

**DEVELOPMENT OF ADDITIVES MATERIALS FOR
CONTROLLING TRACE ELEMENTS LEACHING FROM COAL
FLY ASH**

**石炭フライアッシュからの
微量元素溶出抑制材の開発**

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

by

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Preface

Coal fly ash is a by-product of the combustion process which uses coal as a fossil fuel in a power plant. Based on Energy education encyclopedia in 2015, coal is the primary source of electricity generation in the world. Coal-fueled power plants currently fuel 38% of global electricity. Global coal demand as a source of energy expected to keep stable until 2024, reported by the International Energy Agency (IEA). It means coal fly ash will be produced during the use of coal.

The utilization of coal as fossil fuel in the combustion process to generate electricity has been developed for many years to manage better and keep strict environmental impact and save the operational cost. The use of such coal includes in the cement concrete industry, in the road construction, as the soil stabilization, etc. However, almost the coal fly ashes discharged from the coal combustion process will dump in an open pond. Then, this condition will trigger the pollution of the environment.

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. The dumping of fly ash in the disposal pond could cause a profound environmental impact. Arsenic (As), selenium (Se), boron (B), fluorine (F), and Chromium (Cr) have been recognized as the most troublesome hazardous elements in coal fly ash. Therefore, acceptable waste management practices are needed to sustain a healthy environment.

This thesis is consisting of six chapters. The first chapter introduces coal fly ash, trace element, additive materials, and the research objective. Chapter 2 discusses additives' effect for controlling As, Se, B, and F leaching from coal fly ash. Three types of additive materials used as a single and mixture additive have been tested to kind of coal fly ash. Chapter 3 describes calcium performance in paper sludge ashes as an additive material for controlling trace elements leaching from fly ash. Characterization of PS ash and its calcium compound content from 9 kinds of paper sludge ashes have been investigated. The PS ash, which contains the higher level of calcium compound and has the same level capability for controlling trace element leaching (result from chapter 3) tested to 14 types of fly ash, investigated the role of calcium compound on

fluorine leaching concentration. It discusses in Chapter 4. Chapter 5 investigated the effect of additive material on controlling chromium (Cr) leaching from coal fly ash. Finally, chapter 6 is delivered the conclusions as well as the future perspectives of this research.

Chapter 1 Introduction

1.1 Coal Fly Ash

Coal remains a crucial contributor to the global energy supply in electricity generation worldwide. Coal-fueled power plants currently fuel 38% of global electricity. Global coal demand as a source of energy expected to keep stable until 2024, reported by the International Energy Agency (IEA) [1, 2]. Energy education encyclopedia said in 2015 that coal is the primary source of electricity generation in the world, followed by natural gas, hydro, and nuclear, as shown in Figure 1.1.

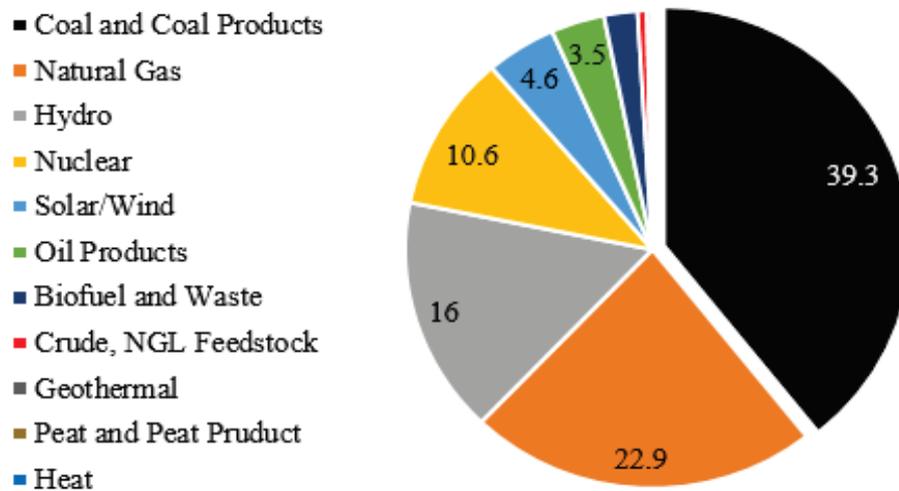


Figure 1.1. World electricity generation 2015 (24254.8 TWh) [3]

Coal as a fossil fuel in a power plant is used in the combustion process. The process of the coal power plant is describing in Figure 1.2. Coal-fired plants produce electricity by burning coal in a boiler to produce steam. The steam then travels through a turbine, causing it to rotate extremely fast, spinning a generator and producing electricity. The electricity can then be input to the electrical grid for use by society. Besides producing steam, the combustion process also has two kinds of ash: bottom ash and fly ash. Most of the trace elements in coal will distribute in fly ash. Then, Fly ash is transported from the combustion chamber by electrostatic precipitator.

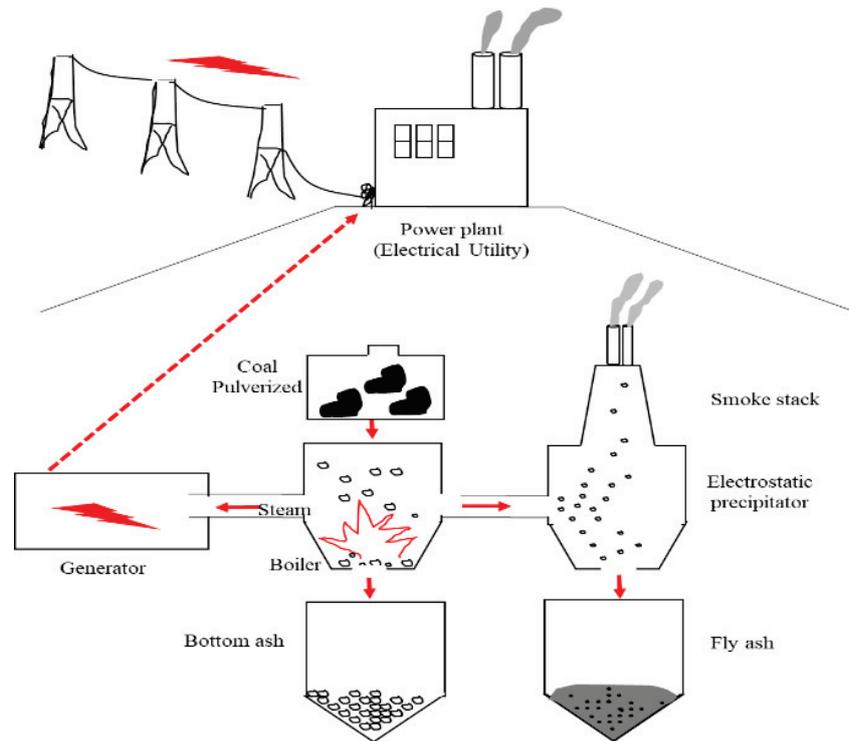


Figure 1.2. Schematic diagram of coal combustion power generation process

Due to the increase in energy demand, coal fly ash production expects to grow. Recently, the utilization of coal fly ash in several fields is developing. It uses cement raw material, embankment, backfills, building construction, agriculture land, bricks and tiles, reclamation, concrete, etc. [4 - 6]. Table 1 provides the worldwide production and utilization of fly ash. The average of fly ash utilization is 40.15%. It is mean the Utilization of fly ash is not optimal yet. The other remain of fly ash still dumped in a landfill.

Table 1.1. Coal fly ash production and utilization in different countries

No.	Name of Countries	Production (Million Tons/Y)	Utilization (Million Tons/Y)	Utilization (%)
1	Australia	59	25	42.37
2	China	150	52	34.70
3	Germany	78	40	51.28
4	India	132	48	36.36
5	Japan	55	29	45.45
6	Russia	102	32	31.37
7	South Africa	78	57.9	74.42
8	Spain	58	26	44.82
9	UK	60	34	56.67
Mean				40.15

Source: International Journal of Science and Research (IJSR) [7]

1.2 Trace Elements

Coal fly ash (CFA), which is not utilized, is considered waste and a possible source of toxic elements. During the combustion process, the organic matter in coal was destroyed, and as a result, the concentration of trace elements in coal fly ash enhanced relative to the source coal [8]. It has been reported that the trace element concentrations in fly ash are generally 4–10 times higher than their initial concentrations in coal [9]. 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. The dumping of fly ash in the disposal pond could cause a profound environmental impact. Therefore, acceptable waste management practices are needed to sustain a healthy environment.

Arsenic (As), selenium (Se), boron (B), fluorine (F), and Chromium (Cr) have been recognized as the most troublesome hazardous elements in coal fly ash. First, arsenic, a semi-metallic element that toxic chemicals. Commonly found as As(III) and As(V) compounds. The toxicity of arsenic depends strongly on the valence state. The trivalent oxidation state (As(III)) more toxic than the pentavalent oxidation state (As(V)). Still, overall, arsenic in coal ash is not environmentally stable and can participate in local biogeochemical cycles [10, 11]. Second, selenium in fly ash mainly finds selenite (Se^{4+}) with a minor presence of selenate (Se^{6+}). Selenite and selenate have different toxicity in the other case. In the aquatic environment, generally, Se^{4+} more toxic than Se^{6+} [12]. Permissible limits related to the protection of human health of arsenic, selenium, and its compounds set by the Ministry of the Environment of Japan's government are 10 mg/L. Third, boron, a nonmetallic element with atomic number 5, atomic mass 10.81 g/mole, density 2.3 g/cm³ at 20°C, and a poor electrical conductor at room temperature [13]. The mode of occurrence of this element in coal strongly influences in fly ash because boron is the most mobile trace element in coal ash [14]. Fourth, fluorine, present mainly in an inorganic form on coal fly ash. 55%-60% of the fluorine in fly ash of pulverized-coal-fired boiler were distributed in fly ash particles [15]. Fifth, chromium, a chemical element with the symbol Cr and atomic number 24. The toxicity of Cr also depends strongly on the valence state. The hexavalent (Cr(VI)) oxidation state is both toxic and carcinogenic. Whereas the other common oxidation state of chromium, Cr(III), is considerably less toxic [11].

The leaching of trace elements from fly ash contaminates the aquifer systems and raise the water-environmental problem. Due to the large number of trace elements generated and the effects on the environment, the development of a low-cost treatment for controlling toxic elements is urgently needed.

1.3 Additive Materials

Trace elements can be immobilized by the addition of additive material as an inhibitor. Additive material is a material that consists of high calcium content. It is used in the leaching process to control trace element leaching concentration into the environment. Previous researches had been reported that calcium plays a vital role in interacting with trace elements such as arsenic [16 - 18), selenium, [18 - 20], boron [18, 19], and chromium [17].

Several additive materials from pure calcium compound and material containing high calcium compounds such as calcium hydroxide, paper sludge ash, and blast furnace cement have been investigated singly and mixed in current research. Calcium hydroxide, commonly referred to as slaked lime, is described by the chemical formula $\text{Ca}(\text{OH})_2$. It is an inorganic compound that has a white, powdery appearance in its solid-state. However, $\text{Ca}(\text{OH})_2$ has a colorless appearance in its crystalline form. Molecules of calcium hydroxide are held together via ionic bonds between the calcium ion (Ca^{2+}) and two hydroxide ions (OH^-). Paper sludge (PS) ash is a by-product of the de-inking and re-pulping of the paper industry. It can be obtained by incinerating at temperature 800°celsius. After incinerating, the resultant fly ash may contain reactive silica and alumina (in the form of metakaolin) as well as lime (CaO) [21]. Previous researchers investigated the environmental quality of paper sludge. They found that the primary paper sludge does not represent a major threat to the heavy metal release environment. Also, due to the use of CaCO_3 in industrial during the paper production process, PS ash contains high CaO , which can use for removing heavy metal [22]. Blast furnace (BF) cement is created by adding granulated blast furnace slag with a Portland cement clinker and gypsum. The slag contains the same oxides (SiO_2 , Al_2O_3 , CaO) that makeup Portland cement but indifferent proportions [23]. Based on the EN 197-1:2000 standard, this cement has three types, which are type A, B, and C. Type B of BF cement was applied in this research.

1.4 Objective of The Research

Some researchers have investigated several studies about leaching characteristics of trace elements from coal fly ash. The present research objective focuses on investigating additive material for controlling some trace elements leaching from coal fly ash. Chapter 2 discusses additives' effect for controlling As, Se, B, and F leaching from coal fly ash. Three types of additive materials used as a single and mixture additive have been tested to kind of coal fly ash. Chapter 3 describes calcium performance in paper sludge ashes as an additive material for controlling trace elements leaching from fly ash. Characterization of PS ash and its calcium compound content from 9 kinds of paper sludge ashes have been investigated. The PS ash, which contains the higher level of calcium compound and has the same level capability for controlling trace element leaching (result from chapter 3) tested to 14 types of fly ash, investigated the role of calcium compound on fluorine leaching concentration. It discusses in Chapter 4. Chapter 5 investigated the effect of additive material on controlling chromium (Cr) leaching from coal fly ash.

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Chapter 2 Preliminary Study on Additives for Controlling As, Se, B, and F Leaching from Coal Fly Ash

2.1 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 behaviors 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], 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.

2.2 Materials and Methods

2.2.1 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 (600MWe). Coal fly ash C (FAC) and coal fly ash H (FAH) 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 2.1 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 2.1. 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 ₂ O ₃		22.79	25.63	0.07	15.41	13.32
TiO ₂		2.27	1.99	0.07	0.35	0.19
Fe ₂ O 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 ₂ O		1.20	0.60	0.08	0.02	0.08
K ₂ O		0.80	1.56	0.01	0.15	0.36
P ₂ O ₅		0.07	0.18	0.05	0.10	BDL
MnO		0.06	BDL	BDL	0.04	0.05
V ₂ O 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 CaCO₃ (Figure 2.1).

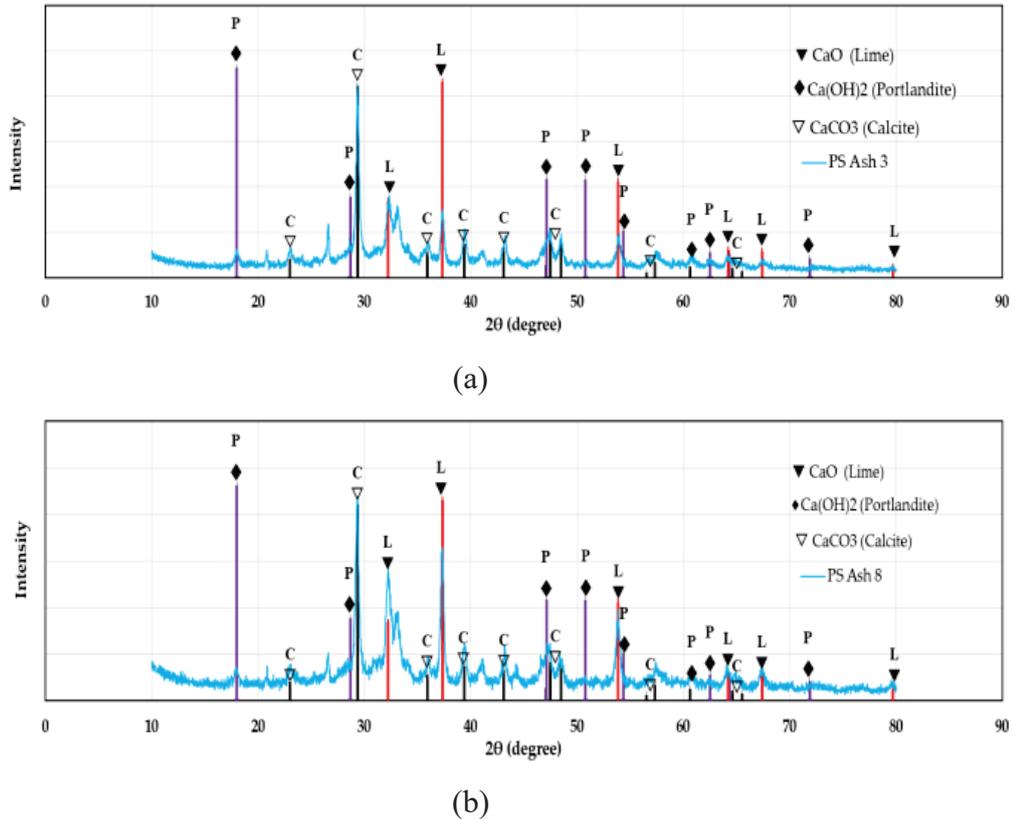


Figure 2.1. The main calcium compounds in (a) PS ash 3 and (b) PS ash 8 by XRD (x-ray diffraction) analysis

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 2.2). 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].

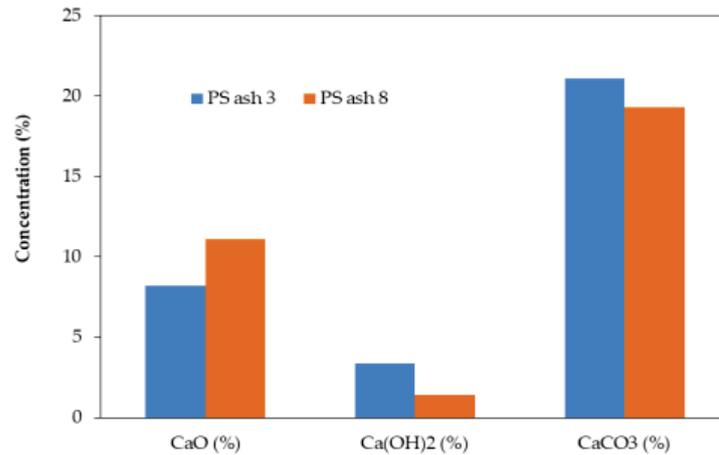


Figure 2.2. Calcium compound concentrations in PS ash 3 and PS ash 8.

2.2.2. Sample Preparation and Leaching Test

Coal fly ash samples were prepared before performing the leaching test process. Figure 2.3 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 mixture was perfectly mixed (~3 min). Table 2.2 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 analyzed by several methods.

Table 2.2. 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

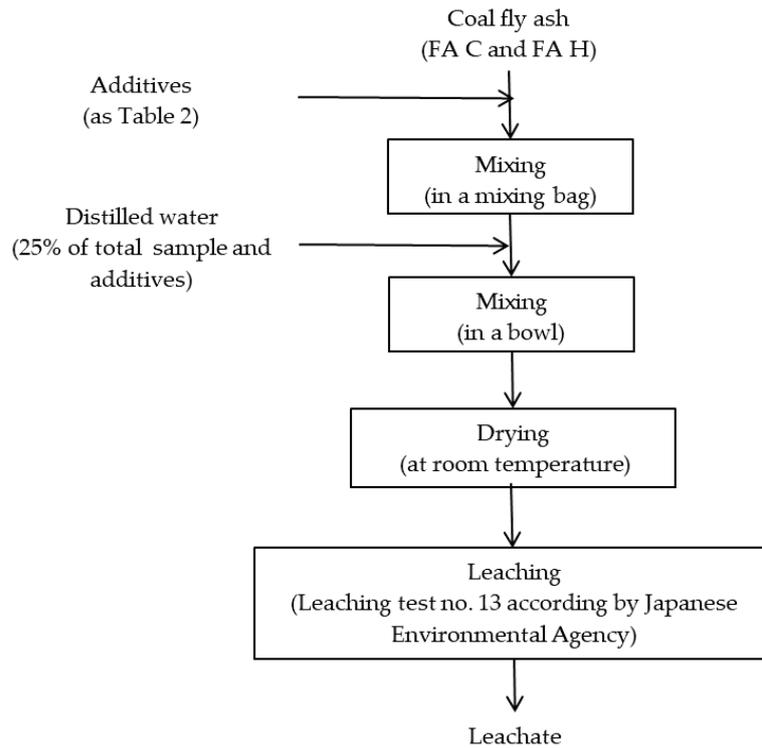


Figure 2.3. Schematic diagram of the sample preparation and leaching test.

2.2.3. 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 analyzed 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).

2.3 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 2.3. 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 2.5. A decrease in leachate concentration indicated that the additive had potential for use in the leaching process.

Table 2.3. Trace element leachate concentrations in coal fly ashes without additives

Leaching concentration	As ($\mu\text{g/L}$)	B (mg/L)	Se ($\mu\text{g/L}$)	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

2.3.1 $\text{Ca}(\text{OH})_2$, 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 decrease 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 2.4 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 $\text{Ca}(\text{OH})_2$, PS ash 8 and BF cement as single additives. The application of $\text{Ca}(\text{OH})_2$ (3% of the total sample) as a native calcium compound in the form of a single additive showed a positive trend. $\text{Ca}(\text{OH})_2$ 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.

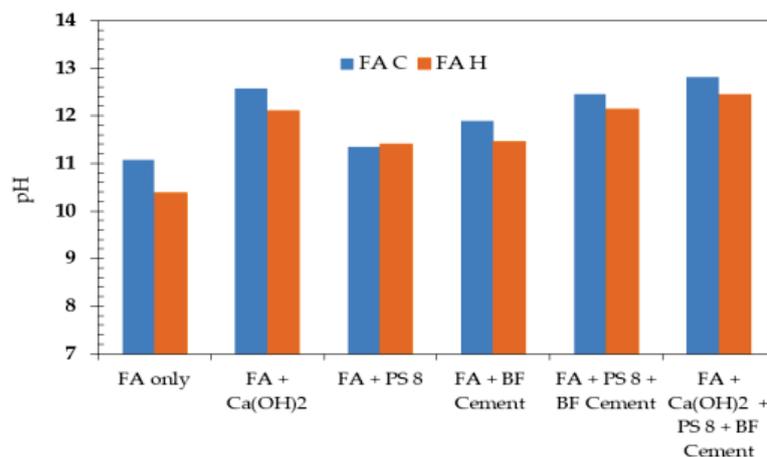
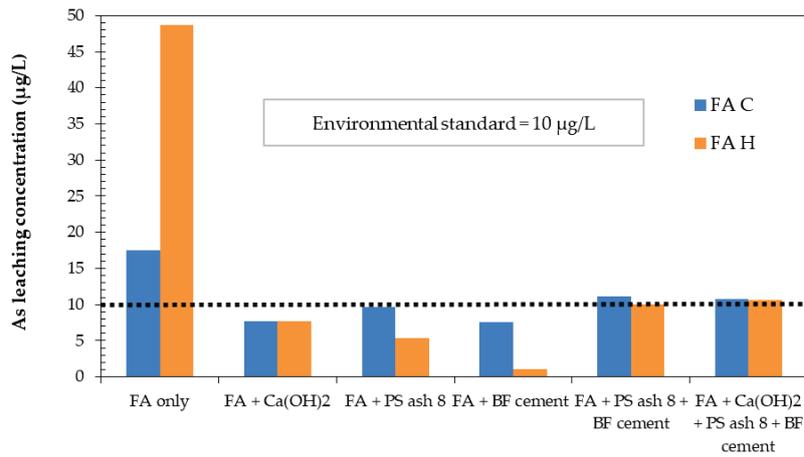


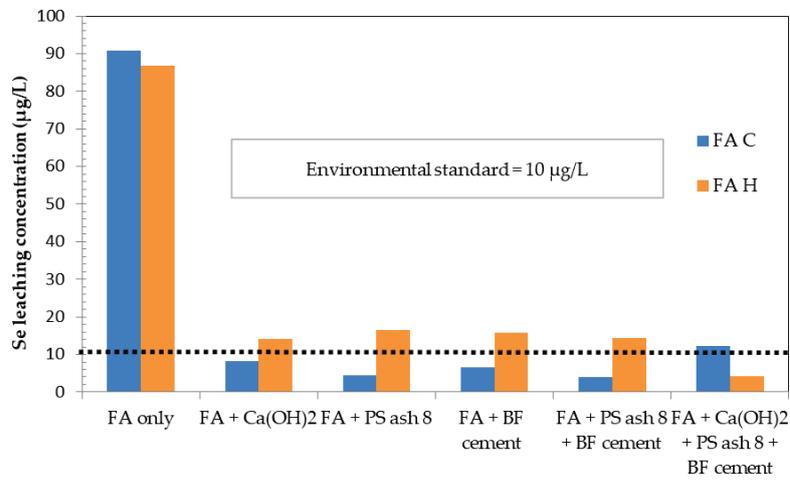
Figure 2.4. The pH of coal fly ashes and mixtures of coal fly ashes and additives.

These varying results led to the conclusion that PS ash 8 and BF cement were not as

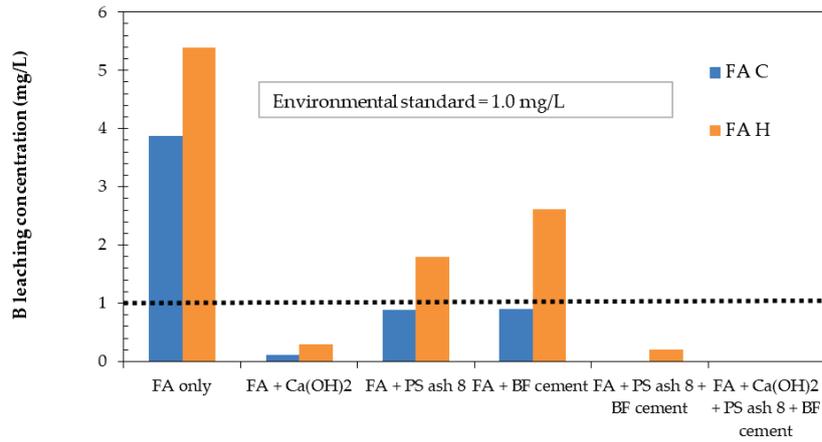
effective as single additives due to the lack of a simultaneous effect in decreasing the leaching of As, Se, B, and F. In fact, the application of Ca(OH)_2 as a single additive was much more effective than that of the other two additives. However, because Ca(OH)_2 is a native calcium compound that was used for comparison with the results of other supplementary materials, this research continued by investigating the application of these three materials as mixed additives.



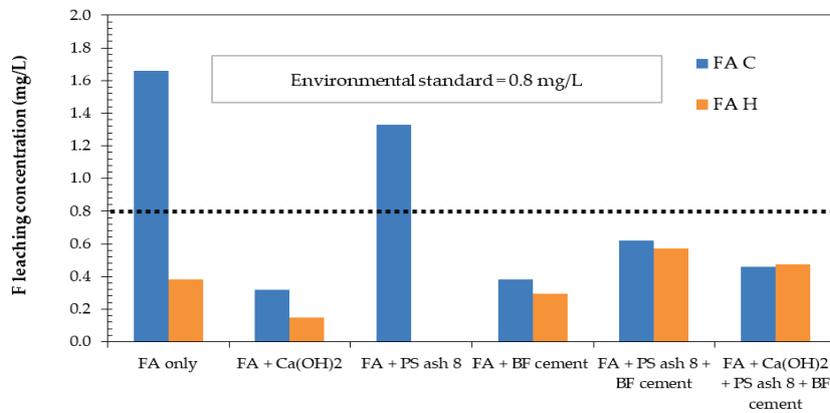
(a)



(b)



(c)



(d)

Figure 2.5. Effect of additive on (a) As, (b) Se, (c) B and (d) F leaching concentrations from two different coal fly ashes.

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

As presented in Figure 2.2, 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 2.6 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.

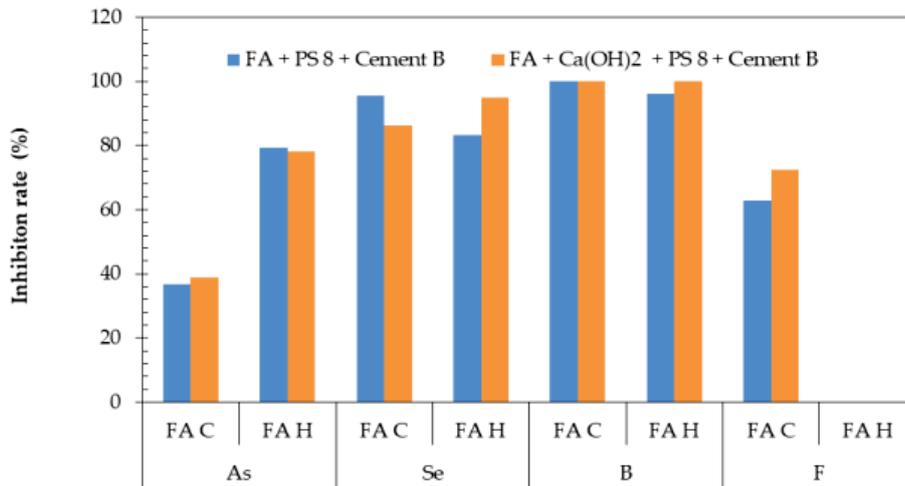


Figure 2.6. Inhibition rate of the mixed additives on the As, Se, B and F leachate concentrations

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 analyzed by XRF (Table 2.4). 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 2.4. Chemical composition of the coal fly ashes and Ca(OH)₂, PS ash 8 and BF cement mixtures before and after leaching

Chemical (%)	FAC		FAH	
	Before leaching with (Ca(OH) ₂ + PS 8 + FB cement	After leaching with (Ca(OH) ₂ + PS 8 + FB cement	Before leaching with (Ca(OH) ₂ + PS 8 + FB cement	After leaching with (Ca(OH) ₂ + PS 8 + FB cement
SiO ₂	56.93	46.11	54.24	48.08
Al ₂ O ₃	22.09	17.74	22.2	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	0.8	0.18	0.46	0.58
K ₂ O	0.57	1.39	1.14	0.78
P ₂ O ₅	0	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	0.5	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 $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ [9,13], CaSeO_3 [9], $\text{Ca}_2\text{B}_2\text{O}_5$, $\text{Ca}_3\text{B}_2\text{O}_6$ [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 ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) 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.

2.4 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 $\text{Ca}(\text{OH})_2$, 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 3 Calcium Performance in Paper Sludge Ash as Suppressing Material

3.1 Introduction

In the next few years, coal will still be an essential source of electricity in Japan and the world. It means Fly ash, as a waste product from the thermal power plants, will be increasing day by day [1]. As the coal burns, toxic pollutants such as arsenic (As), selenium (Se), boron (B) are transferred into the wastes [2]. So, the study to minimize trace elements' effect to the environment still needs to be researched. To decrease the effect of trace elements into the environment, many researchers already investigated role of calcium in leaching mechanism. They said that calcium compound could control the leaching of trace elements from coal fly ash [3]. Another research also states that CaO dominates in the coal fly ash sample directly affects trace elements' mobility by determining pH of the leaching medium [4]. The role of calcium through additives during the leaching of trace elements has been studied in the previous work [5]. The study explained that paper sludge as the additives is a promising solution to minimize the hazardous effect of trace elements into the environment. However, the study also showed that the higher calcium in paper sludge ashes did not always work linearly into a better effect during mechanisms. Paper sludge ash is waste that some industry lately utilized, especially as the cement kiln feed and the cement blending because after incinerating paper sludge at approximately 800°C, the resultant fly ash may contain reactive silica and alumina as well as lime (CaO). The ash composition not only depends on the specific fuel but also on the combustion technology and conditions [6]. There is a specific characteristic of calcium, which may affect leaching mechanisms. Therefore, this research will study the performance of several kinds of paper sludge ashes based on calcium content.

Nine kinds of the paper sludge (PS) ashes will be tried to coal fly ash C to analyze their performance during the leaching mechanisms. The performance of calcium through the addition of paper sludge ashes will be study by the analysis by inductively coupled plasma- Atomic Emission Spectroscopy (ICP-AES) analysis, X-ray Diffraction (XRD) analysis, thermal gravimetric (TG) analysis, and ethylene glycol

(EG) analysis. The result will provide information about the paper sludge ash, which useful in decreasing the As, Se, and B leaching concentration simultaneously.

3.2 Methods

3.1.1 Materials

The fly ash sample which used in this research was Fly ash C (FA C). It is derived from a pulverized coal-fired power plant unit 2 electrostatic precipitator's number 1. This coal fly ash is containing As 26.39 $\mu\text{g/L}$, Se 186.51 $\mu\text{g/L}$, and B 7.85 mg/L based on ICP-AES analysis. PS ash as the suppressing material has been tested for stabilizing As, Se, and B in FA C. Inorganic Chemical composition of FA C and paper sludge ashes could be shown in Table 1.

Table 3.1. Chemical composition in FA C and paper sludge ashes based on XRF analysis.

Samples	FA C	PS Ash									
		3	4	5	6	7	8	9	10	11	
Ash [%]	SiO ₂	64.3	31.47	44.21	42.36	26.03	32.39	28.76	37.82	40.6	26.2
	Al ₂ O ₃	22.8	12.40	22.23	19.8	18.31	15.94	15.41	19.39	19.57	15.04
	TiO ₂	2.27	0.38	2.56	2.11	3.47	0.62	0.35	3.01	2.27	0.42
	Fe ₂ O ₃	3.71	5.13	2.63	5.56	1.58	0.98	0.91	6.11	3.13	-
	CaO	2.71	46.31	18.77	19.51	41.45	44.24	51.22	23.27	24.29	54.76
	MgO	0.85	3.28	3.42	3.3	2.09	2.72	2.76	3.05	2.88	2.56
	Na ₂ O	1.20	0.24	0.95	0.41	-	0.26	0.02	0.41	0.71	0.16
	K ₂ O	0.80	0.20	2.09	1.99	0.93	0.53	0.15	1.87	2.34	0.07
	P ₂ O ₅	0.07	0.18	1.75	1.54	0.94	0.43	0.10	1.32	2.00	0.16
	MnO	0.06	0.03	0.05	0.06	0.04	0.05	0.04	0.06	0.06	0.03
	V ₂ O ₅	-	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	SO ₃	0.35	0.36	1.31	3.33	5.15	1.83	0.27	3.67	2.16	0.56

3.1.2 Leaching Test

Leaching Test for Trace Elements

Leaching test for this experiment based on the procedure of standard leaching test for fly ash notification No.13 by the Environmental Agency of Japan.

Ethylene Glycol Leaching Method

CaO needs a high temperature (>1000°C) to decompose, so it is not easy to measure with thermal gravimetric. In this research, the determination of CaO in paper sludge ash with TG and ethylene glycol has been developed. At the beginning of this method, 1 mg PS ash was weighed and added 25 ml warm ethylene glycol (T=80°C), then stirred at 200 rpm (temperature was kept at 80°C) for one hour. After one hour, the

sample was filtered by 0.45 mm cellulose acetate membrane filter. The concentration of Ca in solution measured by inductively coupled plasma atomic emission spectrometry (ICP-AES).

3.1.3 Instrumentation

Some instruments have been used to analyze calcium compounds in paper sludge ashes. X-ray Diffraction (XRD) labX XRD6100, Shimadzu, Kyoto, Japan, has been used for qualitative analysis. The sample in powder form was pressed into a sample holder so that has a smooth flat surface. The sample was irradiated with Cu K α -radiation between 10° and 80° (2 θ). Scanning speed is 2°/min, at an acceleration voltage of 40kV and tube hazard 30 mA. Software module “DDView and Sleeve,” database PDF – II release 2013 from the International Center for Diffraction Data (ICDD), was used to analyze diffraction patterns after measurement. PDF II means a database that contains full information on a particular phase, including cell parameters. TG/DTA6300 SII EXSTAR 6000, Hitachi, Hongkong has been used to measured Ca(OH)₂ and CaCO₃. The paper sludge ashes sample (9- 12mg) 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 200ml/min flow rate. This instrument work based on the measure of weight/mass change (loss weight) as a function of temperature, time, and atmosphere. Percentage of CaO measured by combining ICP-TG through the ethylene glycol leaching process because CaO needs the high temperature (>1000°C) to decompose, so it is not easy to measure with thermal gravimetric directly. However, not only CaO can dissolve by the ethylene Glycol but also Ca(OH)₂. Therefore, this method has to combine with TG analysis. The content of CaO in a paper sludge is calculated from the amount of calcium determined by the EG method and Ca(OH)₂ obtained by TG.

3.2 Results and Discussion

3.2.1 Effect of Suppressing Material

Each paper sludge ash has been tested on FA C to know the effect of paper sludge ashes with trace element leaching concentration. The result has shown that the addition of paper sludge ash can increase the pH value of leached and decreasing the leaching concentration of trace elements in FA C as demonstrated in Figure 3.1. It was

consentient with the statement [4] that CaO in the coal fly ash sample directly affects the mobility of trace elements by determining pH of the leaching medium. Figure 3.1(a) shows the effect each paper sludge ashes in controlling leaching arsenic (As). Arsenic leaching concentration in FA C without additive material was 17.55 $\mu\text{g/L}$, but after added paper sludge ashes, it could be decreased. All of paper sludge ashes could be decreased As leaching concentration under the environmental standard, but the most effective to reducing Arsenic concentration in FA C was PS ash 11 followed by PS ash 3 and PS ash 6 (0.01 $\mu\text{g/L}$, 1.04 $\mu\text{g/L}$, and 1.65 $\mu\text{g/L}$ respectively). Then, pH also one of the most critical parameters that control the leaching process [8]. Paper sludge ashes could increase the alkalinity of FA C from 8.6 increases until 11.7 pH value by PS ash 11, as shown in Figure 1.1. Selenium (Se) leaching concentration in FA C without additive material was 186.51 $\mu\text{g/L}$. Paper sludge ashes also could keep stabilization selenium in coal fly ash. It proves by figure 3.1(b), selenium leaching concentration decreasing until 0.615 $\mu\text{g/L}$, 14.65 $\mu\text{g/L}$, and 17.02 $\mu\text{g/L}$ by PS ash 11, PS ash 5, and PS ash 9, respectively. Still, only PS ash 11 addition could decrease until under the environmental limit, as shown in Figure 3.1(b). Boron leaching concentration also keeps stable after added paper sludge ashes. Different kinds of paper sludge ashes give different effect stabilization to Boron leaching concentration. Boron leaching concentration without paper sludge ashes was 3.88 mg/L. It could be decreased until 0.38 mg/L, 0.39 mg/L, and 0.64 mg/L by PS ash 11, PS ash 7, and PS ash 8 shown in Figure 3.1(c).

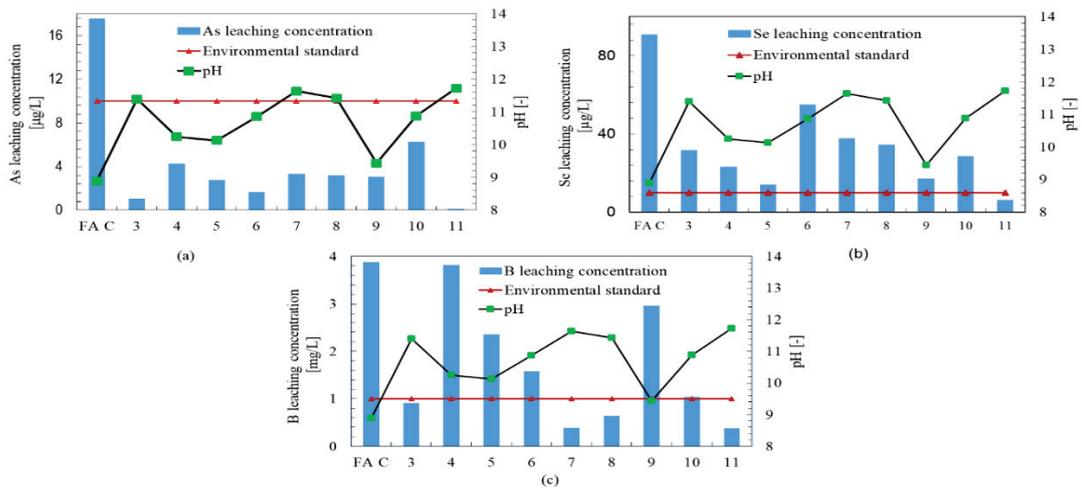


Figure 3. 1. The effect of additive material in controlling trace elements leaching concentration (a) Arsenic, (b) Selenium, and (c) Boron

PS ash 6 good at controlling arsenic, but no in controlling selenium and boron. PS ash 5 and 9 good in selenium but no in controlling boron. PS ash 7 good on boron, but no in arsenic and selenium. Different from PS ash 11, it is useful in three trace elements: arsenic, selenium, and boron. PS ash 3 and PS ash 8 also keep stable for decreasing the leaching concentration of three kinds of trace elements in FA C. To know why some paper sludge ashes, give a good effect. Still, the others no, calcium qualitative and quantitative analysis in FA C has been done.

3.2.2 Qualitative Analysis by XRD

X-ray diffraction analysis was performed to analyze calcium compounds in the paper sludge ashes. Calcium oxide (CaO), Calcium Hydroxide (Ca(OH)₂), and Calcium carbonate (CaCO₃) pure has been used as a standard to analyze calcium compounds in paper sludge ashes. As can be seen from Figure 2.2 raw peak of each paper sludge ash have different intensity. Figure 3.2(a) indicates the height of the diffraction pattern from PS ash 3, 8, and 11 was detected as CaO, Ca(OH)₂, and CaCO₃. Based on Figure 3.2(a), PS ash 3, 8, and 11 predicted to have high calcium compounds. While Figure 3.2(b), the higher intensity of the sample is on different calcium standard intensity. Only a small part of the diffraction peak was detected as a calcium compound. It predicted that PS ash 4, 5, 6, 7, 9, and 10 have low calcium compounds. Quantitative analysis has been done to make sure of this hypothesis.

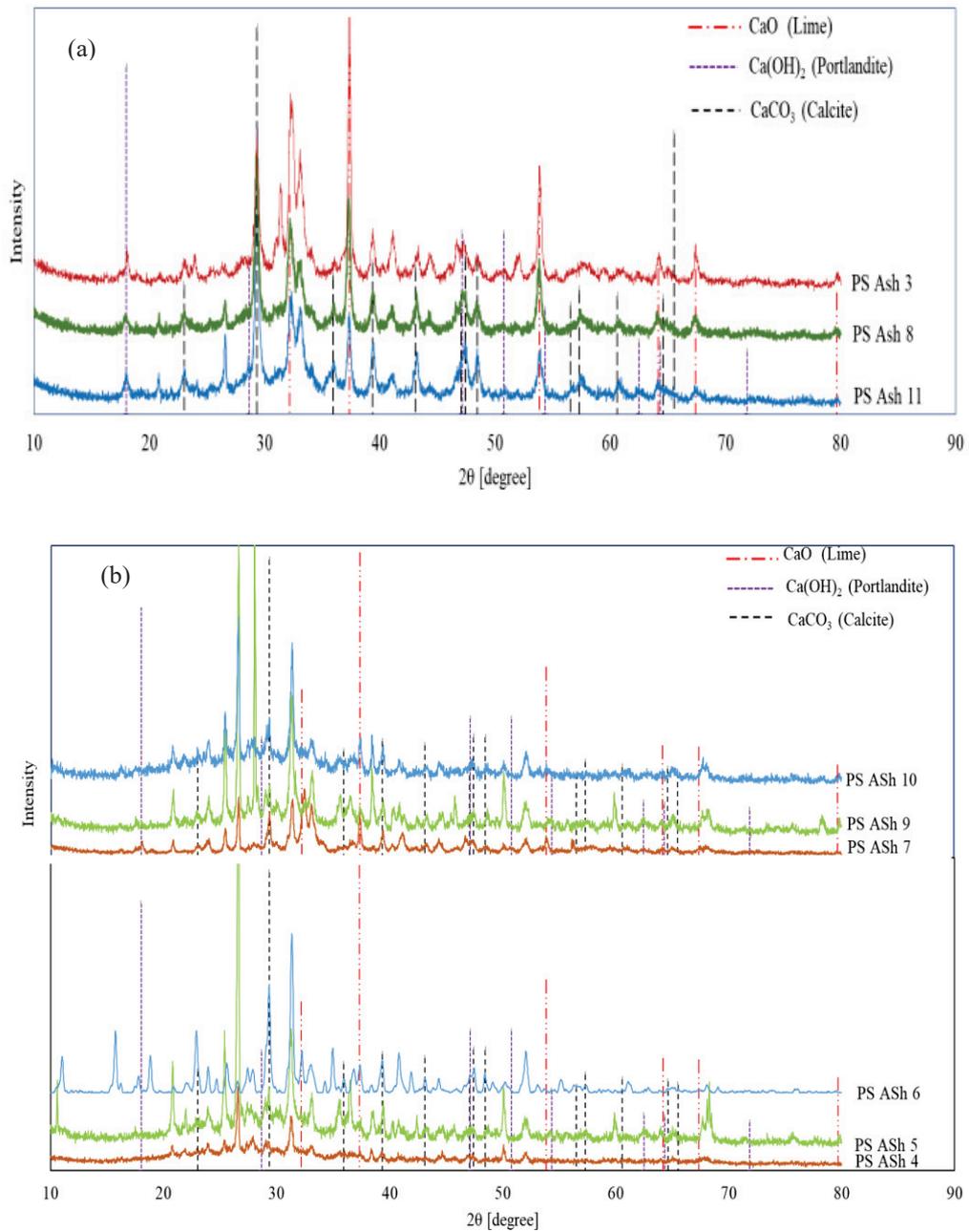


Figure 3. 2. Combination pattern of paper sludge ashes and three of calcium standard; (a) PS Ashes pattern which have generally same peaks with calcium standard, (b) PS Ashes pattern which slightly consist of calcium standard.

3.2.3 Quantitative Analysis by TG and Ethylene Glycol Method

TG analysis was carried out on paper sludge ashes to confirm the percentage of Ca(OH)₂ and CaCO₃ based on weight losses in the TG curve. Ca(OH)₂ starts to lose

weight in the temperature range 350-450°C decomposed into CaO and H₂O. CaCO₃ decomposed into CaO and CO₂ at the temperature around 600-790°C. Both of them have been used as a standard to determine calcium compounds in paper sludge ash. Figure 3.3 shows the decomposition of PS ash 3. A weight loss from the temperature around 355-445°C and 600-780°C for the Ca(OH)₂ and the CaCO₃, respectively. Percentage of each calcium obtained from the calculation of weight loss, molecule weight, and total weight. Since the decomposition temperature of CaO is above 1000°C and cannot be detected by TG only, the analysis was carried out by combining ethylene glycol extraction/ICP-AES. Based on the previous research [8] has been known that CaO and Ca(OH)₂ are dissolved in Ethylene glycol well, but CaCO₃ dissolved hardly. As shown in Table 3.2, it became clear that CaO and Ca(OH)₂ can be extracted entirely by the Ethylene Glycol method. The calcium compound extracted from paper sludge ash by the ethylene method was converted into CaO. The CaO content in the paper sludge ash was determined by subtracting the Ca(OH)₂ amount.

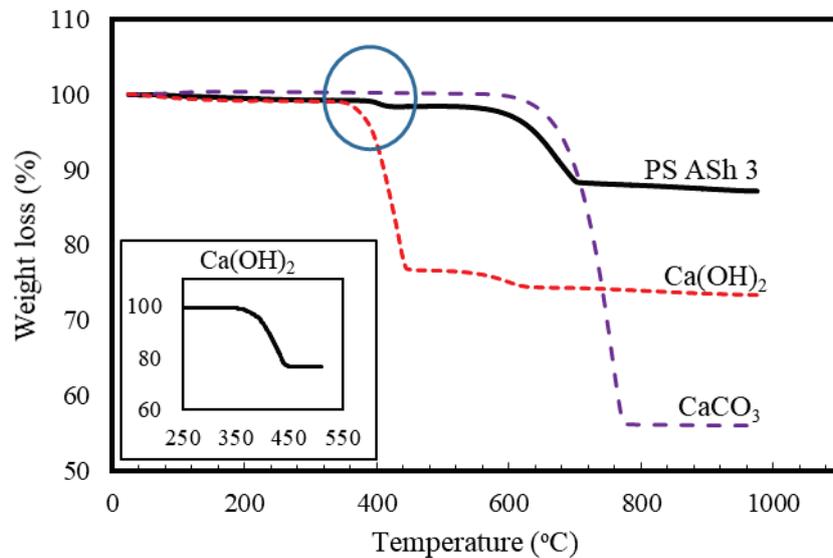


Figure 3.3. Thermal decomposition curves of PS ash 3, Ca(OH)₂ and CaCO₃

Table 3.2. Solubility of CaO, Ca(OH)₂ and CaCO₃ in ethylene glycol

Calcium compound	Dissolve amount (%)
CaO	100.5 ± 0.5
Ca(OH) ₂	96.7 ± 0.6
CaCO ₃	0.1 ± 0.0

3.2.4 Calcium Performance in Paper Sludge Ashes

It has been known that each paper sludge ashes give different effects to control leaching concentration of As, Se, and Boron in coal FA C. In aims to verify the kind of calcium compound, TG analysis and EG method have been done. Figure 3.4 shows the concentration of calcium compounds contained in paper sludge ashes.

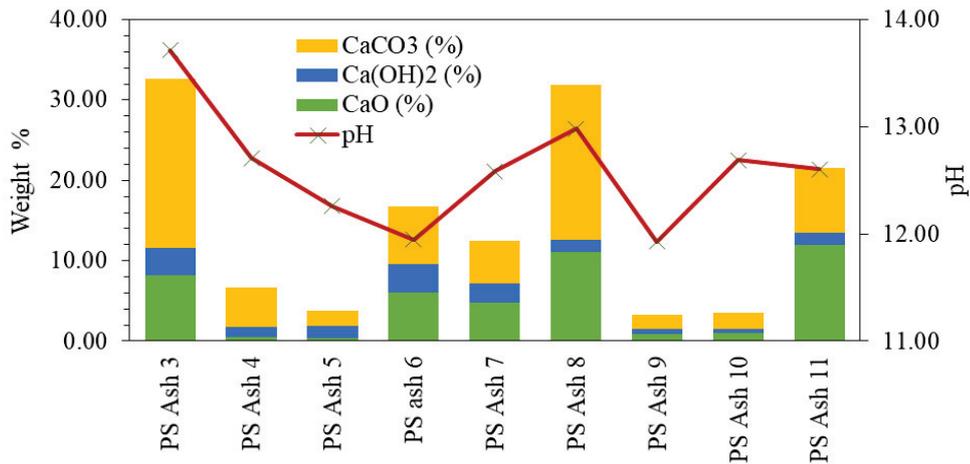


Figure 3.4. Calcium compounds content of paper sludge ashes and its relationship with the alkalinity

The result of Ca(OH)_2 and CaCO_3 got from TG and CaO from the EG method. The lowest calcium concentration was found on PS ash 9, 10, and 5. Otherwise, the highest calcium compound contained on PS ash 3; 32.69%, PS ash 8; 31.86%, PS ash 11; 21.53%, and PS ash 6; 16.81%. The highest calcium compound, 21.12% CaCO_3 , 3.55% Ca(OH)_2 , and 12.03% CaO contained on PS ash 3, 6, and 11, respectively. The alkalinity of paper sludge ashes, which could be increasing pH value in the leaching process of coal fly ashes, also could be seen in figure 3.4. The highest alkalinity found in PS ash 3, 8, and 11 (13.72, 12.98, and 12.61, respectively).

Related to the effect of additive material in controlling leaching concentration of arsenic, selenium, and boron can be known that the highest calcium compound does not give the best performance in preventing leaching concentration simultaneously. Figure 3.5 shows which one is the best PS ashes in controlling As, Se, and B simultaneously.

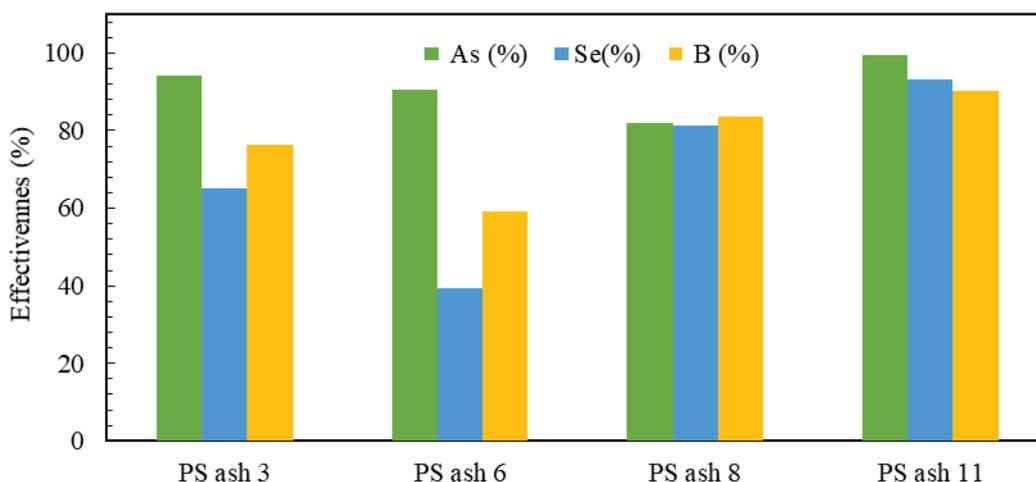


Figure 3.5. The capability of paper sludge ashes in decreasing trace elements

The percentage of effectiveness shows PS ashes' capability, which contains the highest calcium in decreasing trace elements' leaching. PS ash 3, which includes the highest calcium compound and consists of the highest CaCO_3 , only can control leaching concentration As; 94.07%, Se; 65.13%, and B; 76.42%. PS ash 6, which contains the highest $\text{Ca}(\text{OH})_2$, can control leaching concentration of 90.60% As, 39.48% Se, and 59.28% B. PS ash 8, which contains the second highest calcium compound, can control around 80% of As, Se, and B. The most effective control leaching three of As, Se, and B was in PS ash 11. PS ash, which contains the highest CaO , can decrease As; 99.43%, Se; 93.22%, and B; 90.34%.

3.3 Conclusion

Based on the above discussion has been known that each PS ash gives different effect in controlling leach out of trace elements in FA C suitable with kind and total calcium which contained in each PS ash. This research found that PS ash 11 and PS ash 8 are most effective for stabilizing trace elements in coal fly ash because they can control trace elements leaching more than 80% simultaneously.

3.4 Reference

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Chapter 4 The Role of Calcium Compound on Fluorine Leaching Concentration

4.1 Introduction

Coal has been predicted as the largest power generation source in 2040, with a share of almost 30 percent [1]. It means that the production of coal fly ashes will still affect the environment because of the hazardous element containing in the coal fly ash [2]. One of the toxic trace elements consisting of coal fly ash is fluorine. Fluorine is the most reactive of all the chemical elements, including hazardous trace elements in coal. The study reported that about 10-40% of fluorine in coal entered into coal fly ash through the combustion process [3 - 5]. Therefore, the utilization of coal fly ash for various purposes needs to beware of the fluorine effect. Fluoride is the anion of fluorine listed as one of the contaminations in water by the WHO because it could cause many problems in human health [6]. In plants, plants under the natural condition could be absorbed fluorine, and it is bound into insoluble compounds such as CaF_2 [7].

In the development of additives for inhibiting the trace elements' leaching into the environment, a previous study was found that calcium has a positive effect in decreasing trace element leaching concentration [8]. Then, the application of mixture additives was given a good impact in inhibiting the leaching of several trace elements, including the leaching of fluorine [9]. This study was purposed to investigate the calcium compound, which plays a vital role during the fluorine leaching mechanisms. This information will require in controlling the effect of fluorine into the environment.

4.2 Method

4.2.1 Coal Fly Ash

The coal fly ashes sample used in this research were obtained from different coal-fired power plants in Japan. The chemical composition of these fourteen coal fly ashes was 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 4.1. Chemical composition for coal fly ashes by XRF analysis

Fly Ash	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
Power Station	Unit 2				Unit 1										
Chemical Composition [%]	SiO ₂	52.61	51.42	64.34	74.78	55.30	66.99	66.21	59.55	59.21	65.07	56.82	57.32	64.84	63.08
	Al ₂ O ₃	31.35	22.39	22.79	16.68	30.84	26.40	26.65	26.09	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	1.83	1.77	1.11	1.06	0.96	1.12	1.24
	Fe ₂ O ₃	7.06	7.01	3.71	3.93	5.75	2.15	2.57	6.80	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	1.94	2.07	1.43	8.86	8.79	1.39	2.67
	MgO	0.58	1.05	0.85	0.22	0.98	0.51	0.54	0.84	0.91	0.52	0.96	1.02	0.82	1.12
	Na ₂ O	0.38	1.23	1.20	0.38	1.14	0.27	0.29	0.66	0.74	0.44	0.75	0.80	0.52	1.25
	K ₂ O	0.96	1.19	0.80	1.43	1.20	0.58	0.54	1.49	1.44	1.76	1.97	1.97	1.67	1.44
	P ₂ O ₅	0.61	0.22	0.07	0.10	0.19	0.04	0.06	0.19	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	0.09	0.10	-	-	-	0.00	0.07
	V ₂ O 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	0.28	0.28	0.28	0.26	0.44	0.53	0.50	0.35	0.84	0.87	0.35	0.53	

4.2.2 Additives

An additive was used to elevate the calcium content in the coal fly ash sample. There are two kinds of mixture additives used in this research: (1) The mixture of PS ash 8 and BF Cement (2) The blend of Ca(OH)₂, PS ash 8, and BF cement. The previous research presented that these two mixtures were given a promising effect in the leaching of several trace elements from coal fly ash with low calcium content (FA C and FA H). The calcium content in PS ash 8 and BF cement is 51.22% and 48.35% (Table 4.2). The coal fly ash samples mixed with the additives in a certain ratio before the leaching process. The additives' ratio 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.

Table 4.2. Chemical composition for additives by XRF analysis

Chemical Composition	PS ash 8	BF Cement
SiO ₂	28.76	31.03
Al ₂ O ₃	15.41	13.32
TiO ₂	0.35	0.19
Fe ₂ O ₃	0.91	0.44
CaO	51.22	48.35
MgO	2.76	3.77
Na ₂ O	0.02	0.08
K ₂ O	0.15	0.36
P ₂ O ₅	0.10	0.00
MnO	0.04	0.05
V ₂ O ₅	0.02	0.02
SO ₃	0.27	2.39

4.2.3 Analysis and Instrumentation

Ion chromatography analysis (ION ANALYZER IA-300) was performed to determine the fluorine leaching concentration from the 14 different coal fly ashes for before and after applying the additives. Then, the data of leachate alkalinity was provided by pH/ION METER D-53, HORIBA, to probe the effect of pH into fluorine leaching concentration. 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.

4.3 Result and Discussion

4.3.1 Effect of pH in fluorine leaching process

The different calcium compounds on coal fly ashes also affected pH of the leachate. The leachate's pH from the fourteen coal fly ashes before applying mixture additives is linear with the calcium content on each coal fly ashes based on the XRF analysis (Table 4.1). After the application of the mixture additives, the pH of the leachate becomes higher. The leachate pH from the mixture additives PS Ash 8 and BF cement is slightly lower than mixture additives $\text{Ca}(\text{OH})_2$, PS Ash 8, and BF cement (pH around 12, Figure 4.1). This condition proves in the study that explained alkalinity is one factor that affected the trace element leaching concentration into the environment. The high alkaline pH is positively decreasing the trace element leaching concentration [10 - 12].

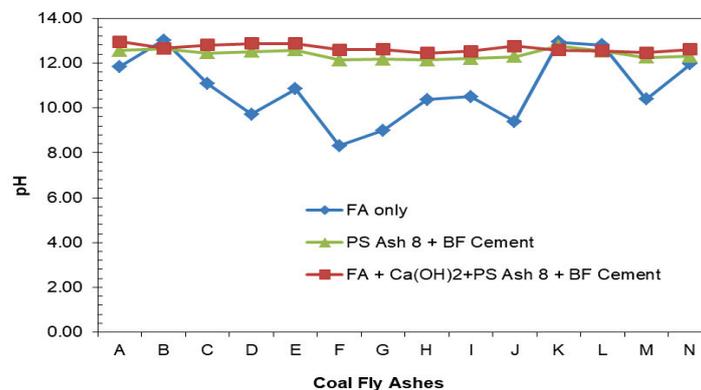


Figure 4.1. Effect of mixture additives into the leachate pH from different coal fly ashes on fluorine leaching process

4.3.2 Effect of additives into fluorine leaching concentration

Based on the pH analysis result, both of the mixture additives have pH in around pH 12. Previous researcher explained in their study that higher pH on the leaching process could lowered the leaching of the fluorine leaching [10, 12]. 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 4.2 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.

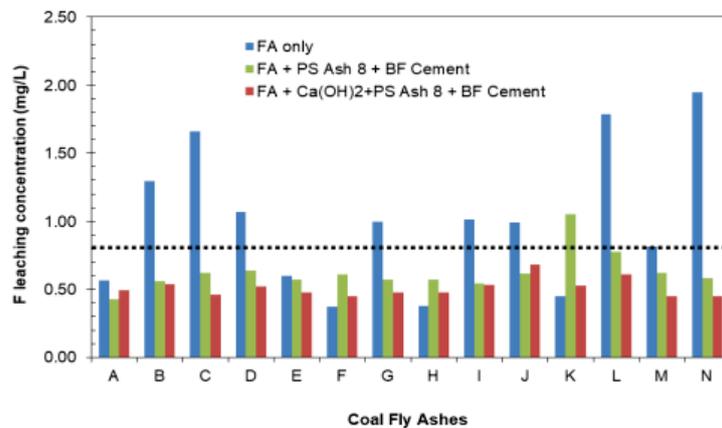


Figure 4.2. Effect of the mixture additives into different coal fly ashes on fluorine leaching concentration

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 4.2). The mixture of $\text{Ca}(\text{OH})_2$, 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 $\text{Ca}(\text{OH})_2$, 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.

4.3.3 The role of calcium in fluorine leaching process

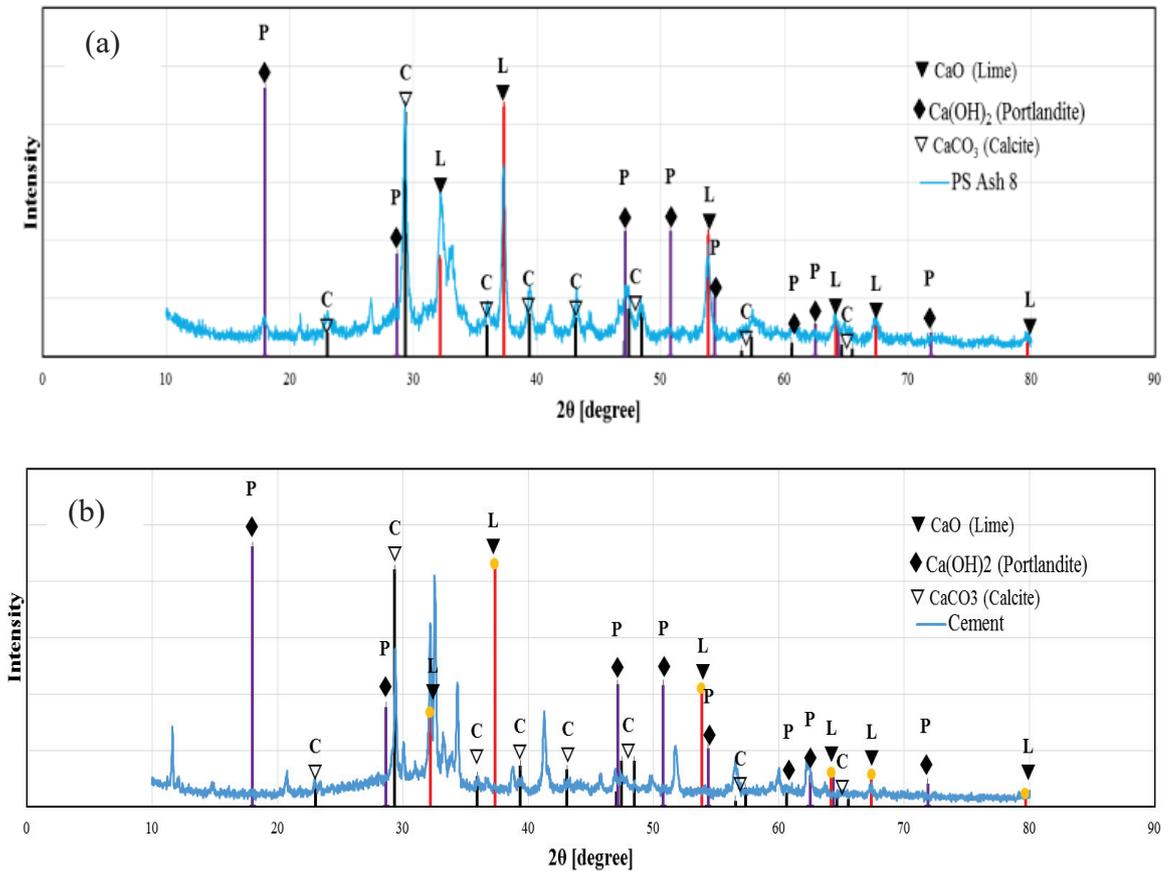


Figure 4.3. XRD patterns of (a) PS ash 8 and (b) Blast Furnace (BF) Cement

Both of the additives' mixtures presented a promising effect in minimizing the effect of the fluorine leaching into the environment. Calcium compound consisting of the coal fly ashes and additives was believed to take an essential role during the fluorine's

leaching. Figure 4.3 showed the XRD analysis result of the PS ash 8 and BF Cement. This figure explained that CaO, Ca(OH)₂, and CaCO₃ were the main calcium content in these additives.

Table 4.3. 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 to find the amount of those calcium compounds in both PS ash 8 and BF cement (Table 4.3). This data explained that the most calcium compound which might affect the fluorine leaching concentration is calcium oxide (CaO) and calcium carbonate (CaCO₃). These calcium compounds will be reacting with other chemical composition, which will stabilize the hazardous heavy metals consisting of coal fly ashes.

Several studies have been researched the calcium and fluorine bearing compounds consisting of coal fly ashes, which might be produced during the combustion process [13 -14]. The study said that mainly fluorine compound in coal is insoluble fluorine such as CaF₂, MgF₂, FeF₃, and AlF₃. These fluorine compounds are the primary occurrence state after the coal combustion process and difficult to break down even at high temperatures. Wang et al. explained that several oxide compounds inside the coal, including CaO in the fly ashes, took part in insoluble fluorides. The previous result confirms that CaO is one of the main calcium compounds that play a role in fluorine leaching.

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 a 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 can decrease the fluorine leaching. The XPS analysis was done into one of the coal fly ash samples (FA C), which was already mixed with Ca(OH)₂. The peak showed that after the mixing process, the estimated calcium compound in the samples is CaF₂ (Figure 4.4). This result only a qualitative analysis so that the exact amount of CaF₂ which might be produced was not well known

yet. However, the leaching process might be affected by the increasing amount of CaF_2 or other insoluble compounds of fluorine, which may cause by the chemical stabilization during the leaching process.

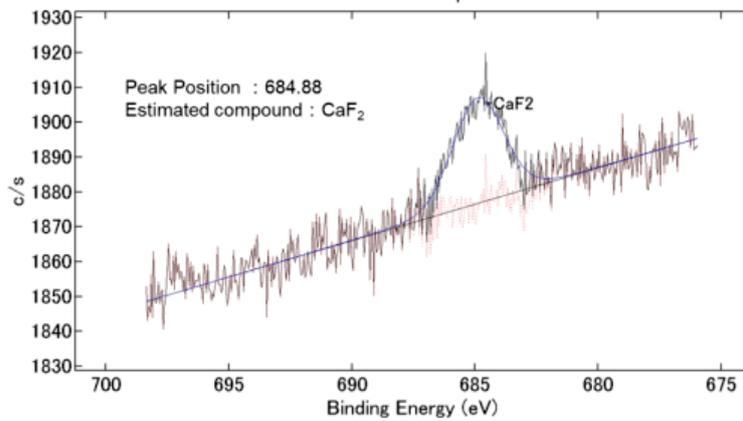


Figure 4.4. XPS analysis result on the mixed coal fly ash sample and additive (FA C and $\text{Ca}(\text{OH})_2$)

4.4 Conclusions

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

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Chapter 5 Effect of Additive Material on Controlling Chromium (Cr) Leaching from Coal Fly Ash

5.1 Introduction

The International Energy Agency predicts that coal will still be the largest source of power supply worldwide (35%) in 2024 [1]. In thermal power plants, coal is used as a fossil fuel in the combustion process. The combustion produces coal fly ash, which contains toxic elements. These elements, once in landfills, then leach into water environments after coming into contact with rain. This condition affects the concentration of toxic elements in water environments in that toxic elements could leach from lignite fly ash into aquatic environments when it comes into contact with water [2]. Concentrations of these toxic elements will increase continuously. One of the toxic elements in coal fly ash is chromium (Cr). The Environmental Protection Agency tested coal ash leachate by obtaining waste from numerous operating power plants and found that many ashes and sludge produce Cr-rich leachate [3]. Permissible limit (for the protection of human health) of chromium set by the Ministry of the Environment of the government of Japan is 50 µg/L.

Some researchers in previous studies have used some material to stabilize chromium. Xue, T. et al [4] used calcium polysulfide (CaS₅) and ferrous sulfate (FeSO₄) for reducing Cr leachability from the soil. As a result, they found that CaS₅ had a better effect than FeSO₄ on the stabilization of chromium. Morales, C et al [5] observed the effects of slag basicity (mass ratio CaO to SiO₂) and the addition of FeSO₄ or FeS₂ into the slag on the stability of the mineralogical species in the slag containing chromium compounds. They found that the lowest chromium concentration levels in the leaching liquors corresponded to slags with CaO/SiO₂ = 1 and high FeS₂ contents, owing to the stable binding of chromium in the compounds FeCr₂O₄, Cr₃S₄, and Ca₃Cr₂Si₃O. Mixing additives in the leaching process could be useful in decreasing As, Se, B, and F leaching concentrations simultaneously from two kinds of fly ash [6]. So, in current research, the utilization of additive material that contained high calcium has been done. The objectives were to use laboratory experiments and FactSage simulations: 1) to determine the Cr leaching levels from different kinds of fly ash, 2) to investigate the effect of additive materials on controlling the Cr leaching from the

different types of fly ash, 3) to examine the influence of pH on Cr, and 4) to identify a suitable additive for controlling the Cr leaching concentration.

5.2 Materials and Methods

5.2.1 Materials

Fly ash samples (FA A–FA N) were obtained from 14 coal-fired power stations in Japan. The primary chemical composition of the samples, which was determined based on X-ray fluorescence (XRF) analysis results (WDXRF S8 Tiger, Bruker AXS), is provided in Table 5.1. The table shows that the samples had different CaO contents. The highest CaO content was found in FA B (10.80%), and the lowest was in FA D (0.45%). Previous research has shown that calcium content has an essential role in the release of trace elements from coal fly ash [7].

Table 5.1. Chemical composition of coal fly ash samples.

Fly Ash	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
Power Station	Unit 2				Unit 1										
Chemical Composition [%]	SiO ₂	52.61	51.42	64.34	74.78	55.30	66.99	66.21	59.55	59.21	65.07	56.82	57.32	64.84	63.08
	Al ₂ O ₃	31.35	22.39	22.79	16.68	30.84	26.40	26.65	26.09	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	1.83	1.77	1.11	1.06	0.96	1.12	1.24
	Fe ₂ O ₃	7.06	7.01	3.71	3.93	5.75	2.15	2.57	6.80	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	1.94	2.07	1.43	8.86	8.79	1.39	2.67
	MgO	0.58	1.05	0.85	0.22	0.98	0.51	0.54	0.84	0.91	0.52	0.96	1.02	0.82	1.12
	Na ₂ O	0.38	1.23	1.20	0.38	1.14	0.27	0.29	0.66	0.74	0.44	0.75	0.80	0.52	1.25
	K ₂ O	0.96	1.19	0.80	1.43	1.20	0.58	0.54	1.49	1.44	1.76	1.97	1.97	1.67	1.44
	P ₂ O ₅	0.61	0.22	0.07	0.10	0.19	0.04	0.06	0.19	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	0.09	0.10	-	-	-	0.00	0.07
	V ₂ O 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	0.28	0.28	0.28	0.26	0.44	0.53	0.50	0.35	0.84	0.87	0.35	0.53

Additive materials containing high calcium content were used to control the leaching concentration of Cr such as calcium hydroxide (Ca(OH)₂), paper sludge (PS) ash 8, and blast furnace (BF) cement. The chemical composition of additive materials is provided in Table 2. The calcium compound Ca(OH)₂ had 95% purity and was obtained from Kanto Chemical Co. Inc. (Gifu, Japan). PS ash is a waste material formed during the paper manufacturing process using wooden pulp in the paper industry. Based on quantitative analysis, PS ash 8 contains 11.10% CaO, 1.44% Ca(OH)₂, and 19.32% CaCO₃ [8]. BF cement is a material formed through the mixing of granulated BF slag with Portland cement clinker and gypsum. These contents in BF cement trigger the formation of a compound that helps preserve trace elements in coal fly ash [6]. Both of PS ash 8 and BF cement was obtained from a manufacturing company in Sendai, Japan.

Table 5.2. Chemical composition of additive materials.

Chemical Composition (%)	Additive Material		
	PS Ash 8	BF Cement	Ca(OH) ₂
SiO ₂	28.76	31.03	0.09
Al ₂ O ₃	15.41	13.32	0.07
TiO ₂	0.35	0.19	0.07
Fe ₂ O ₃	0.91	0.44	-
CaO	51.22	48.35	99.23
MgO	2.76	3.77	0.36
Na ₂ O	0.02	0.08	0.08
K ₂ O	0.15	0.36	0.01
P ₂ O ₅	0.10	0.00	0.05
MnO	0.04	0.05	-
V ₂ O ₅	0.02	0.02	0.03
SO ₃	0.27	2.39	0.01

5.2.2 Sample Preparation and Leaching Test

The fly ash samples mixed with the additives in a specific ratio before the leaching process. The ratio of the additives in the total sample is provided in Table 3.

Table 5.3. Ratio of additive in fly ash for leaching test.

Coal Fly Ash	Additive	
A, B, C, D, E, F, G, H, I, J, K L, M, and N	Single additive	(1) 3% of Ca(OH) ₂
		(2) 10% of PS ash 8
		(3) 10% of BF cement
	Two-mixed additive	(4) 10% PS ash 8 + 10% BF cement
	Three-mixed additive	(5) 3% Ca(OH) ₂ + 10% PS ash 8 + 10% BF cement

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 mixture was perfectly mixed (3 min). After that, it was air-dried for 7 days and then sieved with a 2 mm sieve. The prepared sample was tested by leaching test based on JLT-13 (Environment Agency Notification No.13, 1973). First, 5 g of a sample that had been mixed with additives was added to 50 mL distilled water, and then was shaken for 6 h at room temperature with shaking speed of 200 rpm by Shaker SA400 YAMATO. The solid-liquid was centrifuged by AS-ONE HSIANGTAI

centrifuge for 20 min at a speed of 3000 rpm. A nitrocellulose membrane filter of 0.45 μm was used to separate leachates.

5.2.3 Analysis and Instrumentation

The calcium compound in the additive was measured by thermogravimetric (TG) analysis (TG/DTA6300 SII EXSTAR 6000, Hitachi, Hong Kong, China). A sample of 8–12 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. To determine the Cr leaching concentration, the leachate obtained from the leaching process was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ULTIMA 2, HORIBA, Tokyo, Japan). Cr standard stock solution (1000 mg/L) was purchased from Kanto Chemical Co., Inc., Tokyo, Japan. Working standards of concentrations 0, 50, 100, 150, and 200 $\mu\text{g/L}$ were added to HNO_3 60% and diluting with deionized water. Their absorbances were measured, and five-point linear calibration curves were established. Then, samples solutions were aspirated into the atomic spectrometer and direct readings of total chromium concentrations were recorded. At least two replicate determinations were carried out for each sample resulting in a relative standard deviation lower than 4%. The blanks were also run before chromium determination. The leachate alkalinity was analyzed by a pH ion meter (D-53, HORIBA) to check the effect of pH on the Cr leaching concentration. XRF analysis (WDXRF S8 Tiger, Bruker AXS, Yokohama, Japan) was used to measure the chemical composition of the fly ash samples and the additive materials.

5.2.4 Analysis by FactSage

FactSage 7.2 was employed to predict the Cr speciation based on the minimization of the free Gibbs energy to simulate the chemical reaction equilibrium and processes. FactSage provides information about formed compounds and their phases, mass or mole fraction, and thermodynamic properties for a range of pressures and temperatures. Understanding the effect of temperature on Cr speciation during the combustion process is essential for controlling Cr emissions. The FactSage contains a compound database of all coal fly ash components. These calculations were used to predict the possible Cr-bearing compounds in coal fly ash. The data search used in this analysis

included FactPS and FToxid. In the combustion process, the elemental composition of coal fly ash sample was used as input data. The calculation was performed at different temperature intervals between 100 to 1600 °C, at atmospheric pressure. For the leaching process, the predicted Cr compound from the combustion process was used as input data. Output from these analyses was aqueous, gases, and solid species.

5.3 Results

5.3.1 Analysis of Calcium Compound in Additive Material

Ca(OH)₂ and CaCO₃ were used as standards in analyzing the calcium compounds in the PS ash 8 and BF cement. The Ca(OH)₂, and CaCO₃ in the PS ash 8 and BF cement were thermally decomposed as shown in Figure 1. Ca(OH)₂ started losing weight in the temperature range of 350–450 °C and then decomposed into CaO and H₂O. CaCO₃ decomposed into CaO and CO₂ at temperature around 600–790 °C. The weight of PS ash decreased twice: first from 380 °C to 430 °C (calculated as Ca(OH)₂ decomposition) and then from 600 to 700 °C (as CaCO₃). Similar to PS ash 8, the weight of BF cement decreased twice: from 380 to 400 °C and then from 580 to 680 °C. This condition describes the decomposition of the calcium compound contained in the PS ash 8 and BF cement. Then, the calculation of Ca(OH)₂ and CaCO₃ percentage carried out by Equation (5.1) and Equation (5.2).

$$\%Ca(OH)_2 = \frac{W1}{Mr_{H2O}} \times \frac{Mr_{Ca(OH)_2}}{W_{sample}} \times 100\% \quad (5.1)$$

$$\%CaCO_3 = \frac{W1}{Mr_{CO_2}} \times \frac{Mr_{CaCO_3}}{W_{sample}} \times 100\% \quad (5.2)$$

In this equation, W1 is the weight between temperature decomposition end, and temperature decomposition start. Mr is the relative molecular mass or molecular weight of molecules. From this calculation it was found that PS ash 8 contains 1.44% Ca(OH)₂ and 19.32% CaCO₃. BF cement contains 0.31% Ca(OH)₂ and 6.45% CaCO₃. BF cement contains less calcium compound than PS ash 8. It can be shown in Figure 5.1 that BF cement loses less weight compared PS ash 8.

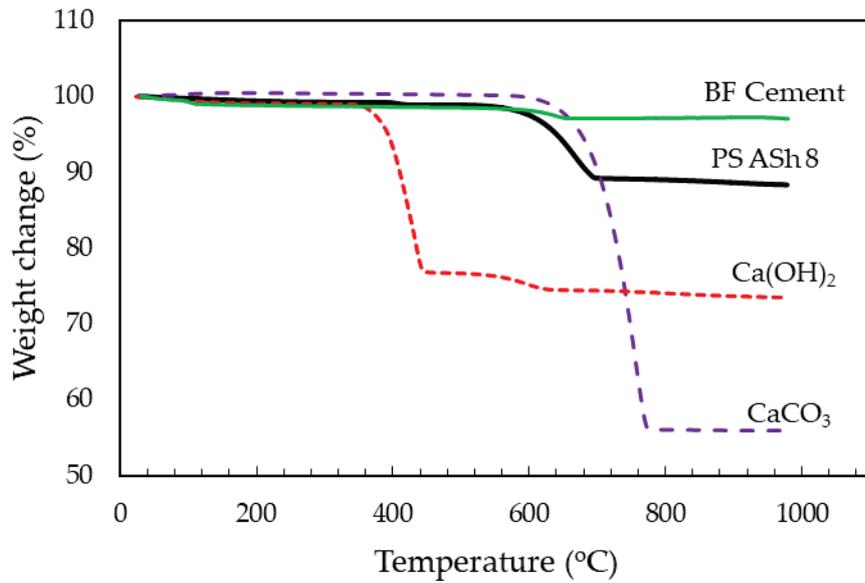


Figure 5.1. Thermogravimetric (TG) curves show the thermal decomposition of Ca(OH)_2 , CaCO_3 , PS ash 8, and BF cement in a N_2 atmosphere.

5.3.2 Effect of Additive on Chromium Leaching Concentration from Fly Ash

The total Cr leaching concentration from the 14 coal fly ash samples was measured by ICP-AES, as shown in Figure 5.2.

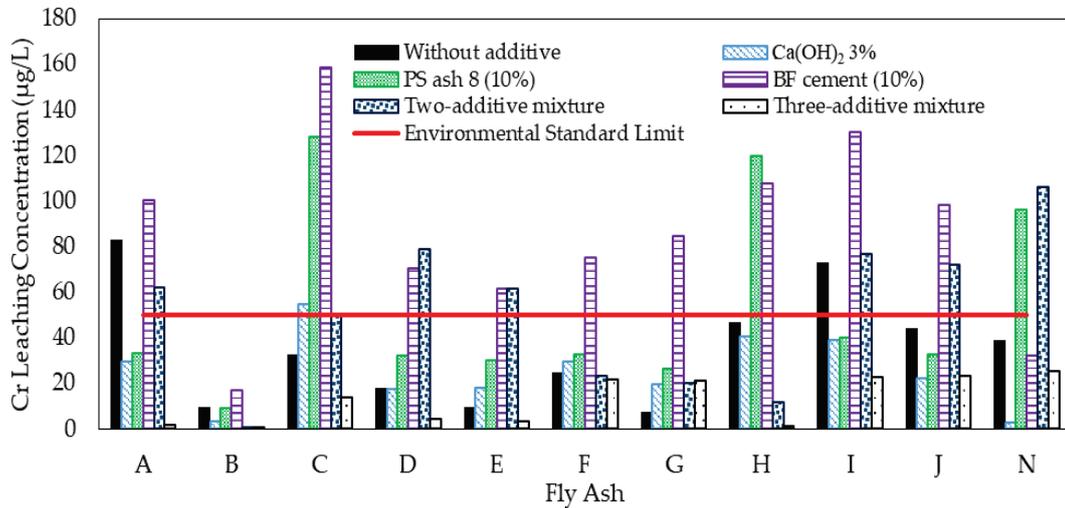


Figure 5.2. Effect of additive on Cr leaching concentration from coal fly ash.

The concentration varied from 0.00 $\mu\text{g/L}$ to 82.93 $\mu\text{g/L}$. The amount of Cr in two fly ash samples (A and I) exceeded the environmental quality standard (50 $\mu\text{g/L}$). In

contrast, Cr was not detected in fly ash samples K, L, and M. Then, the additive materials were added into fly ash samples A, B, C, D, E, F, G, H, I, J, and N to investigate the effect of the additive materials on controlling the Cr leaching concentration. Findings showed that the addition of $\text{Ca}(\text{OH})_2$ can decrease the Cr leaching concentration from fly ash samples A, B, H, I, J, and N. The addition of PS ash 8 can decrease the concentration of only A, I, and J, whereas the BF cement yielded the opposite effect. The Cr leaching concentration increased after the addition of the BF cement. This condition was caused by the Cr leaching concentration from the PS ash 8 and BF cement, which was $0.32 \mu\text{g/L}$ and $228.73 \mu\text{g/L}$, respectively. Therefore, the two-additive mixture cannot decrease all of kinds of Cr leaching concentrations. By contrast, the three-additive mixture had a good effect on decreasing the Cr leaching concentration. The Cr leaching concentration from all the fly ash samples except FA G was decreased by the three-additive mixture. Nonetheless, even though the Cr leaching concentration increased in FA G, it remained under the environmental quality standard. As shown in Figure 5.2, the three-additive mixture gave a significantly decreased concentration compared to the other additives. These results differ slightly from those of our previous research; although not as good as the three-additive mixture, two-additive mixtures can also reduce the level of As, Se, B, and F leaching concentration until under the environmental quality standard [6]. Therefore, the use of a three-additive mixture is beneficial for simultaneously controlling the leaching concentration of As, Se, B, F, and Cr.

5.3.3 Effect of pH on Chromium Leaching Concentration

The pH value is an important factor that can influence the leaching of many potential contaminants from coal fly ash [9–11]. Leaching characteristics of coal combustion by-products under different pH conditions shows Cr elements reach a maximum value under acidic condition, then as the pH increases, the concentration of Cr drops slowly [12]. In the current research, additive materials were applied to increase the pH value. The effect of additive materials on the pH value and the Cr leaching concentration is shown in Figure 5.3.

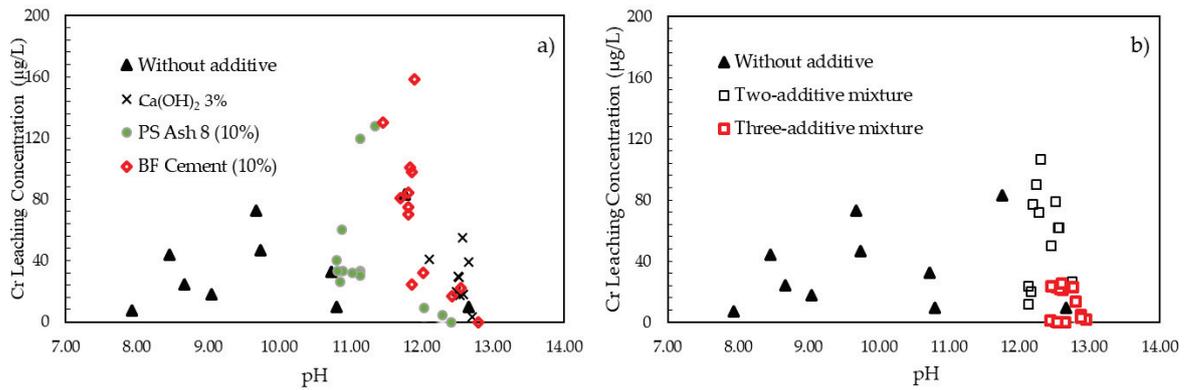


Figure 5.3. Effect of pH on chromium leaching concentration: a) single additives; b) mixed additives.

Figure 5.3a shows the effect of pH on the Cr leaching concentration with single additives. The pH value range of the leachate without additives was 7.94–13.19, with the Cr concentration ranging between 0.00 and 82.93 µg/L. Every single additive material increased the pH value of the leachate, but only Ca(OH)_2 could decrease the Cr leaching concentration and increase the pH value simultaneously. The pH value range with Ca(OH)_2 addition was 12.11–12.72, with the Cr leaching concentration being 3.17–54.95 µg/L. The increase in the Cr leaching concentration with the addition of the PS ash 8 and BF cement was caused by the Cr content in said additives. Figure 5.3b reveals that both additive mixtures could increase the pH value, but only the three-additive mixture could decrease the Cr leaching concentration. The pH value range with the three-additive mixture was 12.44–12.59, with the Cr leaching concentration being 0.00–25.37 µg/L. Increasing the pH enhanced the stability of Cr in the fly ash. Therefore, the role of calcium, which was contained in the additives, was needed to increase the pH value. Although the alkalinity of leachate is strong, it is decreased over time to a pH between 8 and 9 because of carbonate buffering, and a consequent precipitation of calcite in the atmosphere under field conditions has been reported [13], while chromium is transformed into highly stable $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$.

5.3.4 Analysis by FactSage 7.2.

Chromium partitioning behavior characteristics in interaction with mineral in fly ash (FA A) after combustion process, as analyzed using FactSage, was summarized in Table 4.

Table 5.4. Interaction of chromium with mineral compounds in fly ash (FA A) after combustion process (T = 100 °C and P = 1 atm.).

No	Interaction	Species formed
1	Cr + O ₂	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
2	Cr + O ₂ + SiO ₂	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
3	Cr + O ₂ + Al ₂ O ₃	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
4	Cr + O ₂ + TiO ₂	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
5	Cr + O ₂ + Fe ₂ O ₃	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
6	Cr + O ₂ + CaO	CrO ₂ (g), CrO ₃ (g) and CaCr ₂ O ₄ (s)
7	Cr + O ₂ + MgO	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
8	Cr + O ₂ + Na ₂ O	CrO ₂ (g), CrO ₃ (g) Na ₂ CrO ₄ (liq) and Na ₂ CrO ₄ (s)
9	Cr + O ₂ + K ₂ O	CrO ₂ (g), CrO ₃ (g) K ₂ CrO ₄ (liq) and K ₂ CrO ₄ (s)
10	Cr + O ₂ + P ₂ O ₅	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
11	Cr + O ₂ + SO ₃	CrO ₂ (g), CrO ₃ (g) and Cr ₂ (SO ₄) ₃ (s)
12	Cr + O ₂ + K ₂ O + SO ₃	CrO ₃ (g) K ₂ CrO ₄ (liq) and K ₂ CrO ₄ (s)
13	Cr + O ₂ + K ₂ O + SO ₃ + SiO ₂	CrO ₃ (g) K ₂ CrO ₄ (liq) and K ₂ CrO ₄ (s)
14	Cr + O ₂ + K ₂ O + SO ₃ + SiO ₂ + CaO	CrO ₃ (g) K ₂ CrO ₄ (liq) and K ₂ CrO ₄ (s)
15	Cr + O ₂ + K ₂ O + SO ₃ + SiO ₂ + CaO + Al ₂ O ₃	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)
16	Cr + O ₂ + K ₂ O + SO ₃ + SiO ₂ + CaO + Al ₂ O ₃ + Fe ₂ O ₃ + Na ₂ O + MgO + TiO ₂	CrO ₂ (g), CrO ₃ (g) and CrO ₂ (s)

Chromium reacted with CaO, Na₂O, K₂O, and SO₃ to form CaCr₂O₄(s), Na₂CrO₄(s), Cr₂(SO₄)₃(s), and K₂CrO₄(s), respectively, which inhibited chromium volatilization. No reaction or interaction between chromium and SiO₂, Al₂O₃, TiO₂, Fe₂O₃, MgO, and P₂O₅ were observed. The effect of combining minerals on chromium volatilization are also studied as illustrated in interaction no. 12–16 in Table 5.4. In the Cr-O₂-K₂O-SO₃, Cr-O₂-K₂O-SO₃-SiO₂, and Cr-O₂-K₂O-SO₃-SiO₂-CaO, chromium existed as K₂CrO₄(s), by adding Fe₂O₃ to system analysis (Cr-O₂-K₂O-SO₃-SiO₂-CaO-Fe₂O₃), chromium existed as CrO₂(s). In interactions of chromium and all mineral components in fly ash, chromium existed as CrO₂(s) with small contributions of CrO₂ and CrO₃ in gaseous phases. To better understand the combustion process of chromium from fly ash, the possible species of chromium were predicted by a FactSage model, as depicted in Figure 5.4, at different temperatures. All the species studied were present in the gas phase during the combustion stage. CrO₃(g) formed at a temperature above 1100 °C and became the main gaseous species with a small contribution of CrO₂(g). Below 1200 °C, Cr was in the form of Cr₂O₃ and CrO₂ in the solid phase. Cr becomes volatile only at high combustion temperatures, and gaseous species leave the combustion zone and cooling condition [14]. Cr₂O₃(s) became the main species at cooling temperatures

from 1200 to 200 °C. At temperatures below 200 °C, Cr existed in the solid phase in the form of CrO₂, and the formation of CrO₂ increased in the final combustion process (cooling process), indicating that CrO₂ in the solid phase was the chromate species contained in the coal fly ash. This process can be explained by the following reaction of generating CrO₂.

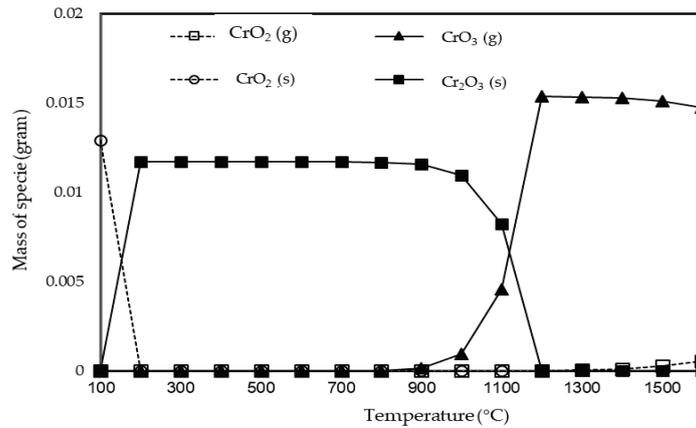


Figure 5.4. Equilibrium composition of Cr considering Cr FA A component interactions.

The coal fly ash, which contained CrO₂ from the combustion process, was tested for the leaching process with additives. The leaching of Cr from coal fly ash during the coal fly ash-water-additive interaction depends on many factors, such as the phases associated with the Cr in the coal fly ash, pH of the leachate, ash properties, leaching environment, and temperature of the leaching process. The possible formation of Cr-bearing species during the leaching process with additives was illustrated in Table 5.5. Once, chromium as CrO₂ reacted with potassium as K₂O to form K₂CrO₄(s) at -5 °C and Cr₂O₃(s) was observed at 25 °C with small contribution of Cr³⁺ and CrO₄²⁻ in aqueous species. On the other hand, the interaction of CrO₂ with SiO₂, Al₂O₃, TiO₂, Fe₂O₃, CaO, MgO, Na₂O, P₂O₅, and SO₃: Cr₂O₃(s) was observed as the same as the interaction of CrO₂ and H₂O, indicating that these minerals are not effective on chromium during the leaching process. In the above multiple interaction analysis, K₂O reacted more easily than other minerals in fly ash and additives. The prediction of chromium species in solution phases is also observed. Five types of chromium species,

Cr^{3+} , CrO_4^{2-} , CrO_7^{2-} , HCrO_4^- , and $\text{Cr}(\text{OH})^{2+}$, in turn appeared along with the increase of temperature studied.

Table 5.5. Interaction of predicted chromium (CrO_2) with mineral components during leaching process.

No	Interaction	Species formed	
		-5 °C	25 °C
1	$\text{CrO}_2 + \text{H}_2\text{O}$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}_2\text{O}_3(\text{s})$
2	$\text{CrO}_2 + \text{H}_2\text{O} + \text{SiO}_2$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
3	$\text{CrO}_2 + \text{H}_2\text{O} + \text{Al}_2\text{O}_3$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
4	$\text{CrO}_2 + \text{H}_2\text{O} + \text{TiO}_2$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
5	$\text{CrO}_2 + \text{H}_2\text{O} + \text{Fe}_2\text{O}_3$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
6	$\text{CrO}_2 + \text{H}_2\text{O} + \text{CaO}$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
7	$\text{CrO}_2 + \text{H}_2\text{O} + \text{MgO}$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
8	$\text{CrO}_2 + \text{H}_2\text{O} + \text{Na}_2\text{O}$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
9	$\text{CrO}_2 + \text{H}_2\text{O} + \text{K}_2\text{O}$	$\text{Cr}^{3+}(\text{aq})$, $\text{CrO}_4^{2-}(\text{aq})$, and $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{CrO}_4^{2-}(\text{aq})$, and $\text{Cr}_2\text{O}_3(\text{s})$
10	$\text{CrO}_2 + \text{H}_2\text{O} + \text{P}_2\text{O}_5$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$	$\text{Cr}^{3+}(\text{aq})$, $\text{HCrO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_3(\text{s})$
11	$\text{CrO}_2 + \text{H}_2\text{O} + \text{SO}_3$	$\text{Cr}^{3+}(\text{aq})$ and $\text{HCrO}_4^-(\text{aq})$	$\text{Cr}^{3+}(\text{aq})$ and $\text{HCrO}_4^-(\text{aq})$

To better understand the leaching process of chromium from fly ash with additive material, the possible species of chromium were predicted, as demonstrated in Figure 5.5a, at different temperatures. It obviously indicates that the leachability of chromium is dependent on the temperature. At a temperature of -5 °C, Cr reacted with K_2O to form K_2CrO_4 and minimize the Cr^{3+} and CrO_4^{2-} released into the water environment. However, an increase in the temperature of the leaching process to 0 °C caused Cr to easily leach into the water environment in the form of Cr^{3+} and CrO_4^{2-} and eliminate the effect of potassium to control the leaching chromium. Here, CrO_4^{2-} tends to

stabilize by increasing temperature in the range 0–25 °C. Immobilization of chromium tends to proceed preferentially under colder conditions; aging at higher temperatures enhances the leachability of chromium in some coal fly ash samples [15]. This analysis indicating that potassium (K) was the most influential factor in Cr transformation. $K_2CrO_4(s)$ was formed from the predicted CrO_2 during the leaching process with K_2O in the additive material at -5 °C, as explained by Equation (5.4).

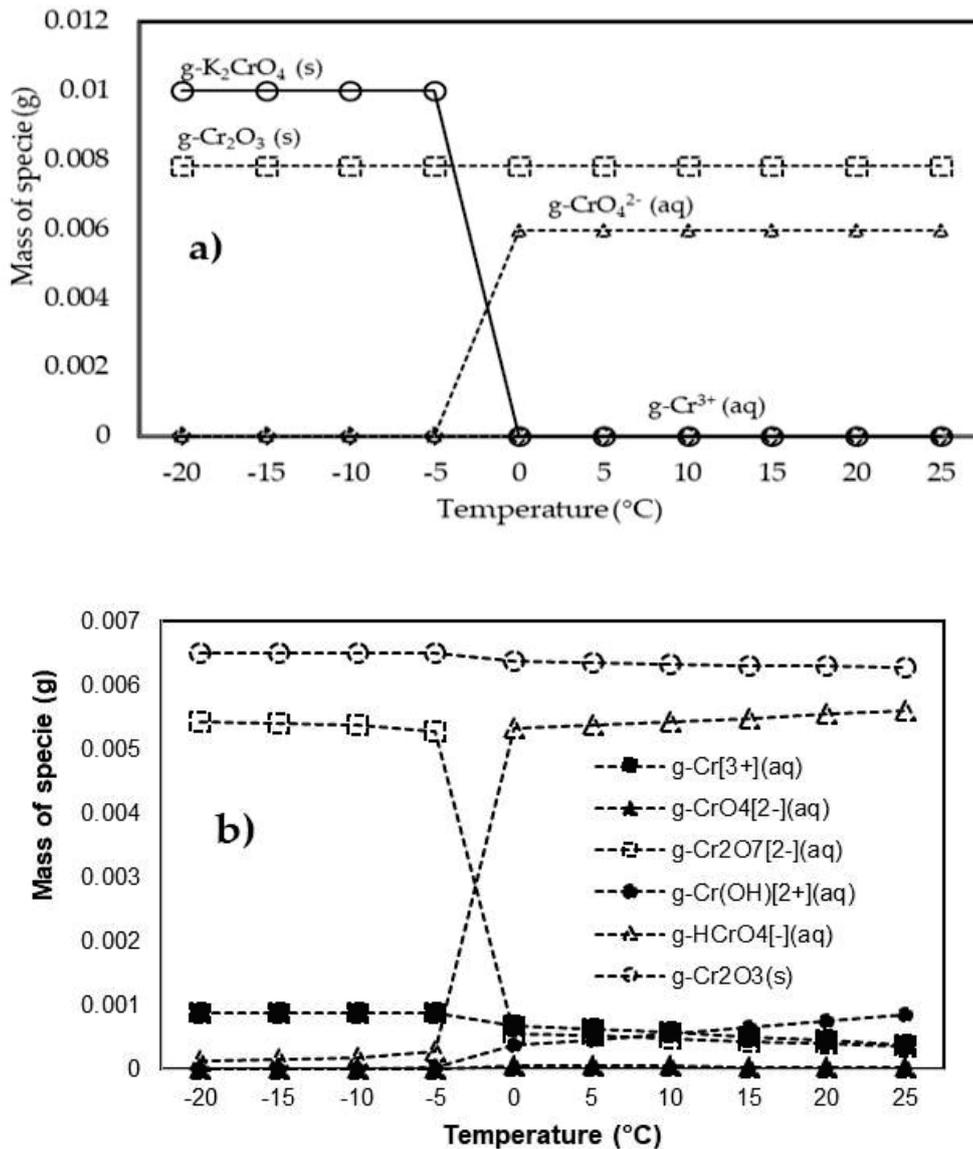
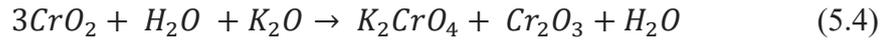


Figure 5.5. Leaching mechanism of predicted chromate (CrO_2) as function of temperature: a) with additive and b) without additive.

On the other hand, the leaching process of chromium without additive material is shown in Figure 5.5b. Regarding the concentration of chromium species in solution, increasing the temperature of the leaching process caused increases of HCrO_4^- , $\text{Cr}(\text{OH})^{2+}$, and CrO_4^{2-} . At the same time, increasing the temperature caused decreased $\text{Cr}_2\text{O}_7^{2-}$ and Cr^{3+} , indicating the leaching process of chromium without additive is not effective to control the leaching of chromium species in to water environment.

According to the above discussion, potassium (K) can control the leaching of Cr from coal fly ash by reacting with the Cr at a temperature of $-5\text{ }^\circ\text{C}$. The effect of the other minerals in the additive materials to control the leaching of Cr^{3+} during the leaching process was also analyzed under different temperatures, as shown in Figure 5.6. Not only K had the potential to control the leaching of Cr^{3+} during the leaching process; Ca, Na, and Mg also interacted with Cr^{3+} . Therefore, K, Ca, Na, and Mg could control the leaching of Cr^{3+} from the fly ash. Previous research has found that the chemical compounds CaO and Mg on fly ash surfaces can control the pH of fly ash and soil leachate [12]. Hydrocaluminate ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$), which form during the leaching process, increase the pH value and also reduce the concentration of heavy metals [16–18].

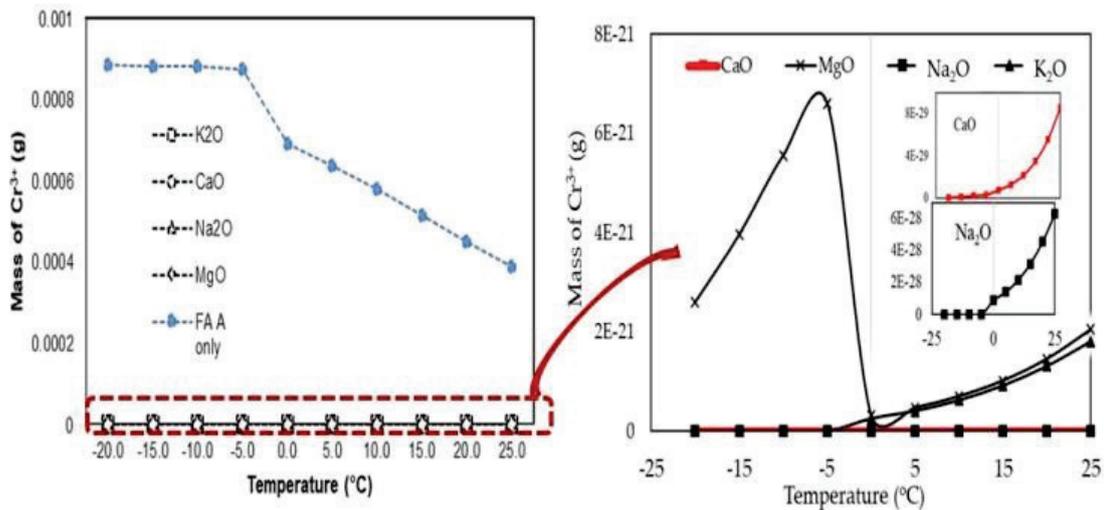


Figure 5.6. Mineral effect on controlling Cr^{3+} during leaching process.

5.3.5 Comparison Result between Experiment and Simulation

Similar to the laboratory experiment, the FactSage simulation was done by the addition of single and mixed additive materials. The result from FactSage also revealed that the three-additive mixture was useful in controlling the Cr leaching concentration from the fly ash. Additive materials' capability is the capability of an additive material to control the Cr leaching concentration from the fly ash. As shown in Figure 5.7, there were no significant differences between the laboratory experiments and FactSage simulations. This figure shows the capability of the three-additive mixture to control the leaching of Cr from fly ash A and B. The Cr controlled from fly ash A by FactSage and the laboratory experiments were 99.98% and 96.91%, respectively; those from FA B were 99.92% and 97.78%, respectively, where error percentages of experimental analysis to FactSage analysis of FA A and FA B were 3.07% and 2.15%, respectively. In a previous research, leaching test results were compared with solution equilibrium calculation results to consider the leaching mechanisms; however, the experimental results were lower than the equilibrium calculation results [19]. The possible reason is the kinetic control during leaching test due to lack of agitation and short residence time [19], therefore, thermodynamic calculation (FactSage 7.2) does not consider the reaction time, which is necessary for the theoretical equilibrium state to be reacted [20].

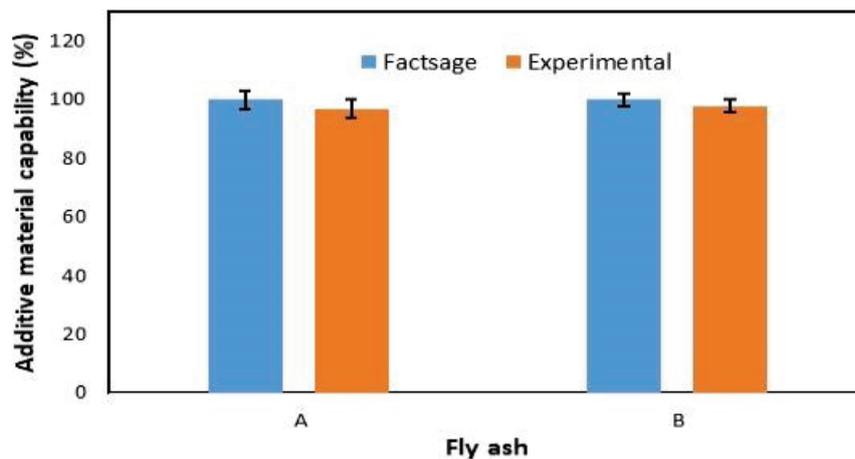


Figure 5.7. Leaching rate comparison between laboratory experiment and FactSage simulation.

5.4 Conclusions

A mixture of the additives Ca(OH)₂, PS ash 8, and BF cement yielded promising effects in controlling the Cr leaching concentration from coal fly ash. An analysis of 14 fly ash samples revealed that this three-additive mixture could reduce the Cr leaching concentration to a level within the environmental quality standard. The pH value also played a role in decreasing the Cr leaching concentration. Analysis by FactSage showed that not only Ca had a role in controlling the concentration; K, Mg, and Na, which are difficult to break down even at high temperatures, were also useful. The results from both laboratory experiments and simulation by FactSage found that the mixture of the three additives decreased the Cr leaching concentration by more than 97%.

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Chapter 6 Conclusions and Future Perspective

6.1 Conclusion

Around 60% of fly ash potential as a source of environmental pollution because of its trace elements still dumped in landfills. Among the trace elements found in coal fly ash, As, B, Se, F, and Cr are the most significant environmental hazards. On the other hand, paper sludge ash, which contains high calcium compound reported, does not represent a major threat for the environment in terms of heavy metals released. In the current research, $\text{Ca}(\text{OH})_2$, PS ash and BF cement B as controller of trace elements of trace element leaching from fly ash has been investigated.

Chapter 2 describes a Preliminary study on additive for controlling As, Se, B, and F leaching from coal fly ash used $\text{Ca}(\text{OH})_2$, PS ash 8, and BF cement as single and mixed additive. Two different coal fly ashes with almost the same calcium content have been tested with additives as single additives and mixed additives. As the single additives, each of calcium hydroxide ($\text{Ca}(\text{OH})_2$), PS ash 8 and 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 $\text{Ca}(\text{OH})_2$, PS ash 8 and BF cement was tested into the both of coal fly ashes. The result indicated that the application of mixed additives could be applicable in controlling the leaching of As, Se, B, and F. The mixture of $\text{Ca}(\text{OH})_2$, PS ash 8, and BF cement showed slightly better decreasing than the mixture of PS ash 8, and BF cement. Trace elements 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 $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$, CaSeO_3 , $\text{Ca}_2\text{B}_2\text{O}_5$, $\text{Ca}_3\text{B}_2\text{O}_6$, and CaF_2 . 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.

Chapter 3 discuss about calcium performance in paper sludge ashes. Nine kinds of PS ash have been tested to FA C for checking the capability of each PS ash to control As, Se, and B. The result shows each paper sludge has a different effect on controlling As, Se, and B. After investigating with the TG and Ethylene glycol methods, it was found that PS ash 3, 8, and 11 contained high calcium compared to others.

Chapter 4 describes the role of calcium compound on Fluorine leaching concentration from fly ash. The mixed additives (the mixture of $\text{Ca}(\text{OH})_2$, PS ash 8, and BF cement) have been tested into 14 different coal fly ashes to study the role of calcium in fluorine leaching concentration. The result confirmed that these mixed additives were applicable in decreasing fluorine leaching concentration. Calcium oxide and calcium carbonate were the main calcium compound that affected the fluorine leaching concentration, and CaF_2 is the fluorine compound formed during the leaching process. CaF_2 is a compound which difficult to break down even with the high temperature.

Chapter 5 focuses on the effect of additive material on controlling chromium leaching from fly ash. Cr leaching levels from 14 kinds of fly ash have been determined. Then, the effect of additive materials, single and mixed additive, and pH influence on controlling the Cr leaching from the different types of fly ash have been investigated. Finally, the result from experimental and simulated was compared. The finding shows that every additive material increased the leachate's pH value, but only $\text{Ca}(\text{OH})_2$ could simultaneously decrease the Cr leaching concentration and increase the pH value. The two-additive mixture cannot reduce all of the kinds of Cr leaching concentrations. By contrast, the three-additive mixture had a good effect on decreasing the Cr leaching concentration. Calcium in additive material reacts with Cr in coal fly ash then transformed into highly stable $\text{CaCr}_2(\text{SiO}_4)_3$. Analysis by FactStage finding show not only Calcium can control Cr leaching concentration but also Mg, Na, and K, which are difficult to break down even at high temperature. The results from both laboratory experiments and simulation by FactSage found that the three additives' mixture decreased the Cr leaching concentration by more than 97%. Based on the above discussion the three-additive mixture ($\text{Ca}(\text{OH})_2$, PS ash 8 and BF cement) has promising effect on controlling As, Se, B, F and Cr leaching concentration from coal fly ash simultaneously.

6.2 Future Perspective

Coal will still be the largest source of power supply worldwide. It means coal fly ash also will be a problem of the environment. Due to this problem, this research needs to develop to prevent environmental pollution. This research proved that calcium plays an essential role in the trace element leaching process, especially in As, Se, B, F, and Cr leaching concentration. The content of calcium compounds within the additive material is the main factor that triggered the chemical stabilization of the trace elements during the leaching process. The three-additive mixture (Ca(OH)_2 , PS ash, and BF cement) has a good effect on controlling As, Se, B, F, and Cr leaching concentration from coal fly ash simultaneously. For further study, the optimum ratio of these mixed additives needs to be found. The role of calcium on other trace elements leaching still needs to be investigated. The effect of Mg, Na, and K on trace elements leaching simultaneously also needs to be proven.

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List of Publication

(1) Research Papers that Form the Basis of Thesis

1. Preliminary Study on Additives for Controlling As, Se, B, and F Leaching from Coal Fly Ash, F. F. Hanum, **E. R. Desfitri**, Y. Hayakawa, S. Kambara, Minerals, 2018.
2. Calcium Performance in Paper Sludge Ash as Suppressing Material, **E. R. Desfitri**, F. F. Hanum, S. Kambara, Y. Hayakawa, IOP Conference Series: Materials Science and Engineering, 543(1), 8pages, 2019.
3. The Role of Calcium Compound on Fluorine Leaching Concentrations, F. F. Hanum, **E. R. Desfitri**, S. Kambara, Y. Hayakawa, IOP Conference Series: Materials Science and Engineering, 543(1), 7pages, 2019.
4. Effect of Additive Material on Controlling Chromium (Cr) Leaching from Coal Fly Ash, **Erda Rahmilaila Desfitri**, Ulung Muhammad Sutopo, Yukio Hayakawa and Shinji Kambara, Minerals, 10(6)-563, 2020.

(2) Other Publications

1) Book (Chapter)

1. Coal Fly Ash Beneficiation, Edited by S. A. Akinyemi and M. W. Gitari, (Chapter 3 Chemical Stabilization of Coal Fly Ash for Simultaneous Suppressing of As, B, and Se Leaching pp. 29-51), S. Hartuti, S. Kambara, A. Takeyama, F. F. Hanum, **E. R. Desfitri**, IntechOpen, 2018.

2) International Proceeding

1. Investigation of Additive Blending Ratio for Controlling Boron and Fluorine from Coal Fly Ash, **E. R. Desfitri**, F. F. Hanum, U. M. Sutopo, Y. Hayakawa, S. Kambara, 12Th Asia-Pacific Conference on Combustion, ASPACC2019-1356, Fukuoka (Japan) 2019
2. Calcium and Arsenic Interaction during Leaching Process of Coal Fly Ash: Analysis by FactSage, U. M. Sutopo, **E. R. Desfitri**, F. F. Hanum, Y. Hayakawa, S. Kambara, 12Th Asia-Pacific Conference on Combustion, ASPACC2019-1265, Fukuoka (Japan) 2019

3) Domestic Proceedings

1. Advanced Study on Additives for Controlling As, Se, B, and F Leaching Concentration from Coal Fly Ash, Farrah Fadhilah Hanum, **Erda Rahmilaila Desfitri**, Yukio Hayakawa, Shinji Kambara 日本エネルギー学会第 55 回石炭科学会議発表論文集, No.1-3-2, 東京, 2018
2. Calcium Mechanism in Controlling Leaching of As and Se from Coal Fly Ash, **Erda Rahmilaila Desfitri**, Farrah Fadhilah Hanum, Yukio Hayakawa, Shinji Kambara 日本エネルギー学会第 55 回石炭科学会議発表論文集, No.1-3-3, 東京, August, 9th 2018

List of Presentation

1. Calcium Mechanism in Controlling Leaching of As and Se from Coal Fly Ash, **Erda Rahmilaila Desfitri**, Farrah Fadhillah Hanum, Yukio Hayakawa, Shinji Kambara 日本エネルギー学会第 55 回石炭科学会議発表論文集, No.1-3-3, 東京, August, 9th 2018 (oral presentation)
2. Calcium Performance in Paper Sludge Ash as Suppressing Material, **Erda Rahmilaila Desfitri**, Farrah Fadhillah Hanum, Yukio Hayakawa, Shinji Kambara, Int. Symp. Indonesian Chemical Engineering, Padang (Indonesia), October 5th 2018 (oral presentation)
3. Investigation of Additive Blending Ratio for Controlling Boron and Fluorine from Coal Fly Ash, **E. R. Desfitri**, F. F. Hanum, U. M. Sutopo, Y. Hayakawa, S. Kambara, 12Th Asia-Pacific Conference on Combustion, ASPACC2019-1356, Fukuoka (Japan), July, 2nd 2019 (oral presentation)

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