312 石炭フライアッシュからの微量金属溶出におけるカルシウムの役割

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

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The effect of calcium into coal fly ash on trace elements leaching concentration has been investigated through the addition of suppressing material. This study aims to provide the useful reference in controlling As leaching concentration into the environment. Suppressing material, as the by-product of other industries which contain high calcium, has been proven in decreasing of arsenic (As) leaching concentration from coal fly ash. There are three suppression materials that have been tested, that is: calcium hydroxide ($Ca(OH)_2$), paper sludge ash (PS3) and filter cake (FC). $Ca(OH)_2$ and PS3 show almost 85-90% decreasing in As leaching concentration based on ICP analysis. Moreover, the XPS analysis results show that calcium oxide (CaO) is consisting in PS3 and calcium carbonate is consisting in fly ash sample H.

Keywords: Coal Fly As, Calcium compound, Suppression material

1. Introduction

Thermal power plant generates large amounts of fly ashes which contain toxic metals. 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 water and soil pollution, disrupt ecological cycles and pose environmental hazards.

The large volume of coal fly ash produced around the world is a potentially significant anthropogenic source of arsenic. Arsenic (As) is one of the most volatile and potentially toxic metals in coal. It is largely released into ambient as gas phase and/or associated with fine ash particulates during coal combustion. Even for the fine ashes which are captured in a power plant, the subsequent treatment through landfilling results in the mobilization of As into aquifer systems, which consequently causes damage to either surface water or groundwater. Japanese government established environmental quality standard in order to prevent health hazard and conserve the living environment. Related to the protection of human health, the permissible limit for As is 0.1 mg/L, and related to environmental quality standard for water pollution the As standard is 0.01 mg/L or less.

Understanding the leaching behavior of As in coal fly ash is significant in evaluating its potential impact on the environment. Calcium is known to play an important role in the release of arsenic from coal fly ash. One hypothesis is that arsenic is reacting with calcium and precipitates as calcium arsenates. 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 leaching concentration, so that it can be used to control the leaching of arsenic into the environment. The role of suppressing materials onto arsenic leaching concentration will be verified by this study. Furthermore, the calcium compound that has influence in the process also will be investigated. X-Ray photoelectron spectroscopy analysis and thermogravimetric analysis have been applied for the qualitative and quantitative analysis of the calcium compounds.

2. Methodology

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, filter cake and calcium hydroxide ($Ca(OH)_2$). 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. Paper Sludge No.3 (PS3) has been tested in this research. Filter cake (FC) comes from lime industry, which is waste in a $CaCO_3$ manufacturing process. Therefore, calcium hydroxide or $Ca(OH)_2$, is chemical compound that have been used to compare the results of both suppressing material above. The percentage of calcium oxide (CaO) which consists in PS3 and FC based on XRF analysis is 46.13% and 59.18%.

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.

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

X-Ray photoelectron spectroscopy (XPS) analysis was applied into the investigation of calcium compound on the surface of coal fly ash and suppressing materials were carried out by XPS Quantera SXM-G and the XPS peak obtained were processed by using of MultiPak sotware.

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

3. Results and discussion

3.1 The effect of suppressing material into As leaching concentration

Arsenic is reacting with calcium and precipitates as calcium arsenates, which is slightly soluble in water. The addition of suppressing material which contains high calcium contents could be enriched the calcium contents in coal fly ashes, so that the leaching of arsenic into the environment could be controlled.

In some suppressing material that has been tested, calcium hydroxide ($Ca(OH)_2$) shows almost 95% of decreasing compared with the leaching concentration of coal fly ash without suppressing material. Paper sludge ash (PS3), shows the closest effect with $Ca(OH)_2$, with the decreasing percentage of arsenic leaching concentration is 85-90%. In the contrary with filter cake (FC) result. The effect of FC into As leaching concentration could not be detected. These results have been insisted with the result from ion chromatography analysis as shown on Fig 2, which explain the relation between the concentrations of calcium ion in leaching solution and As leaching concentration. The effect of calcium into pH also was explained in the figure 1. The determination of pH could be an indicator of the calcium role into As leaching concentration.

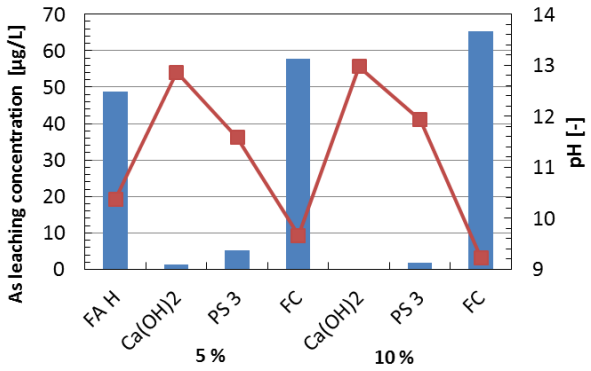

Fig 1. Suppressing material effect into trace elements As leaching concentration

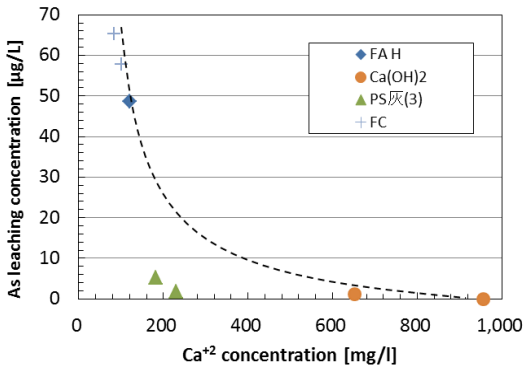

Fig 2. Correlation between Ca^{+2} concentrations into As leaching concentration

3.2 Verifying the effect of calcium compounds on the arsenic leaching concentration

Calcium hydroxide and calcium oxide have been tested as suppressing material into FA H in order to ascertain the effect of calcium into As leaching concentration. Based on the results have been known that calcium affects the As leaching concentration. Moreover, Fig. 3 explained that calcium oxide gives better decreasing on As leaching concentration comparing with calcium hydroxide.

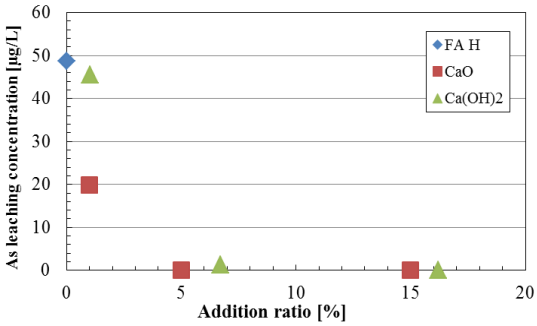

Fig 3. Calcium compounds effect into As leaching concentration

3.3 Investigating calcium compounds in coal fly ash and suppressing materials

Suppressing material (PS3) and calcium oxide have been have been proven could decrease As leaching concentration. In order to know what is the exact calcium compounds that affected the leaching of trace elements, XPS analysis have been done into the coal fly ash sample (FA H) and suppressing materials. Table 1 shows the XPS results of some pure calcium compound.

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

Table 2 shows the XPS analysis result of coal fly ash and the suppressing materials. Compared with the result from the Table 1, the estimated calcium which contain in PS3 and FC are CaO and $CaCO_3$. It was insisted the results before, because PS3 consisting with CaO so that, PS3 was good in decreasing As leaching concentration.

The binding energy of coal fly ash sample (FAH) is in between the binding energy of $CaCO_3$ and $CaSO_4$. So that, the estimated calcium compound of FAH could not be detected directly.

Table 2. Estimated calcium compound on coal fly ash and suppression materials

	Experimental Data	Estimated Ca compound
PS3	346.4	CaO
FC	346.7	$CaCO_3$
FAH	347.1	–

XPS analysis has been carried out into the mixture of $CaCO_3$ and $CaSO_4$ in order to establish the calcium compound composition on FAH. Figure 5 shows the calibration curve of $CaCO_3$ and $CaSO_4$ mixture.

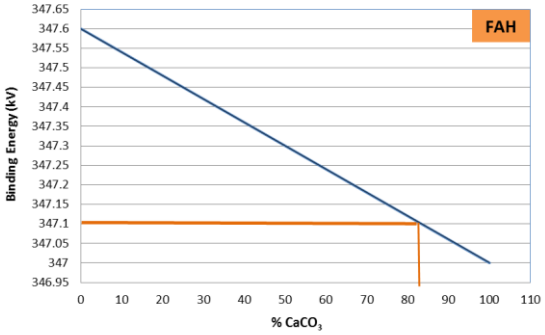

Fig 4. The XPS results of $CaCO_3$ and $CaSO_4$ mixture in $CaCO_3$ percentage

The composition of calcium compound in FAH was expressed in percentage of $CaCO_3$. By plotting the binding energy of FAH on the graph, estimated calcium compound in FAH have been investigated. The ratio of $CaCO_3$ and $CaSO_4$ in coal fly ash sample H in sequentially is 83% and 17%. Table 3 shows the comparison of calcium compound in FAH between calculation result and experimental result (XPS).

Table 3 Comparison between calculation results and experimental results

	Calculations Result	XPS Results
$CaCO_3$ (% wt)	81.45	83
$CaSO_4$ (% wt)	18.05	17

Calculation results is the results which produced by calculated the data from XRF results and ion chromatography results. Based on the result, has been known that the $CaCO_3$ is the highest contents of calcium in coal fly ash samples. The previous result said that PS3, which contain most CaO, is the best suppression material in decreasing As leaching concentration.

3.4 Qualitative analysis for calcium compound in coal fly ash and suppressing material

ICP analysis insisted with thermogravimetry analysis have been used to determine the CaO and $Ca(OH)_2$ ratio in coal fly ash (FA H) and suppressing material. Ethylene glycol extraction method was used as the method to dissolve both of calcium compounds from the sample.

Figure 5 shows that FAH and PS3 contain with CaO and there is no CaO containing in FC. Compare with the XPS analysis results, can be said that the unknown compound in FC and FA H is mostly $CaCO_3$. The amount of CaO which contain in FA H and PS3 is 6.27% and 17.69%.

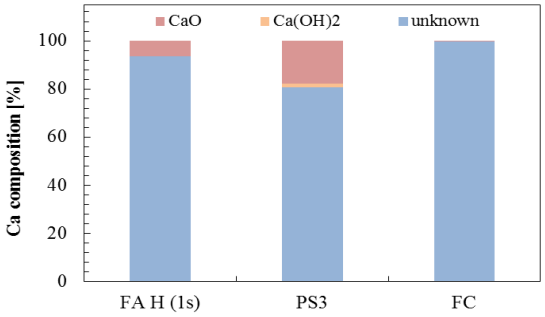

Fig 5. The calcium compounds ratio in coal fly ash and suppressing material

4 Conclusion

Based on this research has been known that suppressing material is affected on As leaching concentration. The most calcium compound which needed in order to decrease the As leaching concentration is CaO. The most calcium compounds in PS3 is CaO, so that PS3 is a best suppressing material for controlling As leaching into the environment. The most calcium compound which consist in FAH is $CaCO_3$.

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