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Investigation of Additive Blending Ratio for Controlling Boron and Fluorine from Coal Fly Ash

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Abstract

Additive material for controlling trace elements from coal fly ash have been developed to expand fly ash utilization. Previous studies found that PS ash 8 and PS ash 11 contain the high calcium compound: 31.86% and 21.53% respectively. Then, the mixture of $Ca(OH)_2$, PS ash 8, and Blast Furnace (BF) Cement became a suitable additive to control arsenic, selenium, boron and fluorine simultaneously. But, pure $Ca(OH)_2$ is expensive material, so it needs to be substitute. Therefore, this research aims to investigate effective blending ratio of additive in order to substitute the use of pure $Ca(OH)_2$ and to increase the use of paper sludge ash to expand utilization. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) used to determine the boron leaching concentration. Fluorine leaching concentration analysis by using ion chromatography. Ca^{2+} and pH have been analyzed to support the result of PS ash effect in controlling trace elements leaching concentration. The result indicated that the enhancement of PS ash percentage commonly could be decreased the leaching concentration of boron and fluorine as same as the mixture of $Ca(OH)_2$ in 25% PS ash addition ratio.

1 Introduction

Coal plays a vital role in electricity generation worldwide. Based on the data from World Electricity Generation in 2015 coal-fired power plants was first ranking generated 39.3% of global electricity in the world followed by natural gas 22.9% [1]. The enhancement of coal utilization increases the production of coal fly ash. Coal fly ash is the waste from combustion process from electric power plants. The management of fly ash disposal still become a problem in coal-fired thermal power plant, because almost all heavy metals such as Ni, Sb, As, B, Cr, Pb, Se, F, etc. generally found in fly ash are toxic in nature [2]. When coal ash comes into contact with water, its toxic constituents can "leach" or dissolve out of the ash and percolate through water. Coal ash has leached from disposal carrying toxic substances into above-ground waterways such as rivers, streams and wetlands, and into underground water supplies [3]. In order to control the leach out of toxic substance the study of leaching control of trace element have been developed. The conclusion from recent publication of our study was the mixture of pure calcium hydroxide ($Ca(OH)_2$, paper sludge ash (PS) ash 8 and blast furnace (BF) cement give simultaneous decreases in trace element concentrations [4]. But, pure $Ca(OH)_2$ no effective for huge application because the price is expensive. In order to substitute the use of pure $Ca(OH)_2$ the ratio of PS ash have been investigated in this research. For preliminary study two-step analysis have been done. First, the chemical composition of fly ash sample and PS ash were analyzed by XRF. Second, the calcium compound in PS ash 8 and 11 carried out by XRD, TG, and Ethylene glycol method.

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2 Material and Methods

2.1 Sample and additive

Three kinds coal fly ashes (FA E, FA G, and FA AC) collected from different coal-fired power plants in Japan (600 MWe) were tested using mixed additive material with varying ratio. Variation of mixed additive consist of $Ca(OH)_2$, BF Cement, and two types of PS ash: PS ash 8 and PS ash 11. PS ash is the residue from the incineration of paper sludge industry. It has already been indicated to have a potential effect as an additive material. The addition of 10% BF cement from total sample triggers the formation of a compound that helps to retain trace elements in coal fly ash samples [4]. 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). The major chemical composition of sample and additive provide in Table 1 based on result from X-ray Florescence analysis (WDXRF S8 TIGER, Bruker AXS).

Chemical Composition		Coal Fly Ash			Additive			
		FA E	FA G	FA AC	$Ca(OH)_2$	PS Ash 8	PS Ash 11	BF Cement
SiO_2	(%)	55.30	66.21	68.98	0.09	28.76	26.2	31.03
Al_2O_3		30.84	26.65	22.53	0.07	15.41	15.04	13.32
TiO_2		1.94	1.77	1.07	0.07	0.35	0.42	0.19
Fe_2O_3		5.75	2.57	3.80	BDL	0.91	BDL	0.44
CaO		2.28	0.81	0.78	99.23	51.22	54.76	48.35
MgO		0.98	0.54	0.51	0.36	2.76	2.56	3.77
Na_2O		1.14	0.29	0.45	0.08	0.02	0.16	0.08
K_2O		1.20	0.54	1.21	0.01	0.15	0.07	0.36
P_2O_5		0.19	0.06	0.18	0.05	0.10	0.16	0.02
MnO		BDL	0.11	0.04	BDL	0.04	0.03	0.05
V_2O_5		0.09	0.02	0.02	0.03	0.02	0.02	0.02
SO_3		0.28	0.44	0.44	0.01	0.27	0.56	2.39

Table 1: Chemical Composition of Coal Fly Ash and Additives

The kind of calcium compound in PS ash 8 and 11 identified by X-Ray Diffraction (XRD) labX XRD6100, Shimazu, Kyoto, Japan. The pattern of PS ash 8 and 11 by XRD shown in Fig. 1. Then, the amount of $Ca(OH)_2$ and $CaCO_3$ determined by Thermal Gravimetric (TG/DTA6300 SII EXSTAR 6000, Hitachi, Hong Kong), the thermal decomposition curves by TG shown in Fig. 2. The amount of CaO measured by combining ICP-TG through ethylene glycol leaching process because CaO needs the high temperature (1000ºC) to decompose, so it is difficult to measure with thermal gravimetric directly. So, after leaching process the concentration of calcium measured by ICP. In addition, not only CaO can dissolve by the ethylene glycol but also $Ca(OH)_2$ [5]. Therefore these methods have to combine.

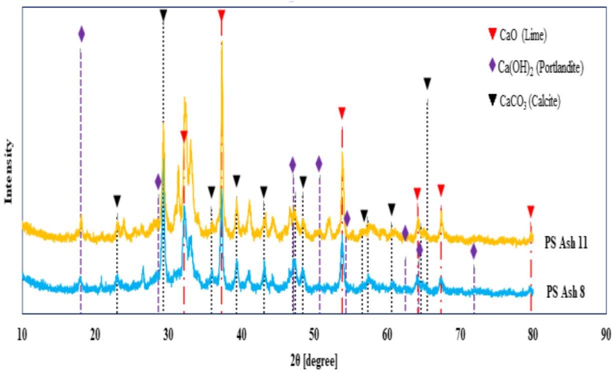


Figure 1: Combining XRD pattern of PS ash with calcium standard

Calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) used as a standard to identify calcium compound in paper sludge ashes. The XRD patterns of PS ash 8 and PS 11 shown in Fig. 1 clearly indicate that both of PS ash 8 and PS ash 11 consist of CaO, $Ca(OH)_2$ and $CaCO_3$.

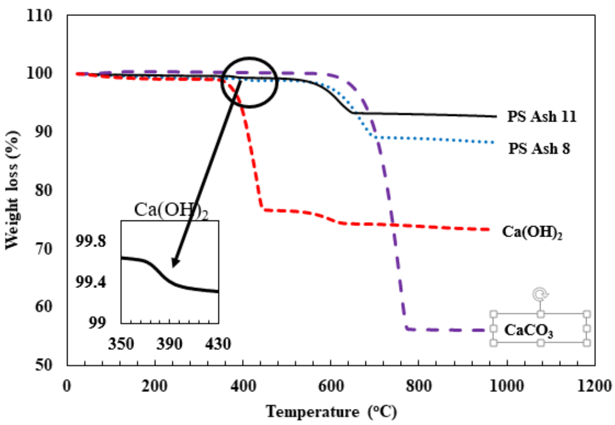


Figure 2: Comparison thermal decomposition curves of PS ash 8 and PS ash 11with $Ca(OH)_2$ and $CaCO_3$ as standard

TG analysis was carried out on paper sludge ashes to confirm percentage of $Ca(OH)_2$ and $CaCO_3$ based on weight losses in TG curve. $Ca(OH)_2$ starts to lose weight in temperature range 350-450°C decomposed into CaO and H_2O. $CaCO_3$ decomposed into CaO and CO_2 at the temperature around 600-790°C. Both of them have been used as a standard to determine calcium compound in PS ash. Figure 2 shows decomposition of PS ash 8, a weight loss from the temperature around 380-430°C and 550-700°C for the $Ca(OH)_2$ and the $CaCO_3$ respectively. PS ash 11 decomposed from 370-410°C and 510-650°C. Percentage of each calcium obtained from 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. Figure 3 shows the calcium compound weight percentage in PS ash 8 and 11. The highest CaO found in PS ash 11; 12.03%, and the highest $Ca(OH)_2$ and $CaCO_3$ shown in PS 8; 1.44% and 19.32%. The total calcium compound in PS ash 8 and 11 is 31.86% and 21.53% respectively.

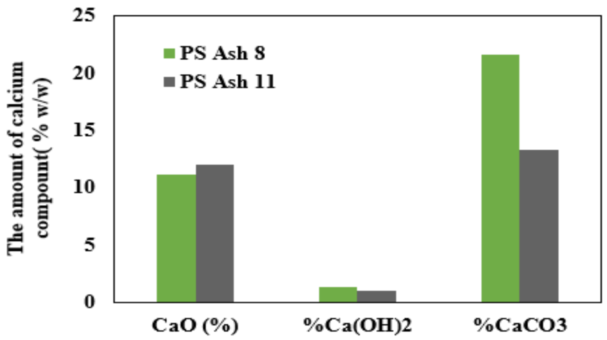


Figure 3: The amount of calcium compound in PS ash 8 and 11

2.2 Preparation Sample and Leaching Test

The amount of additive material was added into each fly ash with ratio provide in Table 2. The percentage of $Ca(OH)_2$ only added to 10% variation of PS ash, while BF cement added 10% to all mixture of sample. The mixture of sample and additive were homogenized in a plastic bag, then was moved into a bowl and added 25% distilled water to the total mixture. The mixture was kneaded for one minute, and then scrapped and continue kneaded for a further two minutes. Finally, the mixture was stored in a plastic tray and air-dried at room temperature. The treated fly ashes and the resulting mixtures were subjected to a leaching test by the Environmental Agency of Japan Notifications No. 13. The treated coal fly ash sample were added distilled water with ratio 1:10, then was shaken at a speed of 200 rpm by Shaker SA400 Yamato for 6 hour. After that, the solid and liquid separate by centrifugation and vacuum filtration using cellulose membrane filters (0.45 μm). At last, the leachate (liquid phase after filtration) was analyzed in order to know the leaching concentration, Ca ion concentration and pH value.

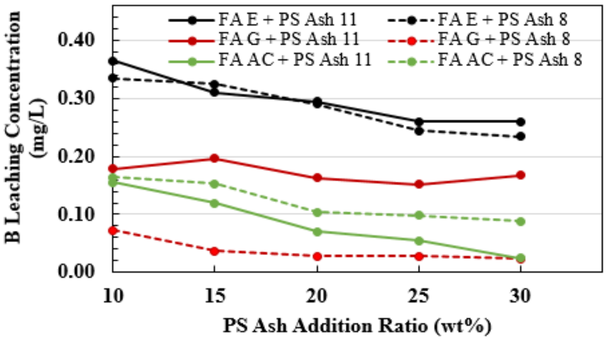
Sample	$Ca(OH)_2$ (10%)	PS Ash (%)		BF Cement (%)
FA E, FA G, and FA AD	1	PS Ash 11	10	10
	0		15	
	0		20	
	0		25	
	0		30	
	1	PS Ash 8	10	
	0		15	
	0		20	
	0		25	
	0		30	

Table 2: Additional ratio of additive material

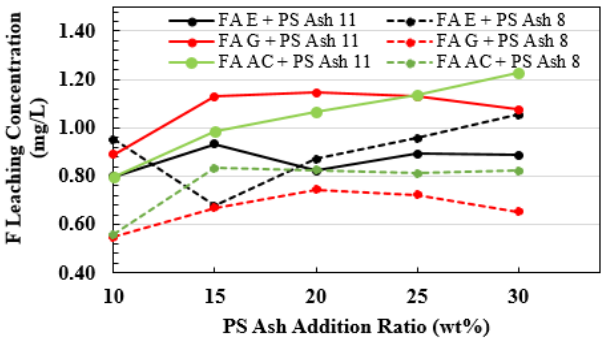
3 Result and Discussion

3.1 The Effect of Various Additive Material Blending Ratio in B and F Leaching Concentration

Three type of fly ash sample, FA E, FA G and FA AD have been tested with five variant of PS ash addition ratio in order to know the optimum addition ratio of PS ash without $Ca(OH)_2$. Figure 4(a) shows the effect of addition ratio of PS ash for boron leaching concentration. FA E with PS ash 11 keep going down until addition 25% and keep stable until addition 30%. Different with PS ash 11, FA E and PS ash 8 increase from addition 10% until addition 15% and keep decrease until addition 30%. FA G sample and PS ash 11 increase from addition 10% until addition 15% then keep decrease until addition 25% next going up until addition 30%. While with addition PS ash 8 keep going down until addition 25% and then keep stable until addition 30%. FA AC sample with both addition of PS ash 8 and 11 keep decreasing until addition 30%.Effect of addition ratio of PS ash for fluorine leaching concentration shown in Fig. 4(b).Even though generally addition of PS ash 8 and 11 increase the fluorine leaching concentration from addition 10% to 15%, except FA E and PS ash 8, but after that could decrease until addition 30% (FA G and PS ash 11; FA G and PS ash 8; FA E PS ash 11). The mixture of FA AC and PS ash 8 show the optimum in addition 25%. As shown in Fig. 4 generally the leaching concentration keep going down until addition 25% then increase in addition 30%. Moreover addition 25% could decrease until lower than addition 10% plus $Ca(OH)_2$ 1%. It is proof that PS ash can substitute $Ca(OH)_2$ as additive material.



(a)



(b)

Figure 4: Effect of Additive Blending ratio for Leaching Concentration; (a) Boron (b) Fluorine

The capability of PS ash in decreasing leaching concentration is different as can be seen in the Fig.4. PS ash 8 could be controlled the leaching concentration better than PS ash 11. Generally the concentration leaching of boron and fluorine with PS ash 8 are below the concentration which use PS ash 11as additive material. This result linear with the total calcium compound which content in PS ash 8 and PS ash 11. PS ash 8 have percentage of calcium higher than PS ash 11 (21.6%, 13.32%) as shown in Fig.1.

This result also support by XRD pattern of FA G before leaching and XRD pattern after leaching which used $Ca(OH)_2$ and PS ash 8 as additive material as display in Fig. 5. Interaction of compound in PS ash 8 cause the transformation of FA G pattern. FA G mainly consist of Al and Si peaks, this is appropriate with XRF result in Table 1 that FA G consist of 66.21% of SiO_2 and follow by 26.65% of Al_2O_3. After added 1% of $Ca(OH)_2$ and %of 10% PS ash 8 the pattern was change. The intensity of Si and Al is decreasing then could be detected the small intensity of Ca. The addition 25% of PS ash 8 into FA G leaching process also could change the peak intensity of FA G. Beside the change of peak intensity of Si and Al, peak intensity also change became higher then addition 1% of $Ca(OH)_2$ and 10% of PS ash 8. This pattern transformation caused by interaction Ca with trace elements became $Ca_3B_2O_6$ and CaF_2 also interaction of Ca with Si and Al became $Ca_3Al_2Si_3O_{12}$.

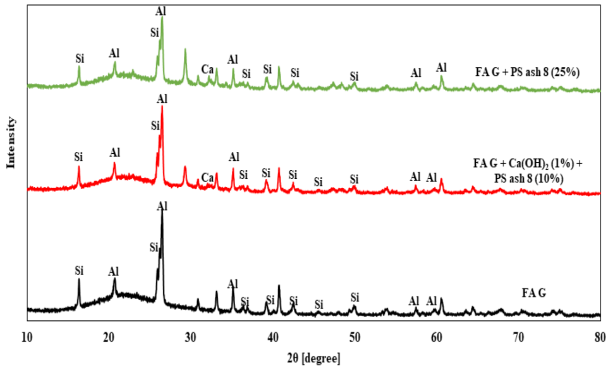


Figure 5: Pattern of FA G before and after added additive material.

3.3 The Effect of Additive Blending ratio for pH in Leaching Process

pH is one important parameter to control the leaching of metals from coal fly ash [6]. Figure 6 shows effect of additive blending ratio for pH value on FA G.

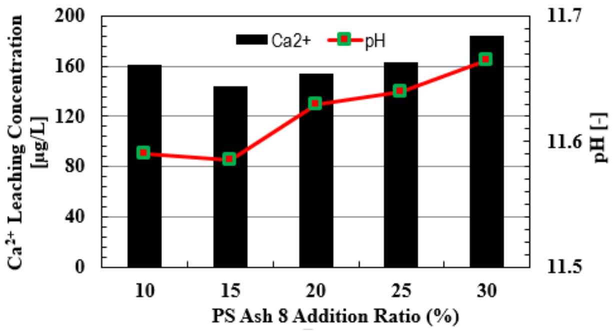


Figure 6: Effect addition ratio for pH value and Ca^{2+} concentration in leaching process from FA G

pH value decrease from addition 10% and $Ca(OH)_2$ 1% to 15% and keep increase until addition 30%. Addition 20% has pH value higher than addition 10% and $Ca(OH)_2$ 1%. Enhancement addition ratio of PS ash can substitute the use of $Ca(OH)_2$. This result also support by cation Ca^{2+} leaching concentration as a source of inhibitor trace elements leaching concentration. As shown in Fig. 5 addition PS ash 25% have Ca^{2+} concentration higher than addition 10% with $Ca(OH)_2$ 1%. Alkaline conditions during the leaching process and the amount of calcium are the main factors for controlling process, because boron and fluorine can react with calcium and form relatively insoluble compounds such as $Ca_2B_2O_5$, $Ca_3B_2O_6$ [7] and CaF_2 [8].

4 Conclusions

Enhancement addition of PS ash can substitute the use of $Ca(OH)_2$ on 25% addition. To upgrade this conclusion, next research will be tested for analyzing arsenic, selenium, and chromium.

5 Acknowledgment

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References

[1] Web Sites: J.M.K.C. Donev et al. (2017). Energy Education - Coal fired power plant [Online]. Available at https://energyeducation.ca/encyclopedia/Coal_fired_power_plant.

[2]M. R. Senapati. Fly ash from thermal power plants - Waste management and overview. Current Science 100 (25) (2011) 1791-1794.

[3] Web Site: United States Affiliate of International Physicians available at https://www.psr.org/wp-content/uploads/2018/05/coal-ash-hazardous-to-human-health.pdf

[4] F. F. Hanum, E. R. Desfitri, Y. Hayakawa, S. Kambara. Preliminary Study on Additives for Controlling As, Se, B, and F Leaching from Coal Fly Ash. Minerals. 8. (2018) 493-504.

[5] M. Kato, T. Hari, S. Saito, M. Shibukawa. Determination of Free Lime in Steelmaking Slags by Use of Ethylene Glycol Extraction/ICP-AES and Thermogravimetry. Japan Science and Technology Agency. 100. (2014) 340-345.

[6] K. Komonweeraket, B. Cetin, A. H. Aydilek, C. H. Benson, T. B. Edil. Effects of pH on the leaching mechanisms of elements from fly ash mixed soils. Fuel. 140. (2015) 788-802.

[7] 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 80 (2010) 881–887.

[8] Wang, G.; Lou, Z.; Zhang, J.; Zhao, Y. Modes of occurrence of fluorine by extraction and SEM method in a coal-fired power plant from Inner Mongolia China. Mineral. 5 (**2015)** 863–869.