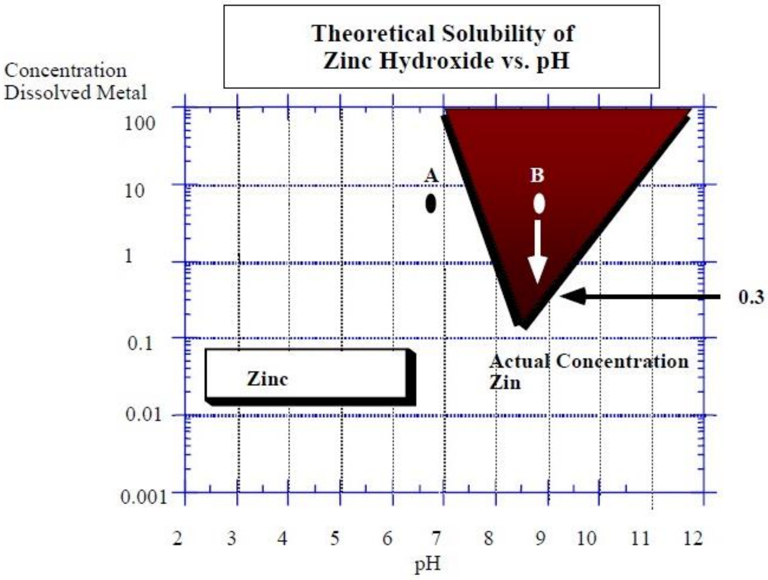


Figure 2.6 Theoretical Solubility of Zinc Hydroxide

2.4 Calculating the leachability of heavy metals

The percentage value of heavy metals leaching methods is calculated by Eq.(1) which compares with microwave assisted digestion method (Neupane & Donahoe, 2013):

$$\%\text{Leaching} = C_o / C_e \times 100 \qquad (1)$$

Where C_o is concentration of an element from TCLP, Jar leaching and column leaching tests (mg/kg) and C_e is concentration of an element from microwave digestion (mg/kg) (EPA 2007).

2.5 Literature Review

2.5.1 Leaching experiments

Wang, W., et al. (2008) studied about column leaching of coal and its combustion residues in China. The results show that most of the elements are more easily leachable from the feed coal as shown in Fig 2.7. The mode of occurrence of elements, time and pH are important role in controlling the leaching behavior of elements from sample. Batch and column leaching were used to investigate the leaching behavior of heavy metals in fly ash. Fly ash content and pH have significant effects on leaching behavior and the leached concentrations of heavy metals from fly ash. (Cetin & Aydilek, 2013; Cetin et al., 2012). Moreover, the results of batch and column leaching tests investigated that different proportions of elements were leached by DI water and SAR (synthetic acid rain) from the fly ash samples. The researchers used jar leaching (120 h), long- term batch (up to 70 weeks), serial batch (35 days) and column leaching test to determine the leaching behaviors of elements from fly ash samples (Neupane & Donahoe, 2013). In Turkey, the elements were studied under two leaching tests, TCLP and ASTM D3987 and characterized by XRD and SEM in terms of the mineralogical/morphological changes (Yılmaz, 2015). In the case of acid digestion, Ilander and Vaisanen (ref) studied arsenic (As) and antimony (Sb) in fly ash using hydride generation ICP-OES. They used three digestion procedures for digesting fly ash samples. Ultrasound method was used in two procedures (US and US-TSD) and the other one used microwave method. The US procedure used aqua regia as digestion solution, while US-TSD (two-step) used nitric acid at the first step and nitric acid with hydro fluoric acid at the second step. Microwave procedure used nitric acid with hydro fluoric acid follow by USEPA method 3052 (Ilander & Vaisanen, 2011). According to Sager, he determined the concentration of heavy metals by graphite furnace, coal vapor, flame and hydride AAs and used nitric, sulfuric, hydrochloric, perchloric and hydro fluoric acid as the digestion solution (Sager, 1993). In China, the researcher studied leachability of heavy metals from lightweight aggregates which are made from sewage sludge and municipal solid waste incineration fly ash (MSWI). The results showed that the leaching concentration of Cr, Cu, Pb and Zn exceed the China Identification Standard for hazardous wastes thus he used stabilization technique for decreasing concentration of toxic metals by adjusting MSWI fly ash/sewage sludge ratio, sintering temperature and sintering time (optimal condition: ratio 2:8, 1100°C and 8 min) (Wei, 2015). The particle of elements (Mn, Ba, Co, Cr, Ni, As, Zn, Pb and Hg) are usually volatile in the combustion process which is inversely proportional to the particle size. A plot of inverse of particle size ($1/d_{32}$) with conductivity of the ions in the leachate solution from Curragh and Tarong fly ashes in Austrlia shows in fig. 2.8 (Iyer, 2002). The processes which involve with leaching process are adsorption and precipitation process. In 2013, the researchers used fly ash as the adsorbent to adsorb heavy metals such as lead, nickel and chromium. They studied equilibrium adsorption, initial metals concentration, contact time, adsorption dose and pH. Moreover, they used the adsorption isotherm to determine and analyze the results of experiments (Shyam et al., 2013).

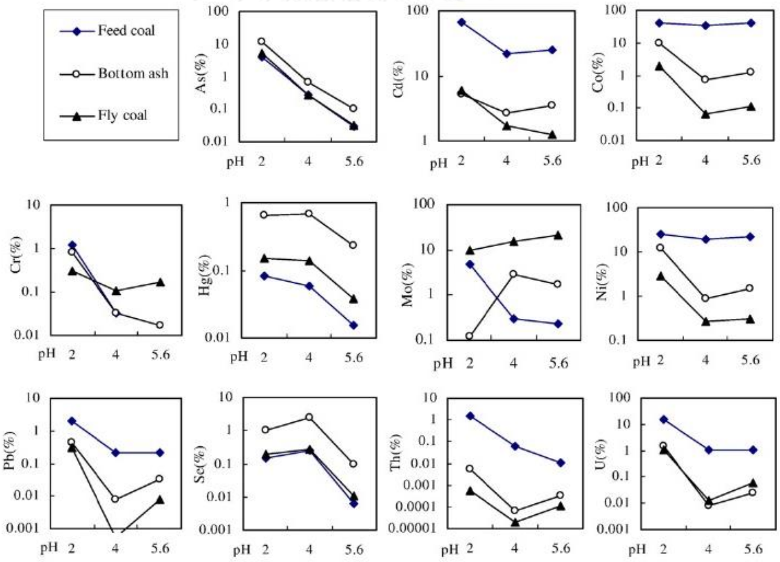


Figure 2.7 Leachabilities (%) of the 11 elements from the feed coal, bottom and fly ashes with pH over 60 h. (Wang et al., 2008)

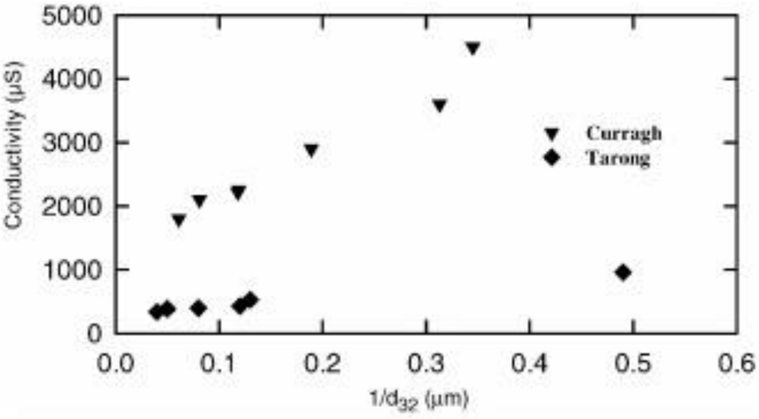


Figure 2.8 The increase in conductivity with increasing $1/d_{32}$ (Iyer, 2002)

2.5.2 Elements

2.5.2.1 Arsenic

The As speciation such as arsenite As(III), arsenate As(V), dimethyl arsenate (DMA) and monomethyl arsenate (MMA) in the aqueous solution in the surface and interstitial water and the solid phase was determined by ion chromatography coupled to inductive coupled plasma mass spectrometry (IC-ICP-MS) (Sajwan et al., 2013). The amount of arsenic is regulated by US EPA for drinking water standard and is used in the environmental impact assessment. Solid/liquid ratio, pH, leaching time and types of ash are factors which affect the leaching of arsenic (Su & Wang, 2011). Arsenic is primarily linked with As-bearing pyrite which can decompose during the combustion process and make a dominant surface in the ash. Arsenic accumulates on the surface of fly ash particles as arsenate species. The maximum solubility of arsenic occurs in the pH 7-11 range. The releasing of arsenic from acidic fly ash increases with pH. On the other hand, this trend is reversed in alkaline fly ash (Izquierdo & Querol, 2012). The leachabilities of arsenic are reversed but dependent on the initial pH of solution from the feed coal, fly ash and bottom ash. Furthermore, the maximum leachability of arsenic in solution is initially at pH of 2.0

for bottom and fly ashes (Wang et al., 2008). Hydride AAs is usually used to detect arsenic in fly ash with the use of1:1 nitric/sulfuric acid as the digestive solution (Sager, 1993). The sensitive instrument which is used to determine the concentration of arsenic in fly ash is hydride generation inductive coupled plasma spectrometry. This technique can separate analyses from the matrix, eliminate interference and increase sensitivity (Ilander & Vaisanen, 2011). Calcium can form a complex with arsenic and form a precipitate as calcium arsenate.. Arsenic is not released until calcium is released. In calcium-rich ash, calcium arsenate is common as the insoluble form (Yudovich & Ketris, 2005). The oxyanionic form of arsenic fit into ettringite structure (Hassett et al., 2005).

2.5.2.2 Chromium

Trivalent chromium accumulates in most bituminous coals and associates in illite (Huggins & Huffman, 2004). According to (Dubikova, 2006), the mobility of alkaline ash is higher with increasing pH. Mobilization of Cr from PD fly ash (alkaline fly ash) showed a bimodal leaching pattern during column leaching test and small amount of Cr was released from the fly ash samples (Neupane & Donahoe, 2013). Cr (VI) concentration from the column percolation test was higher than batch test Adding clay had more effect on reducing Cr (VI) concentration for fly ash samples because the pH of the solution was lower (Chai et al., 2009). Chromium is present during the first flush in column leaching test, and the measured concentrations quickly decreased to below EPA maximum concentration limits (MCLs) regarding drinking water (Cetin et al., 2012). Chromate is likely in the form of chromium under alkaline and oxidizing conditions (Fruchter et al., 1990). In contrast to arsenic, amounts of calcium in solution don’t affect the soluble chromates from being dissolves. The oxygen-rich organic matter in coal may cause of a higher percentage of chromates being formed during combustion (Foscolos et al., 1989).

2.5.2.3 Lead

Lead is associated with sulphide in coal and around 50-60% lead is associated on surface of fly ash (Spears & Martinez-Tarrazona, 2004). According to (Warren & Dudas, 1988) they suggest that the majority of lead associated with internal glassy matrix of fly ash, and is not leached under acidic condition. The findings of Kim et al. (2003) and Moreno et al. (2005) founded that lead was highly insoluble and nearly immobile (<1% and often < 0.1%) in both acidic and alkaline-natured fly ash samples regardless of the pH and leaching test. The precipitation of phosphate minerals which are highly insoluble over a wide pH range can control the mobility of lead (Dublicova et al. 2006). Batch leaching of fly ash from a secondary Pb smelter in solutions of acetic, citric or oxalic acids was performed to simulate the release of toxic metals in rhizophere-like environments. Lead formed chloro- and sulphate-complexes (Vojtech Ettler et al., 2009).

2.5.2.4 Zinc

Acidic conditions can increase the solubility of zinc. Decreasing pH is the cause of increasing the mobility of zinc (Kim et al., 2003). In the case of long-term batch leaching experiments, leachate concentrations of Zn decreased with time from HB and MA fly ash (acidic fly ash in USA) (Neupane & Donahoe, 2013). Zinc form is present in a citrate (Zn-citrate$^-$) complexes which is expected to be less mobile because of sorption onto surfaces of organic matter in acidic soil (Vojtech Ettler et al., 2009).

2.5.3 Toxicity

Arsenic is an extremely toxic metal and also carcinogenic. It can affect respiratory system, skin and liver. The toxic forms of arsenic are As (III) and As (V). As

(III) has highest toxicity. Arsenic was commonly used in industrial workplaces such as pigments in wallpaper and paints (Jula, 1971).

In the case of chromium, the main toxic form of chromium is soluble salts of Cr (VI) ion which releases from alloy, chromium plated objects tannery and galvanization industries. The routes of exposure of chromium are inhalation and dermal skin. It damages blood cells, kidney and liver and causes of allergic (Dayan & Paine, 2001).

Lead is the carcinogenic and is one of the hazardous metals which cause environmental problems. Lead was used in automobiles, paint, ceramics and plastics. It affects almost all the organs such as renal, nervous and cardiovascular systems (Flora et al., 2012).

The routes of exposure of zinc are inhalation from fume industries, dermal skin through powder or concentrated solutions contact. The toxicity of zinc can affect gastrointestinal, cardiovascular and nervous systems. Zinc is not carcinogenic (Nriagu, 2007).

CHAPTER 3

EXPERIMENTAL SECTIONS

3.1 Chemicals, materials and instruments

3.1.1 Chemicals

1. Acetic acid AR PE QREC (CAS: 64-19-7)
2. Nitric acid 65% QREC (CAS: 7697-37-2)
3. Sulfuric acid QREC (CAS: 7664-93-9)
4. Hydrochloric acid 37% QREC (CAS: 7647-01-0)
5. Standard metal solution 1000 mg/L for ICP-OES
6. DI water 15 Ω

3.1.2 Materials

1. Glass fiber filter paper 4.7 cm GF/F WHATMAN
2. Tygon S3 ACF00012 3/16" I.D. x 5/16" O.D. x 1/16" Wall (E-3603 Non-DEHP) 50' Package Length
3. Glassware (Beaker 50 mL, Cylinder, Funnel, Pipette 20 mL and Volumetric flask 500 mL)
4. Centrifuge tube 50 ML

3.1.3 Instruments

1. Inductive Couple Plasma- Optical Emission Spectrometer (ICP-OES) used to analyze the concentrations of chromium, lead and zinc in leachate from leaching methods.
2. Inductive Couple Plasma- Quadrupole Mass Spectrometry (ICP-QMS) used to analyze the concentration of arsenic in leachate from leaching methods.

3. X-ray Fluorescence (XRF) Spectrometer by Bruker AXS, Germany model S4 Pioneer Wavelength dispersive X-Ray Fluorescence (WDXRF) Spectrometry

4. Scanning Electron Microscope

5. pH meter

6. Rotary agitation device

7. Vacuum Filter

8. Shaker

9. Deionized water equipment

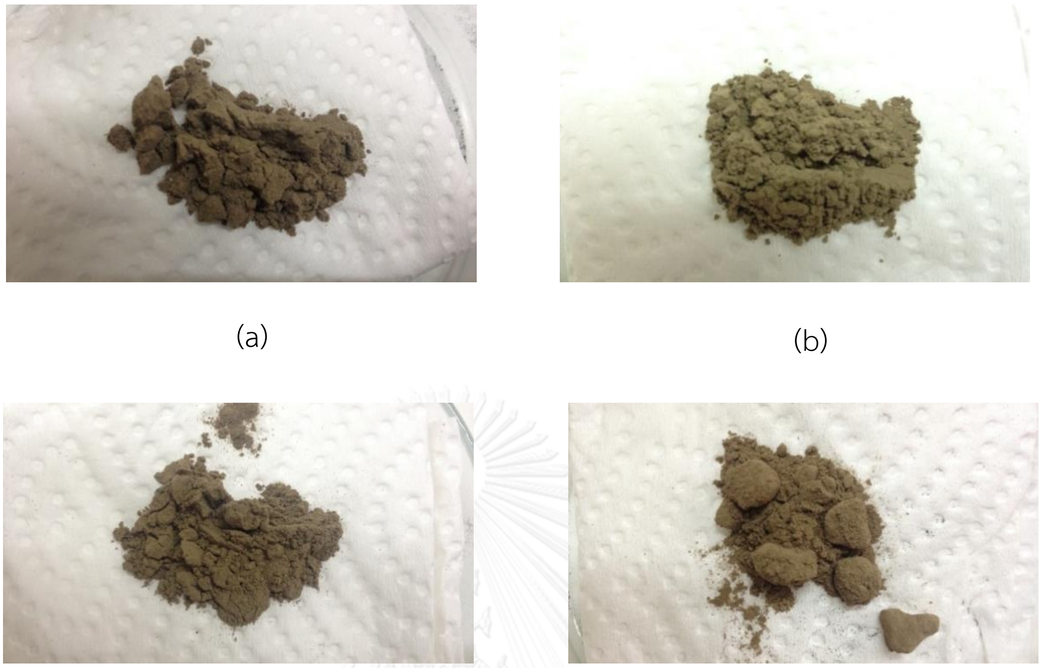
10. Analytical balance

11. Ultrasonic cleaning equipment

12. Peristaltic pump

3.2 Fly ash samples

Lignite coal was dug from Maemoh coal mine. Lignite coal was pulverized and transported to boiler combustion chamber where it was ignited and heated at 900-1000°C. This process used light oil as the catalyst fuel. Boiler tube will remove heat from the boiler, cooling the flue gas. The by-products from coal burning process are bottom ash (wet ash) and fly ash (dry ash). Wet ash fell to the bottom of combustion chamber and transports by scrapper conveyor. Fly ash is separated from hot air by electrostatic precipitator. The ash generated from coal burning process is fly ash (around 80-95%). The bituminous coal fly ash was collected from GHECO-ONE power plant. The treated-bituminous coal fly ash was collected from BLCP power plant. The bituminous coal raw material is imported from Australia and Indonesia. It is heated to1300-1500°C in a boiler furnace during heat generation. For treated-bituminous coal fly ash, it was generated from adding limestone ($Ca(OH)_2$) to bituminous coal fly ash. For municipal solid waste ash, this ash was generated from slag (around 2.5%), bark (around 7.5%), community waste such as paper or plastic (around 10%) and coal (around 80%). Municipal solid waste ash is collected from SCG industry.



(a) (b)

(c) (d)

Figure 3.1 Fly ash samples; (a) Treated-bituminous coal fly ash, (b) Bituminous coal fly ash, (c) Lignite coal fly ash and (d) municipal solid waste ash

3.3 Methodology

3.3.1 Characterization of fly ash samples

3.3.1.1. Ash chemical composition

The objective of this experiment is to analyze percentage of ash chemical compositions on the surface of fly ash samples include major components (silica, alumina and ferric oxide), minor components (potassium oxide, calcium oxide, magnesium oxide, sulfer trioxide, etc.) and trace elements by X-Ray Fluorescence (XRF) spectrometer. These major components were regulated as the chemical composition for fly ash used in construction materials.

3.3.1.2 Microstructure

The objective of this experiment is to analyze shape of fly ash samples and to estimate the particle size by Scanning Electron Microscope.

3.3.1.3 Fly ash pH

The fly ash properties and processes are affected by pH of fly ash such as acidic or alkaline fly ash and the formation of components in fly ash. The fly ash pH is significant for adsorption, leaching and precipitation processes.

In this experiment, a glass electrode was used to measure pH of fly ash. The pH meter was calibrated to use with buffer solutions of pH 4.0 and 7.0. Twenty grams of fly ash was placed in a 50 mL beaker, add 20 mL of DI water, covered and continuously stirred for 5 min. Fly ash suspension was left still for an hour. After one hour, supernatant will be filtered or centrifuged and collected for pH measurement according to US EPA method 9045 part D.

3.3.2 Chemical analysis

3.3.2.1 Toxicity Characteristic Leaching Procedure (TCLP)

TCLP test was used to determine the leaching of heavy metals in the high acidic condition (pH<3) for hazardous wastes. This test was performed at a 1:20 solid: liquid ratio. For this test, 1 g of each fly ash samples was mixed with 20 mL of acetic acid (pH~2.8) in a 50 mL centrifuge tube and rotated at 30 ± 2 rpm for 18 ± 2 hours by rotary agitation device. After 18-hr, each samples was filtered through glass fiber filter, and supernatant was collected and stored at 4°C for further chemical analysis. Moreover, control test using DI water as a leachant is shown in Fig 3.12 (Yılmaz, 2015) (EPA 1992).

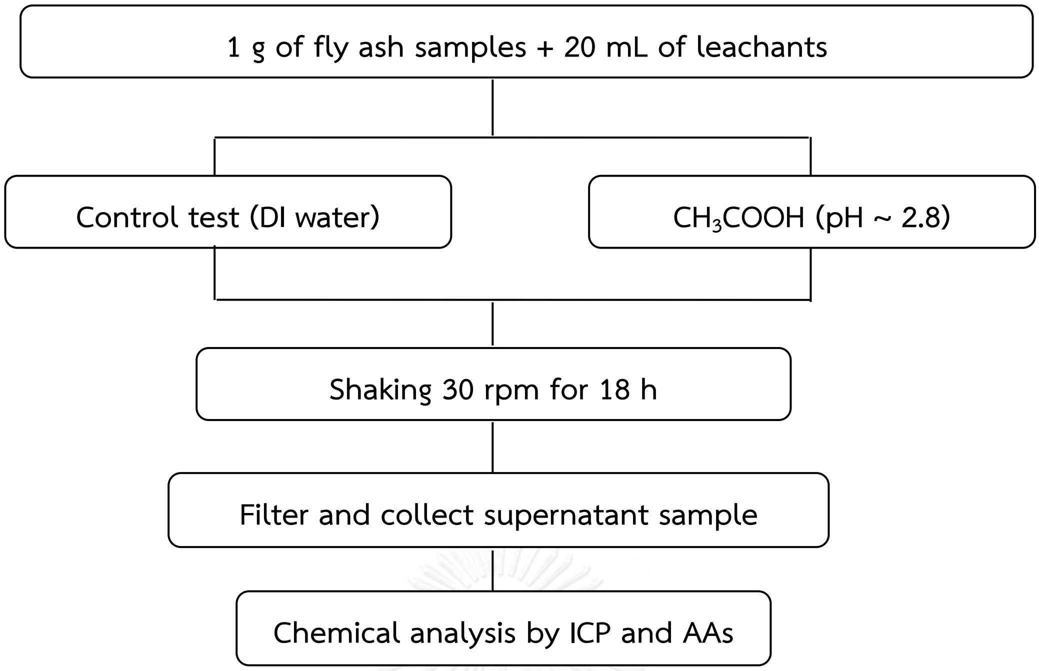


Figure 3.2 Toxicity Characteristic Leaching Procedure

3.3.2.2 Water-based leaching test (Jar leaching test)

The purpose of jar leaching was to determine leaching trends of heavy metals from fly ash samples by using batch reactor (close system). This system is a completely mixed and homogeneous process. According to Fig 3.13, this test was performed at a 1:20 for solid: liquid ratio. 6 g of fly ash samples was mixed with 120 mL DI water in a 200 mL bottle and shake at 200 rpm. The samples was placed still to separate liquid from solid layer. 20 mL of supernatant solution was collected at 1, 2, 3, 4 and 5 days for chemical analysis (Neupane & Donahoe, 2013) (Scott et al., 2003).

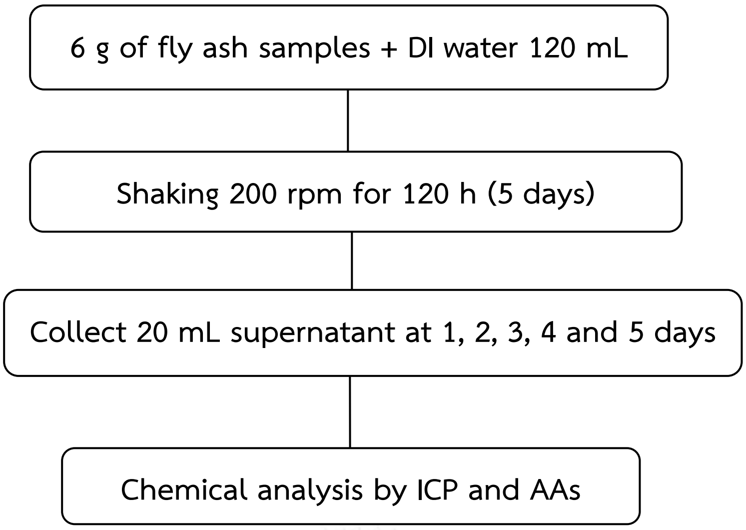


Figure 3.3 Jar Leaching Procedure

3.3.2.3 Column leaching test

Column leaching test (US EPA 1314) was intended to use as part of environmental leaching assessment for evaluating the disposal of fly ash in landfill. g Plug flow condition (open system) represents the scenario happening in the environment. The leachants were pumped through the tubing to the column. Leachant was prepared fresh during the experiment. There was no recycling of leachant. This test used a 9 cm in length and 1 cm in internal diameter for glass column and peristaltic pump for controlling flow of leachant. This test was performed using DI water and synthetic acid rain (pH~4.2) as leachants. About 20 mL of leachant was collected at 0.5, 1.0, 1.5, 2.0, 2.5, 3, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 12, 24, 48 and 72 h. Moreover, control test using DI water as the leachant is shown in Fig 3.14 (Neupane & Donahoe, 2013) (Montour & Survey, 1998).

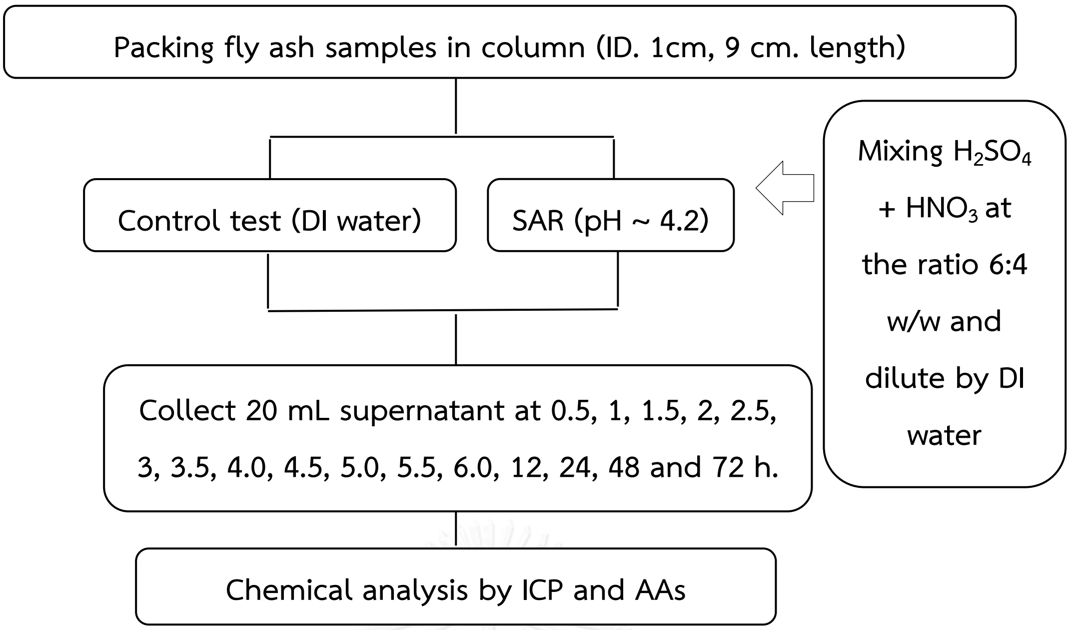


Figure 3.4 Column Leaching Procedure

3.3.2.4 Microwave assisted digestion

Microwave assisted digestion was used to determine pseudo-total concentration of heavy metals from fly ash samples using nitric and hydrochloric acid as digesting solution. The leachants (HCL and HNO_3) cannot digest silica (SiO2) which is the major component of fly ash sample according to XRF results. Hydro fluoric acid (HF) can digest all elements from fly ash but it can damage instruments (ICP or AAs) used to analyze heavy metals concentration. According to Fig 3.15, this test was performed at 0.500 g of fly ash samples with 9 mL concentrated nitric acid and 3 mL concentrated hydrochloric acid in digestion vessels. Fly ash sample was heated higher than 175°C for 5.5 min. Then, the temperature was maintained between 170-180°C for 4.5 min. After 10 minutes, the vessels are left to cool down to room temperature for a minimum of 5 minutes. Then, the sample may be centrifuged and filtered if the particulates exist in the samples. Finally, the digested samples were collected for subsequent chemical analysis (EPA 2007).

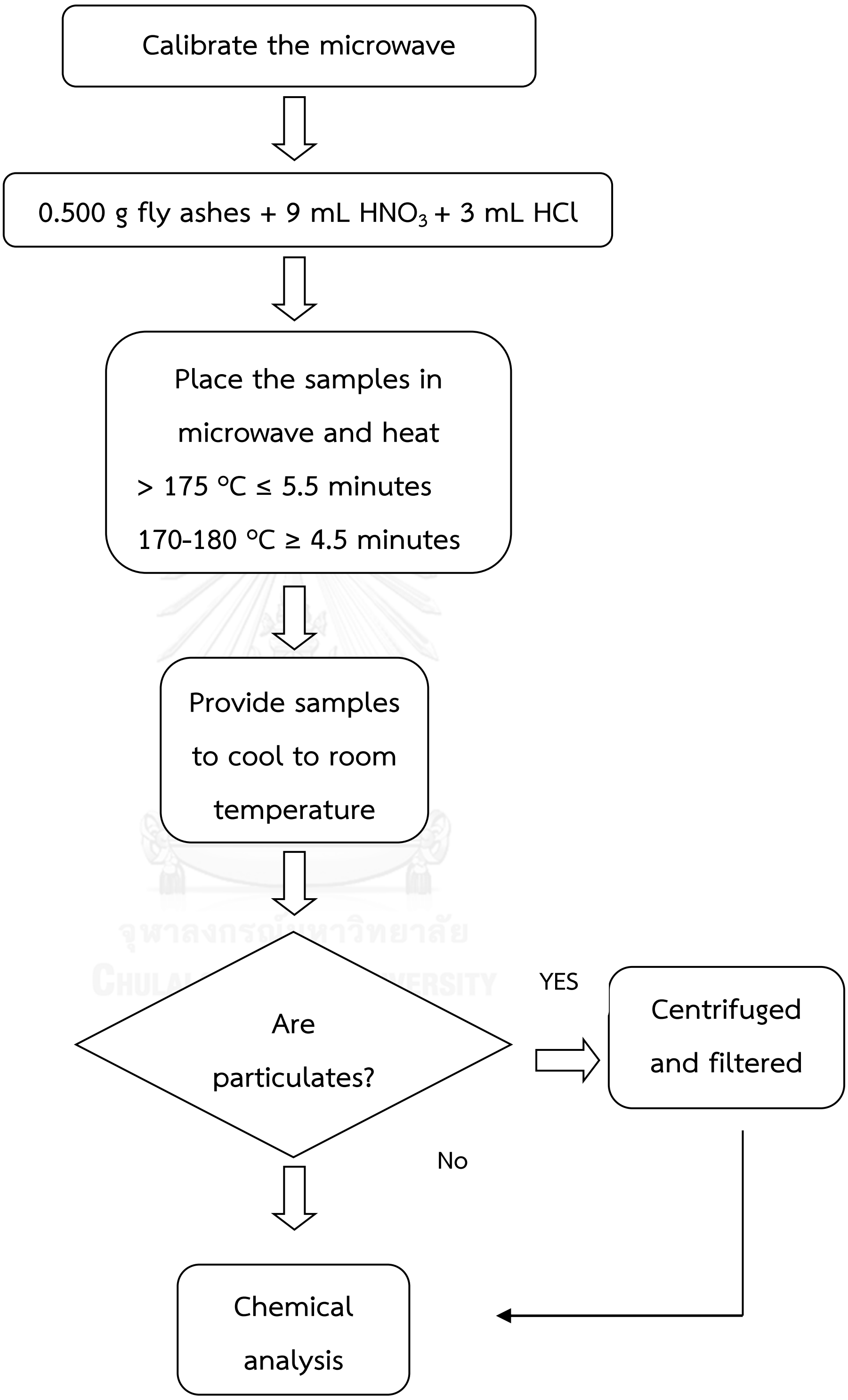


Figure 3.5 Partial Acid Digestion Procedure

3.3.3 Physical analysis

3.3.3.1 Effect of particle size to leachability

This test was to determine the leachability of heavy metals from the three different particle sizes (0.125-0.149 mm, 0.074-0.088 mm and less than 0.044 mm) using coal and municipal solid waste ashes. Sieve number 100, 120, 170, 200 and 325 was used to separate different size of fly ash. Toxicity characteristic leaching procedure (TCLP) was used to determine heavy metal leaching shown in Fig 3.16.

Note: Experiments were repeated three times for all leaching tests except jar leaching and column leaching test

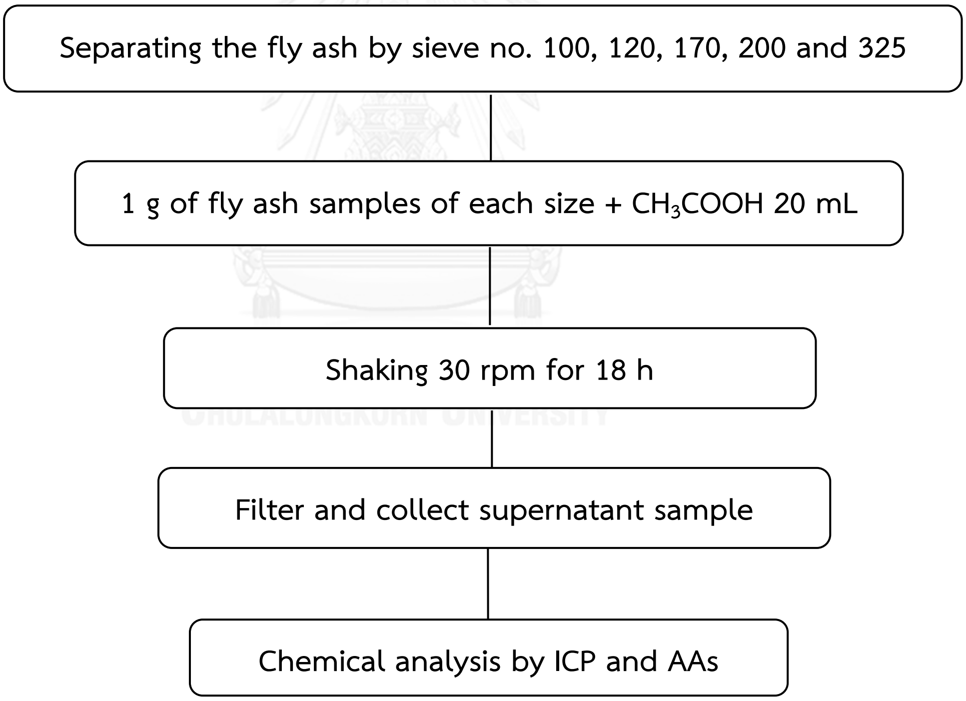


Figure 3.6 Effect of particle size to leachability

3.3.4 Statistical analysis

The statistical analysis was used to get approximate solutions for experiments as research methodology. In this study, the experiments used t-test analysis for approximating some values from some experiments which are different statistical significant level of 0.05 with the other values.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of fly ash

4.1.1 Ash chemical composition

The results showed that the major components of fly ash samples are SiO_2, Al_2O_3 and Fe_2O_3 as shown in Table 4.1. These major components were regulated as the chemical composition for fly ash used in construction materials. LCFA is considered the fly ash class C which has the main components (silica, alumina and ferric oxide) around 60.2% by weight and the remaining is minor components and trace elements including heavy metals (As, Cr and Zn around 0.07%). BCFA and T-BCFA are considered fly ash class F which contain silica, alumina and ferric oxide as a main component (around 82% and 45% by weight), respectively. The heavy metals cannot be detected on the surface of BCFA and T-BCFA. Comparing BCFA in this study with BCFA in China (Wang et al., 2008), both fly ashes had the similar amount of major chemical compositions (SiO_2, Al_2O_3 and Fe_2O_3 around 90%). MSWA is the municipal solid waste ash which has the main components around 53% by weight. Comparing MSWA in this study with MSWA in China, the ash chemical composition was different due to the sources of municipal solid waste used in fly ash generation. For T-BCFA, this fly ash was added with calcium hydroxide to prevent the release of hazardous elements to the environment. So, CaO in T-BCFA was higher than CaO in other fly ashes around 38% by weight and the percentage of heavy metals was lower than the other fly ash samples (Mn, As, Cr, Zn, etc.).

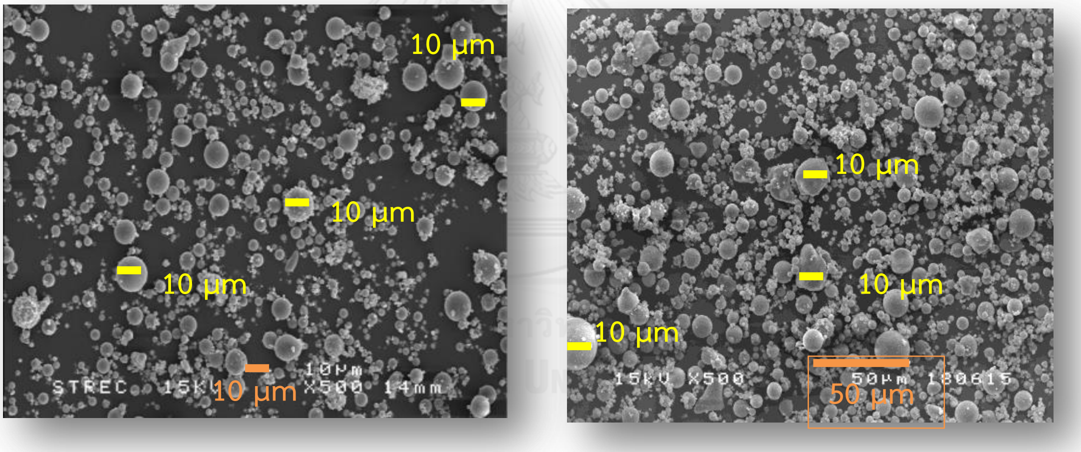
Table 4.1 shows the ash chemical compositions of the fly ash samples measured by X-Ray Fluorescence (XRF)

Chemical compositions (%)	LCFA	BCFA	T-BCFA	MSWA	BCFA (Wang et al., 2008)	MSWA (Wei, 2015)
CaO	27.1	8.467	37.65	32.27	1.5	18.9
SiO_2	26.72	48.55	24.19	26.6	49.5	40.1
Fe_2O_3	18.6	13.4	8.55	10.16	14.4	1.4
Al_2O_3	14.89	20.01	12.51	16.73	25.8	14.8
SO_3	5.582	0.976	7.864	7.091	1.3	ND
K_2O	2.825	2.179	0.929	1.441	1.2	4.1
MgO	1.63	3.406	3.273	2.644	1.3	3.1
Na_2O	1.17	1.37	3.579	1.49	0.4	3.1
P_2O_5	0.26	0.199	0.111	0.365	0.01	ND
MnO	0.158	0.11	0.0517	0.0658	0.06	ND
As	0.056	ND	ND	ND	5.67 (mg/kg)	85 (mg/kg)
Cr	0.0461	ND	ND	ND	38.11 (mg/kg)	142 (mg/kg)
Zn	0.0159	ND	ND	ND	ND	3157 (mg/kg)

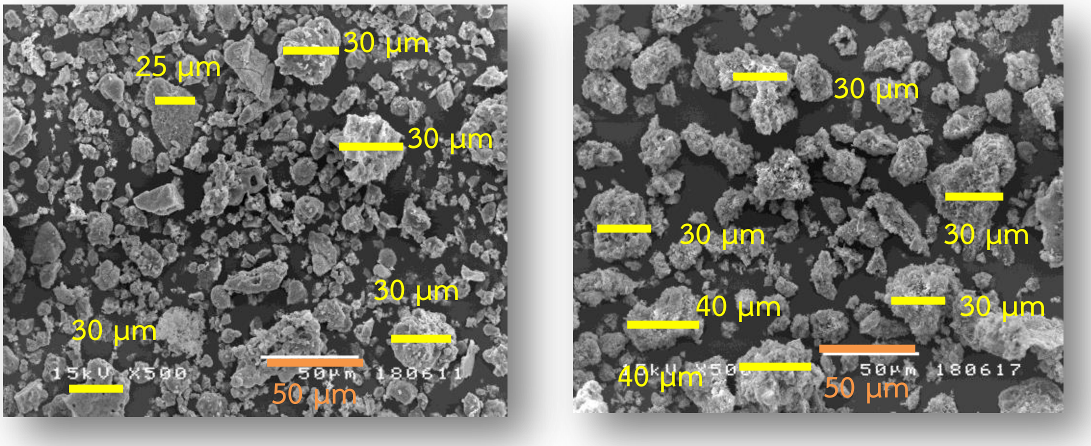
LCFA = Lignite coal fly ash, BCFA = Bituminous coal fly ash, T-BCFA = Treated bituminous coal fly ash, MSWA = Municipal solid waste ash, ND = Not detected

4.1.2 Microstructure

The microstructure and particle size analysis are shown in Fig 4.1. The results showed that the microstructures at 500 magnifications of LCFA and BCFA are sphere but T-BCFA and MSWA are rough and cluster shape because of adding limestone ($Ca(OH)_2$) solution in T-BCFA or depending on burning temperature. Adding $Ca(OH)_2$ can form the complex with the heavy metals so the microstructure of ash particle might change to rough and amorphous. The particle size of fly ash was estimated by image analysis. The particle size of LCFA, BCFA, T-BCFA and MSWA have the particle size in the range 1-10, 1-10, 5-30 and 10-40 µm, respectively. Size of LCFA and BCFA were smallest



a) Lignite Coal Fly Ash b) Bituminous Coal Fly Ash



c) Treated-Bituminous Coal Fly Ash d) Municipal Solid Waste Ash

Figure 4.1 show the microstructure of fly ash samples; (LCFA) Lignite coal fly ash, (BCFA) Bituminous coal fly ash, (T-BCFA) Treated bituminous coal fly ash and (MSWA) Municipal solid waste ash

4.1.3 Fly ash pH

The results show that all fly ash samples are alkaline (pH > 7) as shown in Table 4.2 because most components of fly ash are metal oxide. When fly ash contacted with water, metal hydroxide which is a strong base compound can form. MSWA was the most alkaline, while the least alkaline ash was BCFA.

Table 4.2 pH of the fly ash samples according to USEPA 9045D

Fly ash samples	pH
Lignite coal fly ash (LCFA)	12.61
Bituminous coal fly ash (BCFA)	9.95
Treated bituminous coal fly ash (T-BCFA)	11.46
Municipal solid waste ash (MSWA)	12.77

4.2 Leaching tests

4.2.1 Microwave assisted digestion

The heavy metals from fly ash were extracted by microwave digestion method according to EPA 3051 part A and showed the pseudo-total concentration of trace elements (As, Cr, Pb and Zn) as shown in Table 4.2.1. LCFA was richer in trace elements than other fly ash. Comparing with bituminous coal fly ash from the U.S. (Neupane & Donahoe, 2013), the pseudo-concentration of trace elements was mostly lower than bituminous coal fly ash in this study. It is concluded that BCFA of U.S. was cleaner than BCFA in this study (Neupane & Donahoe, 2013).

Table 4.3 Pseudo-total concentrations of As, Cr, Pb and Zn in fly ash samples according to microwave digestion method (3 replications)

Fly ash	**Concentration of heavy metals (mg/kg)**			
	As	Cr	Pb	Zn
LCFA	214.06±0.06	55.32±0.04	11.16±0.01	232.93±0.97
BCFA	36.91±0.02	70.38±0.00	11.68±0.00	196.59±0.03
T-BCFA	17.33±0.01	31.09±0.03	5.46±0.01	146.69±0.24
BCFA (Neupane & Donahoe, 2013)	17	18	12	69

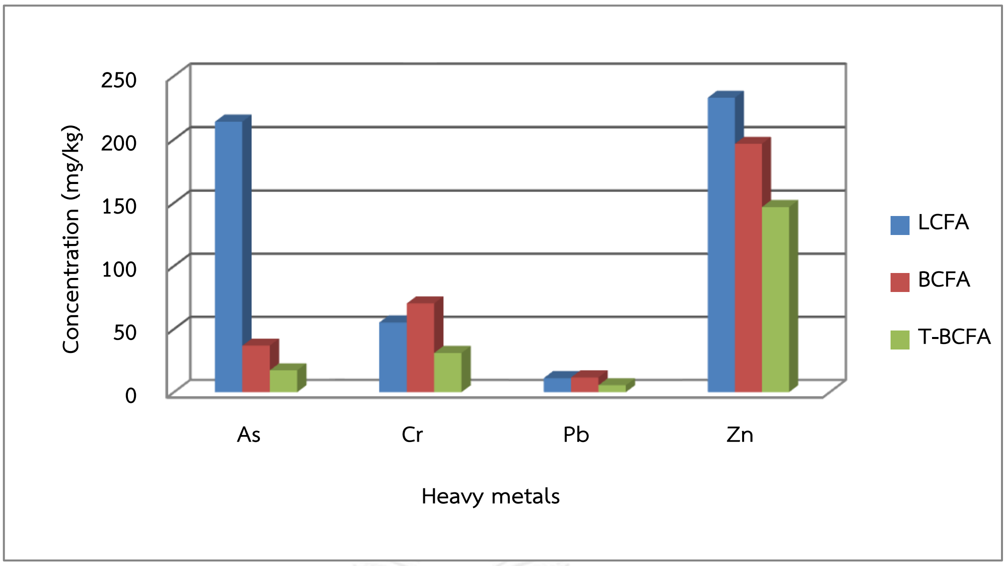


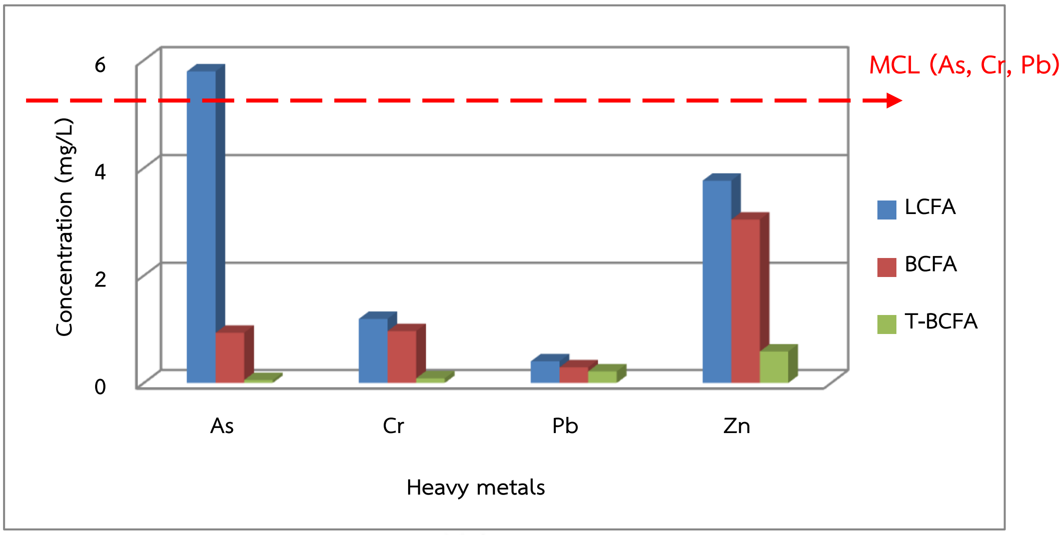
Figure 4.2 Pseudo-total concentrations of As, Cr, Pb and Zn in fly ash samples according to microwave digestion method USEPA 3051A using nitric acid and hydrochloric acid as the leachant)

4.2.2 Toxicity Characteristic Leaching Procedure (TCLP)

The leachate concentrations of As, Cr, Pb and Zn are reported in milligram per liter in Table 4.4 and 4.5 in milligram per kilogram and percentage leaching. The control test using DI water as the leachant is shown in Table 4.6.. The leachate concentrations of heavy metals in LCFA were highest and lowest in T-BCFA. Comparing with bituminous coal fly ash from UK and Austria (Tsiridis et al., 2006), the leaching concentration of Cr, Pb and Zn from UK and Austria BCFA was lower than BCFA in this study. The concentration of As, Cr, Pb in all fly ash was below the regulatory level for TCLP except As in LCFA. The high concentration depended on many factors such as sampling area, sampling date, temperature or contaminated instruments. The percentage leachability of As, Cr and Zn was highest in LCFA. Pb was highest in T-BCFA using acetic acid while percentage leachability of As and Cr from control test were highest from BCFA. Pb and Zn were highest from T-BCFA. Moreover, the leachate concentrations of heavy metals in all fly ash samples from control test were lower than TCLP. This is because acetic acid is a stronger leachant than DI water.

Table 4.4 Leaching concentrations of As, Cr, Pb and Zn in leachate measured by ICP-MS and AAS according to TCLP method USEPA 1311 (mg/L) (3 replicates)

Fly ash	Leaching concentration of heavy metals (mg/L)			
	As	Cr	Pb	Zn
LCFA	5.792±0.205	1.193±0.025	0.402±0.010	3.767±0.108
BCFA	0.935±0.039	0.966±0.031	0.290±0.003	3.043±0.102
T-BCFA	0.055±0.005	0.087±0.001	0.216±0.003	0.585±0.189
BCFA from UK (Tsiridis et al., 2006)	NA	0.013	<0.01	0.86
BCFA from Austria (Tsiridis et al., 2006)	NA	0.082	0.140	0.01



“MCL”- Maximum concentration level of contaminants for TCLP

Figure 4.3 Total concentrations of heavy metals in fly ash samples according to TCLP method

Table 4.5 Concentrations of As, Cr, Pb and Zn in leachate according to TCLP method (mg/kg) using acetic acid as the leachant

Fly ash	Concentration of heavy metals (mg/kg)				% Leaching			
	As	Cr	Pb	Zn	As	Cr	Pb	Zn
LCFA	115.47	23.78	8.01	75.09	53.94	42.99	71.77	32.24
BCFA	18.63	19.24	5.78	60.62	50.47	27.34	49.49	30.84
T-BCFA	1.10	1.73	4.30	11.65	6.35	5.56	78.75	7.94

Table 4.6 Concentrations of As, Cr, Pb and Zn in leachate according to TCLP method (Control test) (mg/kg) using DI water as the leachant (3 replicates)

Fly ash	Concentration of heavy metals (mg/kg)				% Leaching			
	As	Cr	Pb	Zn	As	Cr	Pb	Zn
LCFA	0.1217	1.0770	0.0060	5.6841	0.06	1.95	0.05	2.44
BCFA	0.1156	2.1219	0.0040	1.7733	0.31	3.01	0.03	0.90
T-BCFA	0.0040	0.7178	0.0140	6.3703	0.02	2.31	0.26	4.34

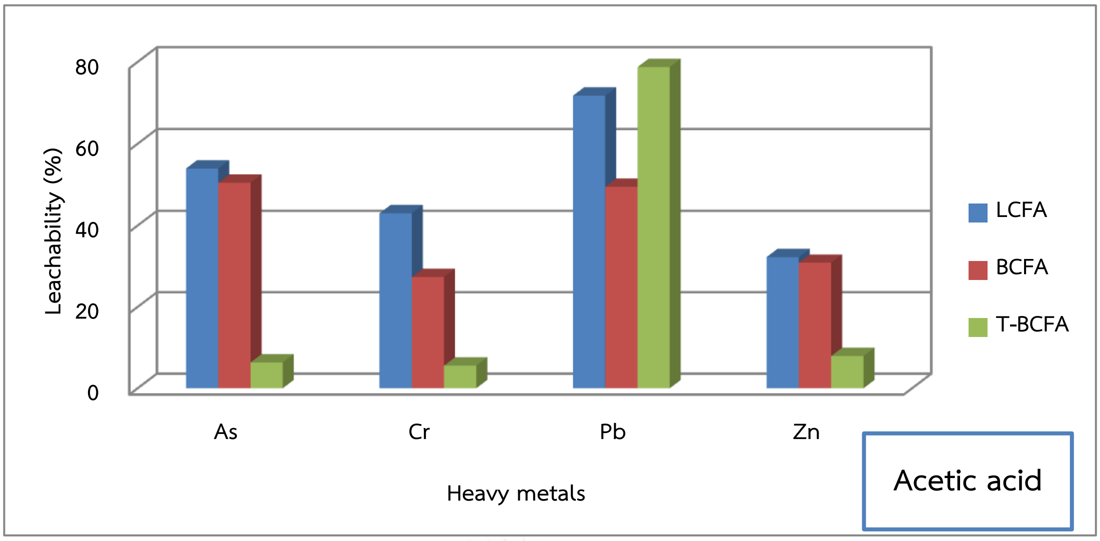


Figure 4.4 Percentage leachability of heavy metals according to TCLP method

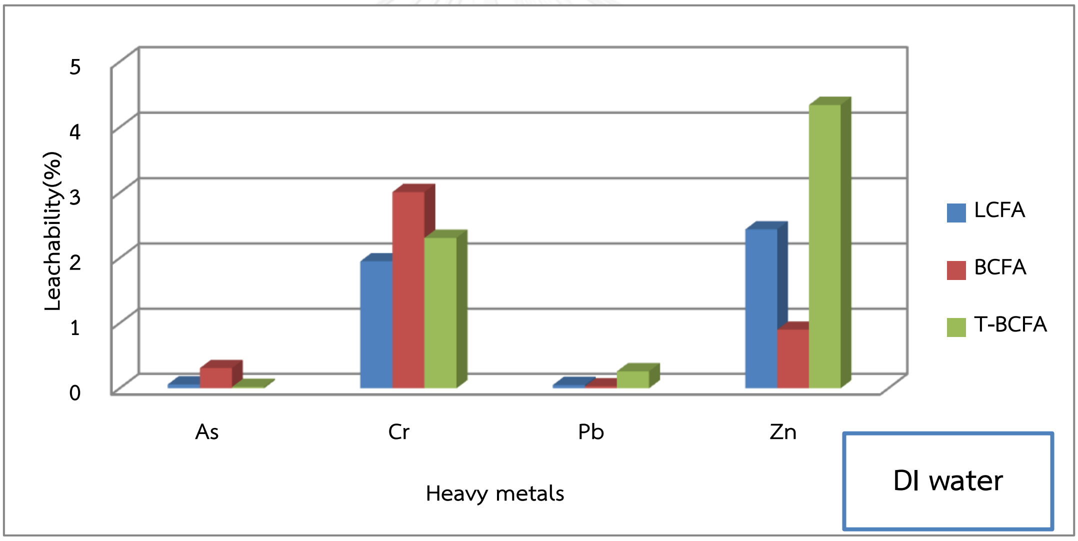


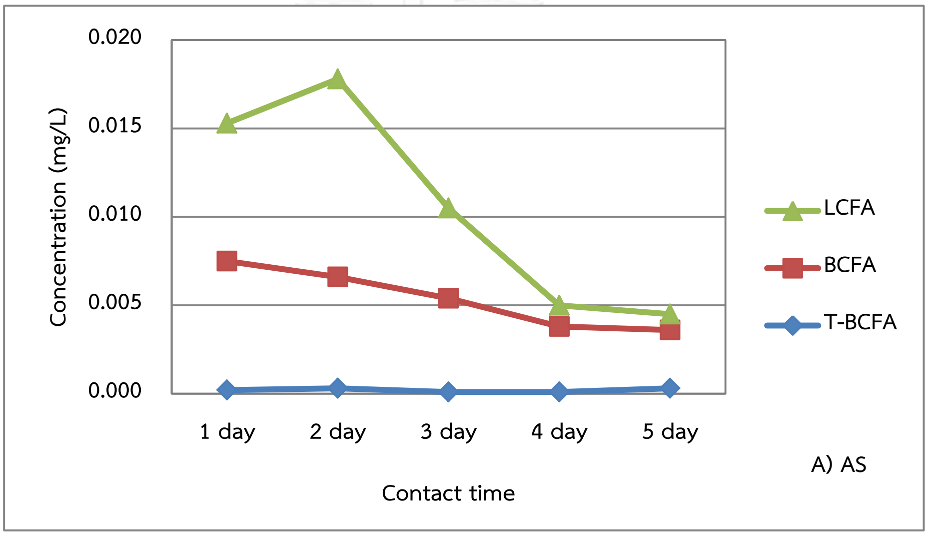
Figure 4.5 Percentage leachability of heavy metals according to TCLP method (Control test)

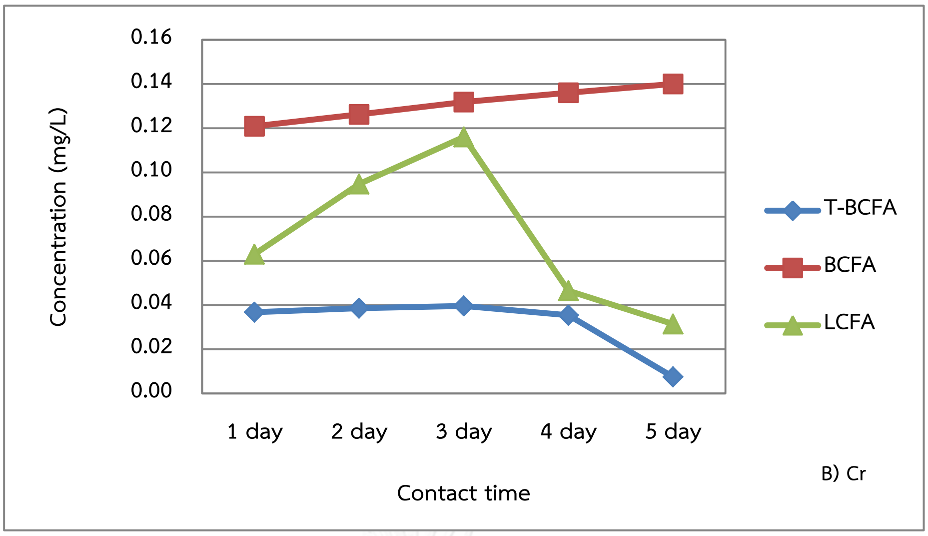
Table 4.7 Regulatory level of maximum concentration of metal contaminants for TCLP method according to USEPA 1311

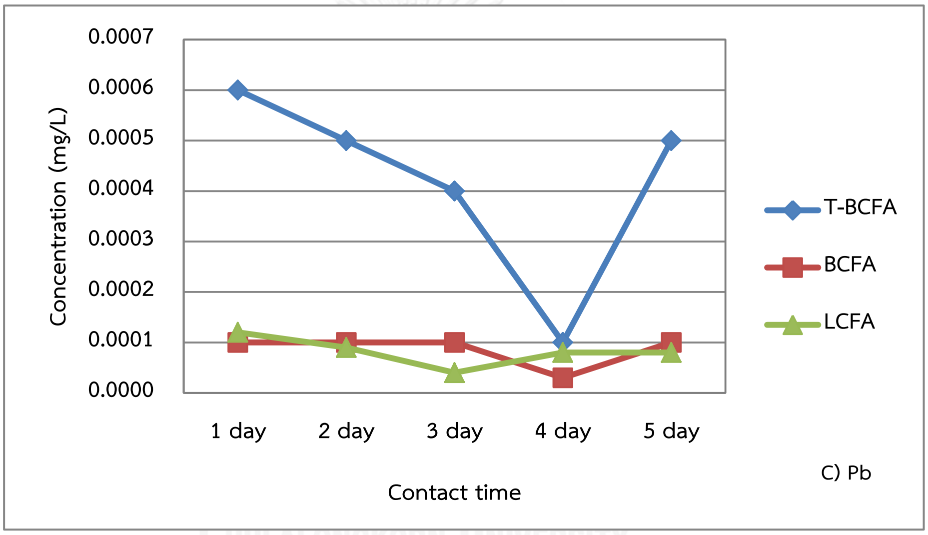
Metal contaminant	**Regulatory level (mg/L)**
As	5.000
Cr	5.000
Pb	5.000

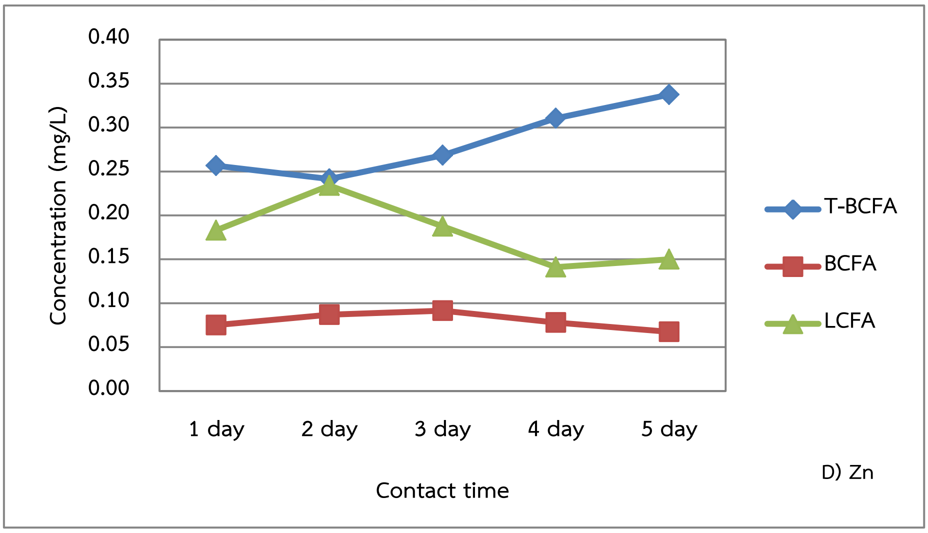
4.2.3 Jar leaching test

The leaching concentrations of As are highest in LCFA on the second day at around 0.0112 mg/L. BCFA was around 0.1401 mg/L at day 5. Cr, Pb and Zn in T-BCFA were around 0.0006 and 0.3375 mg/L at day1 and day 5. Four different trends can be identified which are (1) Leaching concentrations (LCs) increased with increasing contact time, (2) LCs decreased with increasing contact time, (3) LCs were stable over time and (4) LCs fluctuated. Leaching concentration of Cr from BCFA and Zn from T-BCFA showed the increase in mobility from 0.1209 mg/L to 0.1401 mg/L and 0.2565 mg/L to 0.3375 mg/L, respectively. An increase in Cr and Zn in leachant over time may come from the slow dissolution of the particle inside fly ash due to slow diffusion rate of the leachant into the particle. Leaching concentration of As from BCFA and Cr from T-BCFA showed opposite leaching trends (leaching concentration decreased from 0.0073 mg/L to 0.0033 mg/L and 0.0368 mg/L to 0.0075 mg/L, respectively with contact time). According to XRD patterns as shown in Fig 4.7 and 4.8 (Langmuir et al., 2006; Tang et al., 2007), the adsorption and co-precipitation between heavy metals with minerals (quartz, calcite, mullite and hematite) may occur during leaching process. Leaching concentration of As from T-BCFA, Zn from BCFA and Pb from LCFA has similar trend. The concentration was constant over time as shown in Fig 4.6. An increase in leachant contact time did not promote leachability. However, leaching concentration of Cr from LCFA, Pb from T-BCFA and BCFA were unstable and fluctuated. This may be because of the dissolution of trace elements or adsorption of Cr on the surface of fly ash (Wang et al., 2008). For pH trends of these tests, when the contact time increased, the pH of the leachate slightly decreased on second day from 13.85 to 13.07 for T-BCFA, 13.68 to 12.93 for LCFA and 12.45 to 11.95 (for which FA?). The change of pH of unbuffered leachant might slightly affect the adsorption, precipitation and the heavy metals concentration in leachate. However, heavy metals concentrations in leachate were below the industrial effluent standards shown in Table 1.1.




Concentration (mg/L)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
1 day
2 day
3 day
4 day
5 day
Contact time
T-BCFA
BCFA
LCFA
B) Cr


Concentration (mg/L)
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
1 day
2 day
3 day
4 day
5 day
Contact time
T-BCFA
BCFA
LCFA
C) Pb


Concentration (mg/L)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
1 day
2 day
3 day
4 day
5 day
Contact time
T-BCFA
BCFA
LCFA
D) Zn

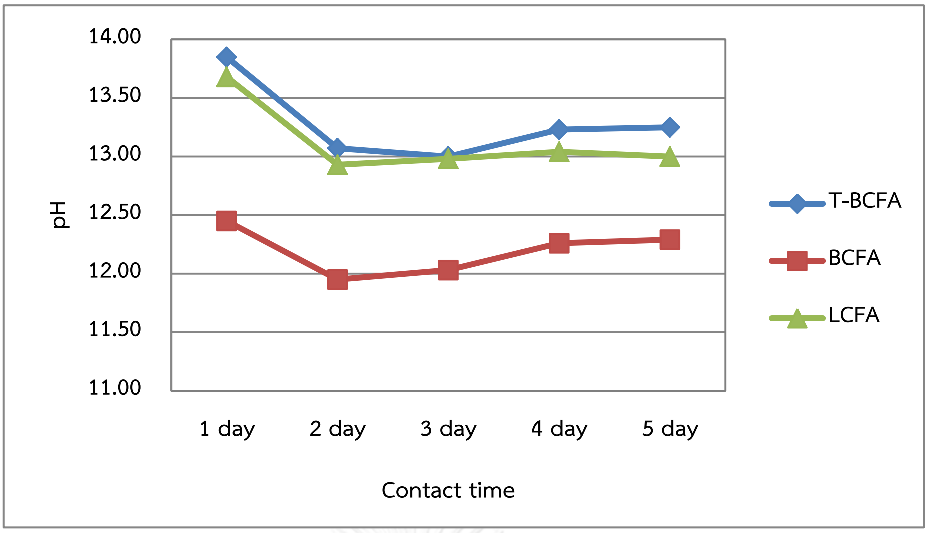


Figure 4.6 Leachate pH trends and leaching concentration of A)As, B)Cr, C)Pb and D)Zn from fly ash samples according to jar leaching test at 25°C (1 replicate)

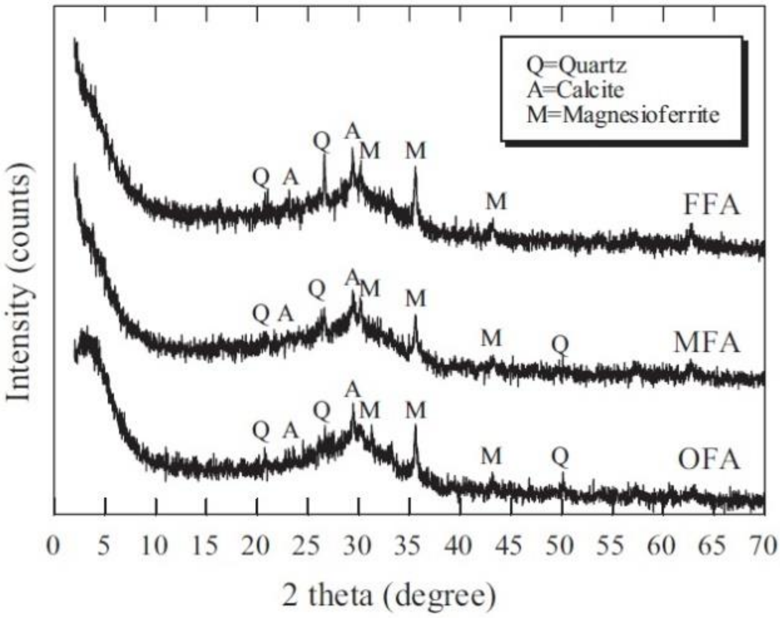


Figure 4.7 XRD pattern of lignite coal fly ash from Maemoh powerplant (Hanjitsuwan et al., 2012)

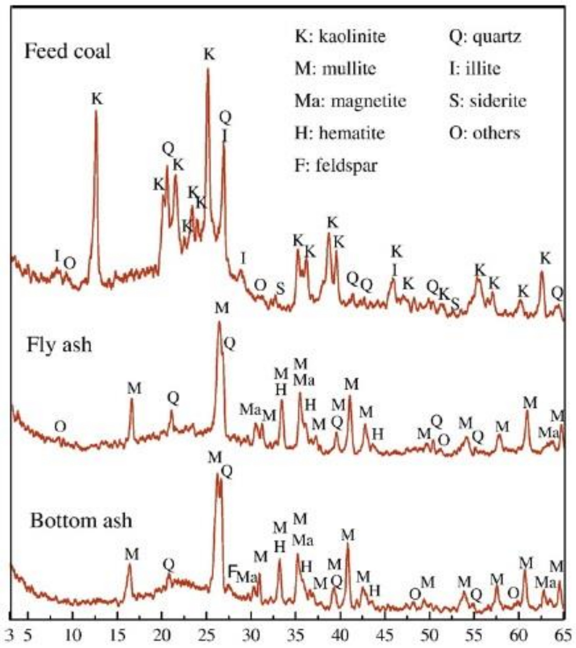


Figure 4.8 XRD patterns of the feed coal, fly ash and bottom ash of bituminous coal fly ash in China (Wang et al., 2008)

4.2.4 Column leaching test

The leaching concentrations of As from LCFA sharply increased from 0.0952 mg/L to 0.5105 mg/L from 24 h to 48 h and decreased to 0.1674 mg/L at 72 h using DI water while increased from 0.1750 mg/L to 0.3137 mg/L at 24 h to 48 h and decreased to 0.2072 mg/L at 72 h using SAR because As may be leached at this time while the leaching concentrations of As from BCFA and T-BCFA still stabilized between 30 min and 72 h. For Cr, the leaching concentration of BCFA sharply decreased from 0.4221 mg/L to 0.0395 mg/L at 30 min to 72 h using DI water, while the concentrations decreased from 0.6024 mg/L to 0.0231 mg/L at 30 min to 72 h using SAR. It was observed that Cr concentration inversely decreased with time. Cr concentrations in LCFA slightly decreased from 0.1203 mg/L to 0.0208 mg/L at 12 h to 72 h using DI water. For SAR, it decreased from 0.0549 mg/L to 0.0194 mg/L at 12 h to 72 h. Cr concentrations from T-BCFA still stabilized. The leaching concentration of Pb from LCFA and BCFA using DI water as the leachant fluctuated and was highest around 0.0060 mg/L for LCFA at 4 h, and 0.0065 mg/L for BCFA at 72 h. While the leaching concentration of Pb from T-BCFA sharply increased from 0.0038 mg/L to

0.0044 mg/L at 6 h to 12 h and decreased to 0.0016 mg/L at 24 h. For Zn, the leaching concentration from BCFA increased from 0.0563 mg/L to 0.3300 mg/L at 30 min to 72 h, while leaching concentration from LCFA fluctuated at 4, 6 h. Zn concentration from T-BCFA stabilized.

For As in LCFA, BCFA and T-BCFA, types of leachant did not affect the leaching trend. For example, the concentration of As in LCFA leached by DI water and SAR sharply increased from 24h to 48h, and decreased afterwards. Moreover, Cr leaching trend in every fly ash was similar when using DI water and SAR as leachant. For instance, the concentration of Cr in BCFA initially decreased and stabilized after 12 h both with DI water and SAR as a leachant.

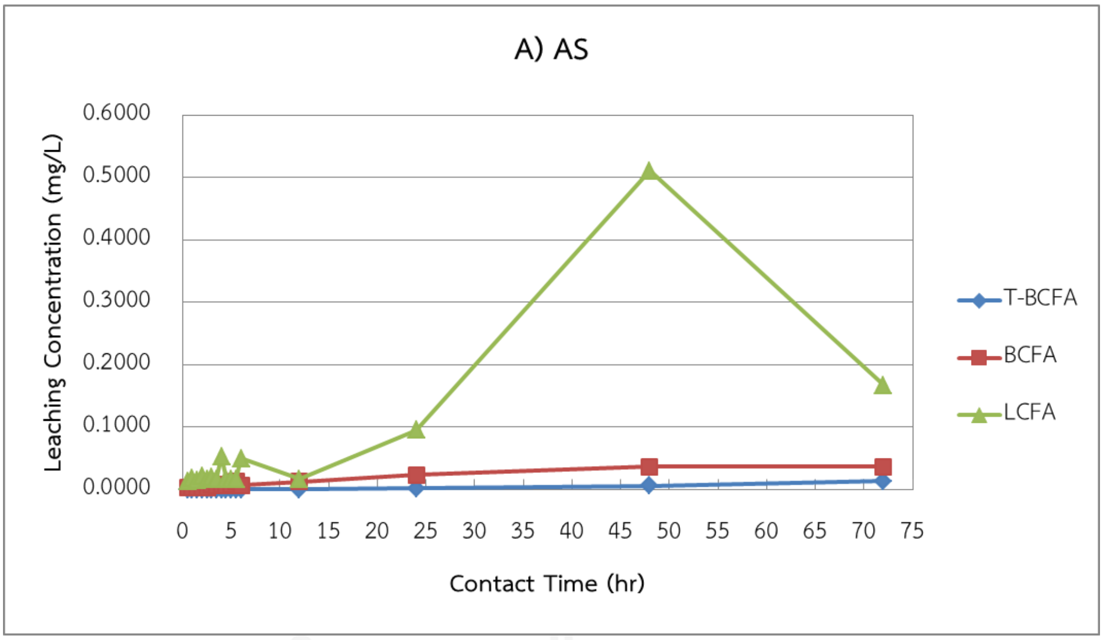
As concentration leached from LCFA was the highest among other types of fly ashes. For example, As concentration was 0.5105 mg/L and 0.3137 mg/L at 48 h using DI water and SAR, respectively. Cr Concentration leached from BCFA was the highest among other types of fly ashes. For example, Cr concentration was 0.4221 mg/L and 0.6024 mg/L at 30 min using DI water and SAR, respectively.

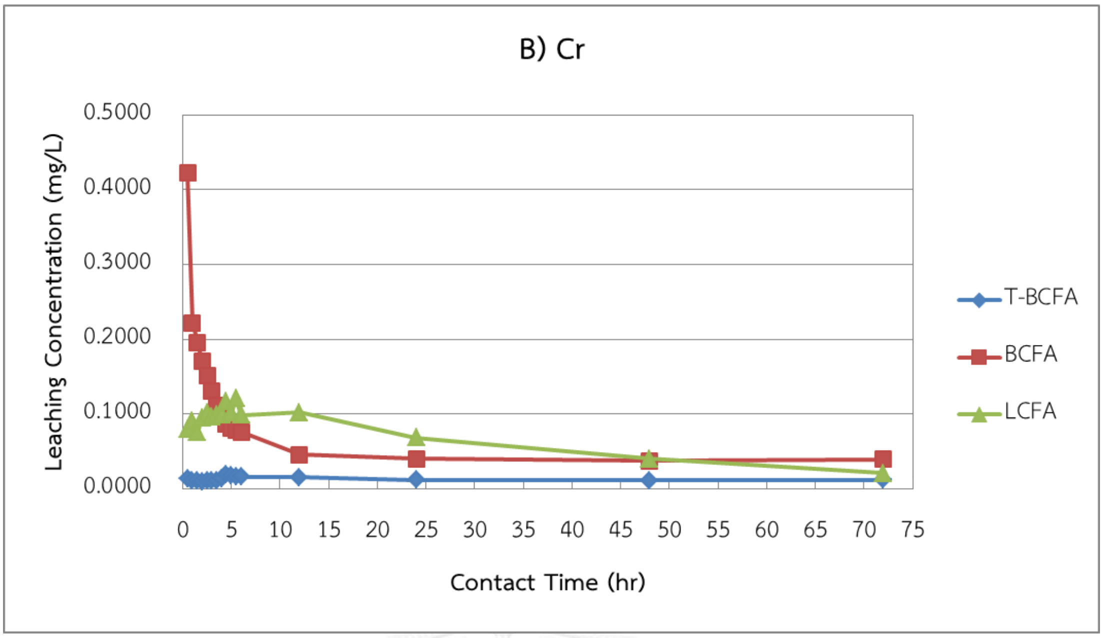
However, Pb and Zn concentrations were found highest in BCFA using DI water as a leachant. For instance, Pb and Zn concentrations in BCFA were 0.0065 mg/L and 0.3300 mg/L, respectively. Pb and Zn concentrations were found highest in LCFA using SAR as a leachant. For instance, Pb and Zn concentrations in LCFA were 0.0030 mg/L and 0.0403 mg/L, respectively.

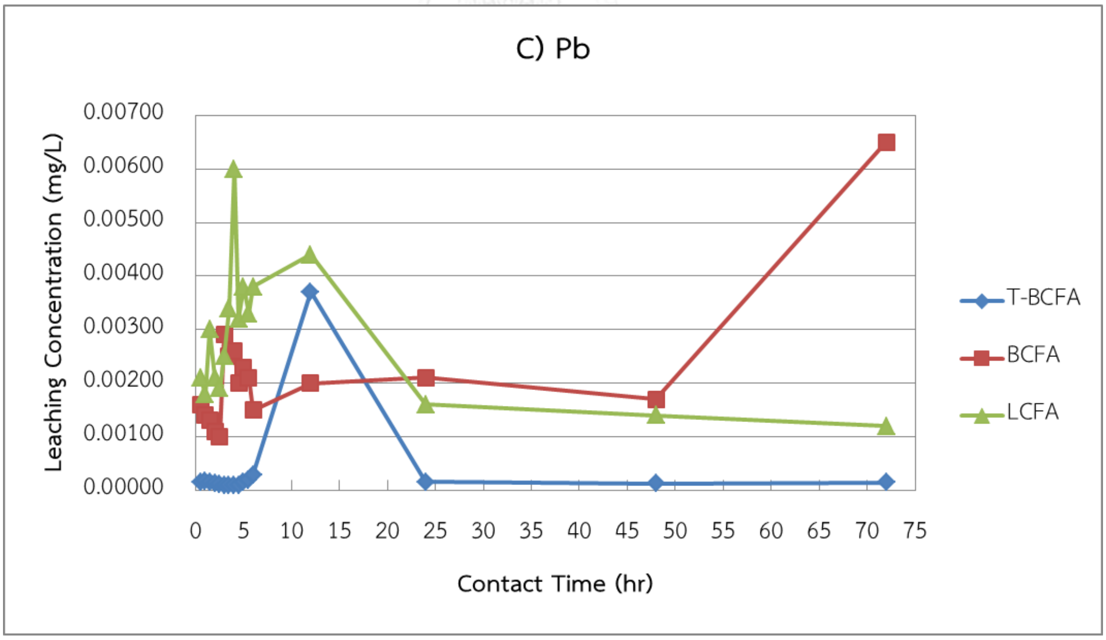
It is observed that most of the leachate concentrations of all heavy metals were below the industrial effluent standards. However, some exceptions may occur. For example, arsenic in LCFA at 48 h for two leachants, chromium of BCFA at 30 min for two leachants and chromium of BCFA at 1 h for SAR as the leachant.

Even though the pH of DI water and SAR is initially different (8 and 4.2, respectively), heavy metal concentrations leached from all fly ashes are not significantly different. For example, As concentrations at 48 h using DI water and SAR as leachant were 0.5105 mg/L and 0.3137 mg/L, respectively.

For pH trends of this test, when the contact time increased, the pH of leachate slightly decreased. For example, the pH of leachate from LCFA using SAR slightly decreased from 13.48 at 2 h to 12.08 at 72 h while using DI water slightly decreased from 13.61 at 2 h to 11.97 at 72 h. Leachate pH of DI water and SAR is not significantly different (P<0.05).




B) Cr
Leaching Concentration (mg/L)
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
Contact Time (hr)
T-BCFA
BCFA
LCFA


C) Pb
Leaching Concentration (mg/L)
0.00700
0.00600
0.00500
0.00400
0.00300
0.00200
0.00100
0.00000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
Contact Time (hr)
T-BCFA
BCFA
LCFA

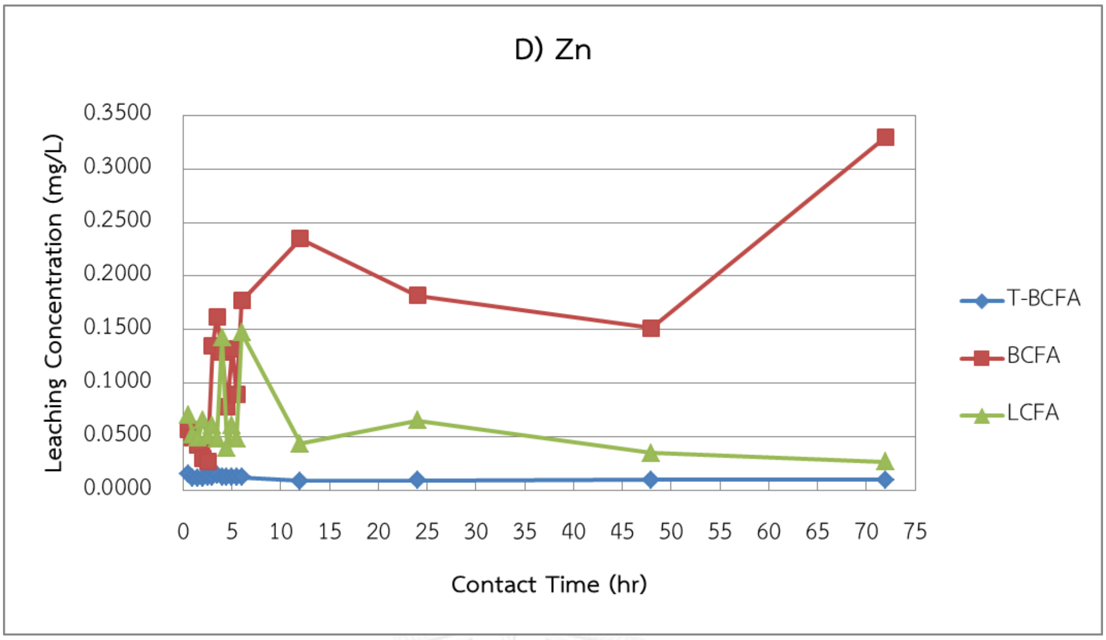
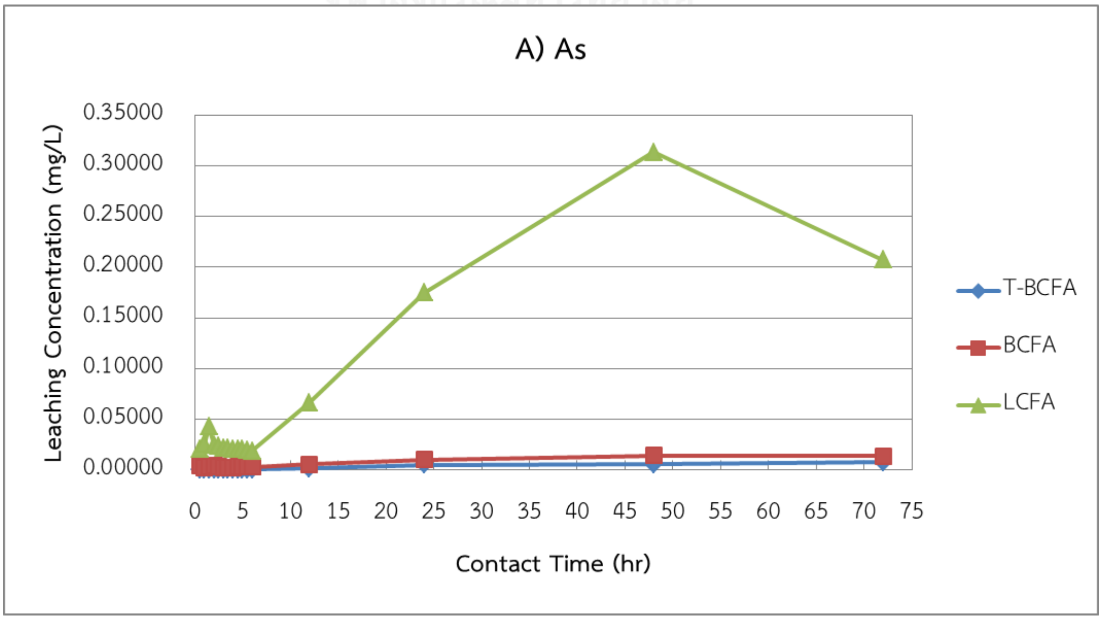
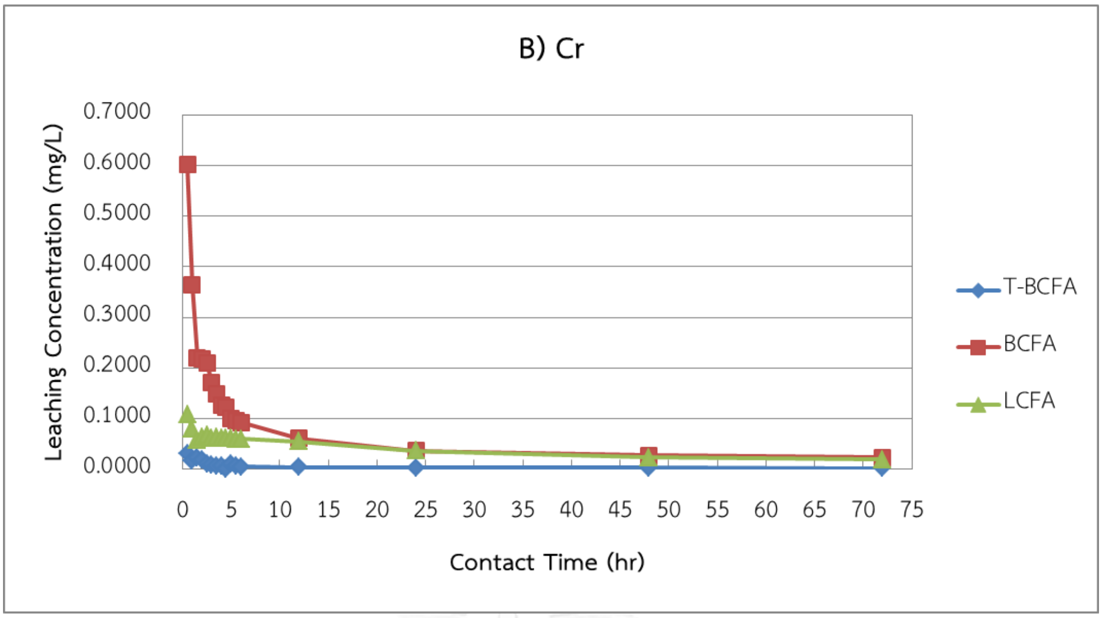
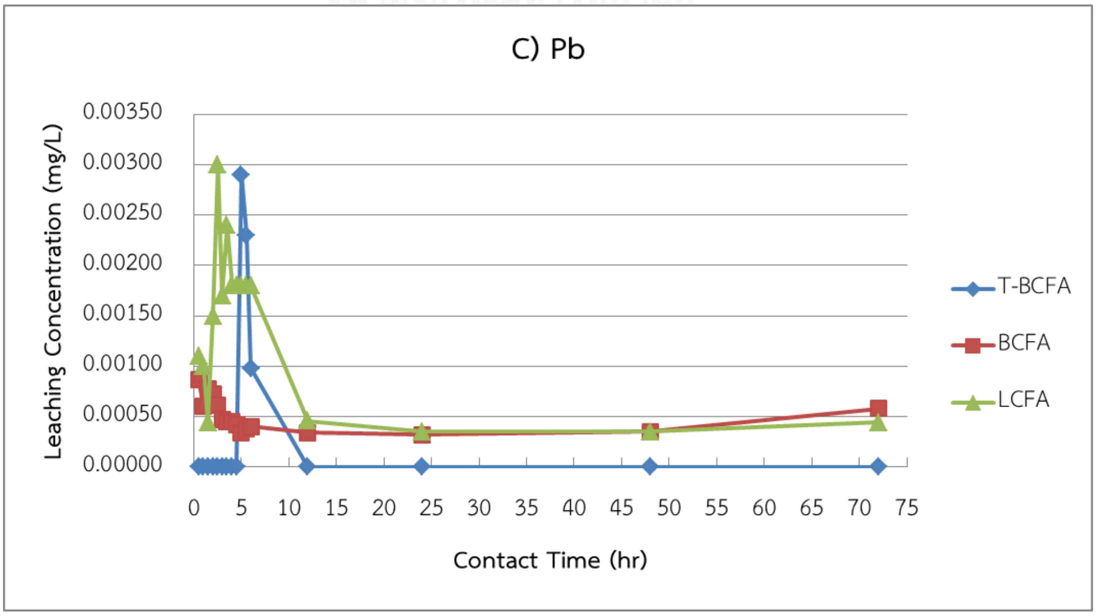


Figure 4.9 Leaching concentration of A) As, B) Cr, C) Pb and D) Zn of fly ash samples according to column leaching test using DI water at 25°C (1 replicate)




B) Cr
Leaching Concentration (mg/L)
0.7000
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
Contact Time (hr)
T-BCFA
BCFA
LCFA


C) Pb
Leaching Concentration (mg/L)
0.00350
0.00300
0.00250
0.00200
0.00150
0.00100
0.00050
0.00000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
Contact Time (hr)
T-BCFA
BCFA
LCFA

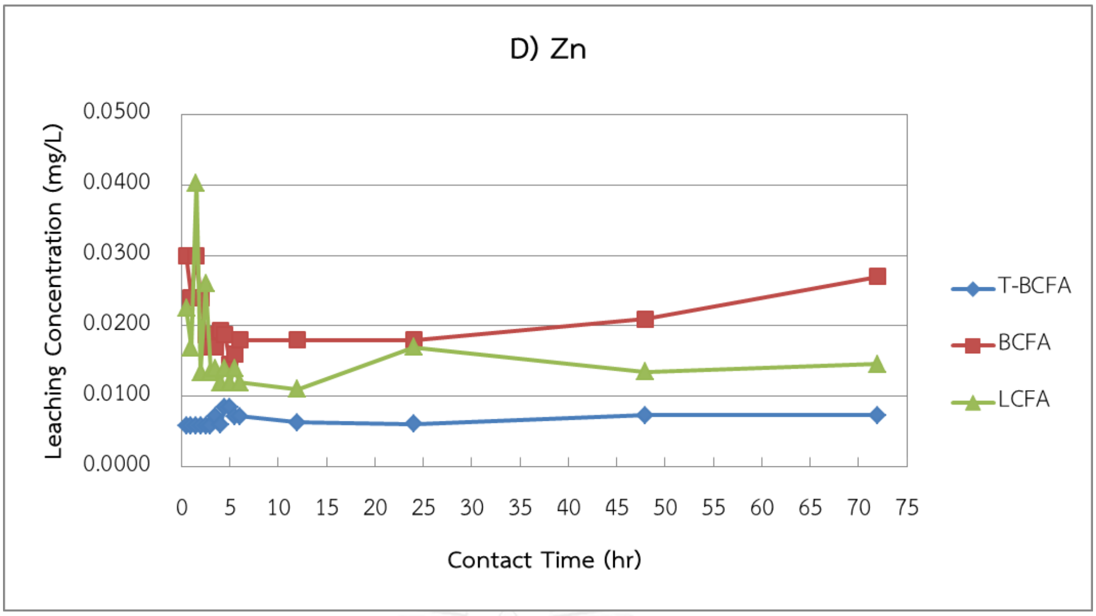
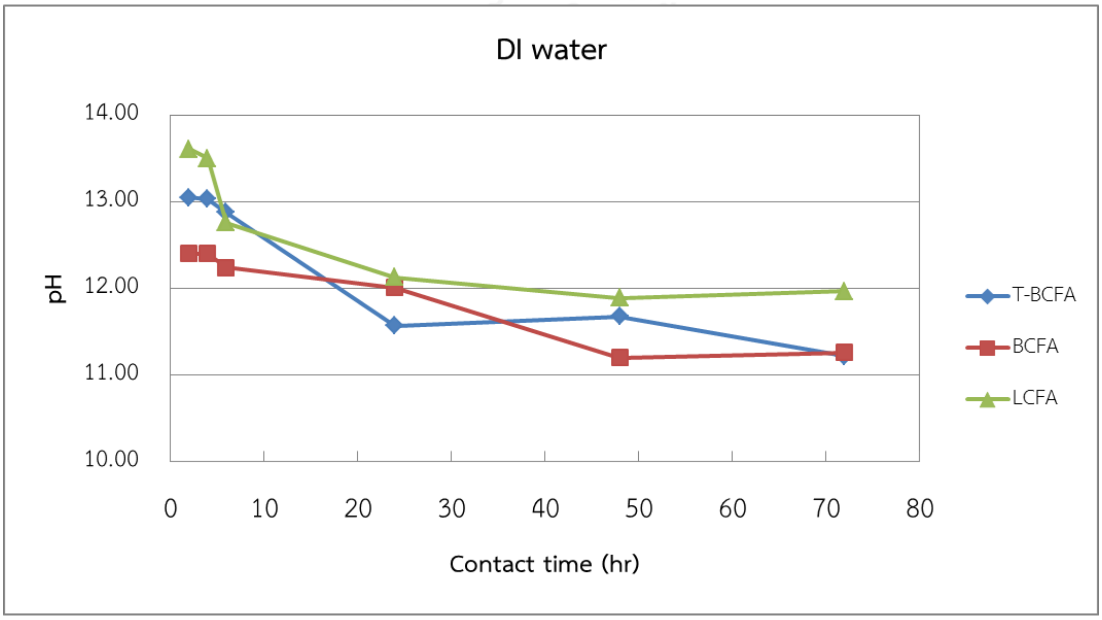


Figure 4.10 Leaching concentration of A) As, B) Cr, C) Pb and D) Zn of fly ash samples according to column leaching test using synthetic acid rain at 25°C (1 replicate)



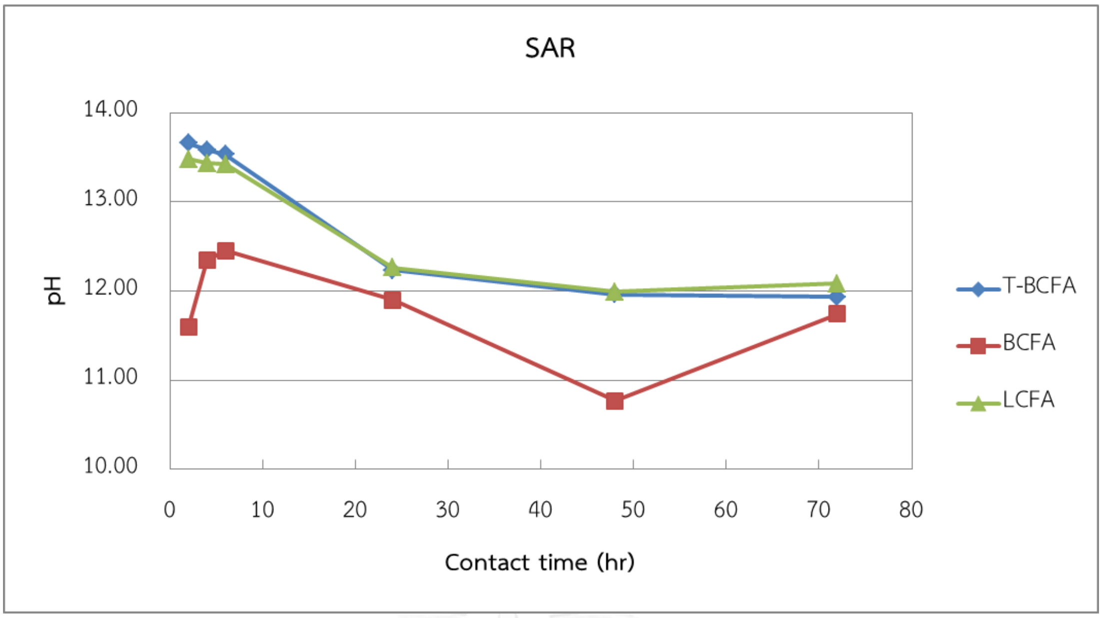


Figure 4.11 Leachate pH trends for column leaching method using DI water and synthetic acid rain at 25°C

4.2.5 Difference between Jar leaching test and column leaching test

The leaching concentration of heavy metals from column was higher than from jar test because column test is a plug flow process in an open system, while jar test is a batch process in a close system (Alinnor, 2007; Nascimento et al., 2009). The contact time of jar test and column test was different. The contact time of jar test was 5 days which was higher than the contact time in a column test (~41min according to $Q(flow\ rate) = \frac{V(volume)}{T(time)}$). Solid to liquid ratio (S/L) of jar leaching test is 1:20 while S/L of column leaching test is around 1:1.5 (according to $\frac{S}{L} = \frac{\text{g of fly ash}}{Volume\ of\ column}$). This high solid to liquid ratio in a column test may lead to higher concentrations of heavy metals in leachants.

4.2.6 Effect of particle size on leachability

This test used municipal solid waste ash for analyzing. Municipal solid waste ash (MSWA) was not used in the leaching tests (microwave digestion, jar leaching test and column leaching test) because the sources of MSWA were generated from the domestic wastes which mostly have low heavy metals so it is not necessary to analyze leachability of heavy metals.. For coal fly ash, it was not used in size analysis because the sizes of coal fly ash samples were tiny and homogenous according to SEM and the resolution of sieves was not small enough to separate the size of coal fly ash samples. Leaching concentrations of heavy metals for three particle sizes from TCLP test were shown in Table 4.8. The results show that leaching concentrations of heavy metals from particle size between 0.074-0.088 mm are higher than the other sizes. It probably causes of the different particle sizes of fly ash don't affect the heavy metals leaching or the sources of this fly ash were generated from different types of wastes such as paper, plastic, etc. Each types of waste may contain different chemical composition which leads to different leachability. For example, the ash particle of plastic may be larger than paper ash.

4.2.7 Effect of composition of fly ash on leachability

According to XRF results, LCFA was richer in trace elements (As, Cr and Zn) on the surface of fly ash than the other ashes, so leaching concentrations of trace elements should be higher than the other ash. According to microwave digestion, LCFA was richest in As and Zn, while BCFA was richest Cr and Pb. According to XRF results, the heavy metals cannot be detected on the surface of BCFA and T-BCFA. So, the trace elements may stay in the interior of particle. For example, leaching concentrations of trace elements were highest for TCLP while leaching concentrations of Cr was highest from BCFA for jar leaching test. It can be concluded that ash chemical composition can affect the leachability. However, the other factors may also affect the leachability especially types of leachants, contact time and shaking speed.

Table 4.8 Leaching concentrations of As, Cr, Pb and Zn for each size of particle according to TCLP method (3 replicates)

Size	Leaching concentration (mg/L)			
	As	Cr	Pb	Zn
0.125-0.149	0.1183±0.0064	0.1246±0.0045	0.0094±0.0005	1.0947±0.0289
0.074-0.088	0.1926±0.0089	0.1398±0.0026	0.0115±0.0004	1.1230±0.0308
< 0.044	0.1360±0.0021	0.1158±0.0011	0.0084±0.0002	1.1140±0.0028

CHAPTER 5

CONCLUSION

The coal fly ash samples were collected from different power plants as lignite coal fly ash (LCFA), bituminous coal fly ash (BCFA) and treated-bituminous coal fly ash (T-BCFA) for using in leaching methods and municipal solid waste ash (MSWA) for analyzing the effect of particle size on leachability. The major components of fly ash samples are SiO_2, Al_2O_3 and Fe_2O_3, while CaO, K_2O and MgO are the minor components. LCFA (fly ash class C) had the main components (silica, alumina and ferric oxide) around 60.2% by weight, while BCFA and T-BCFA (fly ash class F) had the main components around 82% and 45% by weight, respectively. Moreover, MSWA has the main components around 53% by weight. The microstructures at 500 magnifications of LCFA and BCFA were sphere but T-BCFA and MSWA were rough and amorphous. For particle size of ash, LCFA, BCFA, T-BCFA and MSWA had the particle size in the range of 1-10, 1-10, 5-30 and 10-40 µm, respectively.

The environmentally available trace elements in LCFA were richer than the others according to acid digestion method. The leachability of heavy metals (As, Cr, Pb and Zn) was highest in LCFA, and lowest in T-BCFA because LCFA was the lignite coal fly ash (class C) which had more the percentage of trace elements than the bituminous coal fly ash (class F) analyzed by TCLP method. Comparing leachability with regulatory level of contaminant, the leachability of heavy metals of fly ash samples was below the regulatory level except As from LCFA. For particle size analysis of MSWA, leaching concentrations of heavy metals from particle size between 0.074-0.088 mm were highest.

For jar leaching test, the leaching concentrations of heavy metals were highest in LCFA around 0.0112 mg/L at 2 day for As, BCFA around 0.1401 mg/L at 5 day for Cr, Pb and Zn around 0.0006 and 0.3375 mg/L at 1 day and 5 day, respectively for T-BCFA. The leaching concentrations of heavy metals from all fly ash samples were below the industrial effluent standards. For column leaching test, the leaching concentrations of heavy metals were highest in LCFA around 0.5105 mg/L at 48 h for As using DI water and 0.3137 mg/L using SAR. For Cr, BCFA was highest around 0.4221 mg/L at 30 min using DI water and 0.6024 mg/L using SAR. Pb for BCFA was highest around 0.0065 mg/L using DI water and Pb for LCFA was highest around 0.0030 using SAR. Zn for BCFA was highest around 0.3300 mg/L using DI water and Zn for LCFA was highest around 0.0403 mg/L using SAR. The concentration of heavy metals in these tests (using DI and SAR) was close. This means that pH of the leachant didn't play a major role in leaching capacity. Moreover, the leachate concentrations of all heavy metals were below the industrial effluent standards except arsenic from LCFA at 48 h for two leachants. Chromium concentrations from BCFA at 30 min for two leachants,and from BCFA at 1 h for SAR as the leachant were also higher than standard level. The leaching concentration of heavy metals from column leaching test was higher than from jar leaching test.

Suggestion for the future research

Future researcher might analyze the adsorption process which occurs in this study by using X-Ray absorption spectrometry (XAS) or analyze the co-precipitation of heavy metals with fly ash samples by using Scanning Electron Microscope (SEM). For microwave assisted digestion, hydrofluoric acid (HF) may be used for digesting fly ash samples because this acid is stronger than hydrochloric acid (HCl) and nitric acid (HNO_3).

In the cement industry, fly ash is the raw material using in construction of roads and embankments because fly ash is pozzolanic material which can help to increase density, strength and flow of concrete. Another application for fly ash might be used as synthesized zeolite or low cost adsorbent for flue gas treatment and waste water treatment to remove dye, contaminated substance including heavy metals, pollutants and organic matters. The benefits of fly ash utilization include (1) increasing the properties of concrete (strength, density and durability) (2) reduction of energy use and greenhouse gas (3) reduction of coal combustion products and landfill area (4) preservation of natural resources (Ahmaruzzaman, 2010).

APPENDIX

APPENDIX A

Chemical leaching tests results

Table A1 Acid digestion results

No.	Other samples	Mean concentration (mg/l)				Weight (g)
		As	Zn	Pb	Cr	
1	LCFA I	4.2734	4.0100	0.2300	1.1400	0.5067
	LCFA II	4.3557	5.3800	0.2200	1.0900	0.5011
average	LCFA	4.3146	4.6950	0.2250	1.1150	0.5039
SD	LCFA	0.0582	0.9687	0.0071	0.0354	0.0040
RSD	LCFA	1.3488	20.6334	3.1427	3.1709	0.7858
2	T-BCFA I	0.3576	3.2300	0.1200	0.6400	0.5042
	T-BCFA II	0.3426	2.8000	0.1000	0.6500	0.5025
	T-BCFA III	0.3480	2.8400	0.1100	0.5900	0.5046
average	T-BCFA	0.3494	2.9567	0.1100	0.6267	0.5038
SD	T-BCFA	0.0076	0.2376	0.0100	0.0321	0.0011
RSD	T-BCFA	2.1744	8.0346	9.0909	5.1296	0.2213
3	BCFA I	0.7564	3.9440	0.2354	1.4224	0.5065
	BCFA II	0.7322	3.9840	0.2356	1.4159	0.5016
average	BCFA	0.7443	3.9640	0.2355	1.4192	0.5041
SD	BCFA	0.0171	0.0283	0.0001	0.0046	0.0035
RSD	BCFA	2.2991	0.7135	0.0601	0.3239	0.6874

Table A2 TCLP results (Acetic acid)

No.	Other samples	Mean concentration (mg/l)				Weight (g)
		As	Zn	Pb	Cr	
1	LCFA I	5.9928	3.8900	0.4110	1.1700	1.0030
	LCFA II	5.8014	3.7200	0.4020	1.1900	1.0020
	LCFA III	5.5830	3.6900	0.3920	1.2200	1.0050
average	LCFA	5.7924	3.7667	0.4017	1.1933	1.0033
SD	LCFA	0.2050	0.1079	0.0095	0.0252	0.0015
RSD	LCFA	3.5400	2.8635	2.3662	2.1089	0.1522
2	T-BCFA I	0.0612	0.2600	0.2130	0.0867	1.0059
	T-BCFA II	0.0523	0.6040	0.2170	0.0861	1.0022
	T-BCFA III	0.0525	0.5660	0.2190	0.0871	1.0046
average	T-BCFA	0.0553	0.4767	0.2163	0.0866	1.0042
SD	T-BCFA	0.0051	0.1886	0.0031	0.0005	0.0019
RSD	T-BCFA	9.1837	39.5661	1.4122	0.5810	0.1869
3	BCFA I	0.9756	3.1600	0.2930	1.0000	1.0040
	BCFA II	0.9325	2.9700	0.2900	0.9400	1.0040
	BCFA III	0.8981	3.0000	0.2870	0.9570	1.0040
average	BCFA	0.9354	3.0433	0.2900	0.9657	1.0040
SD	BCFA	0.0388	0.1021	0.0030	0.0309	0.0000
RSD	BCFA	4.1513	3.3563	1.0345	3.2024	0.0000

Table A3 TCLP results control test (DI water)

No.	Other samples	Mean concentration (mg/l)				Weight (g)
		As	Zn	Pb	Cr	
1	LCFA I	0.0084	0.2865	0.0003	0.0540	1.0052
	LCFA II	0.0046	0.2565	0.0002	0.0539	1.0027
	LCFA III	0.0052	0.3120	0.0003	0.0542	1.0005
average	LCFA	0.0061	0.2850	0.0003	0.0540	1.0028
SD	LCFA	0.0020	0.0278	0.0001	0.0002	0.0024
RSD	LCFA	33.6737	9.7475	21.6506	0.2827	0.2345
2	T-BCFA I	0.0003	0.3615	0.0008	0.0377	1.0047
	T-BCFA II	0.0002	0.2640	0.0007	0.0356	1.0038
	T-BCFA III	0.0002	0.3330	0.0007	0.0348	1.0009
average	T-BCFA	0.0002	0.3195	0.0007	0.0360	1.0031
SD	T-BCFA	0.0001	0.0501	0.0001	0.0015	0.0020
RSD	T-BCFA	24.7436	15.6909	7.8730	4.1566	0.1980
3	BCFA I	0.0050	0.0915	0.0002	0.1083	1.0032
	BCFA II	0.0059	0.0840	0.0002	0.1049	1.0027
	BCFA III	0.0064	0.0915	0.0002	0.1064	1.0056
average	BCFA	0.0058	0.0890	0.0002	0.1065	1.0038
SD	BCFA	0.0007	0.0043	0.0000	0.0017	0.0016
RSD	BCFA	12.3028	4.8653	0.0000	1.5994	0.1544

Table A4 Jar leaching test results

Fly ash	Concentration (mg/L)				pH
	Cr	Pb	Zn	As	
T-BCFA 1 day	0.0368	0.0006	0.2565	0.0002	13.85
T-BCFA 2 day	0.0386	0.0005	0.2415	0.0003	13.07
T-BCFA 3 day	0.0396	0.0004	0.2685	0.0001	13.00
T-BCFA 4 day	0.0354	0.0001	0.3105	0.0001	13.23
T-BCFA 5 day	0.0075	0.0005	0.3375	0.0003	13.25
BCFA 1 day	0.1209	0.0001	0.0750	0.0073	12.45
BCFA 2 day	0.1263	0.0001	0.0870	0.0063	11.95
BCFA 3 day	0.1319	0.0001	0.0915	0.0053	12.03
BCFA 4 day	0.1361	0.00003	0.0780	0.0037	12.26
BCFA 5 day	0.1401	0.0001	0.0675	0.0033	12.29
LCFA 1 day	0.0630	0.00012	0.1830	0.0078	13.68
LCFA 2 day	0.0948	0.00009	0.2340	0.0112	12.93
LCFA 3 day	0.1161	0.00004	0.1875	0.0051	12.98
LCFA 4 day	0.0465	0.00008	0.1410	0.0012	13.04
LCFA 5 day	0.0314	0.00008	0.1500	0.0009	13.00

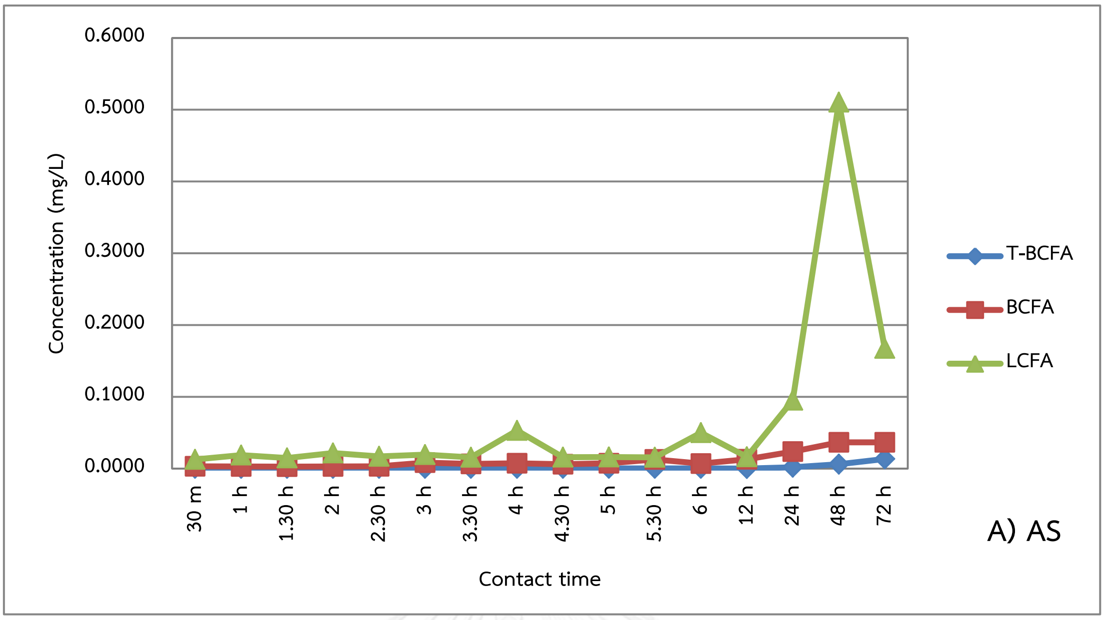
<u>Weight</u>

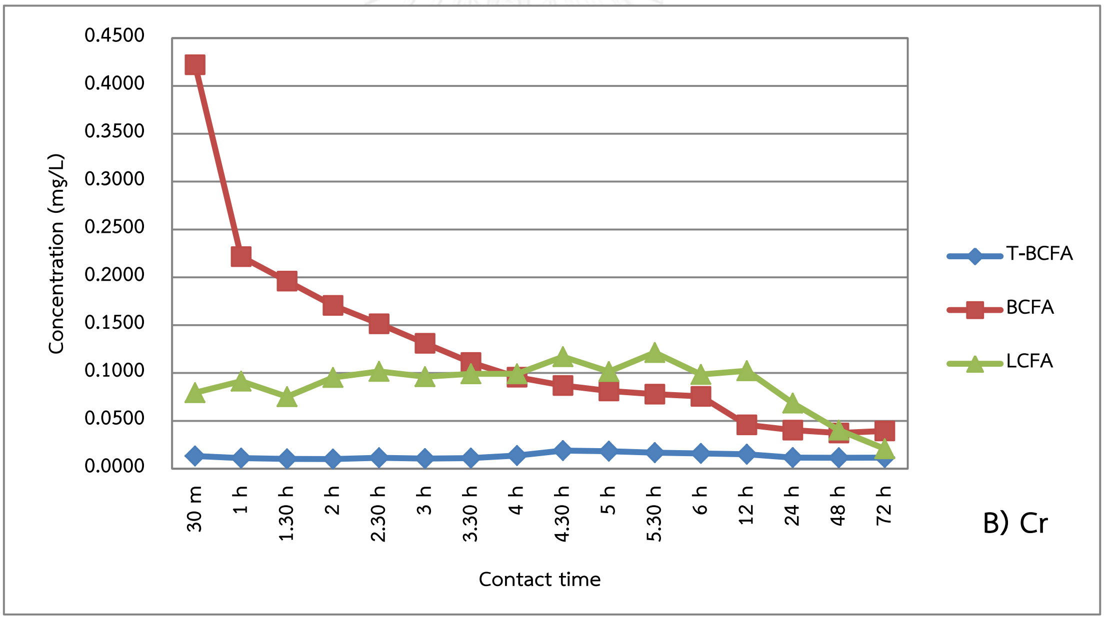
LCFA = 6.0030 g

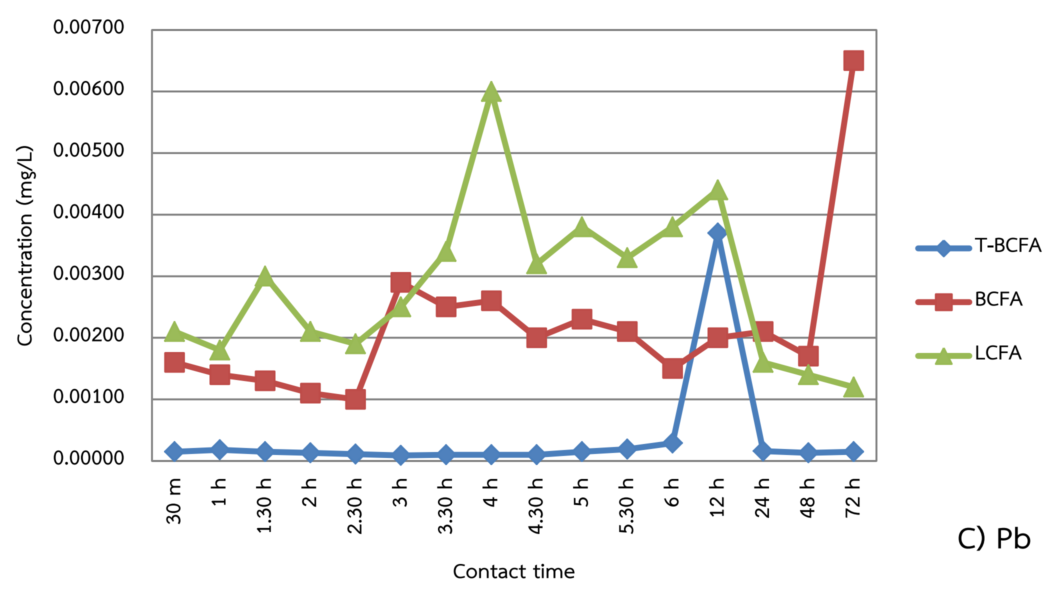
BCFA = 6.0080 g

T-BCFA = 6.0004 g

Fig. A1 Column leaching test (DI water)






0.00700
0.00600
0.00500
0.00400
0.00300
0.00200
0.00100
0.00000
Concentration (mg/L)
30 m
1 h
1.30 h
2 h
2.30 h
3 h
3.30 h
4 h
4.30 h
5 h
5.30 h
6 h
12 h
24 h
48 h
72 h
Contact time
T-BCFA
BCFA
LCFA
C) Pb

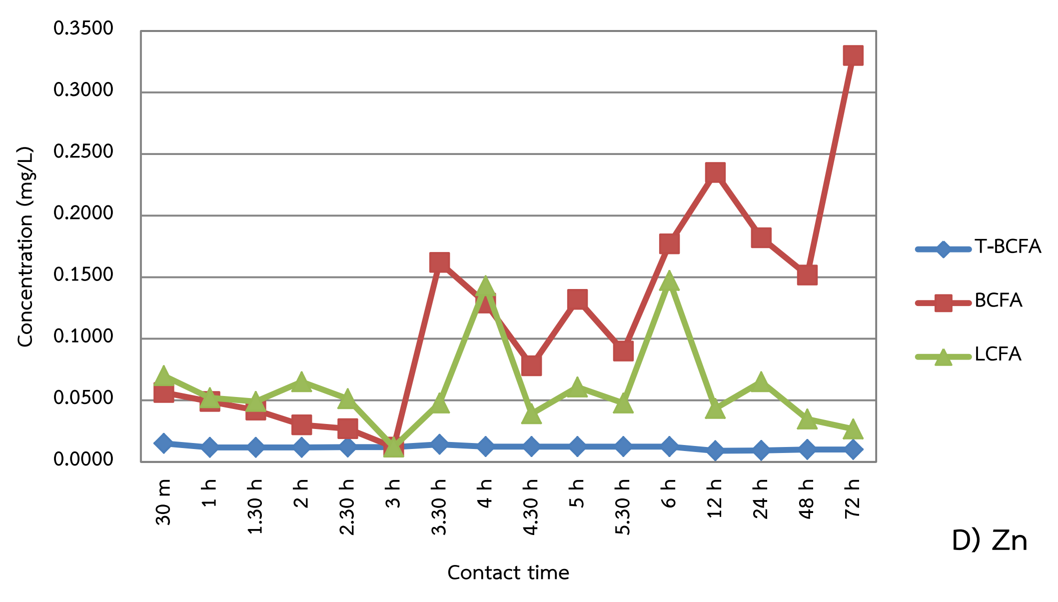
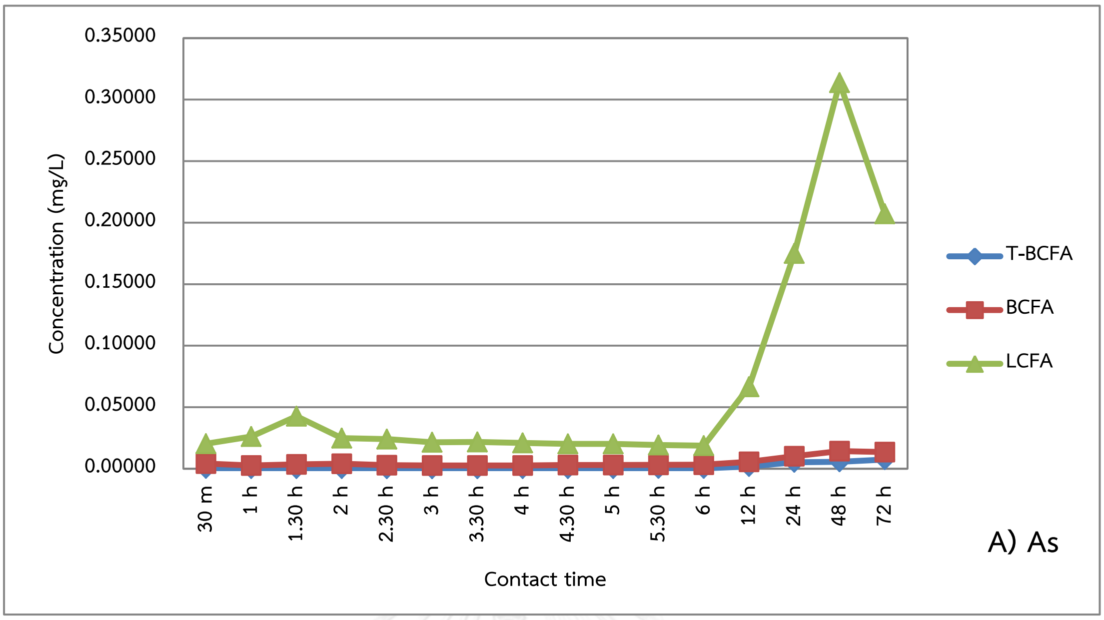
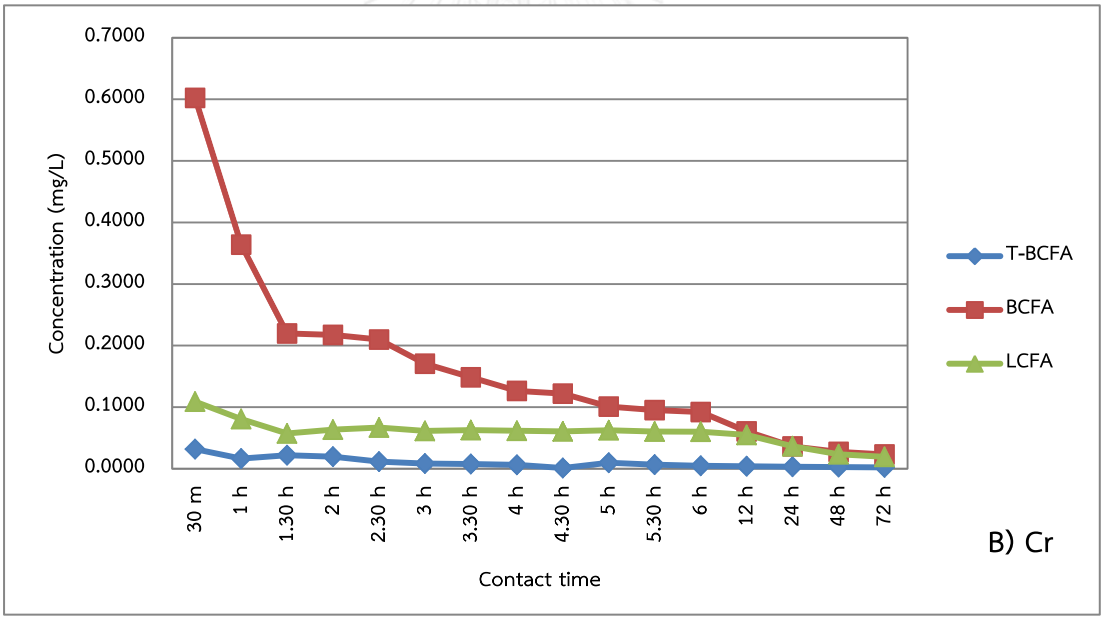
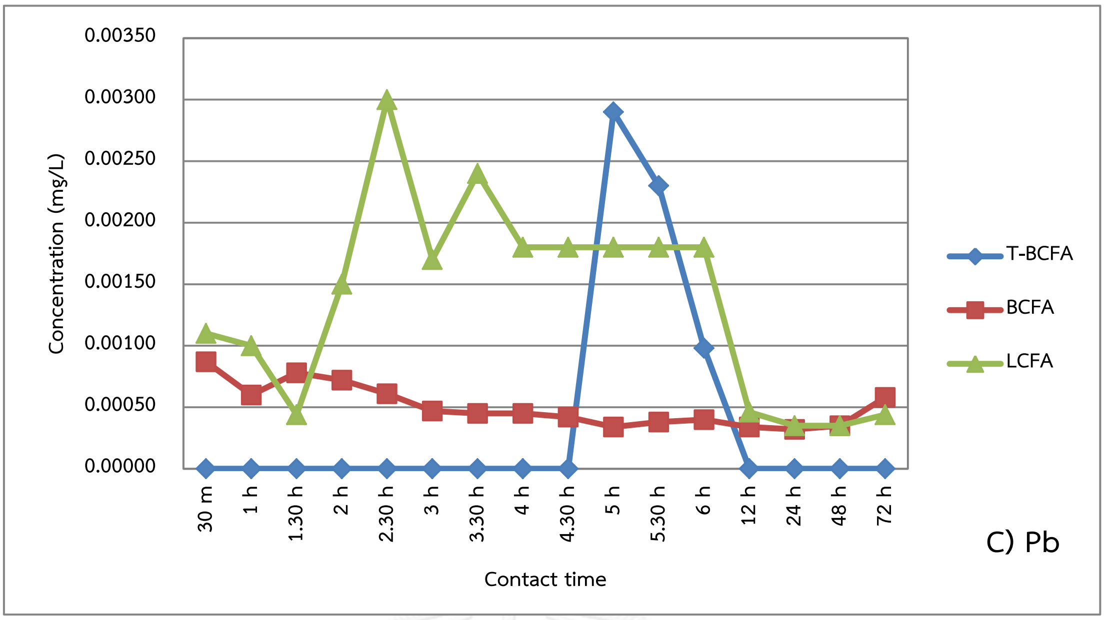

0.3500
0.3000
0.2500
0.2000
0.1500
0.1000
0.0500
0.0000
Concentration (mg/L)
30 m
1 h
1.30 h
2 h
2.30 h
3 h
3.30 h
4 h
4.30 h
5 h
5.30 h
6 h
12 h
24 h
48 h
72 h
Contact time
T-BCFA
BCFA
LCFA
D) Zn

Fig. A2 Column leaching test (SAR)






0.00350
0.00300
0.00250
0.00200
0.00150
0.00100
0.00050
0.00000
Concentration (mg/L)
30 m
1 h
1.30 h
2 h
2.30 h
3 h
3.30 h
4 h
4.30 h
5 h
5.30 h
6 h
12 h
24 h
48 h
72 h
Contact time
T-BCFA
BCFA
LCFA
C) Pb

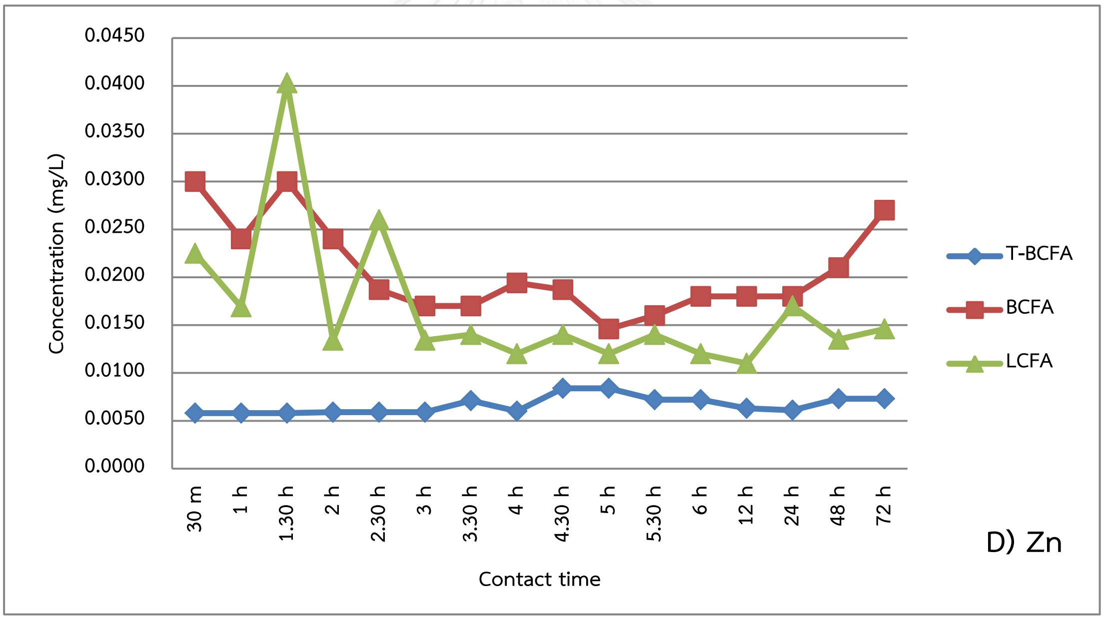

0.0450
0.0400
0.0350
0.0300
0.0250
0.0200
0.0150
0.0100
0.0050
0.0000
Concentration (mg/L)
30 m
1 h
1.30 h
2 h
2.30 h
3 h
3.30 h
4 h
4.30 h
5 h
5.30 h
6 h
12 h
24 h
48 h
72 h
Contact time
T-BCFA
BCFA
LCFA
D) Zn

Table A5 Column leaching test results (Arsenic)

Time	As Concentration (mg/L)					
	SAR			DI water		
	LCFA	BCFA	T-BCFA	LCFA	BCFA	T-BCFA
30 min	0.02030	0.00420	0.00035	0.01280	0.00310	0.00040
1 h	0.02610	0.00270	0.00023	0.01870	0.00300	0.00030
1.30 h	0.04270	0.00350	0.00018	0.01470	0.00280	0.00030
2 h	0.02490	0.00410	0.00013	0.02170	0.00290	0.00030
2.30 h	0.02410	0.00290	0.00009	0.01700	0.00310	0.00030
3 h	0.02150	0.00260	0.00006	0.01950	0.00840	0.00030
3.30 h	0.02180	0.00270	0.00005	0.01560	0.00650	0.00030
4 h	0.02100	0.00270	0.00011	0.05300	0.00750	0.00030
4.30 h	0.02020	0.00300	0.00021	0.01580	0.00620	0.00030
5 h	0.02020	0.00300	0.00023	0.01620	0.00740	0.00030
5.30 h	0.01930	0.00310	0.00031	0.01560	0.01280	0.00020
6 h	0.01870	0.00330	0.00031	0.04990	0.00700	0.00020
12 h	0.06660	0.00560	0.00180	0.01640	0.01290	0.00010
24 h	0.17500	0.01020	0.00525	0.09520	0.02360	0.00190
48 h	0.31370	0.01440	0.00561	0.51050	0.03660	0.00600
72 h	0.20720	0.01360	0.00741	0.16740	0.03660	0.01350

Table A6 Column leaching test results (Chromium)

Time	Cr Concentration (mg/L)					
	SAR			DI water		
	LCFA	BCFA	T-BCFA	LCFA	BCFA	T-BCFA
30 min	0.10910	0.60240	0.03170	0.07950	0.42210	0.01330
1 h	0.08060	0.36390	0.01650	0.09140	0.22160	0.01100
1.30 h	0.05720	0.21960	0.02190	0.07530	0.19600	0.01030
2 h	0.06340	0.21750	0.01950	0.09530	0.17070	0.01000
2.30 h	0.06680	0.20990	0.01160	0.10170	0.15150	0.01150
3 h	0.06150	0.17070	0.00840	0.09620	0.13110	0.01050
3.30 h	0.06260	0.14860	0.00750	0.09920	0.11100	0.01110
4 h	0.06180	0.12630	0.00640	0.09920	0.09570	0.01380
4.30 h	0.06060	0.12210	0.00120	0.11700	0.08700	0.01890
5 h	0.06240	0.10100	0.00980	0.10140	0.08130	0.01820
5.30 h	0.06040	0.09520	0.00650	0.12130	0.07800	0.01680
6 h	0.06000	0.09210	0.00480	0.09840	0.07560	0.01590
12 h	0.05490	0.06060	0.00400	0.10230	0.04580	0.01510
24 h	0.03640	0.03630	0.00320	0.06850	0.04030	0.01160
48 h	0.02340	0.02730	0.00260	0.04030	0.03730	0.01140
72 h	0.01940	0.02310	0.00210	0.02080	0.03950	0.01160

Table A7 Column leaching test results (Lead)

Time	Pb Concentration (mg/L)					
	SAR			DI water		
	LCFA	BCFA	T-BCFA	LCFA	BCFA	T-BCFA
30 min	0.00110	0.00087	0.00000	0.00210	0.00160	0.00015
1 h	0.00100	0.00060	0.00000	0.00180	0.00140	0.00018
1.30 h	0.00044	0.00078	0.00000	0.00300	0.00130	0.00015
2 h	0.00150	0.00072	0.00000	0.00210	0.00110	0.00013
2.30 h	0.00300	0.00061	0.00000	0.00190	0.00100	0.00011
3 h	0.00170	0.00047	0.00000	0.00250	0.00290	0.00009
3.30 h	0.00240	0.00045	0.00000	0.00340	0.00250	0.00010
4 h	0.00180	0.00045	0.00000	0.00600	0.00260	0.00010
4.30 h	0.00180	0.00042	0.00000	0.00320	0.00200	0.00010
5 h	0.00180	0.00034	0.00290	0.00380	0.00230	0.00015
5.30 h	0.00180	0.00038	0.00230	0.00330	0.00210	0.00019
6 h	0.00180	0.00040	0.00098	0.00380	0.00150	0.00029
12 h	0.00046	0.00034	0.00000	0.00440	0.00200	0.00370
24 h	0.00035	0.00032	0.00000	0.00160	0.00210	0.00016
48 h	0.00035	0.00035	0.00000	0.00140	0.00170	0.00013
72 h	0.00044	0.00058	0.00000	0.00120	0.00650	0.00015

Table A8 Column leaching test results (Zinc)

Time	Zn Concentration (mg/L)					
	SAR			DI water		
	LCFA	BCFA	T-BCFA	LCFA	BCFA	T-BCFA
30 min	0.02250	0.03000	0.00580	0.07000	0.05630	0.01500
1 h	0.01690	0.02400	0.00580	0.05200	0.04900	0.01170
1.30 h	0.04030	0.03000	0.00580	0.04900	0.04200	0.01170
2 h	0.01340	0.02400	0.00590	0.06500	0.03000	0.01170
2.30 h	0.02600	0.01870	0.00590	0.05130	0.02700	0.01200
3 h	0.01340	0.01700	0.00590	0.06070	0.13500	0.01200
3.30 h	0.01400	0.01700	0.00710	0.04770	0.16200	0.01420
4 h	0.01200	0.01940	0.00600	0.14300	0.12900	0.01240
4.30 h	0.01400	0.01870	0.00840	0.03900	0.07800	0.01240
5 h	0.01200	0.01460	0.00840	0.06070	0.13200	0.01240
5.30 h	0.01400	0.01600	0.00720	0.04770	0.09000	0.01240
6 h	0.01200	0.01800	0.00720	0.14730	0.17700	0.01240
12 h	0.01100	0.01800	0.00630	0.04330	0.23500	0.00900
24 h	0.01700	0.01800	0.00610	0.06500	0.18200	0.00930
48 h	0.01350	0.02100	0.00730	0.03470	0.15170	0.01000
72 h	0.01460	0.02700	0.00730	0.02670	0.33000	0.01000

Table A9 Column leaching test results (pH)

Time	pH					
	SAR			DI water		
	LCFA	BCFA	T-BCFA	LCFA	BCFA	T-BCFA
2 h	13.48	11.59	13.66	13.61	12.40	13.05
4 h	13.43	12.34	13.58	13.50	12.40	13.03
6 h	13.42	12.45	13.53	12.76	12.24	12.88
24 h	12.26	11.90	12.23	12.13	12.01	11.57
48 h	11.99	10.77	11.96	11.89	11.20	11.68
72 h	12.08	11.74	11.93	11.97	11.26	11.22

Table A10 Column leaching test results (Weight and Flow rate)

Fly ash samples		Weight (g)	Flow rate (mL/h)
Synthetic acid rain (SAR)	LCFA	4.6862	8-10
	BCFA	4.7125	8-10
	T-BCFA	2.9082	40-60
DI Water	LCFA	4.7532	6-10
	BCFA	4.2793	6-10
	T-BCFA	3.1496	20-30

Table A11 TCLP results (Size analysis)

No.	Other samples	Mean concentration (mg/l)				Weight
		As	Zn	Pb	Cr	
1	Size (0.125-0.149 mm) I	0.1256	1.1260	0.0100	0.1289	1.0012
	Size (0.125-0.149 mm) II	0.1138	1.0690	0.0090	0.1250	1.0006
	Size (0.125-0.149 mm) III	0.1154	1.0890	0.0092	0.1199	1.0023
average	**Size (0.125-0.149 mm)**	**0.1183**	**1.0947**	**0.0094**	**0.1246**	**1.0014**
SD	**Size (0.125-0.149 mm)**	**0.0064**	**0.0289**	**0.0005**	**0.0045**	**0.0009**
RSD	**Size (0.125-0.149 mm)**	**5.4124**	**2.6418**	**5.6293**	**3.6222**	**0.0861**
2	Size (0.074-0.088 mm) I	0.1990	1.1280	0.0119	0.1406	1.0006
	Size (0.074-0.088 mm) II	0.1963	1.0900	0.0115	0.1420	1.0036
	Size (0.074-0.088 mm) III	0.1824	1.1510	0.0111	0.1369	1.0038
average	**Size (0.074-0.088 mm)**	**0.1926**	**1.1230**	**0.0115**	**0.1398**	**1.0027**
SD	**Size (0.074-0.088 mm)**	**0.0089**	**0.0308**	**0.0004**	**0.0026**	**0.0018**
RSD	**Size (0.074-0.088 mm)**	**4.6257**	**2.7432**	**3.4783**	**1.8844**	**0.1788**
3	Size (< 0.044 mm) I	0.1360	1.1110	0.0082	0.1150	1.0022
	Size (< 0.044 mm) II	0.1381	1.1145	0.0086	0.1154	1.0014
	Size (< 0.044 mm) III	0.1340	1.1166	0.0083	0.1170	1.0021
average	**Size (< 0.044 mm)**	**0.1360**	**1.1140**	**0.0084**	**0.1158**	**1.0019**
SD	**Size (< 0.044 mm)**	**0.0021**	**0.0028**	**0.0002**	**0.0011**	**0.0004**
RSD	**Size (< 0.044 mm)**	**1.5071**	**0.2539**	**2.4880**	**0.9139**	**0.0435**

APPENDIX B

Physical tests results

Table B1 Sieve analysis

Sieve Size	Mass Retained in each sieve (g)	Cumulative Mass Passed (g)	Total Percent Passed (%)
No.100	372.68	86.94	18.92
No.120	19.03	67.91	14.77
No.170	19.66	48.25	10.50
No.200	23.43	24.82	5.40
No.325	11.46	13.36	2.91
Pan	13.36	0	0
Sum	459.62	459.62	100

APPENDIX C

Statistical analysis (T-test)

Table C1 pH of SAR VS. DI water

	LCFA (SAR)	*LCFA (DI)*
Mean	12.77667	12.64333
Variance	0.541307	0.593267
Observations	6	6
Hypothesized Mean Difference	0	
Df	10	
t Stat	0.306618	
P(T<=t) one-tail	0.382712	
t Critical one-tail	1.812461	
P(T<=t) two-tail	0.765423	
t Critical two-tail	2.228139	

	BCFA (SAR)	*BCFA (DI)*
Mean	11.79833	11.91833
Variance	0.366537	0.305057
Observations	6	6
Hypothesized Mean Difference	0	
Df	10	
t Stat	-0.35868	
P(T<=t) one-tail	0.363647	
t Critical one-tail	1.812461	
P(T<=t) two-tail	0.727293	
t Critical two-tail	2.228139	

	T-BCFA (SAR)	*T-BCFA (DI)*
Mean	12.815	12.23833
Variance	0.73339	0.698537
Observations	6	6
Hypothesized Mean Difference	0	
Df	10	
t Stat	1.18043	
P(T<=t) one-tail	0.132573	
t Critical one-tail	1.812461	
P(T<=t) two-tail	0.265146	
t Critical two-tail	2.228139	

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APPENDIX