LEACHING BEHAVIOUR OF TRACE ELEMENTS FROM FLY ASHES AND DEVELOPMENT OF THE LEACHING INHIBITOR

フライアッシュ中微量元素の溶出挙動と溶出抑制材の開発

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Preface

Coal fueled power plant is one of the major source of the environmental because the discharge of its waste. One of the main wastes of this power plant is from the combustion process, coal fly ash. Several researchers have been studied about the utilization of coal fly ashes such as in the cement concrete industry, in the road construction, as the soil stabilization, and etc. However, almost of the coal fly ashes which discharged from the coal combustion process will dump in open pond. Then, this condition will trigger the pollution of the environment.

Coal fly ash is consisting of several toxic elements which could be leached into the environment after having interaction with weathering and hydrological condition process. Many studies have been discussed the leaching characteristic of the trace element from various coal fly ashes. Our laboratory also studied about the leaching of several trace elements in coal fly ash such as arsenic, selenium, boron, chromium, and fluorine. Then, our laboratory also studied about controlling those toxic materials by the utilization of suppressing material in leaching process.

This thesis is consisting of six chapters. The first chapter is the introduction about coal fly ash, trace element, suppressing materials and brief objective of each study on the next chapter. Then, the second chapter was discussed about the leaching behavior of arsenic leaching concentration. This chapter presented information about that calcium which consisting in coal is one of the main factors in decreasing the arsenic leaching concentration.

The third chapter was started to discuss about additives in leaching process. Based on the information that calcium has strong relation with the trace element leaching concentration, this research was introduced high calcium content material as the additives in the leaching process. This material was added into the coal fly ash before the leaching process in certain addition ratio. Then, the results showed that the trace element leaching concentration could be decreased for about 90% decreasing. Also, the decreasing in arsenic, selenium, and boron leaching concentration was proven to have relation with calcium oxide inside the coal fly samples and additives material.

Then, in the fourth chapter, the further research about the additives material as inhibitor in the trace element leaching concentration was continued. In this chapter, two different coal fly ashes have been tested with additives as the single and mixture additives in order to clarify the effect of the additive materials and also to find an applicable additive which could simultaneously decrease the leaching of arsenic, selenium, boron and fluorine. The result informed that the mixed additives showed better effect as the inhibitor in those trace element leaching concentration.

The fifth chapter was purposed to prove the efficiency of mixed additive in inhibit fluorine leaching concentration. About fourteen coal fly ashes have been tested with the two kinds of the mixed additives. The results was informed that the mixture of $Ca(OH)_2$, PS ash 8 and BF cement could applicable in decreasing fluorine leaching concentration. The results also said that the calcium oxide and calcium carbonate were play important role in the formation of more stable compound during the leaching process. This stable compound is less soluble in water and also difficult to be break.

The last chapter was delivered the conclusions as well the future perspectives of this research. The further application of these additives was possible however the optimum addition ratio of the additives into coal fly ashes is need to be found.

Chapter 1
Introduction

1.1 Coal Fly Ash

Coal plays a vital role in electricity generation worldwide. Based on the BP Energy Outlook 2018, coal-fuelled power plants currently fuel 37% of global electricity. In a coal power plant, steam coal, which also known as thermal coal, use to generate electricity. Coal first milled to a fine powder, which increases the surface area and allows it to burn more quickly. In this pulverized coal combustion (PCC) systems, the powdered coal is blown into combustion chamber of a boiler where it is burnt at high temperature. The hot gases and heat energy produced converts water – in tubes lining the boiler – into steam. The high pressure steam is passed into a turbine containing thousands of propeller-like blades. The steam pushes these blades causing the turbine shaft to rotate at high speed. A generator is mounted at one end of the turbine shaft and consists of carefully wound wire coils. Electricity is generated when these are rapidly rotated in a strong magnetic field.

Trace elements are emitted during this coal combustion process such as arsenic, selenium, boron, chromium, fluorine, cadmium, molybdenum, and vanadium. The quantity, in general, depends on the physical and chemical properties of the elements itself, the concentration of the element in the coal, the combustion conditions and the type of particulate control device used, and its collection efficiency as a function of particle size.

1.2 Trace Elements

Study said that elements present in coal are divided into three groups, which are:
1. Major elements: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S), these occur at >1000 ppm.
2. Minor elements: coal mineral matter: silicon (Si), aluminium (Al), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), iron (Fe), manganese (Mn), titanium (Ti). These may present in concentrations between 100 and 1000 ppm.
3. Trace elements which are the constituents with concentrations <100 ppm. These differ from one coal to another.

Based on partition and enrichment behavior of elements, trace elements could be defined into three basic classes. Class I is the elements approximately equally distributed between the bottom ash and fly ash, or show no significant enrichment or depletion in the bottom ash, such as Ba, Ce, Cs, and Tn. Class II is the elements enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size, such as As, Cd, Pb, Sb, Se,

and Zn. Then, class III is the elements totally emitted in the vapor phase, such as Br, Hg and I.

In the disposal environment, coal fly ashes may react and contact with fluid, such as rainfall, and this condition could release trace elements into groundwater or surface water systems. Numerous experimental leaching studies have been performed to assess the leachability of trace elements from coal fly ash. This study is important in order keep the environment in a good condition.

Arsenic (As), boron (B), selenium (Se) and fluorine (F) have been recognized as the most troublesome hazardous elements in coal fly ash. The dumping of fly ash in disposal pond could cause serious environmental impact. Arsenic compounds cause short-term and long-term effects in individual plants and animals and in populations and communities of organisms. These effects are evident, for example, in aquatic species at concentrations ranging from a few micrograms to milligrams per liter. The nature of the effects depends on the species and time of exposure. The effects include death, inhibition of growth, photosynthesis and reproduction, and behavioral effects. Long-term exposure to arsenic in drinking-water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes such as hyperkeratosis and pigmentation changes. These effects have been demonstrated in many studies using different study designs. In general, inorganic arsenicals are more toxic than organ arsenicals and arsenite is more toxic than arsenate. The mode of toxicity and mechanism of uptake of arsenate by organisms differ considerably. This may explain why there are interspecies differences in organism response to arsenate and arsenite.

Selenium (Se) is a complex species due to its properties of being both essential and toxic, leaving a narrow optimal range within which intake amounts are healthy. Selenium has good photovoltaic and photoconductive properties, and it is used extensively in electronics, such as photocells, light meters and solar cells. The second largest use of selenium is in the glass industry: selenium is used to remove color from glass, to give a red color to glasses and enamels.

Selenium occurs naturally in the environment. It is released through both natural processes and human activities. In its natural form as an element selenium cannot be created or destroyed, but selenium does have the ability to change form. When selenium in soils does not react with oxygen it remains fairly immobile. Selenium that is immobile and will not dissolve in water is less of a risk for organisms. When selenium is more mobile, the chances of exposure to its compounds will be greatly enhanced. Soil temperatures, moisture, concentrations of water-soluble selenium, the season of the year, organic matter content and microbial activity determine how fast selenium will move through soil. In other words, these factors determine its mobility. Humans may be exposed to selenium in several different ways. Selenium exposure takes place either through food or water, or when we come in contact with soil or air that contains high concentrations of selenium. Selenium uptake through food may be higher than

usual in many cases, because in the past many selenium-rich fertilizers have been applied on farmland. People that live near hazardous waste-sites will experience a higher exposure through soil and air.

Boron is a naturally occurring element that is found in nature in compounds called borates. Borates are found in the oceans, sedimentary rocks, coal, shale, and some soils. Borates are naturally released into the environment from the oceans, volcanic activity and other geothermal releases such as geothermal steam, and weathering of clay-rich sedimentary rocks. Boron is also released, to a lesser extent, from sources due to human activity. Boron is an essential micronutrient for plants, with levels of boron required for optimum growth depending on the plant species. Boron deficiency in terrestrial plants has also been observed in many parts of the world. In some plants, there is but a narrow range between boron deficiency and toxicity.

The effect of boron has been determined for several types of organisms in the environment, but more information is available for some types of organism than for others. Some of the information covers the effects of short-term exposure to boron, while other information focuses on long-term or chronic exposure. For humans, boron exposure occurs primarily through the diet and drinking-water. The mean global boron concentration in drinking-water was considered to be between 0.1 and 0.3 mg boron/litre. For the general population, the greatest boron exposure comes from the oral intake of food. The mean daily intake of boron in the diet is about 1.2 mg.

Fluorides are organic and inorganic compounds containing the fluorine element, formed by halogen family (Fluorine F, chlorine Cl, bromine Br and iodine I). Living organisms are mainly exposed to inorganic fluorides through food and water. It is a fact that low amount of fluoride (0.3-1.0 mg/l) in drinking water is helpful in the prevention of dental caries and in treatment of osteoporosis. However, high intake of fluoride (>1.5 mg/l) in drinking water for a prolonged period is known to cause damage to the teeth enamel and eventually leads to skeletal complications that result in fluorosis. Fluoride dust and fumes pollute the environment. Inhaling dust and fumes is as dangerous as consuming fluoride containing food, water or drugs. Industrial fluorosis is a serious problem in the developed western and other industrialized countries. However, in India, the problem of industrial fluorosis is also reaching an alarming state due to rapid industrialization.

1.3 Suppressing Material

Suppressing material is a material which consist high calcium content and use as additives in leaching process in order to control trace element leaching concentration into the environment. Calcium has been known plays important role in the release of trace elements. This material will be added into coal fly ashes in order to increase the calcium content in coal fly ashes. The

presence of excess calcium could trigger the trace elements to form more stable chemical compound. This chemical stabilization forms less hazardous compound of the trace elements. Our laboratory proposed paper sludge ash as the suppressing material. Paper sludge ashes are waste generated by paper making industry. The utilization of this waste is one of the problem solve in reducing environmental waste.

1.4 Objective of the research

Several studies about the utilization of coal fly ashes and about the leaching of trace element from coal fly ashes have been discussed by several researchers. This research was focused on the utilization of suppressing material in controlling the trace element leaching concentration into the environment. In this research, chapter 2 will discuss about the leaching characteristic of the arsenic and will inform the mainly factor that affected the leaching of the trace elements. Then, chapter 3 and 4 will inform about suppressing material. In chapter 3, several suppressing material will be tested and the result will be proved that calcium plays important role in trace element leaching process. Then, chapter 4 will be informed the applicable suppressing material as the additive in controlling the leaching of trace element. Further, in chapter 5, the applicable suppressing material based on the chapter 4 will be tested into 14 different coal fly ashes in order to confirm the effect of this suppressing material and to study the role of calcium during the utilization of this material in the leaching process. The chapter 5 will focus in fluorine leaching concentration.

Chapter 2
Leaching Characteristic of Arsenic in Coal Fly Ash

2.1 Introduction

The discharge of fly ash from coal combustion process has become the matter of concern over last few decades. Coal which is contained significant quantities of many hazardous trace elements burned in boiler of coal-fired power plant to generate electricity. After burning, as the flue gas cools down, trace elements such as As, B, Cr and Se condensed on the surface of the fly ash (collected by electrostatic precipitators) and formed new stable compounds [1]. The collected CFAs (coal fly ashes) by electrostatic precipitators are usually subjected to be reused or disposed. The fly ash is reused 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 such as CFAs having large amount of unburned carbon which are unsuitable as the raw material for cement will be disposed to the landfill. This disposal gives negative impact to the environment, where due to the rainfall the trace elements contained in fly ash will be eluted to the environment [3].

Arsenic, one of the most highly toxic chemicals, is a semi-metallic element commonly found as arsenite and arsenate compounds [4]. The leaching of arsenic from fly ash will contaminate the aquifer systems, and raise the water-environmental problem. It has been described on previous studies that pH, S/L (solid-to-liquid) ratios, leaching time, ash properties (e.g. acidic or alkaline) and the leaching environment are the factors which affect the leaching behavior of arsenic [5-11]. Wang et al. [12] investigated the effect of pH, S/L ratio, calcium addition and leaching time on the leaching behavior of As and Se from two major types of CFAs and they found that leaching of As and Se from CFA generally increased with increases in the S/L ratio and leaching time, and adsorption/desorption played a major role in As and Se leaching from CFA. Jiao et al. [13] studied the leaching characteristics of As in fly ash and they found that the presence of Ca in fly ash plays an important role in the leaching behavior of As, where abundance of free CaO in fly ash generates an alkaline leachate during leaching test and successively reduces arsenic leaching since the precipitate was preferentially occurred via the reaction of arsenic with calcium at high pH leachate. Jankowski et al. [8] performed a long term leaching test for four Australian fly ashes and found that As leaching from both acidic and alkaline ashes was increased with time, after reaching a maximum concentration, As leaching from alkaline ash was decreased.

In this work, leaching characteristic of arsenic in six different CFA samples was investigated.

The samples were collected from a commercial power plant for the leaching experiments. Solution equilibrium calculation was employed to clear the leaching mechanism of arsenic in fly ash, and the calculation results were compared with the experimental results. The influence of time was investigated through a long term leaching test and the effect of leaching rate on the leaching behavior of arsenic was discussed. The overall object of the study was to evaluate more fully the rate of leaching of arsenic and related factors on determining arsenic leaching from different type of CFAs, as a basis for comprehensive assessment of arsenic behavior. The leaching mechanism and the rate of leaching of arsenic were monitored as a basis for finding out the principle of leaching suppression method to prevent the leaching of arsenic. This type of information is different from that produced by simple and standardized leaching tests in which this study involves a long-term leaching process for CFAs, but it is necessary for a more confident approach to aid in the development of sustainable fly ash management strategies.

The novelty of the paper lies in the application of long leaching time of 120 days and observation of leachates during 4 periods to obtain detailed time-series changes in leaching fraction of leachate solutions for monitoring the rate of leaching of arsenic.

2.2 Experimental
2.2.1 CFA Samples

Six CFA samples (G, H, I, J, L, and N) were collected from a pulverized coal fired power plant. Fly ashes H and I derived from the same coal between unit 1 and 2 of coal fired power plants. Table 1 shows the major chemical compositions that were measured by XRF (X-ray fluorescence). Trace element arsenic was measured by ICP-AES. It should be noted that the concentration ranges of As have wide ranges in six CFA samples as shown in Table 1.

2.2.2 Characterization of Elements in CFA Samples

Total concentrations of major chemical compositions were determined using Wavelength Dispersive X-ray Fluorescence Spectrometer (WDXRF S8 TIGER, Bruker AXS). For XRF analysis of CFA samples, a few amount of it (approximately 500 mg) was poured on polypropylene thin-film which was attached previously onto a Plastic-made O-ring sample cup with an outer diameter of 40 mm. The samples were introduced to XRF instrument, and the chemical compositions of samples were determined.

The concentration of arsenic in CFA was determined using microwave-assisted acid-digestion followed by HG-ICP AES (hydride generation-inductively coupled plasma atomic emission spectrometry) analysis. 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. About 0.1 g ash sample was weighted and moved into a pressure- resistant PTFE

(Polytetrafluoroethylene) bottle. An acid mixture capable of completely digesting ash sample was 2 mL of HNO_3 65%, and 4 mL of HF 50% was added, the bottle was then sealed and a digestion program was performed. After cooling and the addition of 5 mL of saturated H_3BO_3, microwave processing was performed again. 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%.

Table 1. Chemical composition of CFA samples.

Fly ash sample		G	H	I	J	K	L	N
Power station		Unit 1	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1
SiO_2		66.21	59.25	59.21	65.07	56.82	57.32	63.08
Al_2O_3		26.65	25.63	26.32	21.83	21.06	20.68	22.73
TiO_2		1.77	1.99	1.77	1.11	1.06	0.96	1.24
Fe_2O_3		2.57	7.49	6.79	7.17	7.23	7.17	5.65
CaO		0.81	2.05	2.07	1.43	8.86	8.79	2.67
MgO	[%]	0.54	0.79	0.91	0.52	0.96	1.02	1.12
Na_2O		0.29	0.60	0.74	0.44	0.75	0.80	1.25
K_2O		0.54	1.56	1.44	1.76	1.97	1.97	1.44
P_2O_5		0.06	0.18	0.18	0.16	0.28	0.27	0.20
MnO		0.11	-	0.10	-	-	-	0.07
V_2O_5		0.02	0.03	0.03	0.15	0.17	0.17	0.04
SO_3		0.44	0.42	0.50	0.35	0.84	0.87	0.53

2.2.3 Leaching Test

The procedure of standard leaching tests for fly ashes Notification No. 13 by the Environmental Agency of Japan was basically employed as the leaching tests in this work. However, in this way, variation in pH of leachate during leaching tests strongly affects leaching concentration of elements, so a buffer solution (pH = 10) was used as a leaching solution, which can keep a constant pH around 10.

Regarding the leaching procedure used in this work, fly ash of 50 g and 500 mL buffer solution (pH = 10), which accounted for a liquid to solid ratio (L/S) of 10, were mixed in a polyethylene bottle, after then, it was shaken for 6 hours at room temperature with a shaking speed of 200 r.p.m. The solid-liquid sample was separated by a filtration using a membrane filter of 0.45 μm to obtain the filtrate. The concentration of arsenic in filtrate was carefully analyzed by HG-ICP AES (ULTIMA2, HORIBA Ltd).

Extended leaching time (long term leaching) has been carried out to elucidate effects of time on the leaching of As. The leaching time was continued for 120 days, in which every 30 days, the concentration of arsenic in the leachate was observed. The value of leaching fraction refers to the percentage of mass of arsenic in leachate to its mass in fly ash.

2.2.4 Thermodynamic Equilibrium Calculation

To consider the leaching fraction of arsenic theoretically in the case of solution equilibrium, the thermodynamic equilibrium software, FactSage 6.0 was used. It has optimized databases for solutions of metals, liquid, and solid, which can be applied for equilibrium calculation in the liquid-solid system. In the equilibrium calculation, chemical composition as shown in Table 1 and liquid conditions (25 ºC, of 1 atm) were set on FactSage 6.0 as calculation input. The databases used include Fact53 and FTmisc, solid species is chosen as an output.

2.3 Result and Discussion

2.3.1 Leaching Characteristics

Figure 1 shows the leaching fraction of arsenic for six CFA samples. The fraction ranges from 0-15%. This low value of leaching fraction exhibits relatively weak relationship between the leaching amount of arsenic and its element concentration in fly ash. As shown in Fig 2. The correlation coefficients (R^2) between leaching amount of arsenic versus its concentration in the solid phase is 0.62.
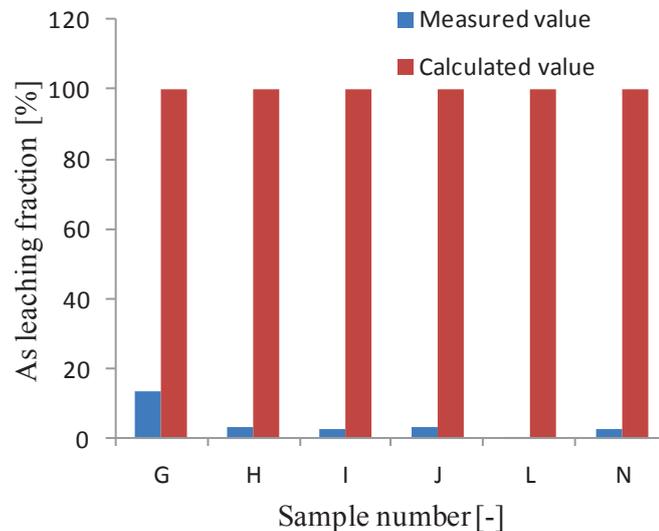

Figure 1. Leaching fractions of arsenic for 6 CFA samples: left bar is experimental result, and right bar is equilibrium calculation.

Sample L has the highest amount of CaO content (Table 1) of all six CFAs tested, has the lowest leaching fraction of 0%, on the other hand, sample G has the lowest amount of calcium has the highest leaching fraction of 15%. A plausible process that responsible to the release of arsenic from fly ash L would be high content of CaO in fly ash L preferentially associates with arsenic to form solid stable compound of $Ca_3(AsO_4)_2$ and the formation of insoluble $Ca_3(AsO_4)_2$ can lead to

a decrease in the dissolved arsenic concentration in the leachate [8,13-16].
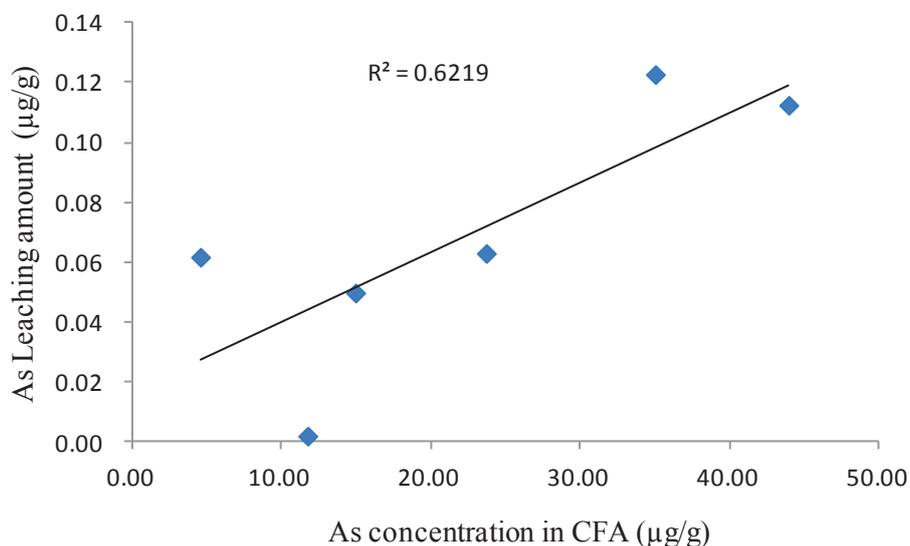

Figure 2. Relationship between leaching amounts and concentration of arsenic in CFAs.

2.3.2 Comparison with Equilibrium Calculation Results

To consider the leaching mechanisms of arsenic, solution equilibrium calculation was performed by FactSage 6.0. In the calculation, the parameter survey has carefully carried out, and the leaching time was assumed as infinite time. The effect of temperatures of the solution and value of pH on the leaching fractions was negligible. As can be seen in Figure 1, the calculation results show the leaching fraction of arsenic were 100% for all fly ash samples, these values were significantly differed with experimental results value. This discrepancy may be depends upon the leaching time because the leaching time has been assumed as infinite time in the equilibrium calculation. This observation indicates that arsenic leaching is time-dependent.

2.3.3 Long-Term Leaching Characteristic

As mentioned in the discussion above, the leaching time is one of the important factors in arsenic leaching mechanism. To investigate the effect of the leaching time, the long-term leaching test was conducted. Fig. 3 shows plot of changes in the leaching fractions of arsenic for 3 CFAs (H, I, and L) at 30th, 60th, 90th and 120th day leaching time. As expected, the leaching fractions were increased with the leaching time for all samples.

As shown in Fig 3. The leaching fractions of sample H and I were much higher than that of the sample L for all terms, most of arsenic in CFA was eluted at 120th day for the sample H and I. Leaching fraction of sample I reached 100% at 120th day, (2.6% at short-term leaching test, see

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Fig. 1). In addition, although fly ashes H and I were derived from the same coal of different unit in power plants, they have different arsenic leaching fraction on the 120th day, fly ash H has a slightly lower leaching fraction than fly ash I. Fly ash L indicated 0% leaching fraction through short-term leaching test as can be seen in Fig. 1, but the leaching fraction was reached about 50% through long-term leaching test as can be seen in Fig.3. It is predicted that the leaching fraction of the sample L will be reached 100 % in longer day.

Therefore, the results of equilibrium calculations were give correct suggestions with this long-term leaching experiment results that the total amount of arsenic will be eluted at the end, and the equilibrium between the solid phase (ash) and the leaching solution was reached in this long-term leaching experiments. This observation is opposite to that reported by Jankowski, who found that the equilibrium between the solid phase (ash) and the leaching solution was not reached in 144 hours (6 days) leaching experiments [8,17-18]. It was concluded that longer leaching test may responsible for this observation, where the diffusion process of arsenic from the inner pores of fly ash to the surface and bulk solution might be resulted from a slow process through a longer term release. [12,19]. From the results shown in Fig. 3, it is clear that a leaching rate is an appropriate factor to evaluate leaching characteristics of arsenic for various types of CFAs.

2.3.4 Evaluation of Leaching Rates of Arsenic

As can be seen in Fig.3 that leaching fraction of arsenic varies depending on coal type, here we calculate the arsenic leaching rate of fly ash H, I and L to investigate the behavior of leaching fraction shown in Fig.3. The leaching rate expressed based on kinetic model of first-order reactions[20], with the rate equation was defined as follows:

$$X = 1 - \exp(-k.t) \qquad (1)$$

where, X [−] is the leaching fraction of arsenic; k is the rate constant and t is time. By this equation, the change in arsenic leaching fraction can be represented freely by changing the rate constant k, but since the leaching fraction of arsenic varies depending on coal type, the behavior of leaching fraction becomes complex, it is required to modify the equation to express the leaching fraction profile for each coal type, the modified equation was defined as follows:

$$X = 1 - \exp(-a.t^b) \qquad (2)$$

where, X [−] is the leaching fraction of arsenic, and constant a and b were variables to express the complex behaviors of leaching fractions for a long-term. The constant a and b are

estimated by data fitting to equation (2). Fig. 4 shows the results of data fitting, and constant a and b indicates in Table 2. As can be seen in Fig.4, the solid line indicates the result of the modified leaching rate equation (2), the trend of the leaching rate equation as a calculation results shows a good agreement with the behavior of leaching fraction as an experimental results.

Table 2. List of constant a and b for 6 different CFAs.

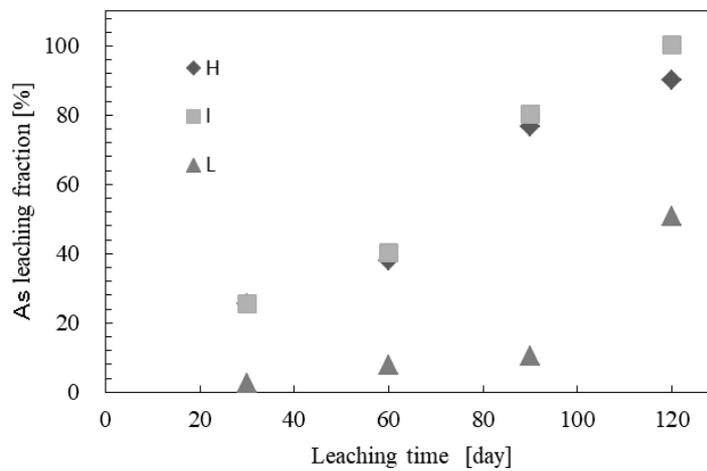|	G	H	I	J	L	N
a	0.2429	0.1627	0.1049	0.2461	0.0043	0.1521
b	0.3429	0.4164	0.7073	0.2582	0.6696	0.2553

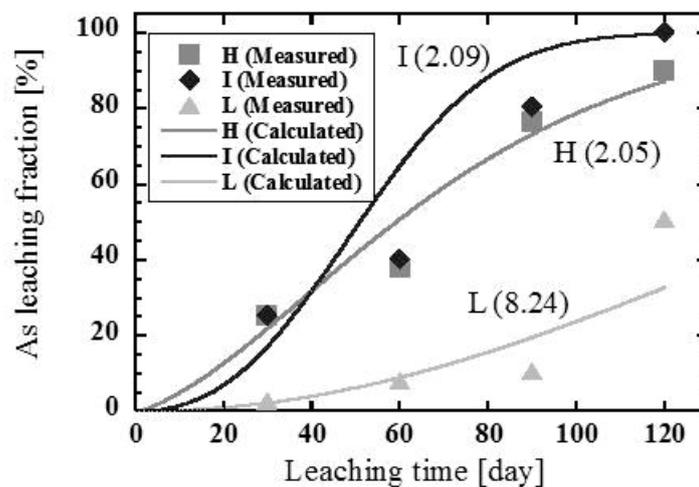**Figure 3.** Effect of leaching time on As leaching fraction

Figure 4. Fitting results by equation (2) for three different CFAs. The value in parentheses is CaO% in the CFA.

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The constants a and b as a variable to express the complex behaviors of long-term leaching fractions is defined to observe the transition of As leaching fraction through locking the value of one constant such as constant b and varying the other constant value such as constant a. Fig.6 shows the As leaching fraction by changing the a is fixed to b, and Fig.7 shows the As leaching fraction by changing the b is fixed to a. As can be seen in Fig.6, Initial As leaching fraction increases with increasing a. On the other hand, there is no change in the initial As leaching fraction in Fig.7, but the leaching rate increases with increasing b. In summary, the coal species having high value of a has a high leaching fraction at initial stage of leaching time (eluted early), while coal species having high value of b has a fast leaching rate. For the sample I which has high value for both constant a and b (Table 2), has a highest As leaching fraction at initial stage of leaching test (eluted early) and has a fast leaching rate. On the other hand, the sample L which has lowest value of a and high value of b, has the lowest leaching fraction at initial stage of leaching test and the leaching rate increased with increasing time. Also, the samples G and J, which are coal the coal types with high value of a, can be evaluated as coal types in which arsenic is eluted much in the initial stage of the leaching test. By substituting the values of a and b into equation (2), the change in leaching fraction X, can be calculated for each number of days.
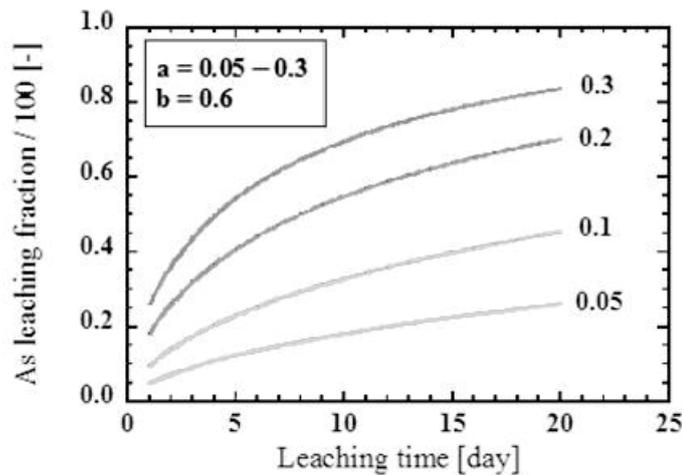

Figure 5. Effect of constant "a" on As leaching fraction and leaching rate equation. The change in As leaching fraction when "a" is changed and "b" is kept constant.

As discussed previously, the leaching fraction of arsenic related with CaO content in fly ash. The relation between CaO content in fly ash and constant a was observed in order to evaluate the correlation between CaO content in fly ash and leaching rate of arsenic. Fig. 7 shows the relation between CaO content in fly ash and constant a. The leaching rate of arsenic (indicated by constant a value) was decreased with an increase of CaO content in fly ash. Therefore, the value of the rate constant a can be said to be the main factor determining arsenic leaching. Arsenic leaching can be
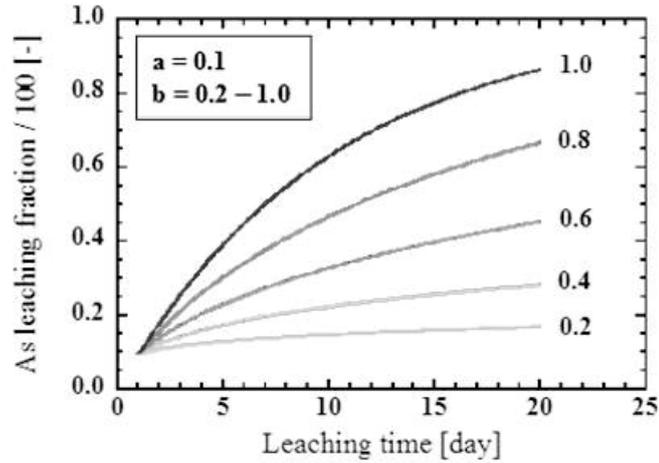
suppressed by controlling this.

Figure 6. Effect of constant "b" on As leaching fraction and leaching rate equation. The change

in As leaching fraction when "b" is changed and "a" is kept constant.

In light of this, it is important to control the amount of CaO for arsenic elution suppression, and it is necessary to add CaO content onto fly ash with an appropriate addition amount to prevent the leaching of arsenic.
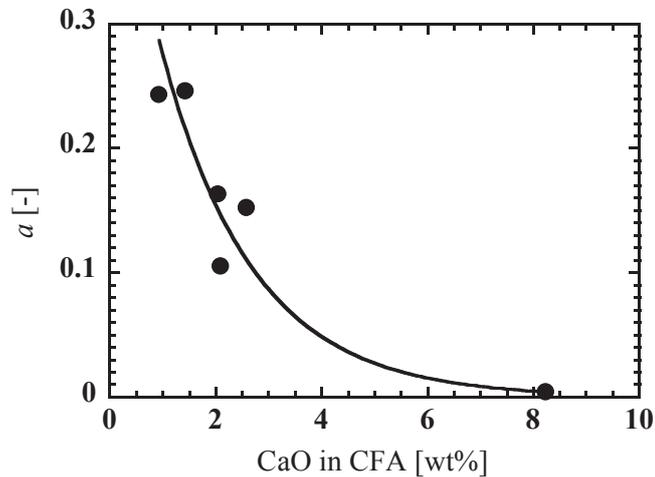

Figure 7. Relation between CaO content in CFA and constant a obtained by data fitting based on equation (2).

2.4 Conclusion

The leaching characteristics of arsenic from CFA were investigated for six different CFA samples that were collected from a large scale power plant in Japan. The arsenic leaching

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fractions were examined through experimental and calculation, the influence of time was investigated and the leaching rate was evaluated. The specific conclusions were described as follows:

1. The leaching fractions of arsenic were low levels below 15%. It was affected by CaO content in CFA.

2. The leaching fractions of arsenic from equilibrium calculation were 100% for all fly ash samples, this results is significantly differed with experimental result. As the time through equilibrium calculation has been assumed as infinite time, this observation indicates that leaching of arsenic is time-dependent.

3. Long-term leaching test shows that whole amount of arsenic was eluted at equilibrium. Most of arsenic in CFA was eluted at 120 days.

4. For the quantitative evaluation of leaching characteristics, the leaching rate equation was defined using modified kinetic model of first-order reactions involving two variables; the constants *a* and *b*. The constants *a* and *b are* estimated by data fitting to the equation.

5. The coal species having high value of *a* has a high leaching fraction at initial stage of leaching time (eluted early) and has a slow speed, while coal species having high value of *b* has a fast leaching rate.

6. It is found that the constant *a* has a good relationship with CaO content in CFAs, in which the constant *a* (indicated leaching rate of arsenic) was decreased with an increase of CaO content in fly ash. Therefore, the value of the rate constant *a* can be said to be the main factor determining arsenic leaching. Arsenic leaching can be suppressed by controlling this.

7. In light of this, it is important to control the amount of CaO for arsenic elution suppression by adding CaO content onto fly ash with an appropriate addition amount to prevent the leaching of arsenic, and it is hoped that more extended study will be made to develop the arsenic leaching suppression method for CFA.

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Chapter 3
Effect of Additives on Arsenic, Boron and Selenium Leaching from Coal Fly Ash

3.1 Introduction

Coal-based power generation is one of the major sources of environmental pollution due to the discharge of large amounts of fly ash into the environment. After burning in a boiler, as the flue gas cools down, trace elements in coal such as As, B, Cr, Sb, and Se condense on the surface of the fly ash and form new stable compounds [1]. Approximately 41% of the production of fly ash worldwide is utilized in various applications, such as a substitute material for Portland cement, structural fills (usually for road construction), soil stabilization, as mineral filler in asphaltic concrete and mine reclamation, and the rest is disposed in landfills [2]. The disposal of fly ash in the environment involves the interaction of fly ash particles with weathering and hydrological processes where rainfall causes trace elements in the fly ash to elute and contaminate the environment. The leaching of As, B, and Se from coal fly ash (CFA) is likely to occur as these elements tend to form hydrophilic oxides that are dissolved as oxyanion forms [3].

The beneficial reuse of fly ash as embankment material in road construction has great potential in minimizing the amount of disposed fly ash [4–6], which will reduce the disposal costs incurred by industry, reduce landfill requirements, minimize damage to natural resources caused by excavating earthen materials for construction, obtain added value from fly ash, and ultimately conserve production energy.

Among the trace elements found in coal fly ash, As, B, Cd, Cr, Hg, Pb, and Se are of the greatest concern as environmental hazards [7]. This study investigated the behavior of As, B, and Se as these elements have recently become a major problem in soil contamination in Japan. Long-term exposure of arsenic-contaminated materials to water may lead to various diseases such as conjunctivitis, hyperpigmentation, cardiovascular diseases, skin cancer, gangrene, and disturbances in the peripheral vascular and nervous systems [8]. Boron can cause nausea, vomiting, redness of the skin, diarrhea, and difficulty swallowing; also, in animals, acute excessive exposure to B may cause rapid respiration, eye inflammation, swelling of the paws, and may affect male reproductive organs [9]. Similarly, excessive Se intake may yield circulatory problems and loss of hair and fingernails in humans [10]. Due to the increased awareness of the environmental impact of fly ash, the leaching of trace elements including As, B and Se needs to be controlled before fly ash utilization. Additionally, the reuse of fly ash as embankment material needs to meet regulations on soil contamination; in Japan, the permissible limits for As, B and Se are 10 µg/L, 1 mg/L, and 10 µg/L, respectively.

Understanding the factors that control the leaching behavior of trace elements is critical in predicting the potential impacts of fly ash on the environment. Several works have been

conducted on the leaching behavior of As, B, and Se from CFA. Jiao et al. [11] studied the leaching characteristics of As in fly ash and they found that the presence of Ca in fly ash plays an important role in the leaching behavior of As. Iwashita et al. [12] suggested that the leaching of B and Se may involve the trapping of B and Se species by the ettringite phase, leading to a decrease in leaching under alkaline conditions. Wang et al. [13] investigated the effect of pH, S/L ratio, calcium addition, and leaching time on the leaching behavior of As and Se from two major types of CFAs and found that the leaching of As and Se from CFA generally increased with increases in the S/L ratio and leaching time; also, adsorption/desorption played a major role in As and Se leaching from the CFA. Van der Hoek et al. [14,15] showed that the leaching of As and Se from acidic ashes could be described by sorption of iron oxide, while the leaching from the alkaline ashes appeared to be controlled by sorption in the alkaline calcium-phase. Our previous study investigated the leaching characteristics of As from six CFA samples, and described a decrease in the As leaching rate with an increase in CaO content in fly ash [16].

Overall, Ca content and the sorption process are known to play important roles in the release of As, B, and Se from CFA. Although there have been extensive studies to explain the effect of calcium on As, B, and Se leaching and adsorption in fly ash [11–19], the application of additives (which contain high levels of calcium) to suppress As, B, and Se release has been less well established. Furthermore, the utilization of paper sludge ash and filter cake—which are generated as waste in the papermaking and lime industry processes—as inexpensive additives to suppress As, B, and Se leaching from CFA has never been tested. Therefore, the aim of this study was to examine the effects of inexpensive additives on suppressing As, B, and Se leaching from CFA. For this purpose, an appropriate amount of paper sludge ash and filter cake were added to fly ash, and the resulting mixture was subjected to a leaching test. The pH of the mixture leachates and the relation of As, B, and Se leaching (with major coexisting ions including Ca, Na, K, and Mg in mixture leachates) are discussed. This new information is expected to help in controlling the release of As, B, and Se into the environment to aid in the development of sustainable fly ash management strategies.

3.2 Experimental
3.2.1 Coal Fly Ash and Additives

A relatively high concentration of trace elements leaching (As 48.66 µg/L, B 5.39 mg/L, Se 86.9 µg/L, detected using ICP-AES) and low calcium content fly ash sample (2.05% of CaO, detected using X-ray fluorescence) named fly ash H (FAH) was collected from a Japanese coal fired power plant (600 MWe) for the leaching test. Paper sludge ash (PS Ash 3, PS Ash 4, and PS Ash 5) and filter cake (FC) (considered as suppressing materials) and pure $Ca(OH)_2$ were used in this experiment as the additives. $Ca(OH)_2$ was applied to compare the

effect of calcium addition among pure calcium-material $(Ca(OH)_2)$ and native calcium-material (PS Ash 3, PS Ash 4, PS Ash 5, and FC). Paper sludge ash is waste generated in the papermaking industry as a by-product of the de-inking and re-pulping of paper, while filter cake comes from the lime industry as a waste from the $CaCO_3$ manufacturing process.

The utilization of paper sludge ash and filter cake was considered due to the relatively high content of calcium they contain. The CaO content detected using X-ray fluorescence (XRF) in PS Ash was varied, ranging from 18.77 to 46.31%. FC had the highest CaO content at 59.18%. Table 1 lists the composition of inorganic elements in FAH and additives.

3.2.2 Fly Ash Treatment and Leaching Test

The additive was added to the FAH sample so as to give a Ca content of 5% and 10% (see Appendix A). The mixture was then moved to a bowl and distilled water at 25% addition ratio of the total mixture was added; the mixture was kneaded for one minute, and then scraped and kneaded for a further two minutes. The mixture was then stored in a sealed plastic bag for seven days, following which the mixture was air-dried and the leaching test was conducted.

Table 1. Composition of inorganic elements in fly ash and additives

Sample			FA H (1)	PS Ash 3	PS Ash 4	PS Ash 5	FC
ash compositition	SiO_2	[%]	26.81	31.47	44.21	42.36	23.31
	Al_2O_3		19.79	12.40	22.23	19.80	13.87
	TiO_2		3.27	0.38	2.56	2.11	0.06
	Fe_2O_3		1.97	5.13	2.63	5.56	2.33
	CaO		37.21	46.31	18.77	19.51	59.18
	MgO		2.04	3.28	3.42	3.30	0.96
	Na_2O		0.18	0.24	0.95	0.41	0.03
	K_2O		0.95	0.20	2.09	1.99	0.25
	P_2O_5		1.47	0.18	1.75	1.54	0.00
	MnO		0.04	0.03	0.05	0.06	0.04
	V_2O_5		0.01	0.01	0.02	0.02	0.02
	SO_3		6.26	0.36	1.31	3.33	0.00
pH of the leachate		[-]	10.38	13.72	12.71	12.26	7.28
Leached of Ca ion		[mg/L]	121	1405	246	597	15.45
Leaching Concentration	As	[µg/L]	48.66				
	B	[mg/L]	5.39				
	Se	[µg/L]	86.9				

Note: FAH (1) means coal fly ash sample H from the chamber 1 of electrostatic precipitator

The procedure of standard leaching tests for fly ash (Notification No. 13 by the Environmental Agency of Japan) was employed as the protocol for leaching tests in this work. The mixture of FAH-additive of 5 g was mixed with 50 mL distilled water, which accounted for a liquid to solid ratio (L/S) of 10, and was shaken for six hours at room temperature with a shaking

speed of 200 rpm. The solid-liquid sample was separated by filtration using a membrane filter of 0.45 μm to obtain the filtrate.

3.2.3 Characterization of the Elements in CFA and Additives

The total concentrations of the major chemical compositions in FAH and additives were determined using a Wavelength Dispersive X-ray Fluorescence Spectrometer (WDXRF S8 TIGER, Bruker AXS, Yokohama, Japan). For XRF analysis of the fly ash and additive samples, a small amount (approximately 500 mg) was poured onto a polypropylene thin-film that was attached previously to a plastic O-ring sample cup with an outer diameter of 40 mm. The samples were analyzed using XRF, and the chemical compositions of samples were determined.

The identification of calcium compounds in the additives was determined qualitatively using thermogravimetric analysis (TG/DTA6300 SII EXSTAR 6000, Hitachi, Hong Kong, China) and X-ray diffraction (LabX XRD6100, Shimadzu, Kyoto, Japan). For thermogravimetric (TG) analysis, a sample of 10–20 mg was heated with a measurement temperature from 30 to 1000 ∘C at a heating rate of 10 ∘C/min under a nitrogen atmosphere at a flow rate of 200 mL/min. For XRD analysis, the sample was irradiated with Cu Kα-radiation between 10 and 80∘ (2θ) with a counting angle at 0.02∘ and slit of 0.3 mm, under a scanning speed of 2∘/min, at an acceleration voltage of 40 kV and current of 30 mA. The diffraction pattern was analyzed with the help of the software module "DDView and Sleve," the phases were viewed and identified by applying the database PDF-2/Release 2013 RDB from the International Center for Diffraction Data (ICDD).

3.2.4 Chemical Analysis

The concentrations of As, B, and Se in the filtrate were carefully analyzed by ICP-AES (ULTIMA2, HORIBA Ltd, Tokyo, Japan). Cations such as Ca^{2+}, Na^+, K^+, and Mg^{2+} were quantified using ion chromatographs IA-300 (DKK-TOA Corporation, Tokyo, Japan). The final pH of the leachate reflected the interaction of the leaching fluid (distilled water) with the buffering capacity of the FAH-additive mixture. The pH measurement was carried out by a pH/ion Meter D-53, HORIBA. After pH meter calibration at pH 4, 7, and 9 using buffer solutions, the pH measurement of samples was carried out.

3.3 Results and Discussion

3.3.1 pH of the Leachates

A strong relationship between the pH of the leachate and CaO content has been recognized since this mineral elevates pH in the leachates [20–23]. Figure 1 shows the effect of including additives in the pH of the leachates, where it increased with the treated amount. However, each additive had a different way of elevating pH that was related to their properties. Of the four

additives discussed (after FAH- Ca(OH)$_2$ mixture leachates), the FAH-PS Ash 3 mixture leachates showed the highest final pH over FAH-PS Ash 5, FAH-PS Ash 4 and FAH-FC mixture leachates for both 5% and 10% Ca content samples, as shown in Figure 1. This indicated that the relatively higher CaO content of PS Ash 3 added into fly ash tended to increase the pH of the mixtures leachates. This was consistent with the previous study in Reference [24], where the release of Ca from CaO minerals yielded Ca(OH)$_2$ in aqueous solutions, which is an oxide mineral that significantly contributes to alkalinity. Conversely, FC, which contained the highest CaO content, did not appear to have any impact on elevating the pH of the mixture leachates.
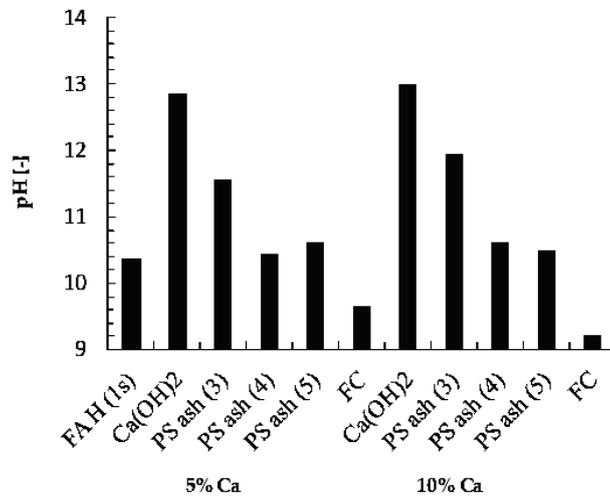

Figure 1. Leachate pH values of fly ash H alone and fly ash H under 5 kinds of additives addition for 5% and 10% Ca content samples.
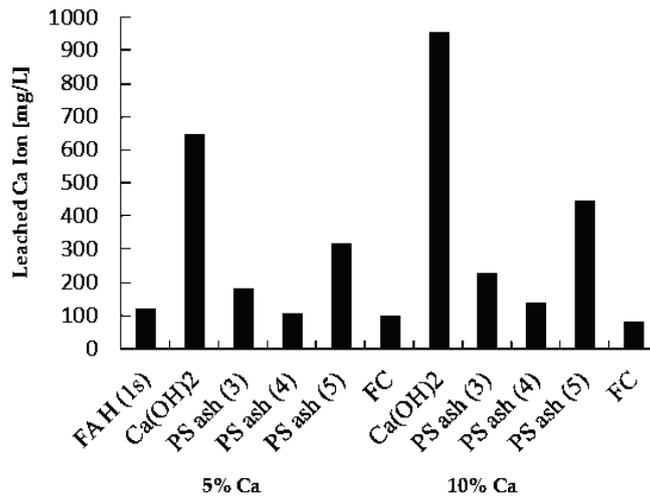

Figure 2. Ca ion leached of fly ash H alone and fly ash H under 5 kinds of additives addition for 5% and 10% Ca content samples.

To probe the effects of FC addition into FAH, the leaching amount of calcium ions in the FAH-FC mixture leachates was examined (Figure 2). As predicted, the amount of Ca ions leached in the FAH-FC mixture leachates was lower than that of other additives. This result indicates that the low amount of leached Ca ion in the FC mixture leachates was not enough to elevate the pH of the leachates. This is relevant with the previous observation in Reference [12], that pH tended to rise when the Ca leaching amount was larger, where the main species of Ca such as CaO elevated the pH in the leachate. Overall, it could be concluded that an increase of CaO content in the additives caused an increase in the leachates pH, and that the leached Ca ions contributed to elevate the leachates pH.

Based on the above discussion, it is clear that the leached Ca ions in the mixture leachates seemingly play an important role in contributing to the alkalinity of the mixture, especially Ca(OH)2, which possessed high solubility during the leaching test given that Ca(OH)2 is composed of completely water-soluble Ca. As the amount of leached Ca ions yielded was varied due to the diverse solubilities of different calcium compounds in the additives, it was important to identify the types of calcium compounds included in the PS Ash 3, PS Ash 4, PS Ash 5, and FC to better understand the effect of the additives on the pH of the leachates. To clarify such a hypothesis, TG and XRD analyses were carried out. The results are shown in Figures 3 and 4.
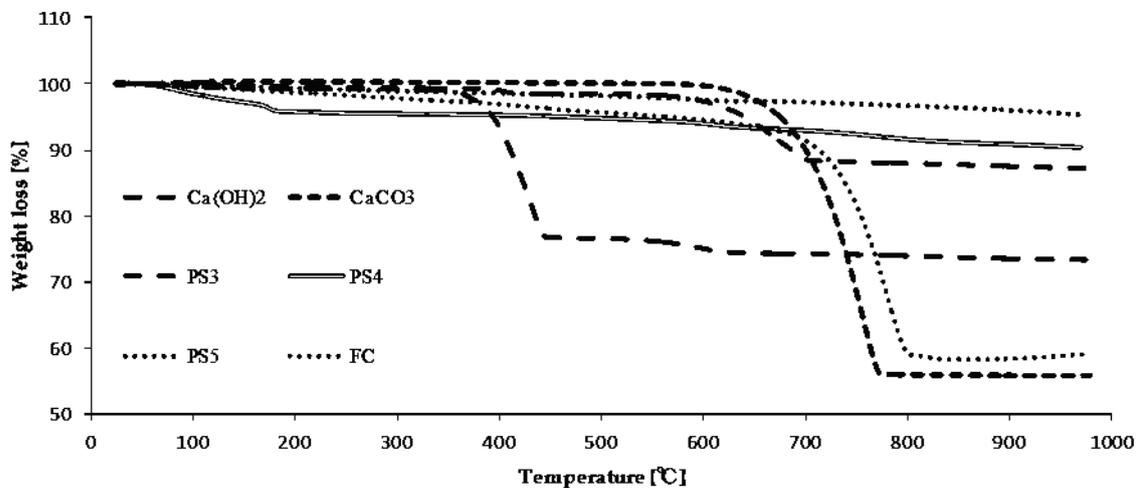

Figure 3. TG curves of thermal decomposition of Ca(OH)2, CaCO3 and additives in N2 atmosphere.

TG was performed on $Ca(OH)_2$ and $CaCO_3$ of 99.9% purity to confirm that the two weight losses in the TG curve of additives were due to the thermal decomposition of $Ca(OH)_2$ and $CaCO_3$. Figure 3 compares the TG curves of each calcium compound and the additives. The TG analysis of $Ca(OH)_2$, $CaCO_3$, and additives was conducted under a nitrogen atmosphere based on

the methods described in References [25,26]. Based on previous study, Ca(OH)2 was thermally decomposed at 330-460oC into CaO [26] and $CaCO_3$ was thermally decomposed into CaO at around 700°C [27]. As seen in Figure 3, the weight losses in PS Ash 3 at around 390°C and 600°C corresponded to the thermal decompositions of $Ca(OH)_2$ and $CaCO_3$. The weight losses in PS Ash 4 (around 600°C), PS Ash 5 (around 500°C), and FC (around 700°C) corresponded to thermal decomposition of $CaCO_3$. From these results, it was found that the $Ca(OH)_2$ and $CaCO_3$ in additives could be detected by TG. Since the decomposition temperature of CaO is above 1000°C [25] and cannot be detected by TG, the analysis of calcium compounds in the additives was performed by XRD method.
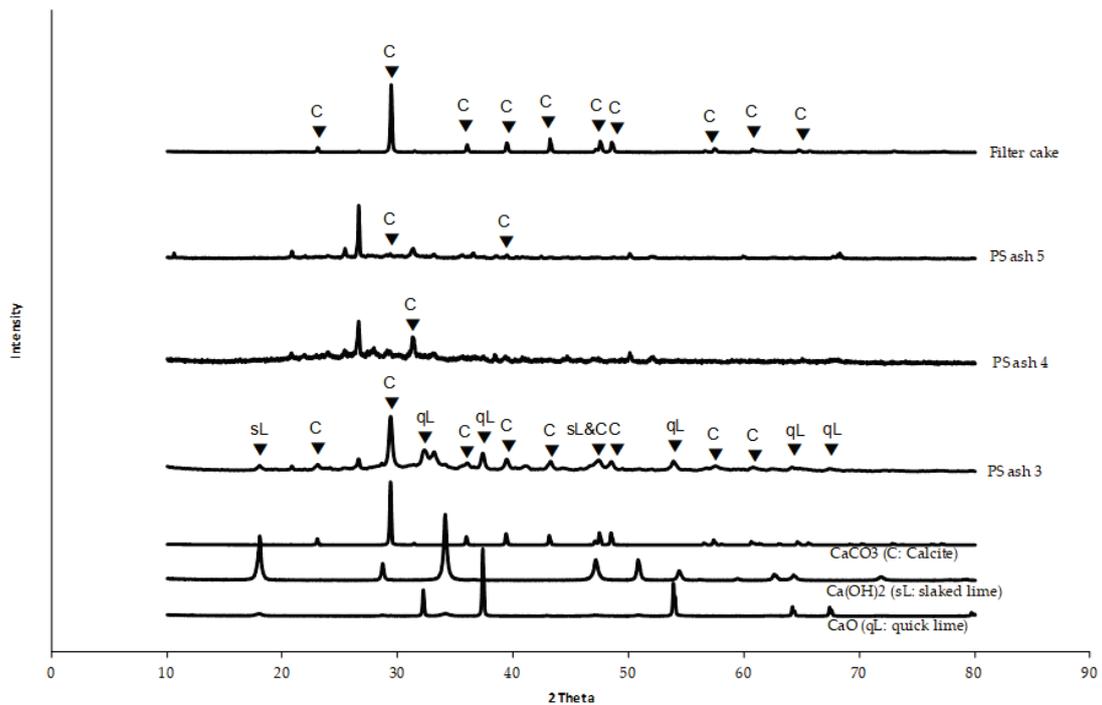

Figure 4. XRD Patterns of several calcium compounds and additives.

Figure 4 shows the X-ray diffraction patterns of several calcium compounds and additives. All of the peaks in the additives were compared with the peaks in each calcium compound. The results showed that PS Ash 3 contained $CaCO_3$, CaO, and Ca(OH)2; PS Ash 4 and PS Ash 5 contained small amounts of $CaCO_3$, while FC contained the most amount of $CaCO_3$. The XRD analysis results were consistent with the TG analysis results described above, and revealed that a relatively high content of $CaCO_3$ in the FC caused this additive to yield low amounts of leached Ca ions and produce a relatively low value of pH mixture leachates, which was considered to be due to $CaCO_3$ being an insoluble substance in pure water. Therefore, the contents of CaO and $Ca(OH)_2$ (as water soluble Ca) in PS Ash 3 caused this additive to yield high amounts of leached

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Ca ions and a higher value of pH mixture leachate than that of PS Ash 4, PS Ash 5, and FC. Regarding the higher amounts of leached Ca ions in PS Ash 5 than in PS Ash 3 (Figure 2), this could be attributed to the relatively high content of SO_3 (detected by XRF) as an acid compound in PS Ash 5 (see Table 2). This is consistent with the reported study by Killingley et al. [28], where the balance between the concentration of alkaline-earth element, Ca, in the ashes, and the proportion of potentially acid generating SO_3 influenced the initial pH and leached Ca ions of the ash-water system.

Table 2. Trace element leaching suppression effect of additives.

Sample	Ca [wt%]	As leaching concentration [μg/L]	Leaching inhibition rate [%]	B leaching concentration [mg/L]	Leaching inhibition rate [%]	Se leaching concentration [μg/L]	Leaching inhibition rate [%]	Final pH
FA H (1s)	1.46	48.66	0.0	5.39	0.0	86.39	0.0	10.38
Ca(OH)2	5	1.26	97.4	0.10	98.1	7.15	91.7	12.86
PS ash (3)	5	5.12	89.5	0.87	83.9	15.00	82.6	11.58
PS ash (4)	5	27.71	43.1	2.83	47.5	26.04	69.9	10.46
PS ash (5)	5	12.06	75.2	1.48	72.6	10.60	87.7	10.63
FC	5	57.75	-18.7	5.55	-3.0	36.04	58.3	9.66
Ca(OH)2	10	0.00	100.0	0.10	98.2	6.16	92.9	12.98
PS ash (3)	10	1.84	96.2	0.41	92.4	8.57	90.1	11.94
PS ash (4)	10	5.66	88.4	2.96	45.1	5.54	93.6	10.62
PS ash (5)	10	6.71	86.2	1.06	80.3	2.80	96.8	10.51
FC	10	65.29	-34.2	5.34	1.0	19.19	77.8	9.23

1 Leaching concentration. 2 Leaching inhibition rate.

3.3.2 Effect of Additives on Arsenic Leaching

The presence of Ca in CFA, pH, and the sorption process are known to play important roles in the leaching behavior of arsenic. Arsenic reacts with calcium to form a new stable compound, which is slightly soluble in water [11,29]. As the additives contained high native-calcium that could enrich the calcium content in CFA, the leaching of arsenic into the environment was expected to be reduced.

Figure 5a shows the arsenic leaching concentration for FAH alone, and for fly ash under five kinds of additives at a 5% and 10% Ca content. The arsenic leaching concentration of FAH is shown on the far left as a comparison standard in Table 2. As seen in Figure 5a, Ca(OH)$_2$ was very effective in suppressing arsenic leaching, and the leaching amount of FAH greatly reduced from 48.7 μg/L

to 1.3 μg/L in the 5% Ca content sample. The leaching inhibition rate was 97.4% and 100% for the 5% and 10% Ca content samples, respectively. The value of the 'leaching inhibition rate' was defined as [(leaching concentration of element in FAH)-(leaching concentration of element in FAH-additives mixture)/(leaching concentration of element in FAH)]. Comparing PS Ash 3, 4

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and 5, it was seen that the arsenic suppressing effect was high in the order of PS Ash 3 > 5 > 4 for the 5% Ca content sample and PS Ash 3 > 4 > 5 for the 10% Ca content sample. In addition, the arsenic leaching concentration was reliably reduced in the Ca 10% sample compared to that in the Ca 5% sample. A plausible reason to describe the dramatic reduction of arsenic leaching concentration could be due to the relatively high Ca ions (Ca^{2+}) in $Ca(OH)_2$ and in the PS Ash mixture leachates that react with oxyanionic species of arsenic at an alkaline pH, which can form precipitates as a new stable compound or trap the oxyanionic species of arsenic through the ettringite phase formed under alkaline conditions, leading to a decrease in the leaching concentration of arsenic from FAH. This is consistent with previous studies that have shown that under a high Ca condition and pH > 11.5 (alkaline leachate), the dominating species, AsO_4^{3-}, formed a precipitate with Ca as a less soluble compound or trapped the arsenic species by the ettringite phase which prevented the leaching of arsenic [11,13]. Figure 6a presents the plots of Ca ion concentration and arsenic leaching concentration in the mixture leachates. The arsenic leaching concentration tended to decrease as the Ca ion concentration increased.

As discussed previously, there was an increase in pH when Ca was abundant in the leachates; Figure 7a shows the relationship between the leachate pH and the arsenic leaching concentration for all samples. Since $Ca(OH)_2$ is completely water-soluble Ca, the pH of $Ca(OH)_2$ was the highest, around 13. Overall, the pH and arsenic leaching concentration showed a linear relationship, where the higher the pH, the lower the arsenic leaching concentration, and arsenic leaching was suppressed as the pH of the leachate became 11.5 or higher. This agrees with the observation reported by Jiao et al. [11] and Wang et al. [13], who claimed that at a pH above 11, AsO_4^{3-} (as the dominating species) forms precipitates with Ca, which provides a suppressing effect on the mobilization of arsenic. Figure 7a shows that arsenic leaching was suppressed in PS Ash 4 and 5 despite a pH lower than 11.5, therefore, it was considered that alkaline elements other than Ca also contribute to suppress arsenic leaching. Thus, the concentration of alkaline elements in the leachates (such as Na, K, and Mg) were measured and the relationships between them and arsenic leaching concentrations were examined. Figure 8a shows the relationship between the Na ion concentration and the arsenic leaching concentration in the mixture leachates. As seen in Figure 8a, the Na ion concentration showed a corresponding correlation with the arsenic leaching concentration, where the arsenic leaching concentration tended to decrease as the Na ion concentration increased. For K and Mg (as shown in Figures A1a and A2a), neither of them were clearly related to the arsenic leaching concentration. This result shows the reason why PS Ash 4 and 5 can be understood to suppress arsenic leaching as an effect of Na ions. The reason why the Na ion concentration as an alkaline element other than Ca influences the arsenic leaching concentration has been insufficiently explored, but warrants further investigation to be able to estimate further mixture compositions of additives for the more effective suppression of arsenic

leaching.

For the arsenic leaching suppression effect on FC, despite the highest Ca content, FC was found to increase rather than decrease arsenic leaching. This could be explained by the relatively low pH of the FAH-FC mixture leachates of around 9.2–9.7, which is not an effective pH value for the suppression of arsenic leaching. Furthermore, the Ca ion concentration was 83–101 mg/L, which is not an effective Ca ion concentration for the suppression of arsenic leaching due to the fact that the composition of FC is calcium carbonate based, which is a relatively stable substance.
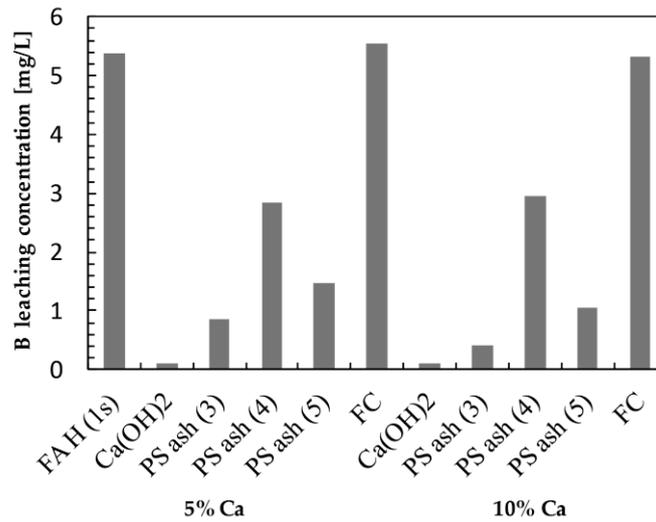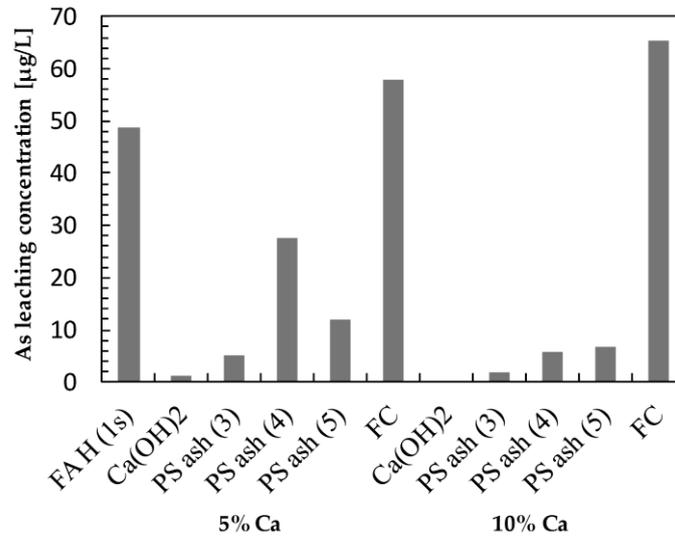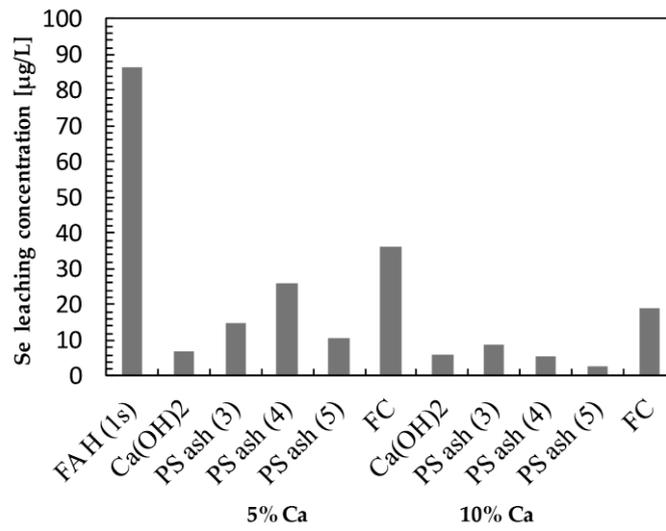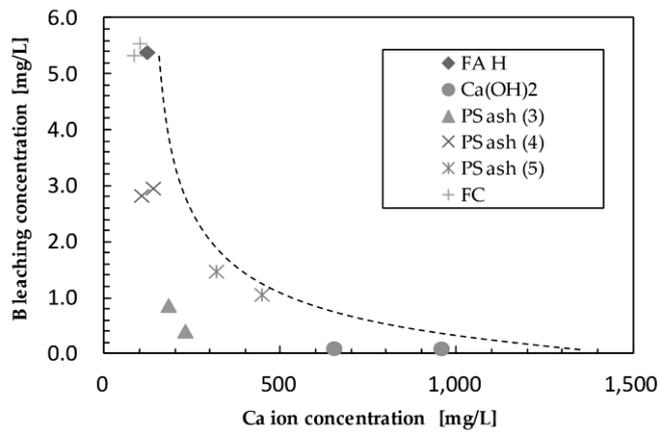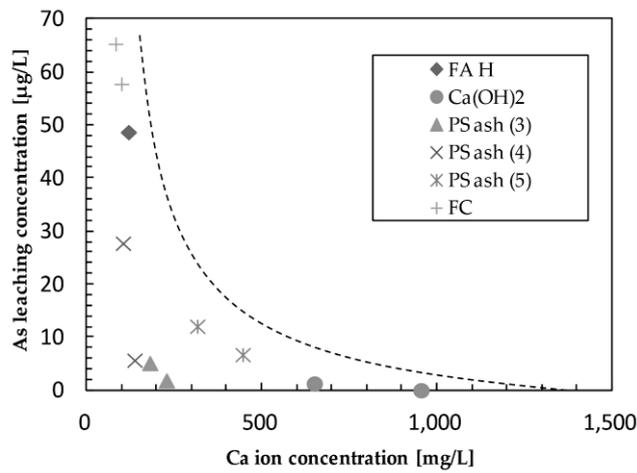
Figure 5. Trace element leaching concentration for fly ash H alone, and fly ash H under five kinds of additives addition for 5% and 10% Ca content samples: (a) arsenic; (b) boron; and (c) selenium
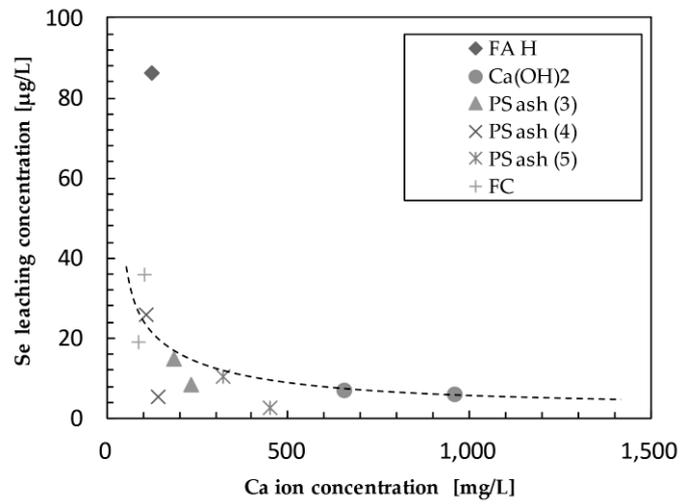
Figure 6. Relationship between Ca ion leaching concentration and trace elements leaching concentration of 5 kinds of additives: (a) arsenic; (b) boron; (c) selenium

Figure 7. Relationship between leachate pH and trace elements leaching concentration of 5 kinds of additives: (a) arsenic; (b) boron; (c) selenium.
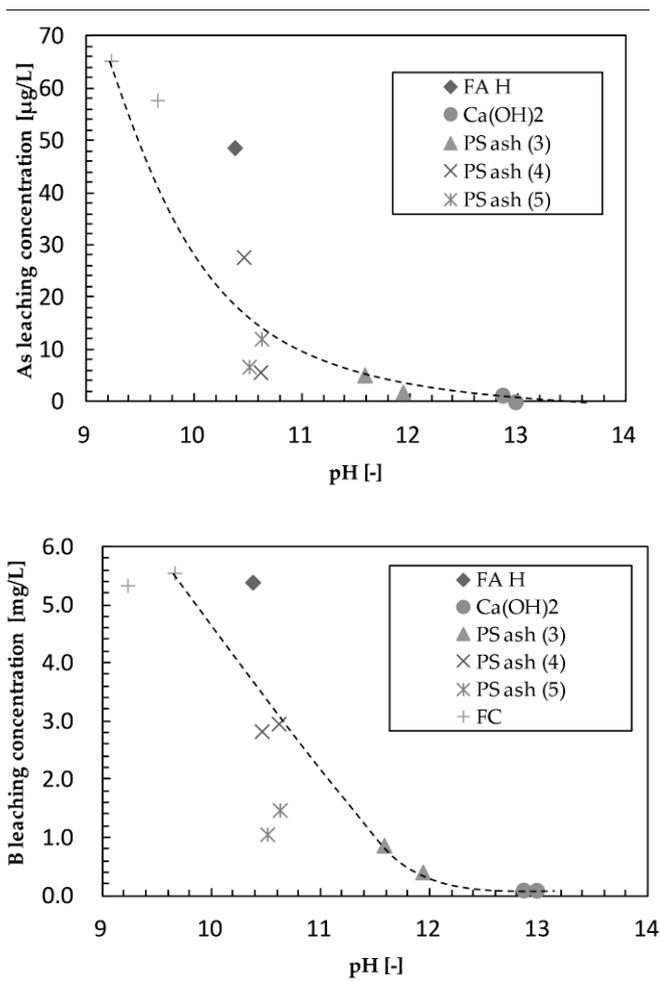
Figure 8. Relationship between Na ion leaching concentration and trace elements leaching concentration of 5 kinds of additives: (a) arsenic; (b) boron; (c) selenium.
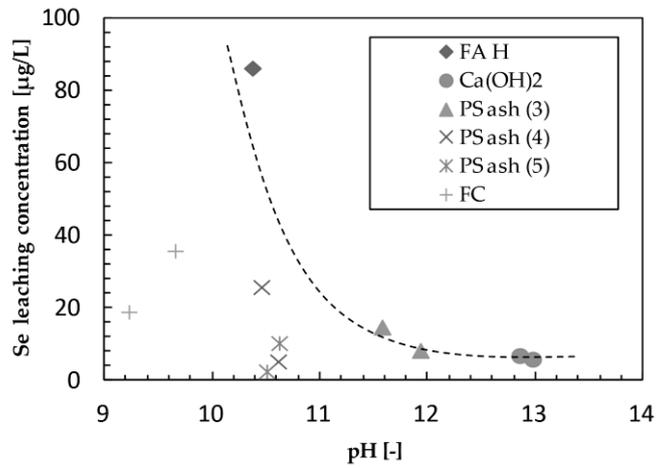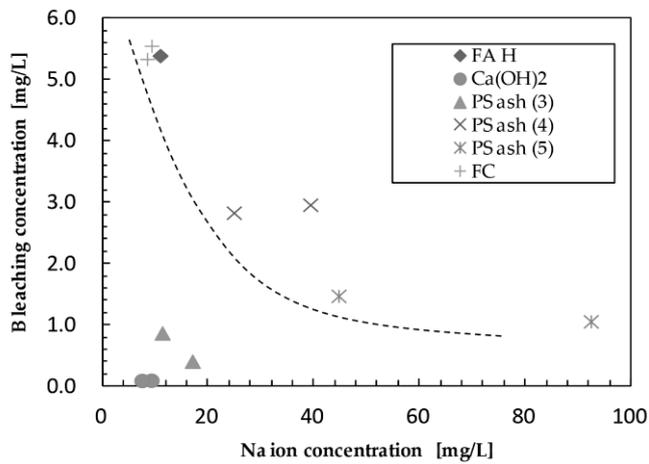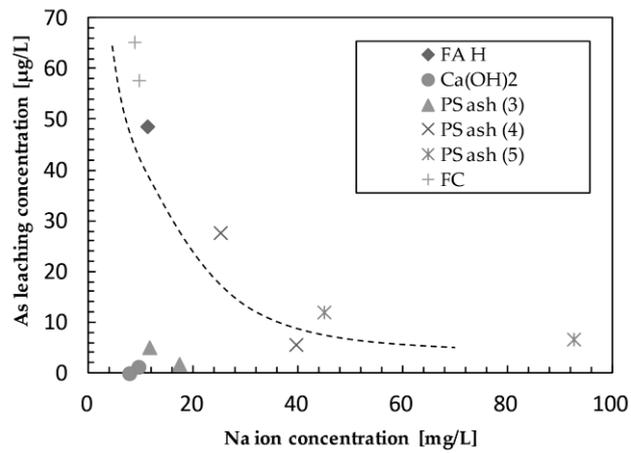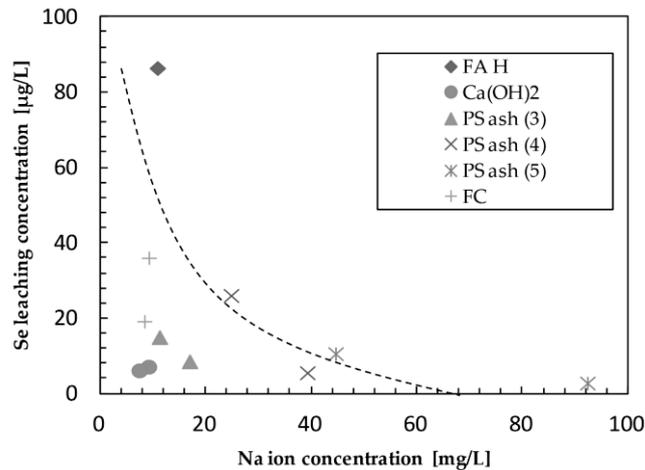
3.3.3 Effect of Additives on Boron Leaching

Figure 5b shows the boron leaching concentration for fly ash H (FAH) alone, and for fly ash under five kinds of additives at 5% and 10% Ca content (as shown in Table 2). As shown in Figure 5b, like arsenic leaching suppression, $Ca(OH)_2$ was also very effective in suppressing boron leaching with a leaching inhibition rate of 98% for both 5% and 10% Ca content, respectively. This result indicated that As and B leaching can be simultaneously suppressed by the addition of $Ca(OH)_2$. A comparison of PS Ash 3, 4, and 5, showed that the boron suppressing effect to be high in the order of PS Ash 3 > 5 > 4 at both 5% and 10% Ca content samples. The dramatic reduction in the boron leaching concentration could be due to the relatively high level of Ca ions (Ca^{2+}) in $Ca(OH)_2$ and in the PS ash mixture leachates that react with oxyanionic species of boron at an alkaline pH, which can form new stable precipitates or trap the oxyanionic species of boron through the ettringite phase formed under alkaline conditions, leading to a decrease in the boron leaching concentration from FAH. This was consistent with a previous study that showed that with a high amount of Ca leaching and a pH >11 (alkaline leachate), the dominating species—in this case, borate—formed a precipitate with Ca that was a less soluble compound or trapped the boron species in the ettringite phase and prevented the leaching of boron [12,30,31]. Figure 6b presents the plots of the Ca ion concentration and boron leaching concentration in the mixture leachates. Like the arsenic results, the boron leaching concentration tended to decrease as the Ca ion concentration increased. Figure 7b shows the relationship between the leachate pH and boron leaching concentration for all samples. Since the leaching test was performed simultaneously with As and Se, the pH data were the same data as As and Se (Table 2). As with arsenic, the pH and boron leaching concentration also showed a linear relationship; the higher the

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pH, the lower the boron leaching concentration, and boron leaching was suppressed as the pH of the leachate became 11.5 or higher. This finding is consistent with Iwashita et al. [20], Hollis et al. [30], and Cetin et al. [31], who claimed that the B concentrations decreased with an increase in pH above 11, where large quantities of Ca minerals in the leachates may have caused the precipitation of B with Ca. In the case of PS Ash 5, it seems that the boron leaching concentration was suppressed despite a pH lower than 11, and it was suggested that alkaline elements other than Ca could also contribute to the suppression of boron leaching. Therefore, the concentration of alkaline elements in the leachate (such as Na, K, and Mg) were measured and the relationships between them and the boron leaching concentrations were examined. Figure 8b shows the relation between the Na ion concentration and boron leaching concentration in the mixture leachates. As shown in Figure 8b, it appeared that the Na ion concentration showed a corresponding correlation to the boron leaching concentration; the boron leaching concentration tended to decrease as the Na ion concentration increased. For K and Mg (as shown in Figures A1b and A2b), neither of them was clearly related to the boron leaching concentration. This result demonstrates why PS Ash 5 could suppress boron leaching as an effect by Na ions. The reason why the Na ion concentration influences the boron leaching concentration has been insufficiently investigated, but it warrants further study in order to estimate the mixture composition of additives for the more effective suppression of boron leaching.

For a boron leaching suppression effect of FC like that observed with arsenic, FC did not have an inhibitory effect on boron leaching. Overall, the mechanism to suppress the leaching of arsenic and boron is similar. Figure 9 shows the relationship between the arsenic leaching concentration and the boron leaching concentration plotted for all samples. In general, they have a good correlation, indicating that As and B can be suppressed simultaneously.
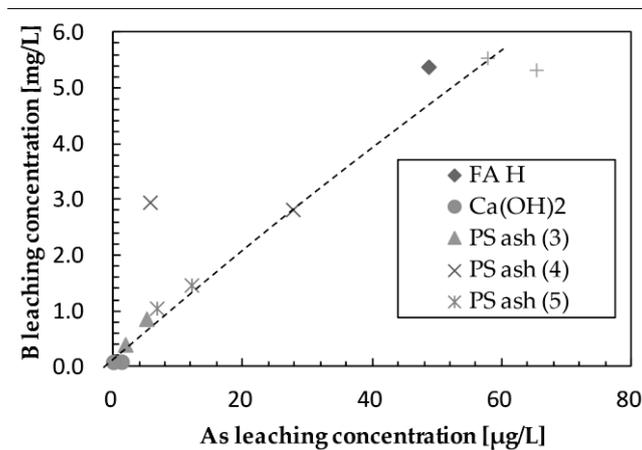

Figure 9. Relationship between arsenic leaching concentration and boron leaching concentration.

3.3.4 Effect of Additives on Selenium Leaching

Figure 5c shows the selenium leaching concentration for fly ash H (FAH) alone, and fly ash under five kinds of additives addition at 5% and 10% Ca content (Table 2). As shown in Figure 5c, $Ca(OH)_2$ was also very effective in suppressing selenium leaching with a leaching inhibition rate of 91% for both 5% and 10% Ca contents, respectively. This result indicated that As, B, and Se leaching could be simultaneously suppressed by the addition of $Ca(OH)_2$. A comparison of the leaching suppression effect by $Ca(OH)_2$ for As, B, and Se showed that the leaching inhibition rate when Ca content was 5% was 97.4%, 98.1%, and 91.7%, respectively. Therefore, the inhibitory effect of Ca was high in the order of B > As > Se. When comparing PS Ash 3, 4, and 5, it could be seen that the selenium suppression effect was increased in the order of PS Ash 5 > 3 > 4 for the 5% Ca content sample, and PS Ash 5 > 4 > 3 for the 10% Ca sample. In addition, it could be seen that the selenium leaching concentration was reliably reduced in the Ca 10% sample compared to the Ca 5% sample. The dramatic reduction of the selenium leaching concentration could be due to the relatively high level of Ca ions (Ca^{2+}) and $Ca(OH)_2$ in the PS ash mixture leachates that react with oxyanionic species of selenium at an alkaline pH, which formed precipitates as a new stable compound or trapped the oxyanionic species of selenium through the ettringite phase formed under alkaline conditions, thus leading to a decrease in the leaching concentration of selenium from FAH. This is consistent with the previous study that under high Ca conditions and a pH > 11 (alkaline leachate), the dominating species, SeO_3^{2-}, formed a precipitate with Ca as a less soluble compound or trapped the selenium species in the ettringite phase and prevented the leaching of selenium [13,32,33]. Figure 6c presents the plots of the Ca ion concentration and selenium leaching concentration in the mixture leachates. Like the results of arsenic and boron, the selenium leaching concentration tended to decrease as the Ca ion concentration increased.

Figure 7c shows the relationship between the leachate pH and the selenium leaching concentration for all samples. As with arsenic and boron, the pH and the selenium leaching concentration also showed a linear relationship; in general, the selenium leaching concentration decreased with increasing pH, and selenium leaching was suppressed as the pH of the leachate became 11 or higher. This finding was consistent with Izquierdo et al. [21], Morar et al. [32], Jankowski et al. [33], and Solen-Tishmack et al. [34], who claimed that the Se concentrations decreased with an increase in pH above 11 due to the substitution of Se in the structure of ettringite. Figure 5c shows that selenium leaching was suppressed in PS Ash 4 and 5. Although the pH was lower than 11, it is thought that alkaline elements other than Ca also contributed to the suppression of selenium leaching. Therefore, the concentration of alkaline elements in the leachate (such as Na, K, and Mg) were measured and the relationships between them and selenium leaching concentrations were examined. Figure 8c shows the relationship between the Na ion concentration and the selenium leaching concentration in the mixture leachates.   As seen

in Figure 8c, it seemed that the Na ion concentration showed a corresponding correlation to the selenium leaching concentration, where the selenium leaching concentration tended to decrease as the Na ion concentration increased. For K and Mg (as shown in Figures A1c and A2c), neither of them were clearly related to the selenium leaching concentration. This result showed why PS Ash 4 and 5 could suppress selenium leaching as an effect of the Na ions. The reasons as to why the Na ion concentration is one of the alkaline elements other than Ca that influence the selenium leaching concentration has also been insufficiently considered, but is needs to be further understood in order to be able to estimate further mixture compositions of additives to more effectively suppress selenium leaching.

In contrast to arsenic and boron, FC showed some effect on selenium leaching suppression. The decrease in selenium leaching may have been due to the presence of Al_2O_3 and Fe_2O_3, as well as the Ca content and leached Ca ion content in FC, as reported by previous observations where Se was controlled by sorption reactions that occurred on the surface of metal oxides such as Al_2O_3 and Fe_2O_3 [35, 36]. These oxides may provide additional surface area to which positively charged ions may attach, resulting in decreased Se concentration in aqueous solutions [37].

Figure 10 shows the relationship between the arsenic leaching concentration and selenium leaching concentration, and Figure 11 shows the relationship between the boron leaching concentration and selenium leaching concentration for all samples. In general, they had good correlation, indicating that As, B and Se could be suppressed at the same time.
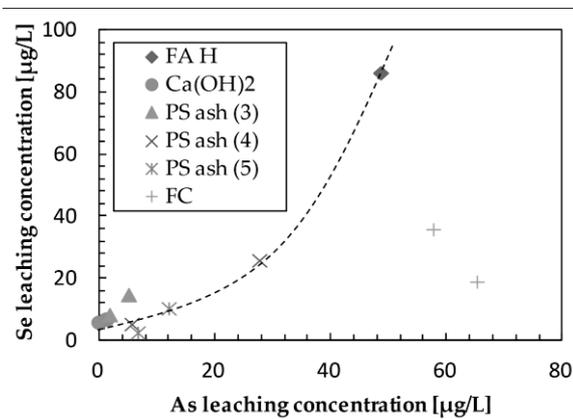

Figure 10. Relationship between arsenic leaching concentration and selenium leaching concentration
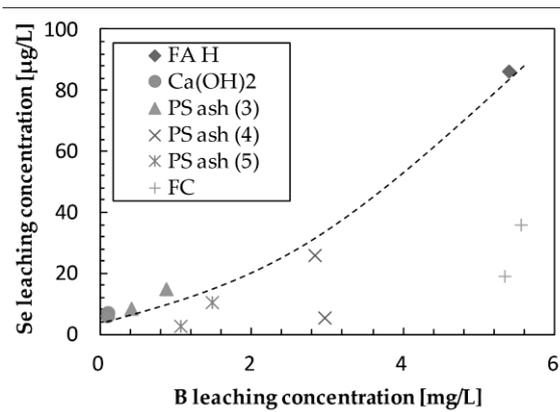
Figure 11. Relationship between boron leaching concentration and selenium leaching concentration

3.3.5 Comprehensive Evaluation of Leaching Suppression Materials

As shown above, PS Ash had the effect of simultaneously suppressing the leaching of As, B, and Se, and it has become clear that it is very promising as a practical leaching suppression material. Although FC had some effect on Se leaching suppression, it did not work for As and B, and was found overall to be inappropriate as a leaching suppression material. Figure 12 plots the leaching inhibition rates of As, B, and Se by the PS Ash as radar charts for the Ca 5% and 10% samples. In these figures, it can be comprehensively evaluated that the one having the largest area had the effect of simultaneously suppressing As, B, Se. From this figure, PS Ash 3 was the most suitable material as a suppression material, followed by PS Ash 5 and PS Ash 4, respectively. For the three elements As, B, Se, the only elution suppression material satisfying the soil environmental standard was PS Ash 3, with a Ca = 10% setting.
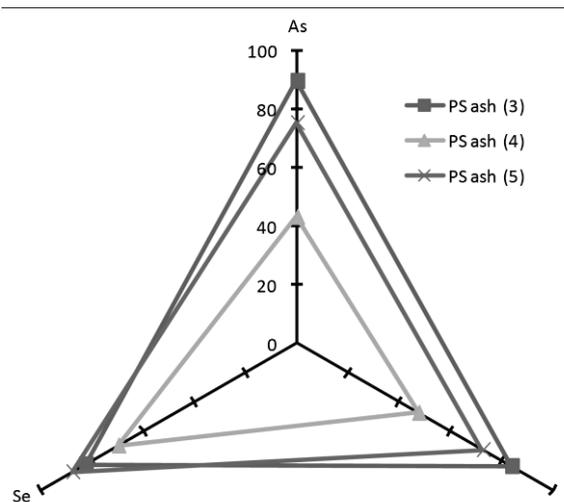
Figure 12. Trace elements (arsenic, boron, and selenium) leaching inhibition rate for (a) 5% Ca content and (b) 10% Ca content samples

3.4 Conclusions

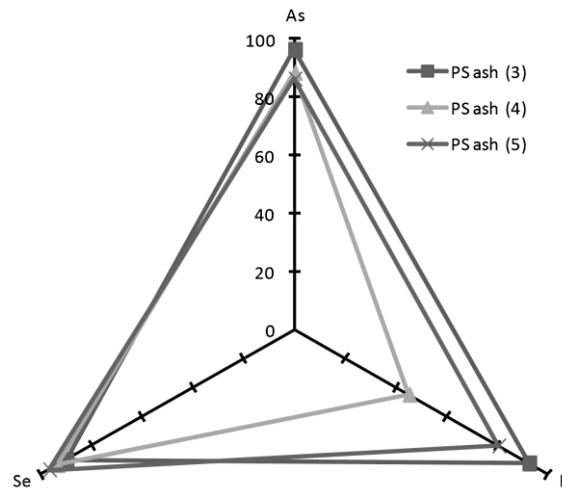This study investigated the effect of additives on the leaching characteristics of As, B, and Se in coal fly ash. We proposed $Ca(OH)_2$, Paper Sludge Ash 3, Paper Sludge Ash 4, Paper Sludge Ash 5, and filter cake as new additives (suppression materials); adjusted the Ca concentration in the finished mixture to 5% and 10%; and verified the simultaneous leaching suppressing effect of As, B, and Se. The results revealed that all additives (other than filter cake) showed a simultaneous leaching suppression effect. However, only the leaching suppression effect of PS Ash 3 satisfied the soil environmental standard with Ca concentration of 10%. Other additives could meet the soil standards by increasing the Ca concentration to a higher level.

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Appendix A

To obtain the Ca content of the finished mixture at 5% or 10%, the amount of each additive and FAH mixed was calculated based on the CaO concentration in the ash (Table 1). For example, when preparing a Ca 5% sample with FAH (x gram) and PS Ash 3 (y gram) based on 100 g of the finished mixture, considering the molecular weight of CaO 56.078 and the molecular weight of Ca 40.078, $x + y = 100$, $2.05 (40.078/56.078) x + 46.31 (40.078/56.078) y = 5$, from the simultaneous equations, the amount of x becomes 88.78 g and that of y becomes 11.22 g.
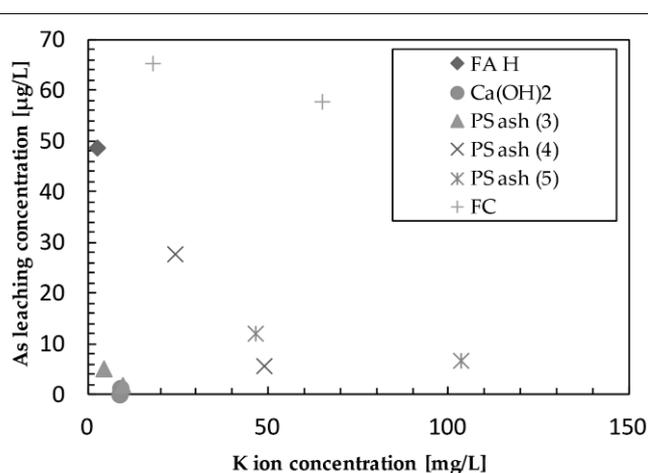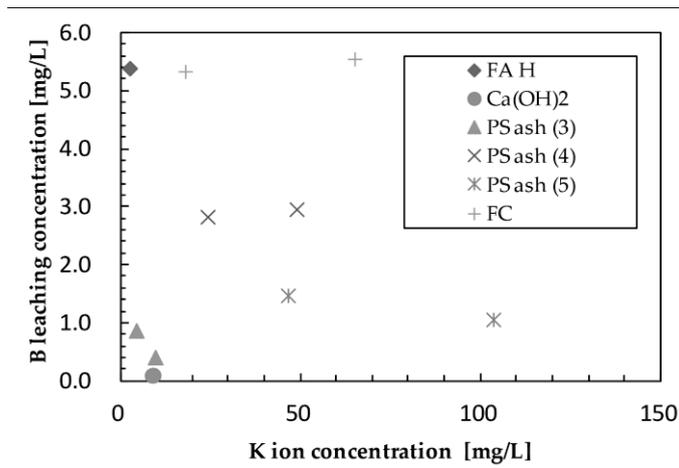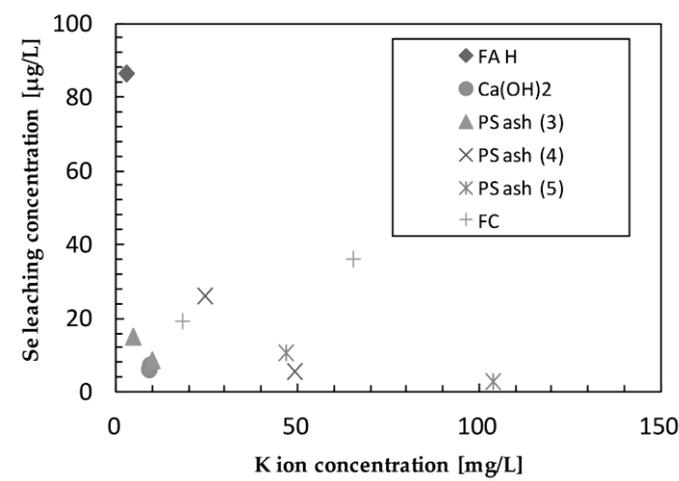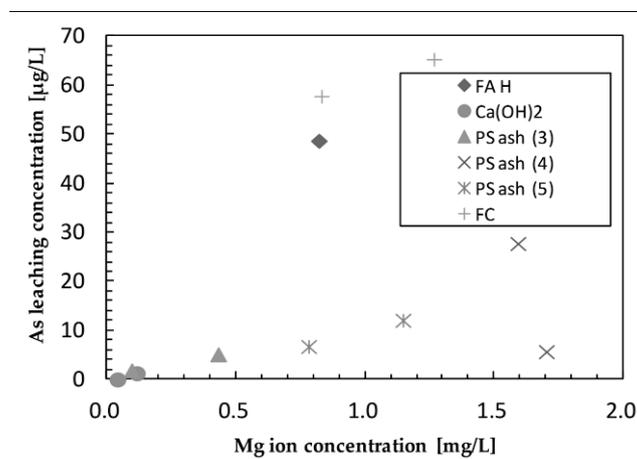
Fig A1. Cont.

Figure A1. Relationship between K ion leaching concentration and trace elements leaching concentration of 5 kinds of additives: (a) arsenic; (b) boron; (c) selenium
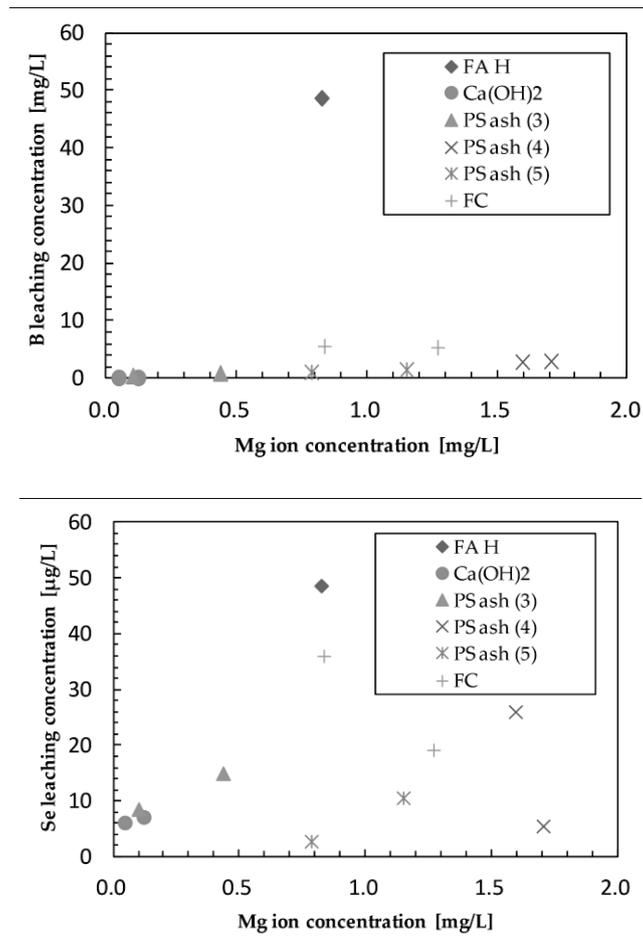
Figure A2. Relationship between Mg ion leaching concentration and trace elements leaching concentration of 5 kinds of additives: (a) arsenic; (b) boron; (c) selenium

Chapter 4
Preliminary Study on Additives for Controlling As, Se, B, and F Leaching from Coal Fly Ash

4.1. Introduction

As reported by the World Energy Council, even though coal production growth was decreasing in 2014, the first decline since the 1990s, almost 40% of the world's electricity was still provided by coal [1]. Coal fly ash is one of the products from the coal combustion process. Approximately 64% of the waste from this process is coal fly ash [2]. Consequently, the study of coal fly ash, especially related to the content of trace metals, such as As, B, Se, Pb, Cd, Cr, Cu, Zn and F in this waste, remains a concern for the next few years.

The leaching behaviour of some heavy metals from various types of coal fly ashes has been discussed by some researchers [3–7]. These studies indicated that the leaching characteristics of each metal are different and that the alkalinity of the leaching solution plays an important role. In addition, the pH of the leachate is believed to be correlated with the calcium content in the coal. Hayashi [8] studied the chemical state of boron in coal fly ash and concluded that boron associated with calcium and magnesium is difficult to leach. Wang [9] stated that As and Se have a high mobility in alkaline pH, and Sri et al. [10,11] stated that leaching of arsenic is related to calcium oxide content in coal fly ash.

Alkalinity and calcium content, especially the calcium oxide content, are the main factors mentioned in several studies. Recent publications from our laboratory [12] studied the effects of additives on the leaching of arsenic, selenium and boron. The introduction of paper sludge ash as an additive is believed to be a promising method for controlling the leaching of heavy metals. Additives are materials containing high levels of calcium and are added to coal fly ash to suppress trace element leaching into the environment. This research aimed to present suitable additives to inhibit the pollution of trace elements, especially As, Se, B, and F, in the environment.

PS ash 8 was chosen as a representative paper sludge ash in this research. In addition, this study proposed BF cement as another high-calcium additive. Blast furnace cement (BF cement) was introduced as a single and mixed-component additive to investigate the role of calcium during the immobilization of heavy metals during leaching. The immobilization process causes trace elements to form more stable chemical compounds, which could lower their hazardous effects [13]. Then, to compare the effect of both suppressing materials, pure calcium hydroxide $Ca(OH)_2$ was used as a native calcium compound.

4.2. Experimental

4.2.1. Coal Fly Ash and Additives

Two coal fly ash samples with a low content of calcium were obtained from different coal-fired power plants in Japan (600 MWe). Coal fly ash C (FA C) and coal fly ash H (FA H) were tested as single and mixed additives in varying ratios. As single additives, calcium hydroxide ($Ca(OH)_2$), paper sludge ash number 8 (PS Ash 8), and blast furnace cement (BF cement) were each added to both coal fly ash samples. Then, mixtures of these three additives were tested. Table 1 provides the major chemical composition information for the coal fly ash and suppressing materials (PS ash 8 and BF cement) based on the results of X-ray fluorescence analysis (WDXRF S8 TIGER, Bruker AXS). Meanwhile, the calcium hydroxide $Ca(OH)_2$ used in this study was a native calcium compound with 95% purity (Kanto Chemical Co., Inc, (Gifu, Japan).

Table 1. Chemical composition of coal fly ash and additives.

Chemical composition		Coal fly ash		Additives		
		FA C	FA H	$Ca(OH)_2$	PS ash 8	BF cement
SiO_2		64.34	59.25	0.09	28.76	31.03
Al_2O_3		22.79	25.63	0.07	15.41	13.32
TiO_2		2.27	1.99	0.07	0.35	0.19
Fe_2O_3		3.71	7.49	BDL	0.91	0.44
CaO		2.71	2.05	99.23	51.22	48.35
MgO	(%)	0.85	0.79	0.36	2.76	3.77
Na_2O		1.20	0.60	0.08	0.02	0.08
K_2O		0.80	1.56	0.01	0.15	0.36
P_2O_5		0.07	0.18	0.05	0.10	BDL
MnO		0.06	BDL	BDL	0.04	0.05
V_2O_5		BDL	0.03	0.03	0.02	0.02
SO_3		0.35	0.42	0.01	0.27	2.39

Paper sludge ash, a potential waste product of paper mill sludge from the de-inking and re-pulping of paper, has already been indicated to have a potential effect as an additive material [12,15]. Due to the amount of calcium contained in this waste, the utilization of paper sludge ash as an additive material in the leaching of trace elements could be an advantageous solution to environmental problems. Moreover, paper sludge ash (PS ash 3) has been proven to suppress the leaching of arsenic, selenium and boron simultaneously [12]. The calcium oxide (CaO) contained in this paper sludge ash has been identified as the calcium compound that plays a role in the trace

element leaching mechanism. Based on qualitative analysis by X-ray diffraction (XRD), the main calcium compounds in both paper sludge ashes were CaO, Ca(OH)$_2$, and CaCO$_3$ (Figure 1). Then, ethylene glycol/ICP analysis and thermal gravimetric analysis (TGA) were performed to determine the concentration of each of these calcium compounds. PS ash 8 was chosen as a supplementary material because the calcium oxide concentration in this paper sludge ash was higher than that in PS ash 3 (Figure 2).
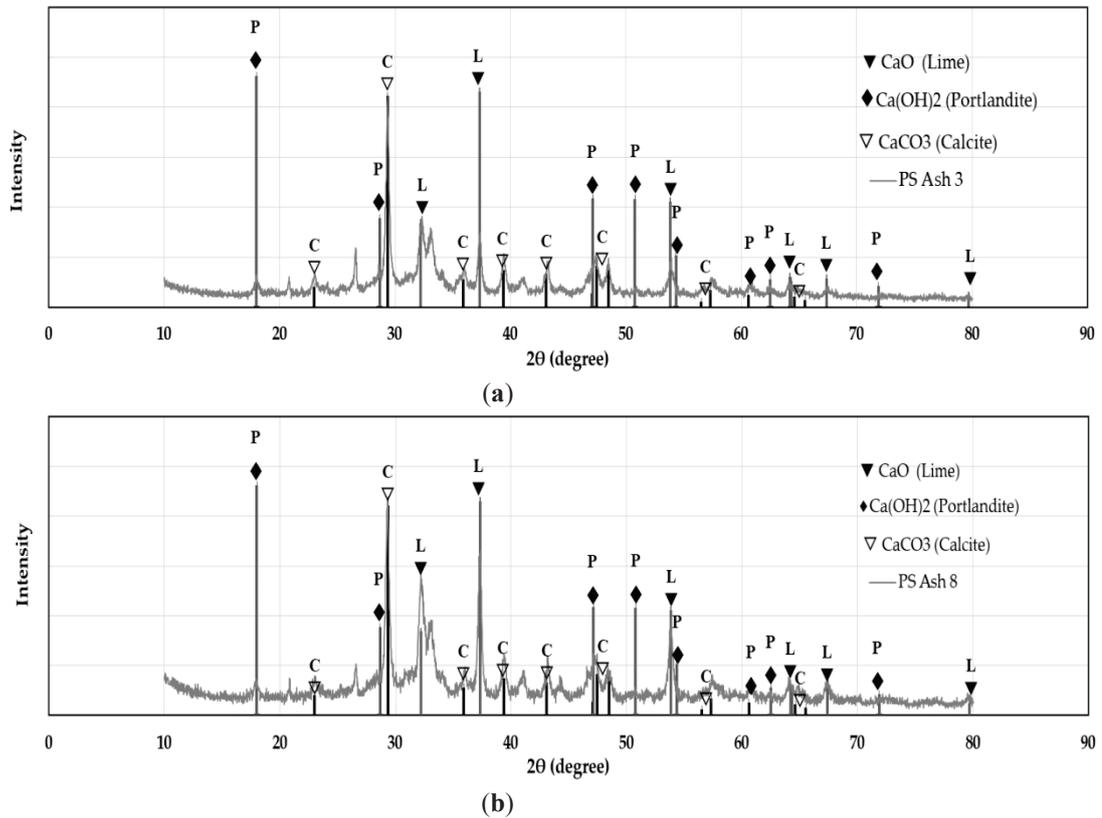
Figure 1. The main calcium compounds in (**a**) PS ash 3 and (**b**) PS ash 8 by XRD (x-ray diffraction) analysis

Blast furnace cement was also applied as an additive in the leaching of trace elements because of the kind and amount of calcium present. Blast furnace cement (BF cement), consisting of granulated blast furnace slag mixed with Portland cement clinker and gypsum, is widely used in Europe and is now increasingly used in the US and Asia, particularly in Japan and Singapore. Based on the EN 197-1:2000 standard, this cement has three types, which are type A, type B and type C. Type B of BF cement was applied in this research. The addition of this type of cement triggers the formation of a compound that helps to retain trace elements in coal fly ash samples [14].

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Figure 2. Calcium compound concentrations in PS ash 3 and PS ash 8

4.2.2. Sample Preparation and Leaching Test

Coal fly ash samples were prepared before performing the leaching test process. Figure 3 shows a schematic diagram of the sample preparation process before carrying out a leaching test. In a mixing bag, various amounts of additives were added to each coal fly ash. The percentage of additive used was based on the total amount of sample (50 g). Then, the mixture was poured into a bowl and distilled water was added (25% of the total sample) until the mixtu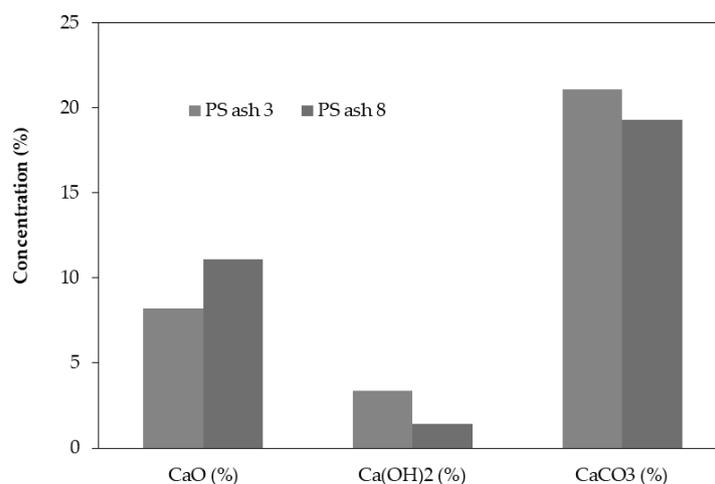re was perfectly mixed (~3 min). Table 2 shows the tested additives and the ratio of each additive used. Before the mixture proceeded to the leaching process, it was air-dried for 7 days and then sieved with a 2 mm sieve. Leaching test No. 13, as established by the Japanese Environmental Agency, was employed as the leaching test. The prepared coal fly ash samples were added to distilled water at a ratio of 1:10. Prior to analysis, this mixture of solid and liquid was shaken at a speed of 200 rpm. for 6 h at room temperature, followed by centrifugation and vacuum filtration to separate the solid and liquid. Cellulose membrane filters (0.45 μm) were used for the filtration process. Next, the leachate (liquid phase after filtration) was analysed by several methods.

Table 2. Ratio of additives in coal fly ash

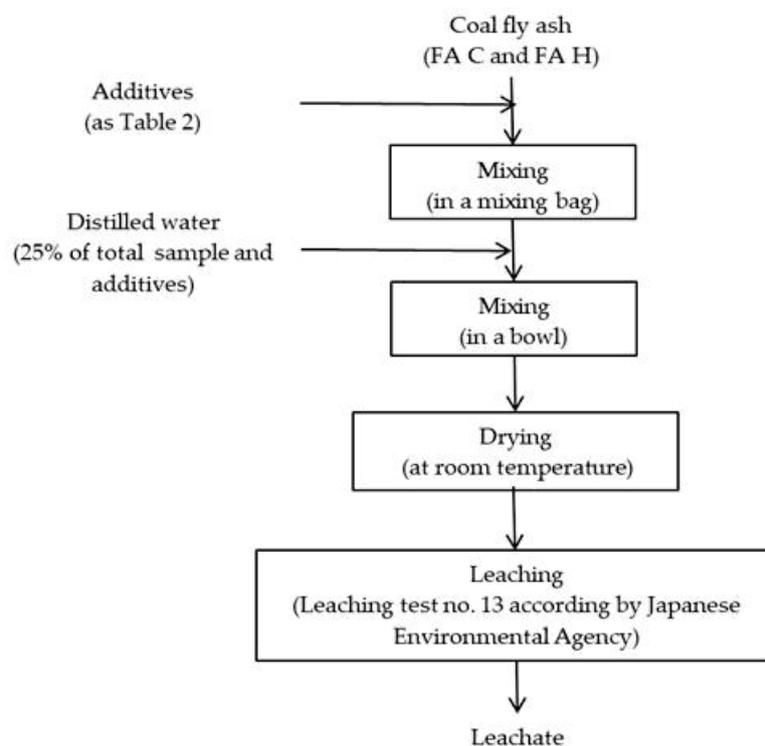| Coal fly ash	Additives
FA C and FA H	(1) 3% of Calcium Hydroxide / $Ca(OH)_2$
	(2) 10% of Paper Sludge Ash / PS ash 8
	(3) 10 % of BF cement
	(4) 10% PS ash 8 + 10% BF cement
	(5) 3 % $Ca(OH)_2$ + 10% PS ash 8 + 10% BF cement

Figure 3. Schematic diagram of the sample preparation and leaching test.

4.2.3. Analysis and Instrumentation

X-ray fluorescence (WDXRF S8 TIGER, Bruker AXS, Yokohama, Japan analysis was carried out to investigate the calcium compounds in the additives. The chemical composition of the mixture of coal fly ash and additives before and after the leaching process was also analysed by this instrument. The effect of additives on the arsenic, selenium, boron, and fluorine leachate concentrations was measured by ICP‑AES (ULTIMA2, HORIBA Ltd, Tokyo, Japan) and ion chromatography (ION ANALYZER IA-300, DKK-TOA Corporation, Tokyo, Japan). The alkalinity of the leachate was determined by using a pH/ion meter (D-53, HORIBA, Tokyo, Japan).

4.3. Results and Discussions

Coal fly ash C (FA C) and coal fly ash H (FA H) without the addition of any supplementary material had different trends in the leaching of arsenic, selenium, boron and fluorine, as shown in Table 3. Coal fly ash H had a higher leachate concentration of arsenic (As) and boron (B), and coal fly ash C had a higher leachate concentration of selenium (Se) and fluorine (F). The fluorine leached from FA H was already under the environmental limit.

The effect of single and mixed additives on the As, Se, B and F leaching concentrations of both of the coal fly ashes is explained in the Figure 5. A decrease in leachate concentration indicated that the additive had potential for use in the leaching process.

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Table 3. Trace element leachate concentrations in coal fly ashes without additives.

Leaching concentration	As (µg/L)	B (mg/L)	Se (µg/L)	F (mg/L)
FAC	17.55	3.88	90.77	1.66
FAH	48.66	5.39	86.9	0.38
Japanese Environmental Limit	10	1.0	10	0.8

4.3.1. Ca(OH)$_2$, PS ash 8, and BF Cement as Single Additives

Our previous study found that the addition of calcium through additives to coal fly ash could inhibit the leaching of trace elements into the environment [12]. Some researchers have also observed that the alkalinity during the leaching process and calcium content are related to decreased leaching concentrations of arsenic, selenium, boron and selenium. Iwashita mentioned that under highly alkaline conditions, the leaching of B and Se tended to decrease [3]. Shun-ichi stated that coal fly ash with better leaching characteristics contained boron in the CaO- and MgO-phases on the surface of coal fly ash particles [8]. Jose and Wang reported that alkaline pH, calcium addition, temperature and the leaching time affected the leaching of As and Se [4,9]. Figure 4 shows the alkalinity of the leachate from coal fly ash C and H before and after the addition of supplementary material. After the addition of the additives in single and mixed forms, the pH of the leachate increased. This could indicate that the application of mixed additives is promising as a suppressing material for the leaching of As, Se, B, and F. Therefore, in relation to the positive effect of alkaline conditions and in relation to the calcium content during the leaching process, this research intended to find suitable and effective suppressing materials that could control the leaching of trace elements into the environment.

First, both coal fly ashes (coal fly ash C and H) were tested with Ca(OH)$_2$, PS ash 8 and BF cement as single additives. The application of Ca(OH)$_2$ (3% of the total sample) as a native calcium compound in the form of a single additive showed a positive trend. Ca(OH)$_2$ could decrease almost all of the trace elements in both of the coal fly ashes, except for Se in coal fly ash H. The application of PS ash 8 (10% of the total sample) only showed satisfying results in suppressing the leaching of As, Se, and B in the FA C sample and the leaching of As in the FA H sample. This research also introduces BF cement as an additive because of the popularity of cement-based methods in the immobilization process in heavy metal stabilization [13, 17–19, 25]. The addition of BF cement to both coal fly ashes as a single additive was not very effective because this addition did not have a simultaneous effect on all of the trace elements. BF cement could decrease the arsenic and fluorine leachate concentration for both of the coal fly ashes but only could decrease the boron and selenium in coal fly ash C. At higher arsenic and selenium

leachate concentrations, the addition of 10% BF cement relative to the total sample was still not representative.
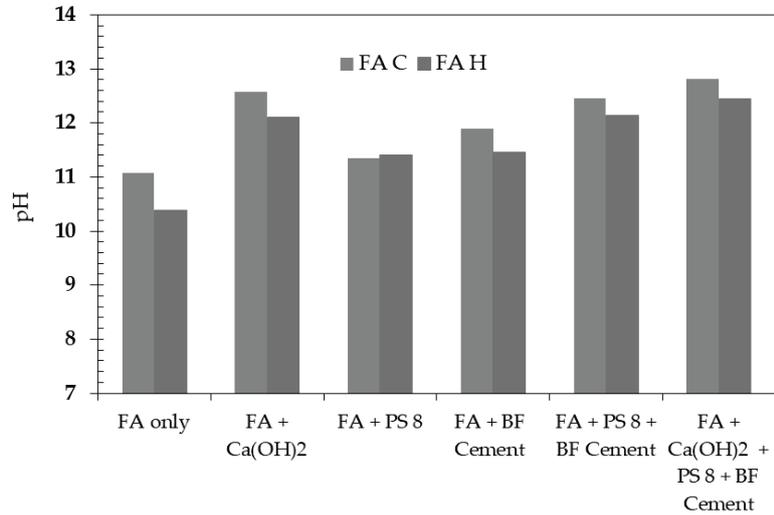
Figure 4. The pH of coal fly ashes and mixtures of coal fly ashes and additives.

These varying results led to the conclusion that PS ash 8 and BF cement were not as effective as single additives due to the lack of a simultaneous effect in decreasing the leaching of As, Se, B, and F. In fact, the application of $Ca(OH)_2$ as a single additive was much more effective than that of the other two additives. However, because $Ca(OH)_2$ is a native calcium compound that was used for comparison with the results of other supplementary materials, this research continued by investigating the application of these three materials as mixed additives.
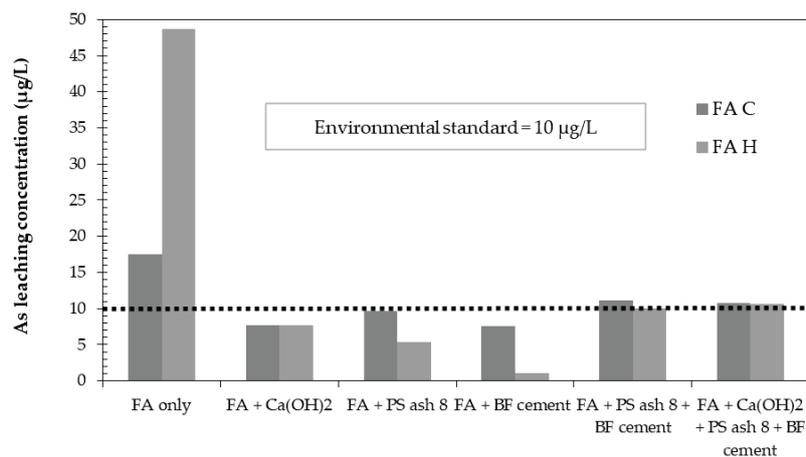
(a)
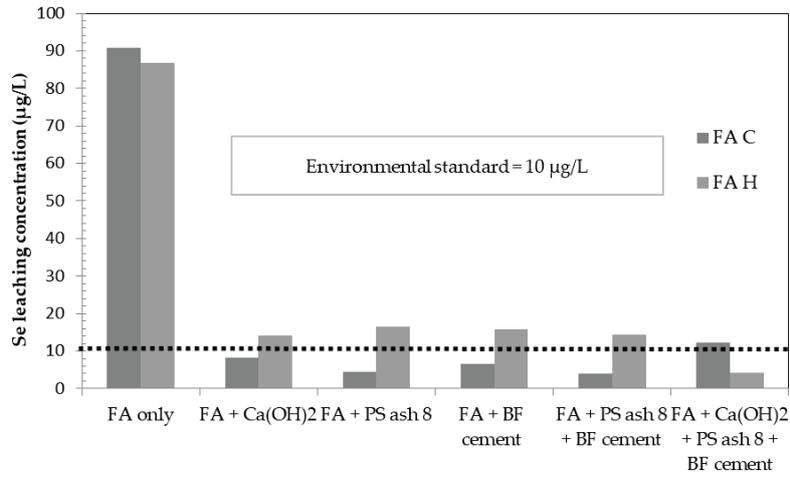
(b)
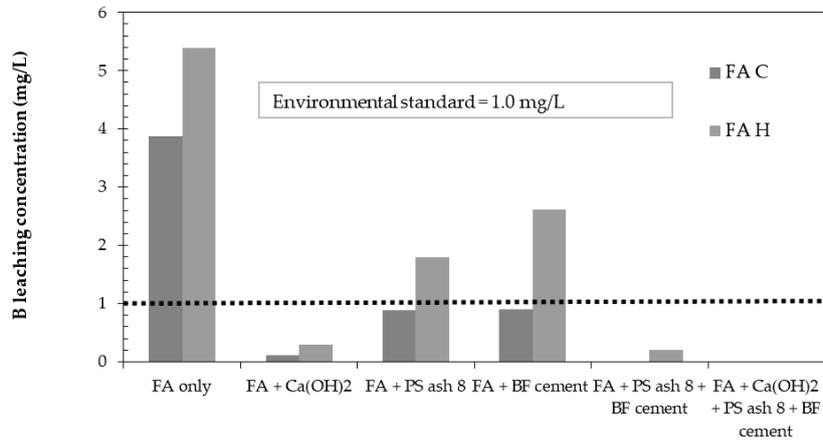
(c)
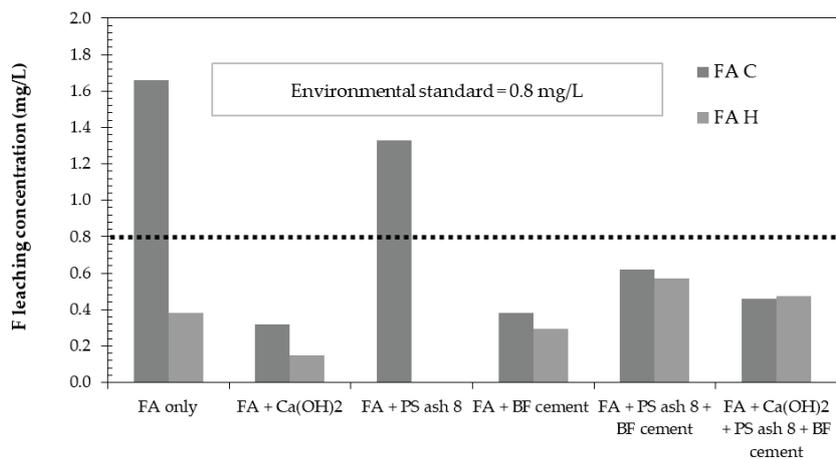
(d)

Figure 5. Effect of additive on (**a**) As, (**b**) Se, (**c**) B and (**d**) F leaching concentrations from two different coal fly ashes.

4.3.2. Ca(OH)₂, PS ash 8, and BF Cement as Mixed Additives

As presented in Figure 2, two types of mixed additive materials were tested in coal fly ash C and H. These included (1) a mixture of PS ash 8 and BF cement and (2) a mixture of $Ca(OH)_2$, PS ash 8 and BF cement. Both of these mixtures have the potential to be applied as a supplementary material in the leaching process because the results presented almost the same patterns. In the leaching of arsenic, the second mixture produced a slightly better decrease than the first mixture. In the leaching of selenium, these two mixtures showed contrary results. The first mixture had a positive effect on decreasing the selenium leachate concentration in coal fly ash C and the second mixture had a positive effect in coal fly ash H. In boron and fluorine leaching, the mixed additives showed a satisfactory decrease for both coal fly ashes.

Figure 6 represents the decrease in trace elements affected by both materials based on the inhibition rate. The inhibition rate explains the ability of the mixture to inhibit the trace element leachate concentration, which is calculated as the percent decrease in leachate concentration before and after the addition of the supplementary material. A lower inhibition rate means that the ability of the additive to suppress the leaching of trace elements is low and a higher inhibition rate means that the additive has a promising effect as a supplementary material.

Based on the inhibition rate, both mixtures had promising effects as suppressing materials in the leaching of As, Se, B and F. However, the second mixture ($Ca(OH)_2$, PS ash 8 and BF cement) was relatively more constant in inhibiting the leaching of trace elements compared to the first mixture (PS ash 8 and BF cement). Note that the value of zero for fluorine in coal fly ash H indicates that there was no inhibition because the initial fluorine concentration in coal fly ash H was lower than the fluorine concentration after leaching in both mixtures.
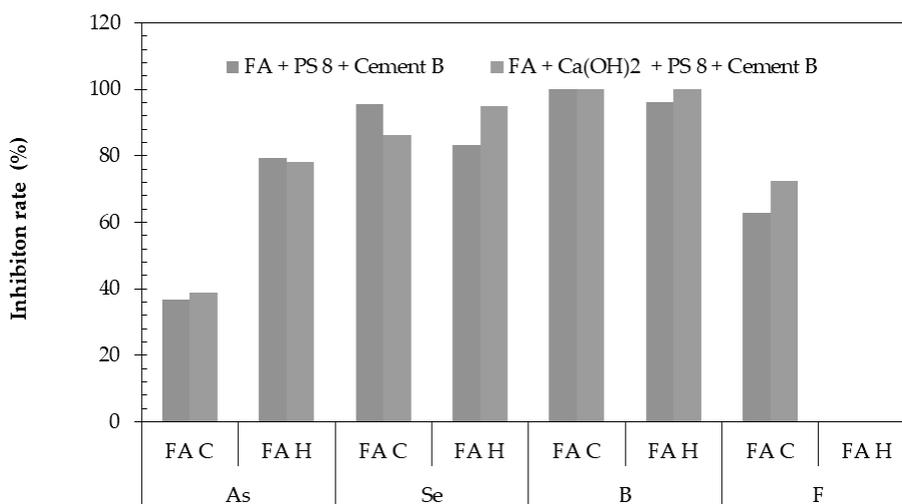

Figure 6. Inhibition rate of the mixed additives on the As, Se, B and F leachate concentrations.

Therefore, the application of mixed suppressing materials as additives for leaching is an

effective solution in controlling the leaching of trace elements into the environment. Additionally, the mixture of Ca(OH)$_2$, PS ash 8 and BF cement was an applicable mixed additive for decreasing the leachate concentration of As, Se, B and F. However, further study of the optimum mixing ratio for the mixture is needed.

This promising result has a strong relationship with the chemical stabilization of trace elements during the leaching process. Chemical stabilization is related to the chemical composition of the coal fly ash and suppressing material mixtures. The changes in chemical composition within coal fly ash C and H before and after leaching were analysed by XRF (Table 4). The results of XRF analysis showed that there were considerable changes in some of the chemical compositions for both coal fly ashes. The change in the amount of several oxides was strongly related to the decrease in the trace element leachate concentrations.

The amount of CaO and MgO in the mixture of coal fly ash and suppressing material triggered an increase in leachate alkalinity [27]. Alkaline conditions are believed to be one of the parameters in the leaching process [3,4,9]. This condition triggered a decrease in the trace element leachate concentration. Moreover, alkalinity might be one of the causes of the decrease in SiO2 because silica can slowly dissolve and form silicic acid [27]. This condition was helpful in controlling pH during the leaching process.

Table 4. Chemical composition of the coal fly ashes and Ca(OH)$_2$, PS ash 8 and BF cement mixtures before and after leaching.

Chemical composition	FA C		FA H	
	Before leaching with (Ca(OH)$_2$ + PS 8 + Cement B)	After leaching with (Ca(OH)$_2$ + PS 8 + Cement B)	Before leaching with (Ca(OH)$_2$ + PS 8 + Cement B)	After leaching with (Ca(OH)$_2$ + PS 8 + Cement B)
SiO$_2$	56.93	46.11	54.24	48.08
Al$_2$O$_3$	22.09	17.74	22.20	18.07
TiO$_2$	1.74	2.73	1.56	2.87
Fe$_2$O$_3$	2.36	11.05	5.96	5.41
CaO	13.65	18.99	12.56	22.21
MgO	1.34	0.86	1.24	1.13
Na$_2$O	0.80	0.18	0.46	0.58
K$_2$O	0.57	1.39	1.14	0.78
P$_2$O$_5$	0.00	0.14	0.11	0.14
MnO	0.04	0.04	0.03	0.03
V$_2$O$_5$	0.02	0.01	0.01	0.02
SO$_3$	0.46	0.76	0.50	0.68
Total	100.00	100.00	100.00	100.00

In addition, excess calcium is directly related to chemical stabilization [13]. Trace elements that are also classified as heavy metals are transformed into less soluble compounds, which makes these trace elements non-hazardous in the environment. As, Se, B, and F can react with calcium and form relatively insoluble compounds such as Ca$_3$(AsO$_4$)$_2$, Ca$_4$(OH)$_2$(AsO$_4$)$_2$·4H$_2$O

[9,13], $CaSeO_3$ [9], $Ca_2B_2O_5$, $Ca_3B_2O_6$ [8] and CaF_2 [29]. Therefore, calcium addition through the use of high‑calcium‑content materials in the leaching process could be applied to control the leaching of trace elements.

In light of the calcium reaction in leaching, not only does chemical stabilization occur between the calcium and the trace element metals directly but the calcium also reacts with the chemical components within the coal fly ash and is then incorporated with the trace elements into the product formed by the reaction. As secondary precipitates during the leaching of alkaline coal fly ashes, hydrocaluminate ($Ca_4Al_2(OH)_{12}(OH)_2·6H_2O$) and ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3·26H_2O$) have been proven to have great a capability in reducing the concentration of the heavy metal anions, including the metals discussed in this research [16–21]. Alkaline conditions during the leaching process, the amount of calcium and the amount of alumina are the main factors in the formation of these materials. The addition of BF cement as an additive in this leaching mechanism was also believed to be strongly related to the formation of these materials.

4.4. Conclusions

The change in chemical composition during leaching is a complicated process. The chemical components are related to each other during the process of leaching. The utilization of mixed additives may have caused a more complex reaction during the process; however, the use of additives also has a great effect in reducing trace element concentrations. This research found that the application of mixed additives in the leaching process could be an effective solution in controlling the leaching of trace elements. Additionally, the mixture of $Ca(OH)_2$, PS ash 8 and BF cement was determined to be an applicable additive in the leaching process because this mixture gives more simultaneous decreases in trace element concentrations than do other suppressing materials; however, the appropriate blending ratio needs to be determined for further applications.

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Chapter 5
The Role of Calcium Compound on Fluorine Leaching Concentration

5.1 Introduction

Coal have been predicted as the largest source of power generation in 2040 with a share almost 30 percent (BP Energy Outlook, 2018). It is means that the production of coal fly ashes will still affected the environment because of the hazardous element containing in the coal fly ash (Puch Bachtrong, 2017). One of the toxic trace element consisting in coal fly ash is Fluorine. Fluorine is the most reactive of all the chemical elements which including into hazardous trace elements in coal, and study was reported that about 10-40% of fluorine in coal entered into coal fly ash through the combustion process (Robertson, 1998; Machado, 2015; Shuang Deng, 2016). Therefore, the utilization of coal fly ash in various purposes need to be beware about the fluorine effect into the environment. Fluoride (the anion of fluorine) has been listed as one of the contamination in water by the WHO because could cause many problems in human health (Jingui He, 2017). In plants, fluorine could be absorbed by plants under natural condition and it is bound into insoluble compounds such as CaF_2 (Szostek R, 2017).

In the development of additives for inhibit the leaching of the trace element into the environment, previous study was found that calcium has positive effect in decreasing trace element leaching concentration (Hartuti, S, 2017). Then, the application of mixture additives was given promising effect in inhibit the leaching of several trace elements, including the leaching of fluorine (Hanum, F F, 2018). This study was purposed to investigate about the calcium compound which plays important role during the fluorine leaching mechanisms. This information will require in controlling the effect of fluorine into the environment.

5.2 Experimental
5.2.1   Coal Fly Ash

Coal fly ashes sample used in this research is obtained from different coal-fired power plants in Japan. The chemical composition of these fourteen coal fly ashes were determined by X-ray fluorescence analysis (WDXRF S8 TIGER, Bruker AXS). Based on the XRF analysis, the coal fly ashes samples consisting of different calcium content from the lowest (FA F, 0.66%) to the highest calcium content (FA B, 10.80%).

Table 1. Chemical composition for coal fly ashes by XRF analysis

Fly Ash (FA)		FA A	FA B	FA C	FA D	FA E	FA F	FA G	FA H	FA I	FA J	FA K	FA L	FA M	FA N
Power station		Unit 2	Unit 2	Unit 2	Unit 2	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1	Unit 1
Chamber of electrostatic precipitator		EP1	EP1	EP1	EP1	EP1	EP1	EP1	EP1	EP1	EP1	EP1	EP1	EP1	EP1
	SiO_2	52.61	51.42	64.34	74.78	55.30	66.99	66.21	59.25	59.21	65.07	56.82	57.32	64.84	63.08
	Al_2O_3	31.35	22.39	22.79	16.68	30.84	26.40	26.65	25.63	26.32	21.83	21.06	20.68	23.28	22.73
	TiO_2	2.08	2.16	2.27	1.14	1.94	2.01	1.77	1.99	1.77	1.11	1.06	0.96	1.12	1.24
	Fe_2O_3	7.06	7.01	3.71	3.93	5.75	2.15	2.57	7.49	6.79	7.17	7.23	7.17	5.81	5.65
	CaO	3.26	10.80	2.71	0.45	2.28	0.66	0.81	2.05	2.07	1.43	8.86	8.79	1.39	2.67
chemical	MgO	0.58	1.05	0.85	0.22	0.98	0.51	0.54	0.79	0.91	0.52	0.96	1.02	0.82	1.12
composition [%]	Na_2O	0.38	1.23	1.20	0.38	1.14	0.27	0.29	0.60	0.74	0.44	0.75	0.80	0.52	1.25
	K_2O	0.96	1.19	0.80	1.43	1.20	0.58	0.54	1.56	1.44	1.76	1.97	1.97	1.67	1.44
	P_2O_5	0.61	0.22	0.07	0.10	0.19	0.04	0.06	0.18	0.18	0.16	0.28	0.27	0.13	0.20
	MnO	0.09	0.18	0.06	0.04	-	0.12	0.11	-	0.10	-	-	-	0.00	0.07
	V_2O_5	0.00	0.00	0.00	0.00	0.09	0.01	0.02	0.03	0.03	0.15	0.17	0.17	0.08	0.04
	SO_3	0.27	1.22	0.35	0.28	0.28	0.26	0.44	0.42	0.50	0.35	0.84	0.87	0.35	0.53

5.2.2 Additives

An additive is used to elevate the calcium content in the coal fly ash sample. There are two kinds of mixture additives used in this researched: (1) The mixture of PS ash 8 and BF Cement (2) The mixture of Ca(OH)2, PS ash 8 and BF cement. The previous researched presented that these two mixtures were given promising effect in the leaching of several trace elements from coal fly ash with low calcium content (FA C and FA H). The calcium containing in PS ash 8 and BF cement respectively are 51.22% and 48.35% (Table 2).

Table 2. Chemical composition for additives by XRF analysis

Chemical composition		Additives	
		PS ash (8)	BF Cement
SiO_2		28.76	31.03
Al_2O_3		15.41	13.32
TiO_2		0.35	0.19
Fe_2O_3		0.91	0.44
CaO		51.22	48.35
MgO		2.76	3.77
Na_2O	[%]	0.02	0.08
K_2O		0.15	0.36
P_2O_5		0.10	0.00
MnO		0.04	0.05
V_2O_5		0.02	0.02
SO_3		0.27	2.39

The coal fly ash samples mixed with the additives in the certain ratio before the leaching process. The ratio of the additives based on the total sample is 3% of calcium hydroxide (Ca(OH)2), 10% of PS Ash 8, and 10% of BF Cement. Then, 1:10 of coal fly ashes and distilled water prepared for the 6 hours leaching in the room temperature.

5.2.3   Analysis and Instrumentation

Ion chromatography analysis (ION ANALYZER IA-300) was performed in order to determine the fluorine leaching concentration from the 14 different coal fly ashes for before and after the application of the additives. Then, the data of leachate alkalinity was provided by pH/ION METER D-53, HORIBA in order to probe the effect of pH into fluorine leaching concentration. In addition the data for thermal gravimetric analysis (TG/DTA6300 SII EXSTAR 6000, HITACHI), ethylene glycol analysis, ICP-AES (ULTIMA2, HORIBA Ltd) and XPS analysis was used to explain the role of calcium onto the fluorine leaching mechanisms.

5.3 Result and Discussion
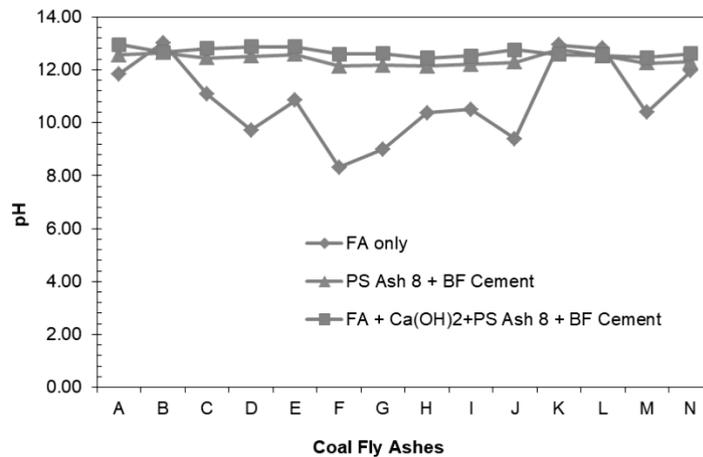### 5.3.1 Effect of pH in fluorine leaching process

Figure 1. Effect of mixture additives into the leachate pH from different coal fly ashes on fluorine leaching process

The different calcium compound on coal fly ashes also affected pH of the leachate. The pH of the leachate from the fourteen coal fly ashes before the application of mixture additives is linier with the calcium content on each coal fly ashes based on the XRF analysis (Table 1). After the application of the mixture additives, the pH of the leachate is become higher. The leachate pH from the mixture additives PS Ash 8 and BF cement is slightly lower than mixture additives $Ca(OH)_2$, PS Ash 8 and BF cement (pH around 12, Figure 1). This is proven the study that

explained alkalinity is one of the factors which affected the trace element leaching concentration into the environment and the high alkaline pH is giving positive effect in decreasing the trace element leaching concentration (Piekos R, 1998; Wang, et al. 2009; Palombo, et al, 2007).

5.3.2 Effect of additives into fluorine leaching concentration

Based on the pH analysis result, both of the mixture additives have pH in around pH 12. Piekos and Palombo et al explained in their study that higher pH on the leaching process could lowered the leaching of the fluorine leaching. As the application of the mixture additives, the pH of the leachate was become higher, so that the additives might have promising effect on the fluorine leaching process. There are fourteen different coal fly ashes were tested in order to study the effect of the additives mixture into fluorine leaching concentration. Figure 2 showed that the leaching of fluorine from coal fly ash B, C, D, G, I, J, L, M, and N without the additives are above the environmental limit. The others have fluorine leaching concentration under the environmental limit. Based on the Ministry of the environment of Japan, the environmental limit of fluorine in Japan is 8 mg/L for other than sea area.
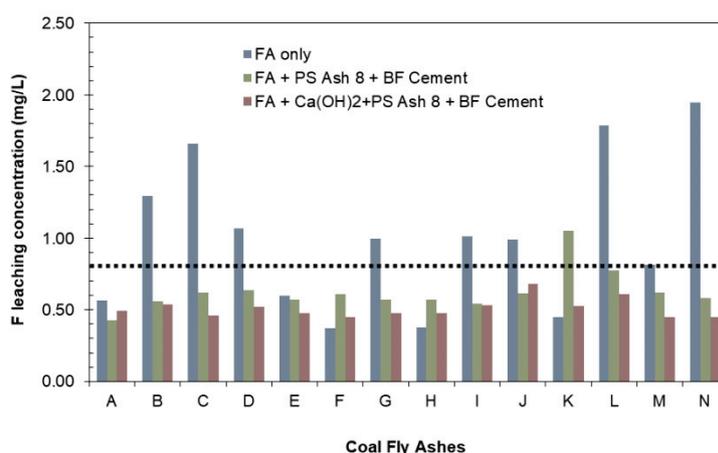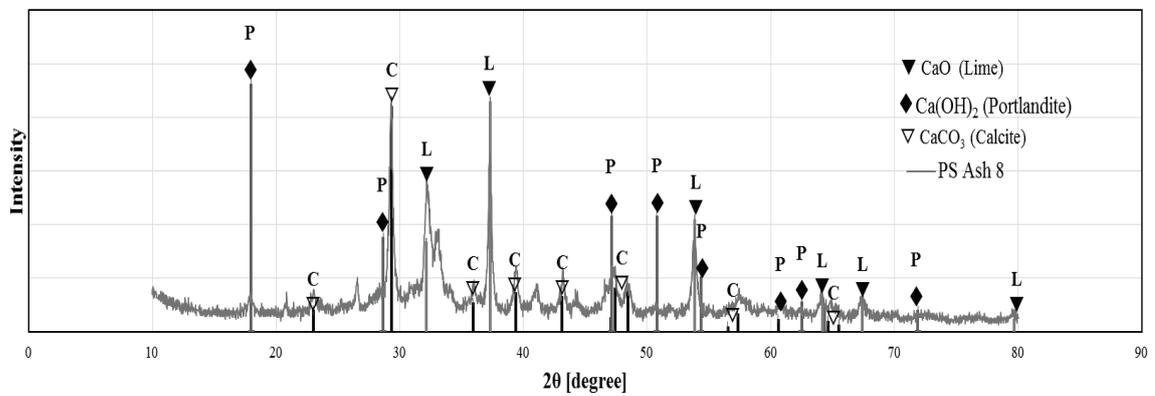

Figure 2. Effect of the mixture additives into different coal fly ashes on fluorine leaching concentration

In addition, amongst the coal fly ashes which have fluorine leaching higher than the standard, the calcium content containing in those coal fly ashes is very various including the lowest (0.81%) and the highest (10.80%) once. This is proven that the amount of calcium consisting in the coal fly ash sample is not linier with the fluorine leaching concentration. Furthermore, this result also stated that calcium compound containing in the coal fly ashes are diverse and there is a specific calcium compound which affected the fluorine leaching concentration. Later, this study will inform the calcium compound which plays an important role during the fluorine leaching concentration.

The both of mixture additives performed a positive decreasing in fluorine leaching concentration into the coal fly ashes which have higher leaching concentration than the environmental standard (Figure 2). The mixture of Ca(OH)$_2$, PS Ash 8 and BF cement could decrease the amount of fluorine in the leachate higher, except on the coal fly ash J (FA J; Ca 1.43%). This result means that the mixture of Ca(OH)$_2$, PS Ash 8 and BF cement is applicable in fluorine leaching mechanisms. In addition, this mixture also containing the calcium compounds which important in inhibit the fluorine leaching concentration, which might be the same with calcium compound that affected the fluorine leaching concentration on the coal fly ashes mentioned before.

5.3.3 The role of calcium in fluorine leaching process

(a)
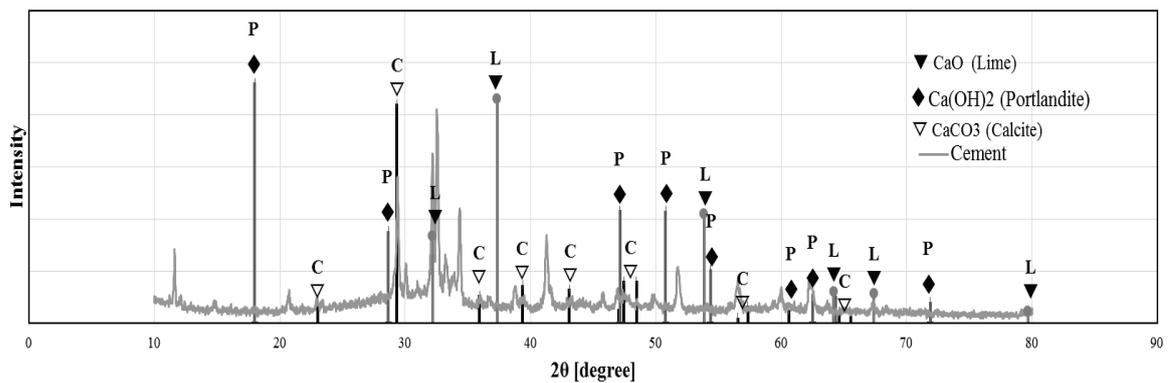
(b)

Figure 3. XRD patterns of (a) PS ash 8 and (b) Blast Furnace Cement (BFC)

The both of the mixture of the additives presented the promising effect in minimizing the effect of the fluorine leaching into the environment. Calcium compound consisting in the coal fly ashes and in the additives were believed to take important role during the leaching of the fluorine.

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Figure 3 showed the XRD analysis result of the PS ash 8 and BF Cement. This figure explained that CaO, $Ca(OH)_2$ and $CaCO_3$ were the main calcium containing on these additives.

Table 3. Calcium compound analysis consisting in the additives materials

Additives material	CaO (%)	$Ca(OH)_2$ (%)	$CaCO_3$ (%)
PS ash 8	11.1	1.44	19.32
BF Cement	1.62	0.31	6.45

Meanwhile, thermal gravimetric analysis (TGA) and ethylene glycol analysis were carried out in order to find the amount of those calcium compounds in the both of PS ash 8 and BF cement (Table 3). This data explained that the most calcium compound which might affected the fluorine leaching concentration is calcium oxide (CaO) and calcium carbonate ($CaCO_3$). These calcium compounds will be reacting with other chemical composition which will stabilized the hazardous heavy metals consisting in coal fly ashes.
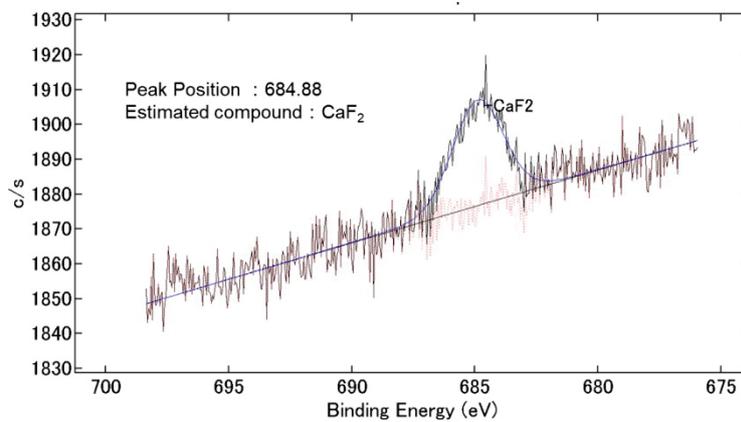

Figure 4. XPS analysis result on the mixed coal fly ash sample and additive (FA C and $Ca(OH)_2$)

Several studies have been researched the calcium and fluorine bearing compound consisting in coal fly ashes which might be produced during the combustion process (Wang, G., 2015; Guo, S., 2006; Xie, P., 2017). The study said that mainly fluorine compound in coal is insoluble fluorine such as CaF_2, MgF_2, FeF_3, and AlF_3. These fluorine compounds are the main occurrence state after coal combustion process and difficult to break down even at high temperature. Wang, et al explained that several oxide compounds inside the coal including CaO in the fly ashes were took part in the formation of insoluble fluorides. This is confirmed the

previous result that CaO is one of the main calcium compound which plays role in fluorine leaching process.

Other than that, based on the XRD analysis data and TG/EG analysis data, the amount of calcium hydroxide is a few. But, calcium hydroxide is native calcium compound to enrich the calcium content on the coal fly ash samples. Even though the amount that little amount of $Ca(OH)_2$, this compound have ability to decrease the fluorine leaching. The XPS analysis was did into one of the coal fly ash sample (FA C) which already mixed with $Ca(OH)_2$. The peak showed that after the mixing process, the estimated calcium compound consisting in the samples is CaF_2. This is only a qualitative analysis, so that the exact amount of CaF_2 which might be produced was not well known yet. However, the leaching process might be affected the increasing amount of CaF_2 or other insoluble compound of fluorine which may cause by the chemical stabilization during the leaching process.

5.4 Conclusions

The application of mixture additive in leaching process has shown promising effect into fluorine leaching concentration. The various kinds of coal fly ashes was treated with the mixture of $Ca(OH)_2$, PS Ash 8 and BF cement as the additives, then the results confirmed that these additive mixtures is appropriate to apply in fluorine leaching concentration. CaO and $CaCO_3$ was mainly the main calcium compound consist in the additives. These calcium compounds was took part in the chemical stabilization of fluorine during the leaching concentration to produce the insoluble fluoride compounds. CaF_2 believed to be the one of fluoride compound consisting in the mixture of coal fly ashes and additives which difficult to break down evens with the high temperature.

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Chapter 6
Conclusions and Future Perspective

6.1 Conclusions

World Energy Council on 2017 reported that almost 40% of the world electricity is still provided by coal. The coal combustion process in coal power generation produced bottom ash and fly ash. Almost 64% of the waste from combustion process is coal fly ash which is one of potential sources of the environmental pollution. The disposal of fly ash in the environment involves the interaction of fly ash particles with weathering and hydrological processes where rainfall causes trace elements in the fly ash to elute and contaminate the environment. Among the trace elements found in coal fly ash As, B, Se, F and Cr are the greatest concern as environmental hazards.

In the study of leaching characteristic of arsenic, six different coal fly ashes which are coal fly ash G, H, I, J, L, and N have been conducted in a long term leaching process. The results showed that the concentration arsenic in the leachate was increased with time and equilibrium between the solid phase and the leaching solution was reached approximately 120 days. This study also found that there is a relation between CaO content in coal fly ash with the arsenic leaching concentration. The leaching rate of arsenic was describe in a kinetic model of first-order reactions by changing the rate constant k with constant a and b. The constant a and b as a variable to express the complex behavior of long term leaching fractions. Based on this equation is found that constant a has a good relationship with CaO content in coal fly ash. The constant a, which is indicated the leaching rate of the arsenic, was decreased with the increasing of CaO content in coal fly ash.

Based on the fact that calcium has strong relation with arsenic leaching concentration, the study about suppressing material in leaching process was carried out. Suppressing material is material which added into coal fly ashes before the leaching process and contains relative high calcium concentration than the coal fly ash. The study about the effect of this additive has been started with the three kinds of paper sludge ashes (PS ash 3, 4 and 5), filter cake (FC) and calcium hydroxide as the suppressing material. These additives were tested into coal fly ash H (FA H). Calcium hydroxide as the native calcium has been used to compare the result from other suppressing material. Calcium hydroxide greatly reduced all the leaching of As, Se, and B until about 91-100% decreasing. Then, the result revealed that all the paper sludge ashes showed simultaneous leaching suppressing effect while the FC did not. However, between all of the paper sludge ash, only PS ash 3 satisfied the soil environmental standard with 10% of Ca concentration. The CaO content in PS ash 3 was proved as the main factor of this satisfying effect. Therefore, this study concluded that the utilization of paper sludge ashes, especially PS ash 3, is a promising

method to control the leaching of As, B and Se into the environment.

The study into paper sludge ash as the additives in controlling the leaching of trace element was continued with a study which aims to find an applicable additive in leaching process. Two different coal fly ashes with almost same calcium content have been tested with additives as single additives and mixed additives. As the single additives, each of calcium hydroxide (Ca(OH)2), paper sludge ash 8 (PS ash 8) and blast furnace cement (BF Cement) was tested into FA C and FA H. Then, as the mixed additives, the mixture of PS ash 8 and BF cement also the mixture of $Ca(OH)_2$, PS ash 8 and BF cement was tested into the both of coal fly ashes. PS ash 8 has higher calcium oxide than PS ash 3, which expected to have better effect in the decreasing of trace elements leaching concentration. Then, the result indicated that the application of mixed additives could applicable in controlling the leaching of As, Se, B and F. The mixture of $Ca(OH)_2$, PS ash 8 and BF cement showed slightly better decreasing than the mixture of PS ash 8 and BF cement.

Performance of calcium through the addition of the additives material has been proven in the leaching of As, Se, B and F. The next study only focused in fluorine leaching concentration. The mixed additives (the mixture of $Ca(OH)_2$, PS ash 8 and BF cement) have been tested into 14 different coal fly ashes in order to study the role of calcium in fluorine leaching concentration. The result confirmed that this mixed additives was applicable in decreasing fluorine leaching concentration. Calcium oxide and calcium carbonate was the mainly calcium compound which affected the fluorine leaching concentration and CaF_2 is the fluorine compound which formed during the leaching process. CaF_2 is a compound which difficult to break down even with the high temperature.

6.2 Future Perspective

These studies proved that calcium plays important role in trace element leaching process, especially in As, Se, B and F leaching concentration. The content of calcium oxide and calcium carbonate within the suppressing material was the main factor that triggered the chemical stabilization of the trace elements during the leaching process. The mixture of $Ca(OH)_2$, PS ash 8 and BF cement was suggested as an applicable suppressing materials in controlling the leaching of As, Se, B and F. For further application, the optimum ratio of this mixed additives need to be found. Also, the role of calcium of the trace elements still needs to be discussed.

List of Publications

1. **Leaching Characteristic of Arsenic in Coal Fly Ash**
   Sri Hartuti, Shinji Kambara, Akihiro Takeyama, Farrah Fadhillah Hanum
   Accepted: July, 2017

2. **Effect of Additives on Arsenic, Boron and Selenium Leaching from Coal Fly Ash**
   Sri Hartuti, **Farrah Fadhillah Hanum**, Akihiro Takeyama, and Shinji Kambara
   Accepted: June 7, 2017

3. **Preliminary Study on Additives for Controlling As, Se, B, and F Leaching from Coal Fly Ash**
   Farrah Fadhillah Hanum, Erda Rahmilaila Desfitri, Yukio Hayakawa, Shinji Kambara
   Accepted: October 19, 2018

4. **The Role of Calcium Compound on Fluorine Leaching Concentration**
   Farrah Fadhillah Hanum, Erda Rahmilaila Desfitri, Yukio Hayakawa, Shinji Kambara

List of Presentations

1. **A role of calcium on leaching of trace elements from coal fly ash.**
   (Oral Presentations) The 26th Symposium on Environmental Engineering.
   Kanazawa, Japan. June 29 - July 1 2016.

2. **A role of calcium on leaching of trace elements from coal fly ash.**
   (Oral Presentations) The 3rd Engineering Science and Technology International Conference (ESTIC 2016).
   Padang, Indonesia. August 30-31, 2016.

3. **Calcium compound characteristics on trace elements leachates from coal fly ash.**
   (Oral Presentations) The 53rd of Coal Science Conference.
   Hiroshima, Japan. October 26-27, 2016.

4. **Calcium compound characteristics in trace elements mechanisms from coal fly ash.**
   (Poster Presentations) The 5th Asian Conference on Innovative Energy and Environmental Chemical Engineering (ASCON-IEEChE).
   Yokohama, Japan. November 13-16, 2018.

5. **Calcium compound characteristics in trace elements mechanisms from coal fly ash.**
   (Oral Presentations) The 27th Symposium on Environmental Engineering.
   Hamamatsu, Japan. July 10-11, 2017.

6. **Advance Study on Additives for Cotrolling As, Se, B and F Leacing Concentration from Coal Fly Ash**
   (Oral Presentations) The 28th Symposium on Environmental Engineering.
   Tokyo, Japan. August, 8-9, 2018

7. **The Role of Calcium Compound on Fluorine Leaching Concentration**
   (Oral Presentations) The 1st International Symposium of Indonesian Chemical Engineering (ISIChem).
   Padang, Indonesia. October 4th-6th, 2018.

List of Awards

1. **Best Young Presenter** in the 26th Symposium on Environmental Engineering by Japan Society of Mechanical Engineering (JSME). 2016.
2. **Best Oral Presenter** in the 3rd Engineering Science and Technology International Conference (ESTIC 2016) by Faculty of Industrial Technology, Bung Hatta University. 2016.