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Direct Quantitative Analysis of Arsenic, its 
Leachability and Speciation in Flyashes from Coal 
Fired Power Plants 

(SRI HARTUTI

March 2015)
Direct Quantitative Analysis of Arsenic, its Leachability and Speciation in Flyashes from Coal Fired Power Plants

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March 2015
Direct Quantitative Analysis of Arsenic, its Leachability and Speciation in Flyashes from Coal Fired Power Plants

A dissertation submitted to the Gifu University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental & Renewable Energy System

By

SRI HARTUTI

March 2015
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Summary

The utilization of coal as fossil fuel in combustion process to generate electricity has been developed for many years in order to perform the better managing regarding to keep strict environmental impact and to save the operational cost. Better knowledge about coal quality may be required to perform the successful in marketing process [1]. Studies of trace elements in coal are needed both for financial and environmental concerns.

Combustion of coal occurs in three phases, namely devolatilisation, combustion of the volatile matter, and combustion of the residual char. Mineral matter may be excluded from the residual char particles due to desegregation and separation in the milling process, or included within the char particle. During combustion, trace elements partition between the bottom ash, the fly ash, and flue gas.

Fly ash as one of coal combustion byproducts generated in the coal fired combustion, contains elevated concentration of several hazardous trace elements with respect to potential health effects. Among the trace elements in coal fly ashes, arsenic, cadmium, copper, mercury, and lead are the greatest concern as environmental hazards. Arsenic, one of the most highly toxic chemicals, is a semi-metallic element commonly found as arsenide and in arsenate compounds. It is an odorless, tasteless, and notoriously poisonous metalloid with many allotropic forms that is dangerous for the environment. Long term exposure of arsenic may cause some diseases such as skin damage or problems with circulatory systems, and
may have an increased risk of getting cancer.

Fly ash has been utilized for some purposes such as cement and concrete but most of them are discarded to the landfill. Rainwater can leach out arsenic and other toxic elements in fly ash and can lead to contamination of groundwater. If the arsenic concentration in the excess water exceeds the environmental limit (0.1 ppb in Japan), the excess water cannot be drained into the sea. This situation is serious, because ash storage must be discontinued.

Given these concerns, it is important to be able to rapidly determine the arsenic content in the fly ash at these sites and understanding the leachability of arsenic from fly ash is significant in predicting the arsenic impact on the drinking water quality and in developing innovative methods to prevent arsenic leaching.

Many studies of arsenic, cadmium, copper, mercury, and lead, have been conducted in recent years, and the analytical methods such as the graphite furnace atomic absorption spectroscopy (GF-AAS) method for direct determination of element in solid sample had been developed. The graphite furnace atomic absorption spectroscopy (GF-AAS) method has been proposed for direct determination of element in solid sample since its appearance as a good alternative to wet methods of analysis in many matrices. Here, we examine the use of GF-AAS for total arsenic determination in coal fly ash from distinct coal mines in Indonesia. Our direct analysis of 21 selected coal fly ashes was not always free of spectral matrix interference (since the characteristic of arsenic is the large difference in the volatility of its compounds, while the oxides are highly volatile, other compounds are very stable, these properties may lead to analyte loss during pyrolisis/ashing and in the first stage of atomization), but through developing the spectroscopic
technique viz. optimized the temperatures of all steps in furnace program, 
investigating the appropriate calibration curve (which has good linearity) and the 
using of matrix modifier gave a good result for total arsenic determination.

A large quantity of research works have been conducted on the behavior of 
As in coal combustion, but it is still far from complete with respect to the 
mechanisms of the partitioning of As during combustion and leaching from fly ash. 
In particular the effect of Ca Content/Ash Content on the leaching characteristics of 
arSENic in fly ash from pulverized coal combustion needs to be further clarified. In 
this work, the leaching characteristics of arsenic (As) in coal fly ash collected from 
two different coal fired power plants (Unit 1 and Unit 2: 600 MWe) have been 
investigated. To determine dominant factors on arsenic leaching from coal fly ash, 
speciation of arsenic during coal combustion was predicted from the perspective of 
thermodynamic equilibrium and leaching test under alkaline condition (pH = 10) at 
solid/liquid ratio of 1:10 was also performed.

The results indicated that, arsenic leaching fractions in unit 1 was higher than 
that of unit 2, it is associated with the amount of reactive calcium oxide (CaO) 
containing in coal fly ash from unit 1 was lower than that from unit 2. As$_2$O$_3$ (gas) 
formed in the boiler reacts with CaO in the fly ash to form calcium arsenate 
Ca$_3$(AsO$_4$)$_2$. Ca$_3$(AsO$_4$)$_2$ is a stable compound formed during combustion, which is 
insoluble in water. Hence the coal fly ash from unit 2 having higher CaO/Ash ratios 
generate more Ca$_3$(AsO$_4$)$_2$ and have lower As leaching fraction than that from unit 1. 
CaO/Ash ratios was a promising index to reduce arsenic leachability from fly ash.
Chapter 1

Literature Review

1.1 Introduction

1.1.1 Coal Utilization

The utilization of coal as fossil fuel in combustion process to generate electricity has been developed for many years in order to perform the better managing regarding to keep strict environmental impact and to save the operational cost. Better knowledge about coal quality may be required to perform the successful in marketing process [1]. Studies of trace elements in coal are needed both for financial and environmental concerns.

The combustion process of coal has the major and minor importance. Generally the majority of it’s combustion is for generating electricity and producing metallurgical coke, while the minor importance is liquefaction and gasification. The suitability of a coal for use in the utilizations can be divided into limitations governed by the organic, and inorganic constituents of coal.

The organic constituents in coal are composed of the elements carbon, hydrogen, oxygen, nitrogen, sulfur and trace amounts of variety of other elements [2] and generally make up the organic fraction of the coal [3]. The industrial properties of the organic fraction of coal are controlled by coal rank. Rank refers to steps in a slow, natural process called coalification during which buried plant matter
changes into an ever denser, drier, more carbon rich and harder material. Coalification is a continuing process involving increases in both temperature and pressure resulting from burial in the earth. The rank of coal is determined by the percentage of fixed carbon, moisture (water), volatile matter, and calorific value in British thermal units (Btu) after the sulfur and mineral-matter content have been subtracted [2].

The inorganic constituents in coal include minerals, mostly silicon, aluminium, iron, sulfur, calcium, and trace elements [4]. The mineral content of coal determines what kind of ash will be produced when it is burned. Generally the inorganic constituents make the utilization of coal limited due to the negative impact on the industrial process or production of environmental pollutants in gases or in solid waste of the power plant. For example, “High” concentrations of chlorine, fluorine, and vanadium in the feed coal may cause corrosion of the combustion equipment [5-8]. High Vanadium coals may cause agglomeration in fluidized bed combustion boilers [9]. A 1 % increase in the concentration of sulphur is thought to increase the coke consumption rate by as much as 32 kg per net ton of hot metal [10] and greatly increase the production of slag. Also, it has long been known that sulphur from coal combustion can cause acid rain [11].

A large quantity of studies have shown that the coal combustion process contribute to the production of trace elements that are toxic to the biosphere, and giving negative health impacts on plants, animals, and humans [12-17]. The concern is that the release of trace elements from coal utilization will result in elemental concentrations exceeding the toxicity threshold of some plants and animals, including humans.
1.1.2 *Fly Ash and trace elements classification*

Coal combustion products predominantly consist of bottom ash, fly ash and flue gas desulfurization residue (FGD) [18]. Ash collected on the down side of the boiler, called bottom ash. Ash that escapes the flue gas control devices and is emitted through the stack, called fly ash. It is called "fly" ash because it is transported from the combustion chamber by exhaust gases. It results from the burning of powdered coal in utility boilers and is carried up and out of the boiler in the flow of flue gases leaving the boiler after the coal is consumed. The fly ash particles are removed from the flue gases using electrostatic precipitators, FGD systems or bag houses and are collected and stored dry for recycling [19].

The ratio between the types of ashes depends on the type of boiler, operating conditions and the efficiency of the flue gas cleaning devices while the emissions of elements into the air depend on the concentration in the coal, the type of boiler, the efficiency of flue gas control devices, the distribution between the types of ashes, and the distribution between the particulate and gaseous phase [20]. A scheme of coal combustion plant can be seen in figure 1.1 below.
A so-called trace element is defined as an element occurring in a very low amount (< 100 ppm). Recently, the topic about trace elements has drawn more interest from scientists because of the great concern for their toxicological on human health and environmental effects.

Based on partition and enrichment behavior of elements [21], three basic classes of trace elements can be defined:

- Class I: Elements approximately equally distributed between the bottom ash and fly ash, or show no significant enrichment or depletion in the bottom ash.
- Class II: Elements enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size.
- Class III: Elements totally emitted in the vapor phase.
Class I elements do not vaporize during combustion and are readily incorporated into the slag. These elements form a melt, which contributes to both fly-ash and slag. The elements involved are partitioned approximately equally between the slag and inlet fly-ash [21].

Class II elements do volatilized, and later condense on and become adsorbed onto the fly ash. Because the slag is quickly removed, Class II elements are not condense on the bottom ash. The Class II elements become concentrated in the inlet fly ash compared to the slag, and in the outlet fly ash compared to the inlet fly ash [21].

Class III elements have a low dew point and tend not to condense anywhere within the power plant. If no flue-gas desulphurization installation are present, virtually all of the Class III elements remain completely in the gas phase and are emitted to the atmosphere [21].

![Vaporization Diagram]

Figure 1.2. Categorization of trace elements based on volatility behavior [22].

<table>
<thead>
<tr>
<th>Boiling PTS, °C</th>
<th>Class I</th>
<th>Class II</th>
<th>Class III</th>
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<tbody>
<tr>
<td>F  -188.1</td>
<td>Hg</td>
<td>Br, Cl</td>
<td>F</td>
</tr>
<tr>
<td>Cl -34.1</td>
<td></td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Se  217</td>
<td>Se</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>SeO₂ 317</td>
<td>Se</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Hg  357</td>
<td>Hg</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>As₂O₃ 465</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>As  613</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>MoO₃ 795</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Zn  907</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Sb₂O₅ 1155</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>B₂O₃ 1800</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>CoO  1800</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Mn  1960</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Cu  2570</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Ni  2730</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Co  2870</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₇ 3000-4000</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>Mo  4660</td>
<td>As₂O₃</td>
<td>Br</td>
<td></td>
</tr>
</tbody>
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1.1.3 Trace elements in fly-ash

Generally, the ash contains the same elements as were present in the coal but they are enriched in the ash by a factor equal to 100/(ash content in %). This factor is called the “coal/ash ratio”. However, the enrichment in the ash also depends on the type of ash and the particular element [20].

The trace elements in fly ash have the trend to deposit on the smaller particle size, due to the greater surface area to volume ratios of fine particles [23]. It means, there is a strong relationship between total particulate emissions from electrostatic precipitators and the emissions of trace elements. Thus highly efficient particulate emission control devices are necessary to control trace element emissions. Unfortunately, the very finest particles may escape even with efficient particle collection devices in place, they are also the most toxic, and are readily inhaled into the lungs of organisms.

1.1.4 Fly-ash Leaching

Fly ash as a byproduct in coal combustion is addressed to be reused or disposed. The fly ash reuse as substitute material for Portland cement, structural fills (usually for road construction), soil stabilization, mineral filler in asphaltic concrete, and mine reclamation has been well recognized [24], but most of the fly ash generated from the power plants is disposed to the landfill. This disposal involve the interaction of the fly-ash particles with weathering and hydrological processes, where due to the rainfall, trace elements that content in fly ash will be eluted to the environment.

The solubility of trace elements into solution will depend on the pH and
redox conditions of leachate [25]. Generally, fly-ash leachate is alkaline in nature, however mobilization of the sulphur on the fly-ash may result in an initial leachate that is slightly acidic. Further, recarbonation (absorbtion of CO₂ from the atmosphere) by alkaline leachates can reduce the overall pH of the leachate to approximately pH 8 [25]. For oxyanions (arsenic, boron, molybdenum, selenium) are most mobile at a pH of about 9 – 11, and cations (cadmium, copper, lead, nickel and zinc) are mobile at pH 4 to 7.

The speciation of some elements is important. Although the arsenate oxyanion is the most stable under oxidizing conditions, at lower redox conditions arsenate may be reduced to the more mobile and more toxic arsenite anion. The arsenite anion is thought to be the most common phase present in leachates [25].

The formation of secondary minerals may also have a profound influence on the elements found in solution. Co-precipitation of selenite with CaCO₃ controls the concentration of that anion in solution under mildly alkaline conditions [25]. Under strongly reducing conditions, insoluble As₂S₃ (orpiment) may form and be incorporated into pyrrhotite or pyrite if sufficient Fe²⁺ is available [39]. Precipitation of Ca₃(ASO₄)₂.6H₂O and Ca₂V₂O₇ has been found to occur as a result of a high concentration of Calcium in solution [26].

1.1.5 Arsenic

Various types of environmentally hazardous substances in raw coal are known to condense on the surface of coal fly ash particles during their formation from coal, depending on their chemical nature and the combustion process. Some of these substances tend to easily elute into the environment [27]. Above all, boron,
fluorine, and arsenic have been recognized as the most troublesome hazardous elements in coal fly ash[27]. Dumping of fly ash in open ash pond causes serious adverse environmental impacts owing to its elevated trace element contents, in particular the arsenic which causes ecological problems[28].

In 1974, Congress passed the Safe Drinking Water Act. This law requires Environmental Protection Agency (EPA) to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water. The MCLG for arsenic is zero. EPA has set this level of protection based on the best available science to prevent potential health problems [29].

In January 2006, the US EPA revised its Maximum Contaminant Level (MCL) for arsenic from 50 μg/L to 10 μg/L (10 ppb or 0.01 mg/L) [29]. The Japanese limit for drinking water is 10 ppb [30] while permission limits for the effluent water quality standard for human protection is 0.1 ppb. The stricter regulation may impact alternatives for disposal and use of arsenic containing wastes and products, including coal fly ash.

Some people who drink water containing arsenic in excess of Environmental Protection Agency/ EPA’s standard over many years could experience skin damage or problems with their circulatory system, and may have an increased risk of getting cancer. Health effects might include thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhea, and liver
effects; cardiovascular, pulmonary, immunological, neurological (e.g., numbness and partial paralysis), reproductive, and endocrine (e.g., diabetes) effects; cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate [29].

Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g. arsenic, selenium, antimony, molybdenum, vanadium, chromium, uranium, and rhenium) in its sensitivity to mobilization at the pH values typically found in groundwaters (pH 6.5-8.5) and under both oxidising and reducing conditions. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5) but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where waters are significantly impacted by industrial pollution [30].

The possible redox states of arsenic and the form of occurrence in alkaline conditions respectively are 0 (As\textsuperscript{0}), +3 (H\textsubscript{2}AsO\textsubscript{3}\textsuperscript{-} and H\textsubscript{3}AsO\textsubscript{4}\textsuperscript{o}) and +5 (AsO\textsubscript{4}\textsuperscript{3-} and HAsO\textsubscript{4}\textsuperscript{2-}). Table 1.3 gives an overview of the total concentration of arsenic in alkaline waste types [31].
Table 1.1 Ranges of total content of oxyanion forming elements expressed in mg/kg in MSWI residues, FFC residues and metallurgical residues.

<table>
<thead>
<tr>
<th></th>
<th>Range (mg/kg)</th>
</tr>
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<tbody>
<tr>
<td>Lithosphere</td>
<td>5</td>
</tr>
<tr>
<td>Soils</td>
<td>1-50</td>
</tr>
<tr>
<td>MSW residues</td>
<td></td>
</tr>
<tr>
<td>Bottom ash</td>
<td>0.1-200</td>
</tr>
<tr>
<td>Fly ash</td>
<td>40-300</td>
</tr>
<tr>
<td>APC residues</td>
<td>20-500</td>
</tr>
<tr>
<td>FFC residues</td>
<td></td>
</tr>
<tr>
<td>Coal bottom ash</td>
<td>0.02-200</td>
</tr>
<tr>
<td>Coal fly ash</td>
<td>2-400</td>
</tr>
<tr>
<td>FGD ash</td>
<td>0.8-50</td>
</tr>
<tr>
<td>Metallurgical slags</td>
<td></td>
</tr>
<tr>
<td>Blast furnace slag</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>Steel slag</td>
<td>5</td>
</tr>
<tr>
<td>Non-ferrous slags</td>
<td>0.2-2</td>
</tr>
</tbody>
</table>

Recent observations and theories on ash particulate formation involving major elements during pulverized coal combustion have invoked two main mechanisms for ash particle formation: (1) evaporation of volatile species and condensation of phases from the vapor, and (2) partial or total fusion and agglomeration of mineral particles. The first mechanism commonly results in the formation of small particles of relatively well defined composition and crystallinity,
such as alkali and alkaline-earth sulfates. The second mechanism results in the formation of partially molten aluminosilicate particles that incorporate varied amounts of basic elements. These latter particles tend to be much larger and are generally at least partially amorphous (glass) upon quenching. In such partially molten deposits, it is likely that AsO$_4^{3-}$ species would be incorporated as a network former in aluminosilicate melts, in much the same way as phosphate anionic species (PO$_4^{3-}$) are incorporated in such melts.

Alkaline-earth orthoarsenates are relatively stable compounds (calcium orthoarsenate melts only at temperatures above 1450°C and magnesium orthoarsenate would be expected to be almost as refractory) and consequently they are prime candidates as condensates from vapor phase arsenic species during combustion, especially of low-rank coals. Under combustion conditions, decomposition of arsenical pyrite or arsenopyrite will be rapid and release arsenic vapor, which should then readily oxidize to vaporous arsenic oxides. In the presence of oxygen, the following solid-vapor reactions will lead to the condensation of calcium orthoarsenate, depending on the oxidation state of arsenic in the vapor phase [32]:

$$\text{As (0): } 3\text{CaO}_{(sol)} + 2\text{As}_{(vap)} + 2.5 \text{O}_2{(gas)} \rightarrow \text{Ca}_3(\text{AsO}_4)_{2(sol)}$$

$$\text{As (III): } 3\text{CaO}_{(sol)} + \text{As}_2\text{O}_3_{(vap)} + \text{O}_2{(gas)} \rightarrow \text{Ca}_3(\text{AsO}_4)_{2(sol)}$$

$$\text{As (V): } 3\text{CaO}_{(sol)} + \text{As}_2\text{O}_5_{(vap)} \rightarrow \text{Ca}_3(\text{AsO}_4)_{2(sol)}$$

It is apparent that these reactions become simpler and involve fewer molecular species with increasing oxidation state of the arsenic. In particular,
regardless of whether the transitory species in the vapor phase is the oxide, As₂O₅, or the anion species, As₂O₅³⁻, no additional oxygen is necessary in reactions involving the As (V) oxidation state as a reactant. Hence, the presence of arsenate in the coal might be expected to facilitate the formation of arsenate compounds during combustion and its capture on particulate matter. Furthermore, arsenate mineral species that are not associated with pyrite or arsenopyrite particles in the coal need not undergo vaporization, but may remain as discrete particles or be assimilated by partial fusion into other particles during combustion [32].

1.2 Methods

1.2.1 Graphite Furnace Atomic Absorption Spectroscopy

Graphite furnace atomic absorption spectrometry (GFAAS) (also known as Electrothermal Atomic Absorption Spectrometry (ETAAS)) [33] is a type of spectrometry that uses a graphite-coated furnace to vaporize the sample.

In atomic absorption (AA) spectrometry, light of a specific wavelength is passed through the atomic vapor of an element of interest, and measurement is made of the attenuation of the intensity of the light as a result of absorption. Quantitative analysis by AA depends on: (1) accurate measurement of the intensity of the light and (2) the assumption that the radiation absorbed is proportional to atomic concentration.

Samples to be analyzed by AA must be vaporized or atomized, typically by using a flame or graphite furnace. The graphite furnace is an electrothermal atomizer system that can produce temperatures as high as 3,000°C [34]. The heated
graphite furnace provides the thermal energy to break chemical bonds within the sample and produce free ground-state atoms. Ground-state atoms then are capable of absorbing energy, in the form of light, and are elevated to an excited state. The amount of light energy absorbed increases as the concentration of the selected element increases. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

GFAA has been used primarily for analysis of low concentrations of metals in samples of water. GFAA can be used to determine concentrations of metals in soil, but the sample preparation for metals in soil is somewhat extensive and may require the use of a mobile laboratory. The more sophisticated GFAAs have a number of lamps and therefore are capable of simultaneous and automatic determinations for more than one element.

Logistical needs include reagents for preparation and analysis of samples, matrix modifiers, a cooling system, and a 220-volt source of electricity. In addition, many analytical components of the GFAA system require significant space, which typically is provided by a mobile laboratory.

GFAAS instruments have the following basic features [34]:

1. a source of light (lamp) that emits resonance line radiation;
2. an atomization chamber (graphite tube) in which the sample is vaporized;
3. a monochromator for selecting only one of the characteristic wavelengths (visible or ultraviolet) of the element of interest;
4. a detector, generally a photomultiplier tube (light detectors that are useful in low-intensity applications), that measures the amount of absorption;
5. a signal processor-computer system (strip chart recorder, digital display, meter, or printer).

The entire analytical procedure of direct solid sampling can be outlined briefly; setting up the spectrometer, separation weighing and introduction of solid test samples for calibration and the unknown laboratory sample to be analyzed, and finally data evaluation.

The analysis of samples in graphite furnace directly from the solid state can be attractive for a number of reasons [35], viz. the sampling, the sample preparation and measurement, the time-consuming decomposition step can be omitted, and the analysis can be carried out without addition of reagents and without any separation and concentration steps; the risks of introducing contaminant and of losing the elements to be determined are thus considerably reduced. Undoubtedly results by solid sample analysis are obtained much faster than those obtained by prior chemical sample preparation. The drawbacks of SS-GFAAS are associated with increasing interferences, difficulties in calibration and sample inhomogenity at the micro levels required [36].

1.2.2 X-Ray Fluorescence (XRF)

X-Ray fluorescence is a good technique in determination the major elemental chemistry of a sample, usually introduced to the instrument as either a fused flat disc or a pressed powder pellet. The technique has been applied for the analysis of both major and trace elements in coal [12, 37]. The detection limit is indicated to be of the order of 10ppm or less [38]. XRF has the advantage of
generally being non-destructive, multi-element, fast and cost effective. It also provides a fairly uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentration. XRF is commonly used to analyse for elements from fluorine to uranium, but more modern equipment can now analyse elements with atomic numbers as low as boron [39].

An incoming X-Ray from an x-ray tube or a radioactive source knocks out an electron from one of the orbitals surrounding the nucleus within an atom of the material. A hole is produced in the orbital, resulting in a high energy, unstable configuration for the atom. To restore equilibrium, an electron from a higher energy, outer orbital falls into the hole. Since this is a lower energy position, the excess energy is emitted in the form of a fluorescent X-Ray. Because each element has a unique set of energy levels, each element produces x-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample.

1.2.3 ICP-AES (Inductively-Coupled Plasma-Atomic Emission Spectrometry)

Analysis by Inductively-Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) requires that the sample be in solution. The solid material had to be dissolved (using strong acids mixture, such as HF/HCL/HNO₃) whilst heated by a microwave oven. Some risk of losing volatile element is apparent. The advantages of ICP-AES are that it can analyse for multiple elements at the same time and has a very low detection limits.

In ICP-AES, the sample is nebulized then transferred to argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. Intensity of the light emitted is measured when the atoms or ions return to lower
levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration [40]. When undergoing ICP analysis, the sample experiences temperatures as high as 10,000°C, where even the most refractory elements are atomized with high efficiency. As a result, detection limits for these elements can be orders of magnitude lower with ICP than with FAAS techniques, typically at the 1-10 parts-per-billion level.

Arsenic is one of element which is difficult to be detected than other elements by conventional pneumatic nebulization with (ICP-AES). One option for improving arsenic detection by ICP-AES is the use of hydride generation. Hydride generation is a technique for determination of arsenic at trace levels. The hydride generation reaction can be nearly 100% efficient. Arsenic is also separated from any non-hydride forming matrix components. It consists of the reaction of some arsenic compounds with sodium tetrahydroborate in acidic medium to produce arsines [41]. The flow chart of arsenic measurement process can be seen in the figure 1.3.

Hydride generation method involves forming hydrides of element such as arsenic as the free metal vapor. The process includes formation of hydrogen free radical and volatile metal hydride.

a. Formation of hydrogen free radical

\[
\text{NaBH}_4 + 3\text{H}_2\text{O} + \text{HCl} \rightarrow \text{H}_3\text{BO}_3 + \text{NaCl} + 8\text{H}^+
\]

b. Formation of the volatile metal hydride (gas)

\[
\text{E}^{m+} + 8\text{H}^+ \rightarrow \text{EH}_n (g) + \text{H}_2 \text{excess}, \text{where E is the volatile hydride forming element. The species EH}_n \text{ is then swept by the nebulizer gas to the ICP-AES for detection. Hydrogen gas (H}_2 \text{) is generated as a by-product of the reaction. This formation of a metal hydride is continuous reaction not a batch process. Being}
\]
volatile, they can more easily be carried by the argon into the plasma [59].

![Flow chart of arsenic measurement](image)

**Fig. 1.3. Flow chart of arsenic measurement.**

### 1.2.4 X-Ray Photoelectron Spectroscopy (XPS, ULVAC-PHI Quantera SXM-GS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is used to determine quantitative atomic composition and chemistry. It is a surface analysis technique with a sampling volume that extends from the surface to a depth of approximately 50-70 Angstroms. Alternatively, XPS can be utilized for sputter depth profiling to characterize thin films by quantifying matrix-level elements as a function of depth. XPS is an elemental analysis technique that is unique in providing chemical state information of the detected elements, such as distinguishing between sulfate and sulfide forms of the element sulfur. The process works by irradiating a sample with...
monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. In this study ULVAC-PHI Quantera SXM-GS was used to measure the chemical form of calcium.

1.2.5 Factsage (Facility for the Analysis of Chemical Thermodynamics)

FactSage [42], was founded over 25 years ago as one of the largest fully integrated database computing systems in chemical thermodynamics in the world, was introduced in 2001 and is the fusion of the FACT-Win/F*A*C*T and ChemSage/SOLGASMIX thermochemical packages. The FactSage package runs on a PC operating under Microsoft Windows and consists of a series of information, database, calculation and manipulation modules that access various pure substances and solution databases. FactSage has several hundred industrial, governmental and academic users in materials science, pyrometallurgy, hydrometallurgy, electrometallurgy, corrosion, glass technology, combustion, ceramics, geology, etc. It is used internationally in graduate and undergraduate teaching and research. Users have access to databases of thermodynamic data for thousands of compounds as well as to evaluated and optimized databases for hundreds of solutions of metals, liquid and solid oxide solutions, mattes, molten and solid salt solutions, aqueous solutions, etc. The FactSage software automatically accesses these databases.

With the various modules one can perform a wide variety of thermochemical calculations and generate tables, graphs and figures of interest to chemical and physical metallurgists, chemical engineers, corrosion engineers, inorganic chemists, geochemists, ceramists, electrochemists, environmentalists, etc.
With FactSage one also can calculate the conditions for multiphase, multicomponent equilibria, with a wide variety of tabular and graphical output modes, under a large range of constraints.

1.3 Objective of the present research

Trace elements in coal fly ash partition between the bottom ash, fly ash, and flue gas during combustion of coal which is a reflection of the volatility of the elements, the element’s mode of occurrence in the coal, collection point and characteristics of the ash.

Coal fly ash as a byproduct in coal combustion is addressed to be reused or disposed. The fly ash reuse as substitute material for Portland cement, structural fills (usually for road construction), soil stabilization, mineral filler in asphaltic concrete, and mine reclamation has been well recognized [24], but most of the fly ash generated from the power plants is disposed to the landfill. This disposal involve the interaction of the fly-ash particles with weathering and hydrological processes, where due to the rainfall, trace elements that content in fly ash will be eluted to the environment.

Arsenic, as one of the most hazardous elements in coal fly ash tends to easily elute into the environment [27]. In January 2006, the US EPA revised its Maximum Contaminant Level (MCL) for arsenic from 50 ppb to 10 ppb [29]. The Japanese limit for drinking water is same with US EPA standard which is 10 ppb [30] while permission limits for the effluent water quality standard for human protection is 0.1 ppb. If the concentration of arsenic over the limit, it can causes several health
problems such as cancer, liver damage, dermatosis, and nervous system disturbances such as polyneuropathy, EEG abnormalities and, in extreme cases, hallucinations, disorientation and agitation [43].

Chapter 2 describes the development of a technique based on Graphite furnace atomic absorption spectrometry (GFAAS) for the direct measurement of arsenic in several coal fly ashes produced from pulverized-coal-fired boilers where the solid samples were directly introduced into the atomizer without preliminary treatment. Emphasis was placed on the optimization of the temperature of the furnace program and the use of chemical modifiers to minimize the potential interference.

The advantages of this technique are good sensitivity with a short analysis time, low cost in comparison with inductively coupled plasma mass spectrometry (ICP-MS) [44], and requires a low sample volume (2–100 μL) [45].

Chapter 3 describes the leaching characteristics of arsenic from fly ashes to be clear effects of the difference in boiler types. The leaching characteristics of arsenic (As) in coal fly ash were carried out from two different coal fired power plants (Unit 1 and Unit 2: 600 MWe). To determine dominant factors on arsenic leaching from coal fly ash, speciation of arsenic during coal combustion was predicted from the perspective of thermodynamic equilibrium and leaching test under alkaline condition (pH = 10) at solid/liquid ratio of 1:10.

Arsenic leaching fractions is associated with the amount of reactive calcium oxide (CaO) containing in coal fly ash. As$_2$O$_3$ (gas) formed in the boiler reacts with CaO in the fly ash to form calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$. $\text{Ca}_3(\text{AsO}_4)_2$ is a stable compound formed during combustion, which is insoluble in water. The coal fly ash
having higher \( \text{CaO}/\text{Ash} \) ratios generate more \( \text{Ca}_3(\text{AsO}_4)_2 \) and have lower As leaching fraction. \( \text{CaO}/\text{Ash} \) ratios was a promising index to reduce arsenic leachability from fly ash.

### 1.4 References


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Chapter 2

Direct Quantitative Analysis of Arsenic in Coal Fly Ash

2.1 Introduction

Coal combustion byproducts predominantly consist of fly ash, bottom ash, and boiler slag [1]. The environmental hazards associated with coal combustion byproducts are of concern with respect to potential health effects [2-4]. Among the trace elements in coal fly ashes, arsenic, cadmium, copper, mercury, and lead are the greatest concern as environmental hazards [5].

Arsenic, one of the most highly toxic chemicals, is a semi-metallic element commonly found as arsenide and in arsenate compounds. It is an odorless, tasteless, and notoriously poisonous metalloid with many allotropic forms that is dangerous for the environment [6]. Long-term exposure of arsenic contaminated materials to water may lead to various diseases such as conjunctivitis, hyperkeratosis, hyperpigmentation, cardiovascular diseases, disturbance in the peripheral vascular and nervous systems, skin cancer, gangrene, leucomelonosis, non-pitting swelling, hepatomegaly, and splenomegaly [7].

In Japanese coal-fired power plant sites, the ash storage area usually holds seawater and rainwater (excess water); therefore, some elements in the fly ash, including arsenic, are leached out into the excess water. If the arsenic concentration in the excess water exceeds the environmental limit (0.1 mg L$^{-1}$ in Japan), the
excess water cannot be drained into the sea. This situation is serious, because ash storage must be discontinued.

Given these concerns, it is important to be able to rapidly determine the arsenic content in the fly ash at these sites. Graphite furnace atomic absorption spectrometry (GFAAS) is one of the most reliable and powerful analytical techniques for the determination of trace elements in water, soil, clinical, and biological samples [8,9]. It offers good sensitivity with a short analysis time, low cost in comparison with inductively coupled plasma mass spectrometry (ICP-MS) [8], and requires a low sample volume (2–100 μL) [9].

However, most of the reported methods for arsenic determination based on GFAAS require preconcentration, separation [10-13], and dilution steps [10,13-15]. These steps are disadvantageous with respect to cost and are also time-consuming [16]. Therefore, it is necessary to establish a simpler procedure for the accurate determination of arsenic in solids using GFAAS. However, there have been only limited studies on the determination of arsenic using a direct sampling system with solid samples [15,17,18].

Therefore, the present paper focuses on the development of a technique based on GFAAS for the direct measurement of arsenic in several coal fly ashes produced from pulverized-coal-fired boilers. Emphasis was placed on the optimization of the temperature of the furnace program and the use of chemical modifiers to minimize the potential interference.
2.2 Experimental

2.2.1 Instrumentation

A single-beam atomic absorption spectrometer (model novAA400, Analytik Jena) equipped with a monochromator was used for the measurements. This instrument has a Czerny-Turner mount with a plain holographic grating system (1800 lines/mm) that covers the wavelength range from 185 to 900 nm. The spectrometer combines a new transverse–heated graphite furnace atomizer with high-aperture optics and fast background compensation based on an optimized deuterium hollow cathode lamp. The optics system provides efficient background compensation by means of the transillumination of equal absorption volumes for both measurement and correction. Solid and liquid sample introduction modes are possible with a quick change and realignment of the system. For solid samples, an automatic sample weighing system (Sartorius microbalance) and pyrolytically coated graphite tubes with platform boats were used as the sample carriers.

2.2.2 Standards and Reagents

2.2.2.1 Construction of the Calibration Curve

Standard samples for the calibration of solid samples (coal fly ash) were prepared from the certified reference material NIST 1633b (Arsenic conc. = 136.2 ± 2.6 mg kg$^{-1}$). The NIST 1633b material was diluted with α-Alumina (α-Al$_2$O$_3$) powder to prepare samples of different concentrations. A matrix modifier was prepared by dissolving palladium nitrate (Pd(NO$_3$)$_2$, 100 ppm) in 40% HNO$_3$ and distilled water.
Standard samples for the calibration of liquid samples were prepared from reference solutions of As$_2$O$_3$ (Merck, pro-analysis). The standard arsenic solutions were prepared in 60% HNO$_3$ and distilled water. The matrix modifier was composed of Pd(NO$_3$)$_2$ (100 ppm) in 3.75% HNO$_3$ and distilled water.

2.2.2.2 Coal Fly Ash Samples

Twenty-one objective samples of coal fly ashes were collected from the electrostatic precipitator in a pulverized-coal-fired power generation process (1000 MWe) using raw coal imported from distinct Indonesian coal mines (Kalimantan Island, Indonesia). To analyze the arsenic concentration in these coal fly ashes, the samples, with added Pd(NO$_3$)$_2$ (100 ppm), were directly introduced into the GFAAS without any pretreatment (known as direct solid sampling).

To complete the validation of the method, the calculation of the mass balance for arsenic was required. This calculation involved the determination of the arsenic concentration in the raw coal samples.

2.2.2.3 Pretreatment of Raw Coal Samples.

The raw coal samples are the source fuel for the fly ash samples described above. The arsenic concentration in the raw coal samples must be analyzed to validate the accuracy of the determination of the arsenic concentration in the fly ashes. However, because the arsenic concentration in the raw coal samples was too high for GFAAS detection, a dilution process was necessary.

The raw coal samples were prepared through wet destruction procedures using several concentrated acids, followed by heating (200 °C), cooling, and
filtering processes. The concentrated acids included 60% HNO₃, 60% H₂SO₄, 3.5 % HCl, and 30% HF. Other reagents used for the treatment included 2.5 % KMnO₄ and 5%FeCl₃. Following the wet destruction, the final raw coal samples were obtained in the liquid phase. Five raw coal samples served as the source of the twenty-one coal fly ash samples analyzed in the study.

2.2.3 Measurement Conditions

The optical parameters used for the direct analysis of arsenic in coal fly ash (solid sampling system) and in the raw coal samples (liquid sampling system) were as follows: wavelength, 193.7 nm; slit width, 1.2 nm; lamp intensity: 6.0 mA. Quantification was carried out by the analysis of the peak area, and pyrolytically coated graphite tubes with platform boats were used for sample introduction.

The optimization sequence for the furnace program used to analyze the different concentrations of the selected certified reference material NIST 1633b is presented in Table 2.1, and the details of the optimum furnace program developed for the analysis of all of the coal fly ash samples is presented in Table 2.2.

With respect to the liquid samples, the optimization sequence for the furnace program used to analyze the reference solutions containing different concentrations of As₂O₃ in NaOH·HCl are listed in Table 2.3, and the details of the optimum furnace program developed for the analysis of all of the raw coal ash samples is presented in Table 2.4.

The weight of the fly ash samples ranged from approximately 0.5 to 2 mg and was determined using a microbalance. The appropriate amount of the raw coal sample (as a liquid) was determined on the basis of the analyte sensitivity and
ranged from approximately 10 to 20 μL. After weighing a sample, the appropriate matrix modifier solution containing palladium nitrate was injected into the sample boat, and the boat was introduced into the furnace. The furnace was then heated according to the specified furnace program and settings for the atomic absorption measurement device.
Table 2.1 Optimization of the furnace program for the analysis of coal fly ash (solid sampling system).

<table>
<thead>
<tr>
<th>Integration time (s)</th>
<th>Ashing temperature (s)</th>
<th>Ashing rate (°C s⁻¹)</th>
<th>Hold time (s)</th>
<th>Ar gas flow rate L min⁻¹</th>
<th>Atomizer temperature (°C)</th>
<th>Atomizer rate (°C/s)</th>
<th>Hold time (s)</th>
<th>Ar gas flow rate L min⁻¹</th>
<th>Correlation Coefficients</th>
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<td>600</td>
<td>100</td>
<td>20</td>
<td>Max</td>
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<td>1000</td>
<td>5</td>
<td>mid</td>
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</tr>
<tr>
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<td>100</td>
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<td>Max</td>
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<td>1000</td>
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<td>Max</td>
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<td>5</td>
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<td>20</td>
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<tr>
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<td>500</td>
<td>7</td>
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<tr>
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<td>100</td>
<td>20</td>
<td>Mid</td>
<td>2150</td>
<td>500</td>
<td>7</td>
<td>mid</td>
<td>0.9349</td>
</tr>
</tbody>
</table>

*Coefficients: min: 0.1 L min⁻¹, mid: 1.0 L min⁻¹, max: 2.0 L min⁻¹*
Table 2.2 Optimized furnace program for the analysis of coal fly ash (solid sampling system).

<table>
<thead>
<tr>
<th>Step</th>
<th>Parameters</th>
<th>Ar gas</th>
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</thead>
<tbody>
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<td>Ashing</td>
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<td>100</td>
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<td>Ashing</td>
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<td>100</td>
</tr>
<tr>
<td>Ashing</td>
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<td>100</td>
</tr>
<tr>
<td>Autozero (AZ)</td>
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</tr>
<tr>
<td>Atomization</td>
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<td>500</td>
</tr>
<tr>
<td>Cleaning</td>
<td>2600</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 2.3 Optimization of the furnace program for the analysis of raw coal (liquid sampling system).

<table>
<thead>
<tr>
<th>Integration</th>
<th>Pyrolysis</th>
<th>Rate</th>
<th>Hold time</th>
<th>Ar gas</th>
<th>Atomizer</th>
<th>Rate</th>
<th>Hold time</th>
<th>Ar gas</th>
<th>Correlation</th>
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</thead>
<tbody>
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<td>temperature (s)</td>
<td>(°C s⁻¹)</td>
<td>(s)</td>
<td>temperature (°C)</td>
<td>(°C s⁻¹)</td>
<td>(s)</td>
<td>L min⁻¹</td>
<td>Coefficients</td>
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<tr>
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<td>30</td>
<td>max</td>
<td>2500</td>
<td>1000</td>
<td>6</td>
<td>stop</td>
<td>0.9960</td>
</tr>
</tbody>
</table>

mid: 1.0 L min⁻¹, max: 2.0 L min⁻¹
Table 2.4 Optimized furnace program for the analysis of raw coal (liquid sampling system).

<table>
<thead>
<tr>
<th>Step</th>
<th>Parameters</th>
<th>Ar gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Rate (°C s⁻¹)</td>
</tr>
<tr>
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</tr>
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<td>Drying</td>
<td>120</td>
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</tr>
<tr>
<td>Pyrolysis</td>
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<td>100</td>
</tr>
<tr>
<td>Autozero (AZ)</td>
<td>1500</td>
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</tr>
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<td>Atomization</td>
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</tr>
<tr>
<td>Cleaning</td>
<td>2600</td>
<td>1000</td>
</tr>
</tbody>
</table>
2.3 Results and Discussion

2.3.1 Optimization of Instrumental Parameters for Solid and Liquid Sample

Introduction

There are two wavelengths available for arsenic elemental analysis: 193.7 nm and 197.2 nm. The second most sensitive wavelength for arsenic was selected because of the relatively high arsenic content in the coal fly ash and the certified reference material as determined during the analysis performed using the atomic absorption spectrometry device.

At 193.7 nm, the sample was completely atomized (100% based on the instrument sensitivity), but with high interference, while at 197.2 nm, the sample was only partly atomized (53%) with low interference. To achieve optimum results, analysis at 193.7 nm was selected to ensure that a relatively large quantity of arsenic was available for detection. High interference is associated with the characteristic of arsenic, which has the large difference in the volatility of its compounds, where the oxides are highly volatile, and other compounds are very stable. These properties may lead to analyte loss during pyrolysis and even in the first stage of atomization which made some compounds possible to evaporate together with other element; therefore, the background signals from other elements in the coal and fly ash increased [19]. To overcome this problem, a chemical modifier (palladium nitrate) was added to reach satisfactory stabilization of arsenic at high temperatures and to reduce the background signals [20]. When the same experiment was repeated, the background wavelengths were not selected, leading to a better signal-to-noise ratio.
While this approach is not specific to a particular coal sample, it can be applied in general to all samples.

The lamp slit makes it possible to adjust the light intensity, which is produced using a hollow cathode lamp. With a high slit, the intensity is high, and with a low slit, the intensity is low.

The integration time is the length of time during which the atomized sample is in contact with the light passing through it. The integration time for the liquid and solid samples was different because of the difference in properties of the two types of samples.

2.3.2 Development of a Direct Quantitative Analysis Method

To ensure the quality of the analytical results, all of the parameters of each step in the furnace program were optimized, and appropriate calibration graphs were obtained.

The optimization efforts were focused on the pyrolysis/ashing and atomizing steps. The optimum pyrolysis temperature is the maximum temperature at which no losses of the analyte occur, and maximum analyte absorbance and minimum background noise are achieved during atomization. The optimum atomization temperature is the minimum temperature at which a complete and fast evaporation of the analyte is achieved and a reproducible signal (in terms of height and shape of the peak) is recorded.

For the coal fly ash samples, the experiments was carried out using the optimized furnace program shown in Table 2. The optimization of the furnace program was focused on the ashing and atomization steps. Two previous drying
steps were carried out to achieve the correct dryness so that the matrix modifier solvent (distilled water) did not cause splattering. For dry ashing, a high temperature between 500 and 1200°C was used to vaporize any remaining water and other volatile materials and convert any organic substances in the presence of the oxygen in the air to CO₂, H₂O, and N₂ [21].

For each step, the hold time and flow of inert argon gas were studied. In the ashing step, a maximum flow of the inert gas was chosen because it was necessary for the decomposition of the sample matrix to gaseous products. For the atomization step, a temperature of 2150°C was used on the basis of the need to evaporate arsenic, maintain a low background signal that did not disturb the measurement, and achieve a good level of sensitivity for the signal peak of the analyte. For the liquid sampling system (raw coal sample), the experiments was carried out using the optimized furnace program shown in Table 4. The optimization of this furnace program was also focused on the pyrolysis and atomization steps. Drying steps were again carried out to achieve the correct dryness so that the solvent of the matrix modifier (distilled water) did not cause splattering. For the dry pyrolysis procedure, a high temperature 1500°C was used to vaporize the remaining water and other volatile materials and to convert any organic substances in the presence of the oxygen in air to CO₂, H₂O, and N₂. For each step, the hold time and inert (argon) gas flow rate were studied. In the pyrolysis step, the maximum flow of inert gas was again chosen because it was necessary for the decomposition of the sample matrix to gaseous products. For the atomization step, a temperature of 2500°C was used in this case to achieve a low background signal that did not disturb the measurement and a good level of sensitivity for the signal.
peak of the analyte.

2.3.3 Establishment of the Quality Parameters for Solid and Liquid Sample

Introduction

A calibration curve was constructed by plotting the average peak area against the concentration, and the regression equation was computed. The total absorbance and background signals were recorded during the atomization step of the furnace program when arsenic was evaporated and split from molecules into atoms. The instrument recorded the absorption generated by each given concentration.

For the solid samples, the linearity was measured by analyzing four different concentrations (136.2, 68.1, 34.05, 17.02, and 0 mg kg\(^{-1}\)) of the certified reference material NIST 1633b. The correlation coefficient \((r)\) obtained from the analysis was 0.9699 (Figure 2.1). For the liquid samples, the linearity was measured by analyzing four different concentrations (10, 2, 1, 0.5, and 0 mg L\(^{-1}\)) of reference solutions of \(\text{As}_2\text{O}_3\) in NaOH-HCl. The correlation coefficient \((r)\) obtained from this analysis was 0.9980 (Figure 2.2).
Fig. 2.1 Calibration for solid sample determination by GFAAS.

Fig. 2.2 Calibration for liquid sample determination by GFAAS.
Table 2.5 Arsenic concentration (mg kg$^{-1}$).

<table>
<thead>
<tr>
<th>Samples Code</th>
<th>As content Raw Coal (mg L$^{-1}$) *</th>
<th>Fly Ash (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FA EP 1</td>
</tr>
<tr>
<td>E</td>
<td>1.58</td>
<td>9.34</td>
</tr>
<tr>
<td>F****</td>
<td>1.37</td>
<td>10.55</td>
</tr>
<tr>
<td>G****</td>
<td></td>
<td>42.94</td>
</tr>
<tr>
<td>H****</td>
<td>4.2</td>
<td>9.22</td>
</tr>
<tr>
<td>J****</td>
<td></td>
<td>40.85</td>
</tr>
<tr>
<td>J</td>
<td>2.65</td>
<td>18.57</td>
</tr>
<tr>
<td>K</td>
<td>1.34</td>
<td>10.96</td>
</tr>
</tbody>
</table>

*Five raw coal samples.
**Twenty-one fly ash samples.
***F and G were the same raw coal samples.
****H and I were the same raw coal samples.

2.3.4 Quantity of Arsenic in the Coal Fly Ash Samples

The optimized furnace program allowed the determination of arsenic in the coal fly ash and raw coal samples. The obtained results for the analysis of the 21 fly ash and 5 raw coal samples can be seen in Table 2.5.

The arsenic concentration in the EP 3 samples tended to be greater than that in the EP 2 samples, and the arsenic concentration in the EP 2 samples tended to be greater than that in the EP 1 samples. This trend can be explained by the differences in the particle sizes of the samples; the particle size increased in the order EP 3 < EP 2 < EP 1. The surface area of the smaller particle sizes enables a higher absorption of arsenic in the samples.

The data for the raw coal samples were used to validate the accuracy of the method. The mass balance (distribution rate of arsenic in the coal fly ash) was calculated by the following formula:
\[ P_{As} = \frac{A_{S_{ash}}}{A_{S_0}} \times 100, \quad (1) \]

\[ A_{S_0}' = \frac{A_{S_0}}{A_{sh}} \times 100, \quad (2) \]

where \( P_{As} \) is the distribution fraction of arsenic [%], \( A_{S_{ash}} \) is the average arsenic concentration in the fly ash (EP1, 2, 3) [mg kg\(^{-1}\)-coal, dry basis], \( A_{S_0} \) is the arsenic concentration in the raw coal [mg kg\(^{-1}\)-coal, dry basis], \( A_{S_0}' \) is the arsenic concentration in the raw coal on an ash basis [mg kg\(^{-1}\)-coal, dry basis], and \( A_{sh} \) is the ash content in the raw coal [%, dry basis].

The results for the mass balance values for each raw coal sample (E, F, G, H, I, J, and K) are shown in Table 2.6.

Table 2.6 Mass balance data for arsenic (%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass balance (%) of As</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>113.2</td>
</tr>
<tr>
<td>F</td>
<td>112.3</td>
</tr>
<tr>
<td>G</td>
<td>113.3</td>
</tr>
<tr>
<td>H</td>
<td>110.7</td>
</tr>
<tr>
<td>I</td>
<td>101.9</td>
</tr>
<tr>
<td>J</td>
<td>101.8</td>
</tr>
<tr>
<td>K</td>
<td>119.0</td>
</tr>
</tbody>
</table>

2.4 Conclusion

Based upon the obtained results, we conclude that the direct quantitative analysis of arsenic in solid samples (coal fly ash) is possible using the developed graphite furnace atomic absorption spectroscopy (GF-AAS) method. The determined validation parameters for the developed method are in the commonly
acceptable range for this type of analysis, and the good percentages for the mass
balance indicate the accuracy of the method. Hence, the proposed method is a
simple, accurate, rapid technique that can be employed to routinely determined the
amount of arsenic in coal fly ash.

2.5 Acknowledgments

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absorption spectrometer.

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Chapter 3

Arsenic Leachability and Speciation in Flyashes from Coal Fired Power Plants

3.1 Introduction

Coal as a kind of fossil fuel contains toxic trace elements. The major importance of coal combustion to generate electricity has lead the major sources of environmental pollution due to the discharge of coal combustion products the environment. After burning in boiler, coals produce bottom ash, fly ash and flue gas [1], however most amount of trace elements in coal are distributed in fly ash.

Fly ash as a byproduct in coal combustion is addressed to be reused or disposed. The fly ash reuse as substitute material for Portland cement, structural fills (usually for road construction), soil stabilization, mineral filler in asphaltic concrete, and mine reclamation has been well recognized [2], but most of the fly ash generated from the power plants is disposed to the landfill. This disposal involve the interaction of the fly-ash particles with weathering and hydrological processes, where due to the rainfall, trace elements which contained in fly ash will be eluted to the environment [3].

Among the trace elements in fly ashes, arsenic, cadmium, copper, mercury, and lead are the greatest concern as environmental hazards [4]. Arsenic, one of the
most highly toxic chemicals, is a semi-metallic element commonly found as arsenite and in arsenate compounds. In Japanese coal-fired power plant sites, the ash storage area usually holds seawater and rainwater (excess water); therefore, arsenic and some elements in fly ash, are leached out into the excess water. If the arsenic concentration in the excess water exceeds the environmental limit (0.1 mg L\(^{-1}\) in Japan), the excess water cannot be drained into the sea. This situation is serious, because ash storage must be discontinued. Given these concerns, it is important to find leachability of arsenic from the flyashes for various coal types for the development of advanced control technology to reduce the negative impacts of this element on the environment.

The mode of occurrence of arsenic in a raw coal have been summarized in some review papers [5]. In general, the majority of As in a coal exists as pyritic, organic and arsenate. Arsenic partitioning is dependent on many factors such as the initial concentration of As in a coal, combustion conditions (types of coal fired boilers) and ash properties [6, 7]. Arsenic in raw coal was released as vapor at high temperature during combustion, and generated gaseous arsenic oxide reacted with calcium oxide on fly ash. Consequently, Ca\(_3\)(AsO\(_4\))\(_2\) is formed on fly ash surface, which is the most thermodynamically stable calcium–arsenic compound under conditions of coal fired boilers [8].

Although many works have been conducted on the behavior of As in coal combustion [5, 9-11], but it is still far from complete with respect to the mechanisms of the partitioning of As during combustion and leaching from fly ash. In particular the effect of Ca/Ash Content on the leaching characteristics of arsenic in fly ash from pulverized coal combustion needs to be further clarified.
The purpose of this present study is to investigate the leachability of As for various coal flyashes collected from two different coal fired power plants (Unit 1 and Unit 2: 600 MWe). Emphasis was placed on the the effects of Ca and boiler types on As leachability.

3.2 Experimental

3.2.1 Description of coal fired power plants and properties of coal and fly ash

Six fly ash samples were carefully collected from each coal fired power plants (Unit 1 and Unit 2: 600 MWe). Fly ash F and G, and fly ash H and I came from the same coal between unit 1 and 2 of coal fired power plants. Table 3.1 lists coal properties and ash composition.

Fig. 3.1 depicts the process flow of the plants, ash collection locations, and typical gas temperatures between the boiler exit and the low temperature electrostatic precipitator (ESP). Each unit (boiler) is connected to a three-field electrostatic precipitator (chamber #1, #2, and #3) whose removal efficiency is approximately 85% in chamber 1, 10% in chamber 2 and 5% in chamber 3. To prevent contamination of samples, after enough time from coal switching, the ash sampling was began at each chamber (#1, #2, and #3) of ESP.

The difference between unit 1 and unit 2 is placed on the availability of DeNox (SCR) system technology, only in unit 2 has a DeNOx (SCR) system. While, for controlling DeNox in unit 1, low combustion temperature is applied in order to inhibit the formation of thermal NOx. In another words, it could be said that the temperature of boiler in unit 1 is lower than that in unit 2.
Fig. 3.1 Process flow of the coal fired power plants and ash collection points.

Table 3.1 Properties of raw coals and flyashes collected from #1 chamber of ESPs.

<table>
<thead>
<tr>
<th>Power Station</th>
<th>Key</th>
<th>Raw coal (on dry basis)</th>
<th>Fly ashes (on dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C (wt%)</td>
<td>Ash (wt%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(wt%)</td>
<td>(wt%)</td>
</tr>
<tr>
<td>Unit 1</td>
<td>E</td>
<td>67.91</td>
<td>14.28</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>71.52</td>
<td>13.29</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>68.32</td>
<td>10.37</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>69.59</td>
<td>9.66</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>70.93</td>
<td>13.04</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>76.48</td>
<td>9.54</td>
</tr>
<tr>
<td>Unit 2</td>
<td>G</td>
<td>71.52</td>
<td>13.29</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>68.32</td>
<td>10.37</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>67.92</td>
<td>13.86</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>73.08</td>
<td>10.33</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>72.99</td>
<td>9.70</td>
</tr>
<tr>
<td></td>
<td>Q</td>
<td>74.02</td>
<td>9.54</td>
</tr>
</tbody>
</table>

3.2.2 Characterization of sample

Major elemental compositions of ash were quantified using Sequential X-ray Fluorescence Spectrometer (XRF-1800, Shimadzu).

The concentration of arsenic in fly ash was analyzed using HGICP-AES with the assistance of acid digestion. Sample digestion was carried out in a microwave oven (MDS 2000) fitted with an exhaust unit and a microprocessor to control the power and thermal program. Briefly, about 0.1 g ash sample was
weighted and moved into PTFE bottle. An acid mixture capable of completely digesting ash sample were 2 ml of HNO₃ 65%, 4 ml of HF 50% and 5 ml of saturated H₃BO₃. Boric acid was added after dissolution to neutralize the corrosive hydrofluoric. After cooling, the residue was dissolved and diluted to 50 mL using HCl 10% and KI 20%.

The concentration of arsenic in raw coal was analyzed using HGICP-AES with the assistance of wet destruction procedures using several concentrated acids. Prior to analysis coal sample was first grinded, about 0.5 g raw coal sample was weighted and moved into Erlenmeyer, involve heating (200ºC), cooling and filtering procedures. Concentrated acids which is used were HNO₃ 60%, H₂SO₄ 60%, HCl 10%, HF 30 %, and another reagents which is used were KMnO₄ 2.5 % and FeCl₃ 5%.

Speciation of Ca in fly ash samples was quantified using X-Ray Photoelectron Spectroscopy (XPS, ULVAC-PHI Quantera SXM-GS).

3.2.3 Leaching tests

To simulate pH of the excess water, a buffer solution adjusted pH = 10 was prepared as a leaching solvent. In brief, the ash sample of 1 g was mixed with the leaching solvent (10 mL) and the slurry was shaken (200 rpm) for 30 minutes at room temperature. Filtration was performed to separate the fly ash using a filter (Advantec No.2). The concentration of arsenic in filtrate was measured by HGICP-AES.
3.2.4 Thermodynamic equilibrium calculation

To predict the speciation of arsenic during coal combustion theoretically, we employed the thermodynamic equilibrium software, FactSage 6.0, where the databases used were ELEM, FACT and Fact53 and the calculation input was the elemental compositions of ash.

3.3 Results and Discussion

3.3.1 Arsenic partitioning

In coal combustion systems, the partitioning of arsenic between the vapor and solid phases is determined by the interaction of arsenic vapors with fly ash compounds under post-combustion conditions. Previous studies shown that trace elements can be classified into three broad groups according to their partitioning during coal combustion [12], arsenic has classified as Group II elements which are not incorporated into the bottom ash but it vaporized during combustion and chemically condensed onto particle surfaces in the flue gas stream during cooling process [13].

To compare arsenic partitioning in the unit 1 and 2, relation between modified arsenic concentration in the raw coals, \[ \frac{\text{As}_0}{\text{Ash}^{0.65}} \], and arsenic concentration in flyashes, \( \text{As}_{FA} \), for the unit 1 and 2 was investigated. \( \text{As}_0 \) and \( \text{Ash} \) are As concentration \([\text{mg/kg-coal, db}]\) and ash content \([\%\text{, db}]\) in the raw coals, respectively. As shown in Fig. 3.2, arsenic shows similar partitioning behavior between unit 1 and 2 of coal fired power plants. From the relationship obtained, arsenic concentration in flyashes, \( \text{As}_{FA} \), can be accurately estimated by the parameter \[ \frac{\text{As}_0}{\text{Ash}^{0.65}} \].
3.3.2 Arsenic leaching

According to the above results, all of arsenic presents in raw coals for unit 1 and 2 are distributed to fly ash, hence clarifying the leaching characteristics of arsenic in fly ash is important.

To clarify the leaching characteristics of arsenic, the leaching test was conducted. Fig. 3.3 shows the leaching fraction of arsenic, $L_{As}$, in the fly ash collected from two coal fired power plants (Unit 1 and Unit 2).
Fig. 3.3 Variation in As leaching fraction for various fly ash samples in unit 1 and 2.

The leaching fraction refers to the mass of arsenic in leachate to its mass in fly ash in percent. Clearly, the $L_{As}$ in the fly ash from combustion of coal in unit 1, range of 3–30%, is much higher than that in unit 2, range of 2–8%. Particularly, for the fly ash F and G, which derived from the same coal between unit 1 and 2 of coal fired power plants, has different $L_{As}$ value. $L_{As}$ in fly ash F (21%) is quite higher than that in fly ash G (7%), indicating that the leaching of arsenic from fly ash is affected by boiler types.

### 3.3.3 Dominant factors on arsenic leaching

To understand the dominant factor on arsenic leaching, the possible form of arsenic functional form during cooling process of the power plants need to be clarified. Thermodynamic equilibrium calculation was conducted to predict the formation of arsenic functional form during the coal combustion and cooling process of the power plants. As demonstrated in Fig. 3.4, indicates that calcium is the most influential factor on arsenic transformation. As can be seen in Fig. 3.4, during the combustion process, any arsenic in the feed coal is vaporized at
temperatures above 1400 °C, and at these temperatures is present in the gas phase as arsenic trioxide (As$_2$O$_3$). During the cooling process, at temperature below 800 °C, the flue gases cool and As$_2$O$_3$ formed in the boiler reacts with ash carried contains CaO in the flue gases to form stable compounds calcium arsenate Ca$_3$(AsO$_4$)$_2$.

Fig. 3.4 Prediction of As functional form during the cooling process of the power plants.

Arsenic preferentially combines with calcium to form Ca-As compound.

From the above result, it is clear that calcium content has a significant effect on arsenic transformation. To better know the main species of calcium in both units, speciation of calcium in fly ash samples was investigated. Chemical form of calcium was identified from fly ash F, G, H, I using X-Ray Photoelectron Spectroscopy (XPS, ULVAC-PHI Quantera SXM-GS). Those four fly ash samples were chosen to be identified by reason of they came from the same coal between unit 1 and 2 of coal fired power plants. As shown in Fig. 3.5 and 3.6, the main species of calcium is CaCO$_3$, followed by small amount of CaSO$_4$.

As can be seen in Fig. 3.5, 3.6, and 3.7, Fly ash F and H from unit 1 has higher
amount of CaSO₄ than that of fly ash Fly ash G and I from unit 2. High amount of CaSO₄ can be considered as reducing the amount of Ca₃(AsO₄)₂ as the main chemical species of arsenic in the fly ash, and in turn can be considered resulting more arsenic leaching.

The possible explanation for sulfation and arsenate reaction of the above result is CaO derived from the decomposition of CaCO₃ during coal combustion, as shown in Eq. (1) [14] reacts with SO₂ through Eq. (2) to form CaSO₄ [14, 15] and with arsenic vapor through Eq. (3) to form Ca₃(AsO₄)₂ [15].

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \quad \text{(Decomposition)} \\
\text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 & \rightarrow \text{CaSO}_4 \quad \text{(Sulfation)} \\
3\text{CaO} + \text{As}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{Ca}_3(\text{AsO}_4)_2 \quad \text{(Arsenate reaction)}
\end{align*}
\]

As reported by Wang et al [14], that the value of calcium conversion (\(\eta\)) of CaCO₃ to the sulfation of CaSO₄ is affected by temperature in air combustion, where the value of \(\eta\) is higher at lower temperature (500–1100) °C and lower at higher temperature (1200 °C). This is relevant with the experimental results as shown in Fig. 3.5, 3.6 and 3.7 that the amount of sulfation products (CaSO₄) is higher for fly ash F and H which derived from low combustion temperature (unit 1) than that of fly ash G and I which derived from high combustion temperature (unit 2).

As also shown in Fig. 3.5 and 3.6, another information that we may point out here is that, it seems that the fly ashes (G and I) produced from a boiler (unit 2) applying DeNOx (SCR) system which has high combustion temperature contain much volatile calcium (CaCO₃) than that in the fly ashes (F and H) produced from a
boiler (unit 1) without applying DeNOx system which has low combustion temperature. In turn, that calcium (CaCO₃) will decompose to CaO and reacts with arsenic trioxide (As₂O₃) to form stable compound of Ca₃(AsO₄)₂. Hence, Fly ash G and I from unit 2 (shown in Fig. 3.5 and 3.6), have high content of CaCO₃, decomposed and derived higher CaO than F and H from unit 1 (Fig. 3.5 and 3.6), lead to form more Ca₃(AsO₄)₂, and in turn can be considered resulting lower arsenic leaching.

3.3.4 Effects of boiler types on arsenic leaching

We can explain the effect of boiler types on arsenic leaching from the above discussion.

To further clarify the effect of boiler types (unit 1 and 2), variation in $L_{As}$ for all fly ash samples and CaO content in raw coal as a function of $CaO/Ash \times 100$, where $CaO$ is ash composition in the raw coal, was investigated. As shown in Fig. 3.8, $L_{As}$ in fly ash decreased with the increase of $CaO/Ash$ ratios. $L_{As}$ increased under the $CaO/Ash$ of 50 in both units. $CaO/Ash \times 100$ of fly ash F and G is same, 6.28, shows that both fly ashes which derived from the same coal between unit 1 and 2 of coal fired power plants have high $L_{As}$ value. However, $L_{As}$ of fly ash F (21%) from unit 1 is much higher than that in fly ash G (7%) from unit 2. This trend can be explained by the difference of CaO content in fly ash between unit 1 and 2. To confirm such a hypothesis, CaO content in fly ash was also determined. As shown in Fig. 3.9, CaO content in fly ash F from unit 1 is lower than that in fly ash G from unit 2; therefore CaO/Ash ratio of the unit 1 was lower than that of unit 2 as shown in Fig. 3.8. It is supposed that high $L_{As}$ of the fly ashes in unit 1 is owing to the loss of calcium
during combustion. Abundant of CaO/Ash ratio in fly ashes of unit 2 preferentially associates with arsenic to form stable compound, Ca$_3$(AsO$_4$)$_2$, and thus reduce the leaching of arsenic. This observation clearly indicates that CaO in coal is favorable for reducing the leachability of arsenic. It is also relevant with the previous investigation by Jiao F. et al [16].

Fig. 3.5 XPS of fly ash F from unit 1 (a) and G from unit 2 (b). The major calcium-bearing compounds are CaCO$_3$, followed by small amount of CaSO$_4$.

Fig. 3.6 XPS of fly ash H from unit 1 (a) and I from unit 2 (b). The major calcium-bearing compounds are CaCO$_3$, followed by small amount of CaSO$_4$.

CaO is the most important factor both in arsenic vapor capture during coal combustion from
pulverized coal fired power plants and prevention of its leaching from fly ash. Through controlling $CaO/Ash$ ratio can efficiently inhibit the leaching of arsenic [16].

![Bar chart showing CaSO$_4$ in fly ash samples](image)

Fig. 3.7 Quantity of CaSO$_4$ in 4 flyashes samples. Lower combustion temperature in unit 1, lead to form more CaSO$_4$ than that in unit 2 which has higher combustion temperature. High amount of CaSO$_4$ can be considered as reducing the amount of Ca$_3$(AsO$_4$)$_2$ as the main chemical species of arsenic in fly ash, and in turn can be considered resulting more arsenic leaching.

![Graph showing variation in $L_{As}$%](image)

Fig. 3.8 Variation in $L_{As}$ % as a function of CaO/Ash ratios for the unit 1 and 2.
3.4 Conclusion

The leaching characteristics of arsenic from flyashes were examined to be clear effects of the difference in boiler types of coal fired power plants. The findings of this study are summarized as follows:

1. Arsenic partitioning in the unit 1 and unit 2 represented the same behavior. Arsenic vaporized during combustion and chemically condensed onto particle surfaces in the flue gas stream during cooling process.

2. Most of arsenic in the raw coal associated with the fly ash for various coal types. However, leaching of arsenic was different for each boiler types.

3. $CaO/Ash$ ratio in raw coal affects the retention of arsenic in fly ash through the chemical reactions of arsenic vapor with CaO. Unit 2 has higher $CaO/Ash$ caused a significant reduction on the emission of arsenic, in comparison with unit 1.
3.5 Acknowledgment

The authors thank to Ms. Michiko Endo for all of X-Ray Photoelectron Spectroscopy (XPS) analytical work.

3.6 References


Conclusions

1. The direct quantitative analysis of arsenic in solid samples (coal fly ash) is possible using the developed graphite furnace atomic absorption spectroscopy (GF-AAS) method. The determined validation parameters for the developed method are in the commonly acceptable range for this type of analysis, and the good percentages for the mass balance indicate the accuracy of the method. Hence, the proposed method is a simple, accurate, rapid technique that can be employed to routinely determined the amount of arsenic in coal fly ash.

2. Arsenic partitioning in the unit 1 and unit 2 represented the same behavior. Arsenic vaporized during combustion and chemically condensed onto particle surfaces in the flue gas stream during cooling process. Most of arsenic in the raw coal associated with the fly ash for various coal types. However, leaching of arsenic was different for each boiler. CaO/Ash ratio in raw coal affects the retention of arsenic in fly ash through the chemical reactions of arsenic vapor with CaO. Unit 2 has higher CaO/Ash caused a significant reduction on the emission of arsenic, in comparison with unit 1.
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Fig. 3.6 XPS of fly ash H from unit 1 (a) and I from unit 2 (b). The major
calcium-bearing compounds are CaCO$_3$, followed by small amount of CaSO$_4$.

Fig. 3.7  Quantity of CaSO$_4$ in 4 flyashes. Lower combustion temperature in unit 1, lead to form more CaSO$_4$ than that in unit 2 which has higher combustion temperature. High amount of CaSO$_4$ can be considered as reducing the amount of Ca$_3$(AsO$_4$)$_2$ as the main chemical species of arsenic in fly ash, and in turn can be considered resulting more arsenic leaching.

Fig. 3.8  Variation in $L_{As}$ % as a function of CaO/Ash ratios for the unit 1 and 2.

Fig. 3.9  Different in CaO% in the flyashes between the unit 1 and 2.
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Table 2.1 Optimization of the furnace program for the analysis of coal fly ash (solid sampling system).

Table 2.2 Optimized furnace program for the analysis of coal fly ash (solid sampling system).

Table 2.3 Optimization of the furnace program for the analysis of raw coal (liquid sampling system).

Table 2.4 Optimized furnace program for the analysis of raw coal (liquid sampling system).

Table 2.5 Arsenic concentration (mg kg$^{-1}$).

Table 2.6 Mass balance data for arsenic (%).

Chapter 3

Table 3.1 Properties of raw coals and flyashes collected from #1 chamber of ESPs.
List of publications


List of presentations

1. Sri Hartuti, Shinji Kambara, Hiroshi Mortomi.

2. Sri Hartuti, Shinji Kambara, Hiroshi Mortomi.

3. Sri Hartuti, Akihiro Takeyama, Shinji Kambara.

4. Sri Hartuti, Akihiro Takeyama, Shinji Kambara.
Curriculum Vitae

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Sri Hartuti