A role of calcium on leaching of trace elements from coal fly ash

Farrah Fadhillah Hanum [1,*], Akihiro Takeyama [1], Shinji Kambara [1]

[1]*Environmental and Renewable Energy System, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan*
**E-mail: farrah_fh@yahoo.co.id*

Abstract

Calcium has been known has a good decreasing in the leaching concentration of arsenic (As) and selenium (Se). This study aims to provide the useful reference in controlling As and Se leaching concentration into the environment through the effect of suppressing material addition. Suppressing material, as the by-product of some industries which contains of high calcium and there are three suppressing materials that have been tested, that are: paper sludge ash (PS 3 and PS 4) and filter cake (FC). PS 3 shows the closest effect to $Ca(OH)_2$ which is used as the standard, it shows almost 80-90% decreasing in As and Se leaching concentration based on ICP analysis. FC did not show an effect in As leaching concentration, but in the contrary with Se leaching concentration, it shows almost 60% decreasing. Calcium oxide has been known as the almost calcium compound which is containing in PS 3 and also known has the best decreasing on As and Se leaching concentration amongst the others calcium compound tested. Could be concluded that CaO is the most wanted calcium compound in controlling the As and Se leaching concentration into the environment.

1. Introduction

The large volume of coal fly ash produced around the world is a potentially source of trace elements, such as arsenic, selenium, boron, chromium, and etc. Thermal power plant generates large amounts of fly ashes. Presently, a substantial amount of these wastes is disposed in landfills and only 16% of total ash worldwide is potentially utilized for various applications such as cement production, synthesis of zeolite, mine backfill, and road-sub-base. If not properly disposed of, it can cause soil pollution and damage to either surface water or groundwater.

Arsenic (As) is one of the most volatile and potentially toxic metals in coal. Selenium is a striking example of a contaminant which is predominantly (there are exceptions) referred to as a potentially hazardous contaminant. The toxic potential and availability of selenium compounds is related to chemical form, since it can be very complex in the natural environment. They are largely released into ambient as gas phase and/or associated with fine ash particulates during coal combustion.

Environmental quality standard is a value, generally defined by regulation, which specifies the maximum permissible concentration of a potentially hazardous chemical in an environmental sample, generally of air or water. The values vary from country to country in order to prevent health hazard and conserve the living environment. Related to the protection of human health, Japanese government established the permissible limit for As and Se are 0.1 mg/L, and related to environmental quality standard for water pollution the As and Se are 0.01 mg/L or less.

Understanding the leaching behavior of As and Se in coal fly ash are significant in evaluating their potential impact on the environment. Calcium is known to play an important role in the release of arsenic and selenium from coal fly ash. Suppressing material is by-products from industries which contains of high calcium contents. In this research, leaching experiments have been done by the addition of some amounts of suppressing material into the coal fly ash sample. This addition is intended to decrease the arsenic and selenium leaching concentration, so that it can be used to control their leaching into the environment. The role of

calcium will be verified by the addition of suppressing materials. Furthermore, the calcium compound that has influence in the process also will be investigated.

2. Experimental

2.1 Coal fly ash and suppressing materials

Coal fly ash sample H (FA H), is collected from a coal fired power plant (600MWe). It decided to use as the sample based on the low calcium contents (2.05% of CaO, measured by X-ray fluorescence; XRF), and high arsenic leaching concentration (48.66 μg/L, measured by ICP –AES/OES ULTIMA2, HORIBA Ltd).

Three kinds of suppressing material which have been tested in this research, they are paper sludge ash (PS 3 and PS 4), filter cake (FC) and pure calcium hydroxide ($Ca(OH)_2$). Calcium hydroxide is chemical compound that have been used to compare the results of both kinds of suppressing material above. The percentage of calcium oxide (CaO) which consists in PS 3, PS 4 and FC based on XRF analysis in sequentially is 46.13%, 18.77% and 59.18%.

Paper sludge ash is waste generated by the paper recycling industry. It is produced when dewatered waste paper sludge, a by-product of the de-inking and re-pulping of paper. It is combusted, to reduce waste volume and to produce energy. Filter cake (FC) comes from lime industry, which is waste in a $CaCO_3$ manufacturing process. Other than calcium hydroxide, some pure calcium compounds (CaO, $CaCO_3$, and $CaSO_4$) also have been tested into FA H in order to investigating calcium compound which affect the leaching mechanism.

2.2 Sample preparation and leaching test

Coal fly ash was mixed with suppressing material in the mixed bag. The addition ratio of suppressing material is 5% and 10% of total mixture. This mixture was going into the leaching experiment by distilled water as the solvent. Leaching test No. 13 which notified by the Japanese Environment agency were basically employed as the leaching test in this work. Amounts of coal fly ash will was mixed with distilled water (the ratio 1:10) and it was shaken with the shaking speed 200 r.p.m for 6 hours in room temperature. Solid-liquid sample was separated by a filtration using membrane filter of 0.45 μm to obtain the filtrate. The arsenic concentration in the filtrate was measured by ICP-AES. The final pH of leachate was measured by pH/ION METER D-53, HORIBA.

2.3 Instrumentation

Ethylene glycol extraction insisted with ICP-AES analysis and thermogravimetric analysis has been carried out in the determination of calcium oxide and calcium hydroxide in coal fly ash and suppressing materials for the quantitative analysis.

X-Ray photoelectron spectroscopy (XPS Quantera SXM-G) and X-Ray Diffraction (Shimazu LabX XRD-6110X Smartlab) analysis was applied into the investigation of calcium compound on the surface of coal fly ash and the XPS peak obtained were processed by using of MultiPak sotware.

3. Result and Discussion

3.1 The effect of suppressing material into As and Se leaching concentration

As the different calcium characteristic which is consisting in suppressing material, their effect into arsenic and selenium leaching concentration also be different. Calcium hydroxide ($Ca(OH)_2$) shows the rapidly decreasing in the leaching concentration of As and Se. In this research, $Ca(OH)_2$, as the standard calcium compound, has been use to compare the results of other suppression material. It shows almost 95% of decreasing

compared with the leaching concentration of coal fly ash without suppressing material. It is proven the addition of suppressing material take an important part in controlling trace elements (As and Se) leaching concentration.

Paper sludge ash (PS3), shows the closest effect with $Ca(OH)_2$, with the decreasing percentage of arsenic and selenium leaching concentration is about 80-90%, while the PS4 only shows about 50% of decreasing. In the contrary with filter cake (FC) result. The effect of FC into As leaching concentration could not be detected but different with the result of selenium, it shows almost 60% of decreasing. The different effect of suppressing material into leaching concentration is related to their calcium characteristic.

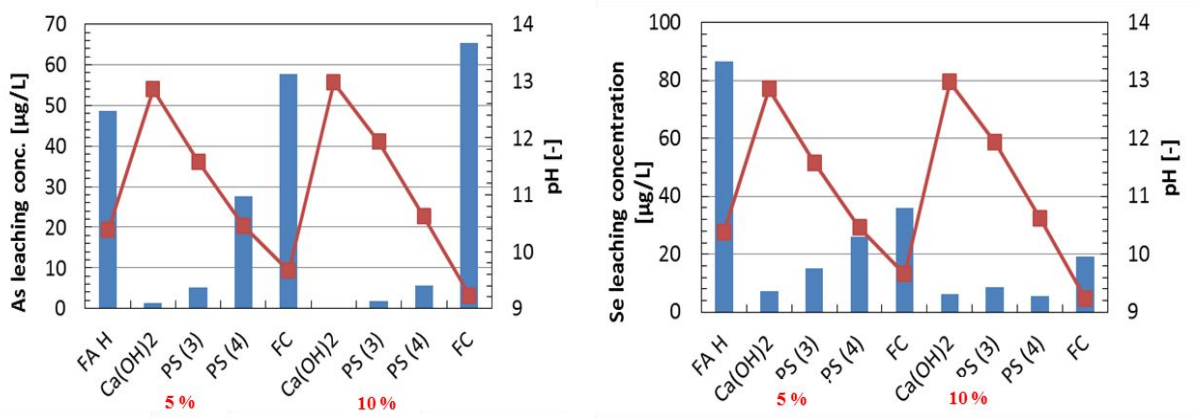

Fig. 1. Suppressing material effect into As (left) and Se (right) leaching concentration

This hypothesis has been insisted with the result from ion chromatography analysis as shown on Fig 2, which explained the relation between the concentrations of calcium ion in leaching solution and leaching concentration of As and Se. The higher calcium ion concentration in solution will decrease the As and Se leaching concentration.

The calcium contents will be affected the pH of environment. Comparing with other suppression material, $Ca(OH)_2$ shows the highest pH after the leaching experiment was done. The pH of leaching solution after the leaching experiment is about 10-13. This pH is still higher than the permissible pH for environment.

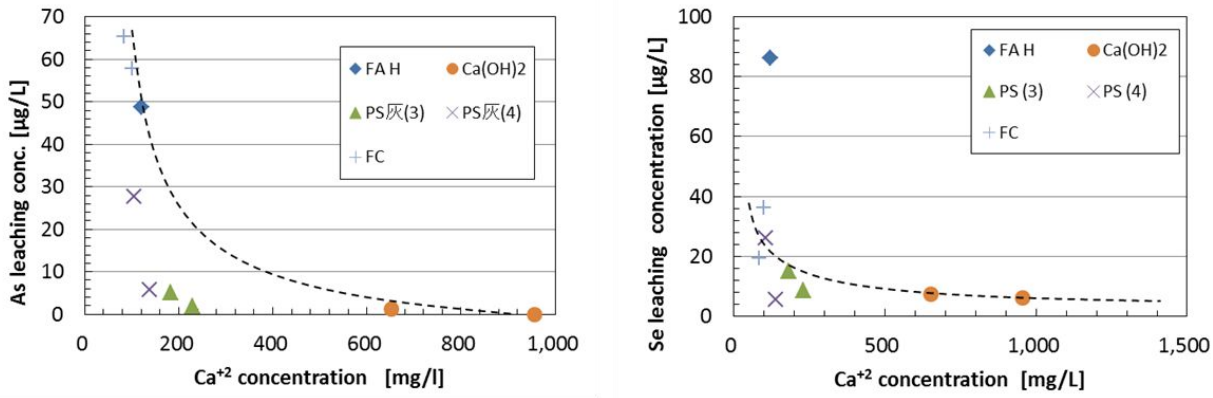

Fig 2. Correlation between Ca^{+2} concentrations into As (left) and Se (right) leaching concentration

3.2 Investigating calcium compounds in coal fly ash and suppression material

Some calcium compounds have been tested as suppressing material into FA H in order to order to ascertain the effect of calcium into leaching concentration. Based on the results have been known that calcium affects the As leaching concentration. Moreover, Fig. 3 explained that calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$) gives better

decreasing on As leaching concentration comparing with calcium carbonate ($CaCO_3$) and calcium sulphate ($CaSO_4$). Therefore, could be hypothesized that PS3 and PS4 may contains CaO or $Ca(OH)_2$ and FC contains $CaCO_3$ or $CaSO_4$. Some analysis and instrumentation have been done to investigate the exact calcium compound in the suppression materials and coal fly ash itself. In order to investigate the calcium compound which affect in suppressing the leaching of trace elements, XPS and XRD analysis was done into coal fly ash and suppressing material.

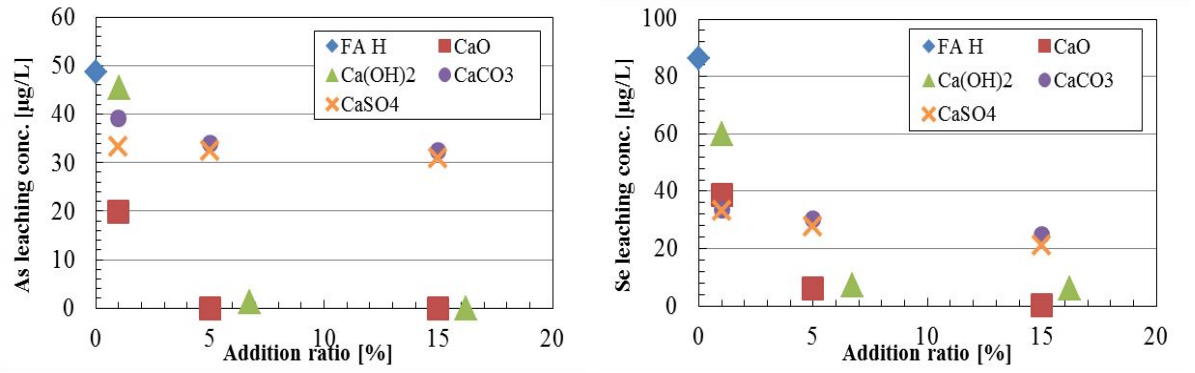

Fig. 3. Calcium compounds effect into As (left) and Se (right) leaching concentration

XPS analysis had been carried out into some pure calcium compounds and two suppressing materials, PS and FC, which showed the contrary effect each other. Table 1 shows the XPS results of some pure calcium compound which will be used to compare the binding energy of coal fly ash and the both suppressing materials mentioned above.

Table 1. Binding energy data of pure calcium compounds

	Experimental Data	Data Base
CaO	346	346.2
$Ca(OH)_2$	346.1	-
$CaCO_3$	347	346.8
$CaSO_4$	347.6	347.4

By comparing the result from the Table 1 with the binding energy data of FAH and suppressing material, the estimated calcium which contain in PS3, PS 4 and FC are CaO and $CaCO_3$. Because the low calcium composition in coal fly ash, estimated calcium compound in FAH had been done into the mixture of $CaCO_3$ and $CaSO_4$ and was expressed in percentage of $CaCO_3$. The ratio of $CaCO_3$ and $CaSO_4$ in coal fly ash sample H in sequentially is 83% and 17%.

In order to insist the hypothesis about the calcium contents in suppressing material and coal fly ash, analysis by XRD also had been done by comparing the XRD peak result of calcium compounds standard (CaO, $Ca(OH)_2$, $CaCO_3$, and $CaSO_4$) with the peak data of FAH and suppressing materials. The results said that almost the same with the XPS analysis result. The estimated calcium compound which is containing in PS 3 and FC are almost calcium oxide and calcium carbonate. But, different with paper sludge ash result, estimated calcium in FAH and PS 4 could not be detected by XRD analysis directly since the low content of calcium. Therefore, could be said that PS 3 is a good suppressing material because it is affected by the CaO contents. Figure 4 shows the peak of PS 3 after comparing with the calcium standard peak.

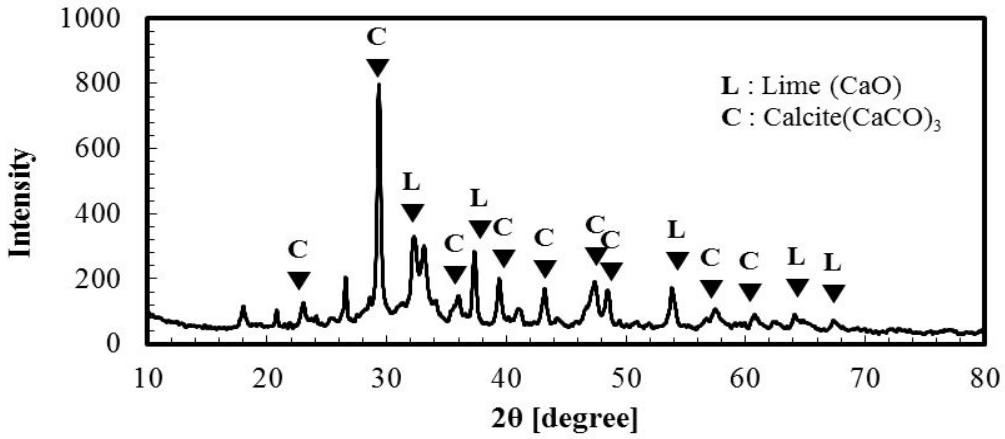

Fig.4. XRD analysis peak of paper sludge ash (PS 3)

3.3 Quantitative analysis for calcium compound in coal fly ash and suppressing materials

The leaching experiment by ethylene glycol analysis has been conducted in order to know the amount of calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$) content in leachate from the mixture of FA H and the three suppressing materials below. The results of this analysis will be measured by ICP analysis and insisted with thermogravimetric analysis.

Figure 5 shows that only PS 3 which is consisting of $Ca(OH)_2$ and PS 3 also content higher calcium oxide than the two others suppressing materials, 8.19%. FA H is containing 0.13% of CaO but based on the previous discussion, almost of the calcium contents in FA H is CaCO3. Therefore, could be hypothesized that the unknown compound in the figure 5 is calcium carbonate ($CaCO_3$).

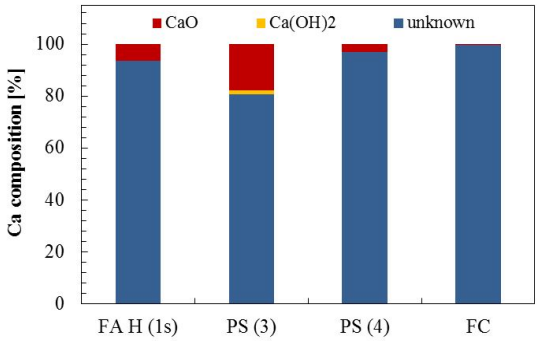

Fig. 5. The calcium compounds ratio in coal fly ash and suppressing materials

4. Conclusion

Based on this research has been known that suppressing material is affected on As and Se leaching concentration. CaO had been shows the best effect in controlling leaching of As and Se from coal fly ash into the environment. Since the CaO is the estimated calcium compound in PS 3, could be said that paper sludge ash 3 is a good suppressing material in controlling the As and Se leaching concentration into environment.

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