minerals

MDPI

Article

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

Farrah Fadhillah Hanum, Erda Rahmilaila Desfitri, Yukio Hayakawa and Shinji Kambara *

Environmental and Renewable Energy System Division, Graduate School of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan; farrah_fh@yahoo.co.id (F.F.H.); rahmilaila01@gmail.com (E.R.D.); h_yukio@gifu-u.ac.jp (Y.H.)

* Correspondence: kambara@gifu-u.ac.jp; Tel.: +81-58-293-2581

Received: 7 September 2018; Accepted: 19 October 2018; Published: 1 November 2018

check for updates

Abstract: The application of paper sludge ash as an additive in controlling the leaching of trace elements has been satisfactorily effective to date. Previous studies have found that paper sludge ash has a promising effect in controlling the leaching of arsenic, selenium and boron. The content of calcium oxide in paper sludge ash is believed to be one of the important factors in decreasing the concentration of trace elements in leachate. Therefore, this study aimed to verify the effect of paper sludge ash in the leaching process and to propose an effective and applicable suppressing material that can control the leaching of As, Se, B and F simultaneously. In light of this aim, $Ca(OH)_2$, PS ash 8 and blast furnace cement (BF cement) were tested as single and mixed additives in two different coal fly ashes (FA C and FA H). The results indicate that the application of a mixture of additives is necessary to control the leaching of trace elements. A mixture of PS ash 8, $Ca(OH)_2$ and blast furnace cement (BF cement) was proposed to be an applicable and suitable additive that could suppress arsenic, selenium, boron, and fluorine leaching simultaneously.

Keywords: additives; calcium; paper sludge ash; coal fly ash

1. Introduction

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

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

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

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

2. Materials and Methods

2.1. Coal Fly Ash and Additives

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

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

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

Paper sludge ash, a potential waste product of paper mill sludge from the de-inking and re-pulping of paper, has already been indicated to have a potential effect as an additive material [12,14,15]. 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 [14]. Based on qualitative analysis by X-ray diffraction (XRD), the main calcium compounds in both paper sludge ashes were CaO, $Ca(OH)_2$, and $CaCO_3$ (Figure 1). Then, ethylene glycol/ICP analysis and thermal gravimetric analysis (TGA) were performed to determine the concentration of each of these calcium compounds. PS ash 8 was chosen as a supplementary material because the calcium oxide concentration in this paper sludge ash was higher than that in PS ash 3 (Figure 2).

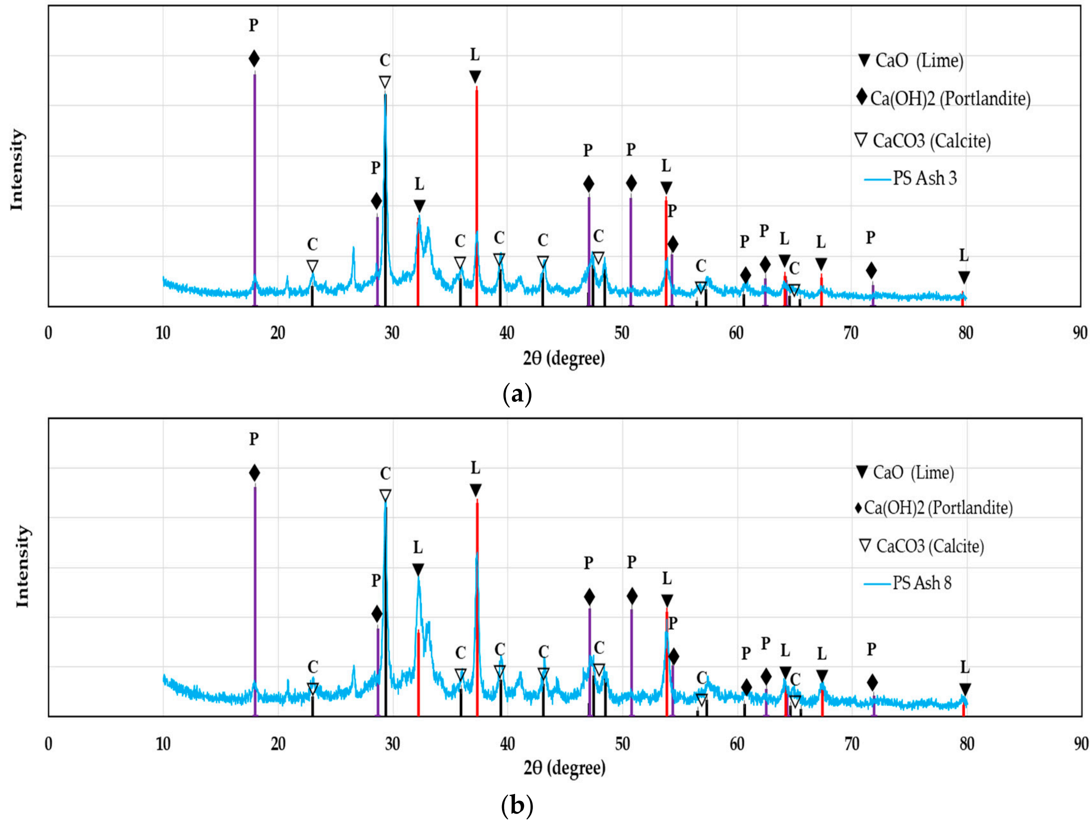


Figure 1. The main calcium compounds in (**a**) PS ash 3 and (**b**) PS ash 8 by XRD (x-ray diffraction) analysis.

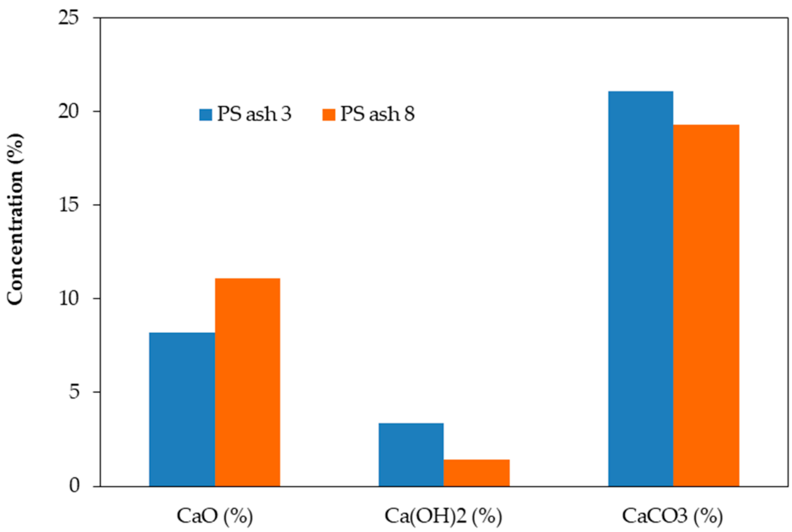


Figure 2. Calcium compound concentrations in PS ash 3 and PS ash 8

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.

2.2. Sample Preparation and Leaching Test

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

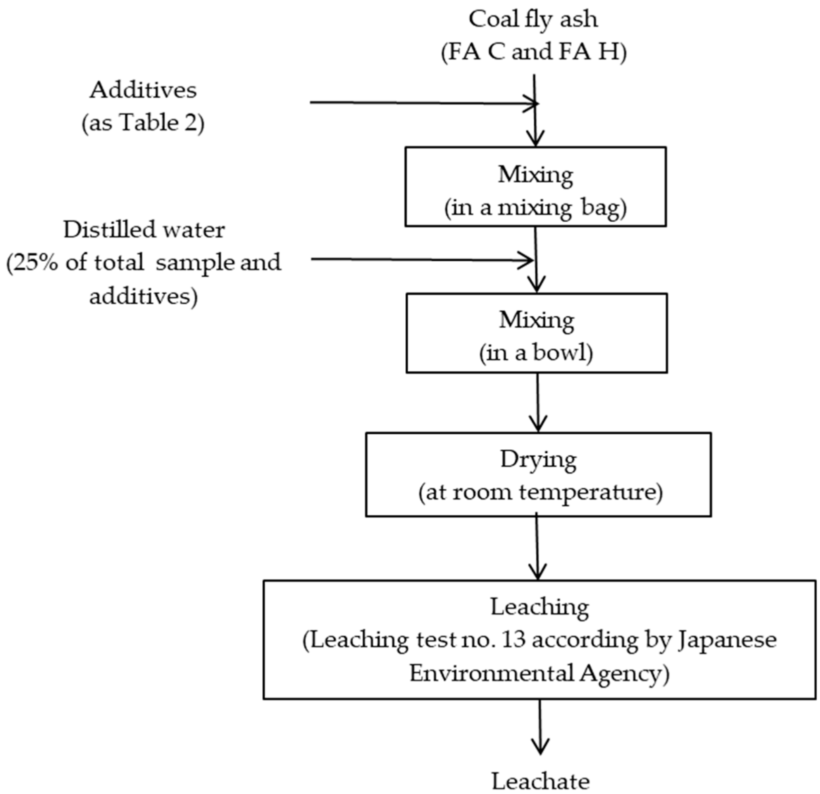


Figure 3. Schematic diagram of the sample preparation and leaching test.

Table 2. Ratio of additives in coal fly ash

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

2.3. Analysis and Instrumentation

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

3. Results

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

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

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

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

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

Our previous study found that the addition of calcium through additives to coal fly ash could inhibit the leaching of trace elements into the environment [12]. Some researchers have also observed that the alkalinity during the leaching process and calcium content are related to decreased leaching concentrations of arsenic, selenium, boron and selenium. Iwashita mentioned that under highly alkaline conditions, the leaching of B and Se tended to decrease [3]. Shun-ichi stated that coal fly ash with better leaching characteristics contained boron in the CaO- and MgO-phases on the surface of coal fly ash particles [8]. Jose and Wang reported that alkaline pH, calcium addition, temperature and the leaching time affected the leaching of As and Se [4,9]. Figure 4 shows the alkalinity of the leachate from coal fly ash C and H before and after the addition of supplementary material. After the addition of the additives in single and mixed forms, the pH of the leachate increased. This could indicate that the application of mixed additives is promising as a suppressing material for the leaching of As, Se, B, and F [15–18]. 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.

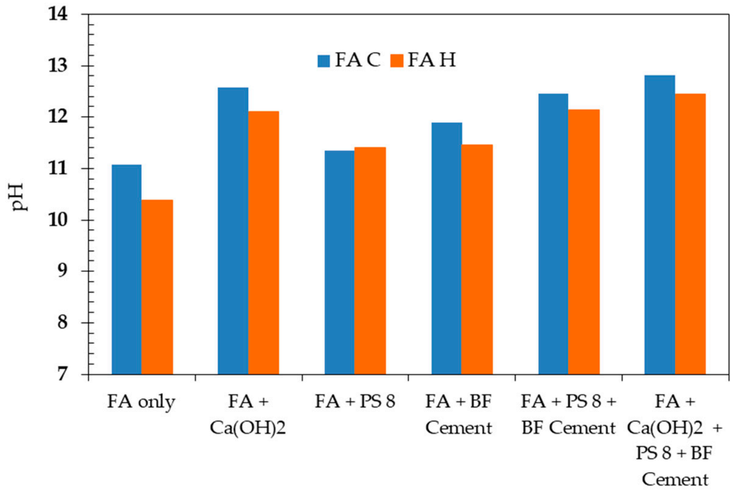
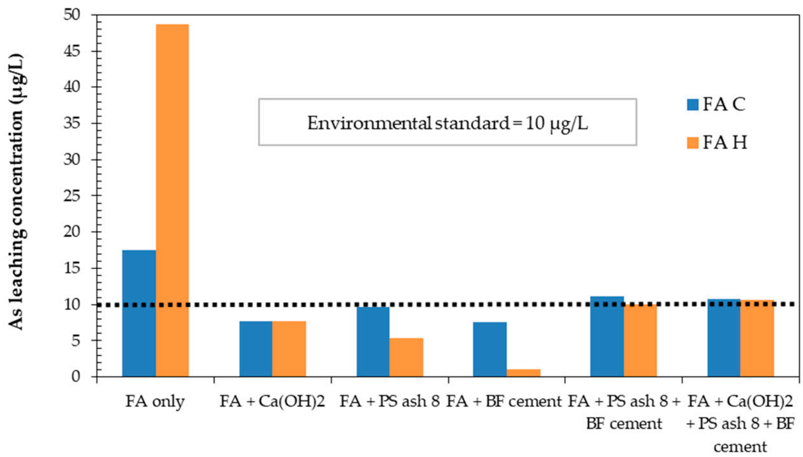


Figure 4. The pH of coal fly ashes and mixtures of coal fly ashes and additives.

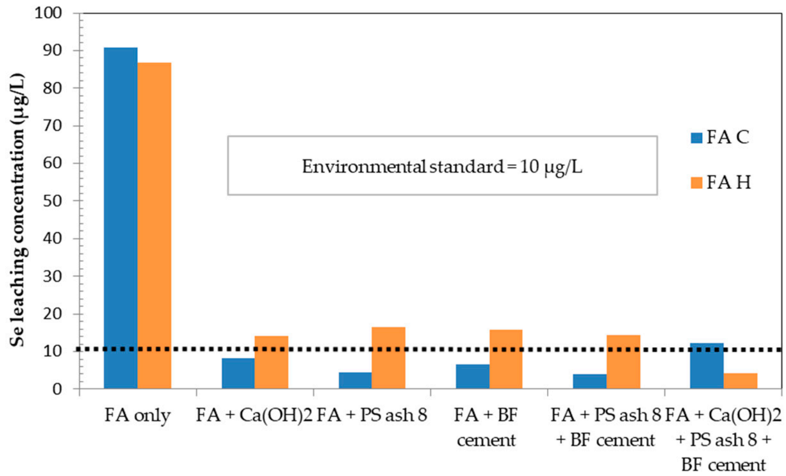
First, both coal fly ashes (coal fly ash C and H) were tested with $Ca(OH)_2$, PS ash 8 and BF cement as single additives. The application of $Ca(OH)_2$ (3% of the total sample) as a native calcium compound in the form of a single additive showed a positive trend (Figure 5). $Ca(OH)_2$ could decrease almost all of the trace elements in both of the coal fly ashes, except for Se in coal fly ash H. The application of PS ash 8 (10% of the total sample) only showed satisfying results in suppressing the leaching of As, Se, and B in the FA C sample and the leaching of As in the FA H sample. This research also introduces BF cement as an additive because of the popularity of cement-based methods in the immobilization process in heavy metal stabilization [13,19–22]. 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.

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.

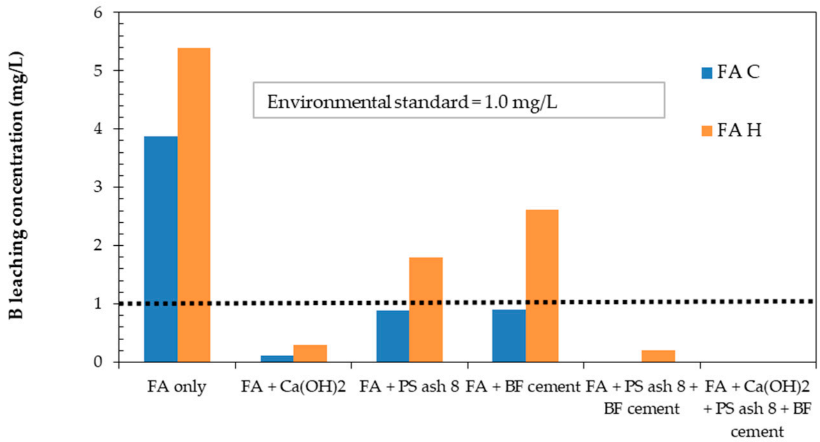


(a)

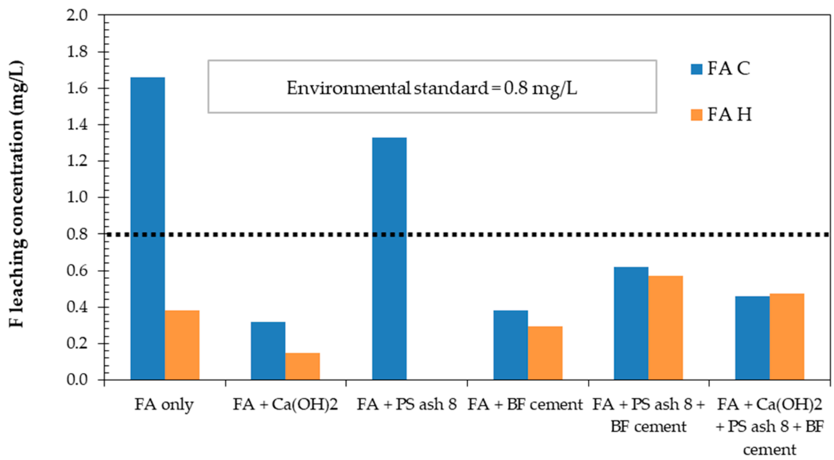
Figure 5. *Cont.*



(**b**)



(**c**)



(**d**)

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

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

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

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

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

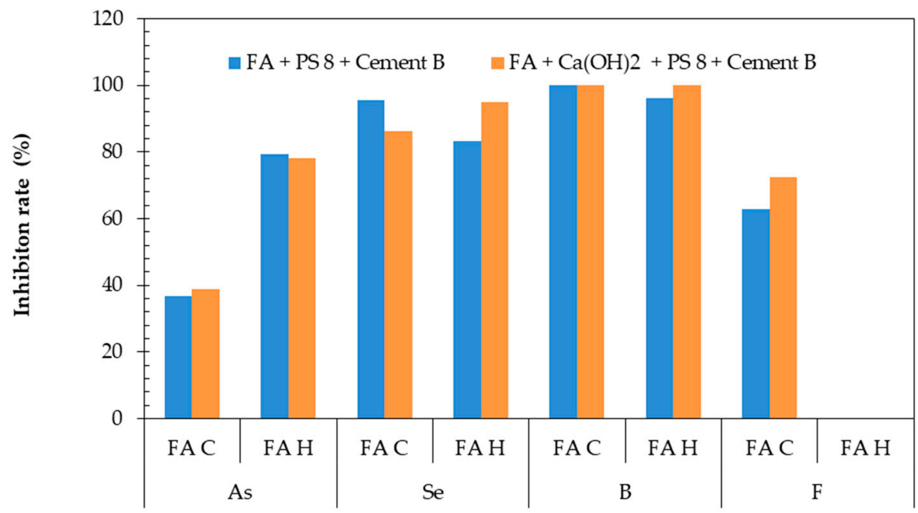


Figure 6. Inhibition rate of the mixed additives on the As, Se, B and F leachate concentrations.

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

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

The amount of CaO and MgO in the mixture of coal fly ash and suppressing material triggered an increase in leachate alkalinity [23]. 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 SiO_2 because silica can slowly dissolve and form silicic acid [23]. This condition was helpful in controlling pH during the leaching process.

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

Chemical Composition	FA C		FA H	
	Before Leaching with ($Ca(OH)_2$ + PS 8 + Cement B)	After Leaching with ($Ca(OH)_2$ + PS 8 + Cement B)	Before Leaching with ($Ca(OH)_2$ + PS 8 + Cement B)	After Leaching with ($Ca(OH)_2$ + PS 8 + Cement B)
SiO_2	56.93	46.11	54.24	48.08
Al_2O_3	22.09	17.74	22.20	18.07
TiO_2	1.74	2.73	1.56	2.87
Fe_2O_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_2O	0.80	0.18	0.46	0.58
K_2O	0.57	1.39	1.14	0.78
P_2O_5	0.00	0.14	0.11	0.14
MnO	0.04	0.04	0.03	0.03
V_2O_5	0.02	0.01	0.01	0.02
SO_3	0.46	0.76	0.50	0.68
Total	100.00	100.00	100.00	100.00

In addition, excess calcium is directly related to chemical stabilization [13]. Trace elements that are also classified as heavy metals are transformed into less soluble compounds, which makes these trace elements non-hazardous in the environment. As, Se, B, and F can react with calcium and form relatively insoluble compounds such as $Ca_3(AsO_4)_2$, $Ca_4(OH)_2(AsO_4)_2{\cdot}4H_2O$ [9,13], $CaSeO_3$ [9], $Ca_2B_2O_5$, $Ca_3B_2O_6$ [8] and CaF_2 [24,25]. Therefore, calcium addition through the use of high-calcium-content materials in the leaching process could be applied to control the leaching of trace elements.

In light of the calcium reaction in leaching, not only does chemical stabilization occur between the calcium and the trace element metals directly but the calcium also reacts with the chemical components within the coal fly ash and is then incorporated with the trace elements into the product formed by the reaction. As secondary precipitates during the leaching of alkaline coal fly ashes, hydrocaluminate ($Ca_4Al_2(OH)_{12}(OH)_2{\cdot}6H_2O$) and ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3{\cdot}26H_2O$) have been proven to have great a capability in reducing the concentration of the heavy metal anions, including the metals discussed in this research [26–29]. Alkaline conditions during the leaching process, the amount of calcium and the amount of alumina are the main factors in the formation of these materials. The addition of BF cement as an additive in this leaching mechanism was also believed to be strongly related to the formation of these materials.

4. Conclusions

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

Author Contributions: S.K. conceived and designed the experiment and contributed to the materials, reagents and instrumentation; F.F.H. and E.R.D. performed the experiments; F.F.H., E.R.D. and Y.H. discussed and analysed the data; and F.F.H. wrote the paper.

Acknowledgments: The author would like to thank Akihiro Takeyama for his valuable contributions in data analysis.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. World Energy Council. *World Energy Resources Report 2016*; World Energy Council: London, UK, 2016.
2. Kalyoncu, R.S.; Olson, D.W. Coal Combustion Products. ACAA International: Last Modified 29 November 2016. Available online: https://pubs.usgs.gov/fs/fs076-01/fs076-01.html (accessed on 14 September 2017).
3. Iwashita, A.; Sakaguchi, Y.; Nakajima, T.; Takanashi, H.; Ohki, A.; Kambara, S. Leaching characteristics of boron and selenium for various coal fly ashes. *Fuel* **2005**, *84*, 479–485. [CrossRef]
4. Otero-Rey, J.; Mato-Fernandez, M.; Moreda-Piñeiro, J.; Alonso-Rodríguez, E.; Muniategui-Lorenzo, S.; López-Mahía, P.; Prada-Rodríguez, D. Influences of several experimental parameters on As and Se leaching from coal fly ash samples. *Anal. Chim. Acta* **2005**, *531*, 299–305. [CrossRef]
5. Kadir, A.A.; Hassan, M.I.H.; Abdullah, M.M.A.B. Investigation on leaching behaviour of fly ash and bottom ash replacement in self-compacting concrete. *Mater. Sci. Eng.* **2016**, *133*, 012036. [CrossRef]
6. Akar, G.; Polat, M.; Galecki, G.; Ipekoglu, U. Leaching behavior of selected trace elements in coal fly ash samples from Yenikoy coal-fired power plants. *Fuel Process. Technol.* **2012**, *104*, 50–56. [CrossRef]
7. Yilmaz, H. Characterizations and comparison of leaching behaviors of fly ash samples from three different power plants in Turkey. *Fuel Process. Technol.* **2015**, *137*, 240–249. [CrossRef]
8. Hayashi, S.; Takahashi, T. Chemical state of boron in coal fly ash investigated by focused-ion-beam time-of-flight secondary ion mass spectrometry (FIB-TOF-SIMS) and satellite-transition magic angle spinning Nuclear magnetic resonance (STMAS NMR). *Chemosphere* **2010**, *80*, 881–887. [CrossRef] [PubMed]
9. Wang, T.; Wang, J.; Tang, Y.; Shi, H.; Ladwig, K. Leaching characteristics of arsenic and selenium from coal fly ash: Role of calcium. *Energy Fuel* **2009**, *23*, 2959–2966. [CrossRef]
10. Hartuti, S.; Kambara, S.; Takeyama, A. Arsenic leachability of coal fly ashes from different types of coal fired power plants. *J. Mater. Sci. Eng.* **2017**, 169–177. [CrossRef]
11. Hartuti, S.; Kambara, S.; Takeyama, A.; Hanum, F.F. Leaching characteristic of arsenic in coal fly ash. *J. Mater. Sci. Eng.* **2017**, *7*, 19–26.
12. Hartuti, S.; Fadhillah Hanum, F.; Takeyama, A.; Kambara, S. Effect of additives on arsenic, boron, and selenium leaching from coal fly ash. *Minerals* **2017**, *7*, 99. [CrossRef]
13. Mavroulidou, M.; Bouluki, G.; Unsworth, C. Incorporating Waste Water Paper Sludge Ash As Partial Cement Replacement in Concrete. In Proceedings of the 13th International Conference of Environmental Science and Technology, Athens, Greece, 5–7 September 2013.
14. Catalfamo, P.; Pasquale, S.D.; Corigliano, F.; Mavilia, L. Influence of the calcium content on the coal fly ash features in some innovative applications. *Resour. Conserv. Recycl.* **1997**, *20*, 119–125. [CrossRef]
15. Palumbo, A.V.; Tarver, J.R.; Fagan, L.A.; McNeilly, M.S.; Ruther, R.; Fisher, L.S.; Amonette, J.E. Comparing metal leaching and toxicity from low pH, high pH and high ammonia fly ash. *Fuel* **2007**, *86*, 1623–1630. [CrossRef]
16. Janskowki, J.; Ward, C.R.; French, D.; Groves, S. Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems. *Fuel* **2006**, *85*, 243–256. [CrossRef]
17. Sun, W.; Renew, J.E.; Zhang, W.; Tang, Y.; Huang, C.H. Sorption of Se (IV) and Se (VI) to coal fly ash/cement composite: Effect of Ca^{2+} and high ionic strength. *Chem. Geol.* **2016**, *464*, 76–83. [CrossRef]
18. Nabajyoti, S.; Kato, S.; Toshinori, K. Behavior of B, Cr, Se, As, Pb, Cd, and Mo present in waste leachates generated from combustion residues during the formation of ettringite. *Environ. Toxicol. Chem.* **2006**, *25*, 1710–1719.
19. Vhahangwele, M.; Mugera, G.W.; Hlanganani, T. Adsorption of As, B, Cr, Mo and Se from coal fly ash leachate by Fe^{3+} modified bentonite clay. *J. Water Reuse Desalin.* **2016**, *6*, 382–391. [CrossRef]
20. Harashima, A.; Ito, K. The conditions of ettringite formation by the reaction of a blast furnace slag with aqueous alkaline solutions. *ISIJ Int.* **2016**, *56*, 1738–1745. [CrossRef]

21. Cetin, B.; Aydilek, A.H. pH and fly ash type effect on trace metal leaching from embankment soils. *Resour. Conserv. Recycl.* **2013**, *80*, 107–117. [CrossRef]
22. Guo, Q.; Tian, J. Removal of fluoride and arsenate from aqueous solution by hydrocaluminate via precipitation and anion exchange. *Chem. Eng. J.* **2013**, *231*, 121–131. [CrossRef]
23. Iyer, R. The surface chemistry of the leaching of coal fly ash. *J. Hazard. Mater.* **2002**, *93*, 321–329. [CrossRef]
24. Wang, G.; Lou, Z.; Zhang, J.; Zhao, Y. Modes of occurence of fluorine by extraction and SEM method in a coal-fired power plant from Inner Mongolia China. *Mineral* **2015**, *5*, 863–869. [CrossRef]
25. Radoslaw, S.; Zdzislaw, C. Effect of soil contamination with fluorine on the contents of calcium and magnesium in the biomass of crop plans. *J. Elm.* **2017**, *20*, 731–742.
26. Zhang, M.; Reardon, E.J. Removal of B, Cr, Mo and Se from wastewater by incorporation into Hydrocalumite and Ettringite. *Environ. Sci. Technol.* **2003**, *37*, 2947–2952. [CrossRef] [PubMed]
27. Kumarasathan, P.; McCarthy, G.J.; Hasset, D.J.; Pflughoet-Hassett, D.F. Oxyanion substituted ettringites; synthesis and characterization and their potential role in immobilization of As, B, Cr, Se and V. *MRS Proc.* **1989**, *178*, 83. [CrossRef]
28. Tian, J.; Guo, Q. Thermal decomposition of hydrocalumite over a temperature range 400–1500 °C and its structure reconstruction in water. *J. Chem.* **2014**, *2014*, 1–8. [CrossRef]
29. Guo, B.; Liu, B.; Yang, J.; Zhang, S. The mechanism of heavy metal immobilization by cementitious material treatments and thermal treatment: A review. *J. Environ. Eng.* **2017**, *193*, 410–422. [CrossRef] [PubMed]