Calcium Performance in Paper Sludge Ash as Suppressing Material

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Calcium Performance in Paper Sludge Ash as Suppressing Material

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Abstract. Paper sludge (PS) ash is a waste material collected from the paper industry, which containing calcium compound. In the previous research, several paper sludge ashes have been tried into coal fly ashes in order to suppress the leaching of trace elements such as As, Se, and B into the environment. The result showed that paper sludge ashes has potential effect in inhibit the leaching of these trace elements because of the calcium contains in the paper sludge ashes. Therefore, this research provide information about the amount of calcium in paper sludge ash as suppressing material. Nine kinds of paper sludge ashes tested into coal fly ash C (FA C) in order to know the ability of each paper sludge ash in suppressing the leaching of trace elements. Inductively coupled plasma (ICP-AES) used to determine the leaching concentration of As, Se, and B. Then, the kind of calcium in paper sludge ashes were analysed by X-ray diffraction (XRD). Thermal gravimetric analysis (TG) used to determinate $Ca(OH)_2$ and $CaCO_3$. The percentage of CaO in paper sludge ashes analysed by combination ethylene glycol, ICP-AES and TG. This research found the kind of PS which most influential for controlling leached out of trace elements.

1. Introduction

Fly ash, a waste product from the thermal power plants, is increasing day by day [1]. So, in the next few years, coal will be still an important source of electricity, not only in Japan but also in the world. As the coal burns, toxic pollutants such as arsenic (As), selenium (Se), boron (B) are transferred into the wastes [2]. Because of this, the study about how to minimize the effect of trace element into the environment still needs to be researched. In order to decrease the effect of trace element into the environment, many researchers already found that calcium is affected trace elements leaching mechanism said that calcium compound could control the leaching of trace element from coal fly ash [3]. Another research also states that CaO dominates in coal fly ash sample directly affects the mobility of trace elements by determining pH of the leaching medium [4].

The role of calcium through the addition of 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 one of the promising solution in minimize the hazardous effect of trace element into the environment. However, the study also showed that the higher calcium in paper sludge ashes did not always linier into a better effect during mechanisms. Paper sludge ash is waste which lately was utilized by some industry, 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 (in the form of metakaolin) as well as lime (CaO). The composition of the ash not only depend on the specific fuel, but also on the combustion technology and conditions [6].

There are specific characteristic of calcium which may affect the leaching mechanisms. Therefore, this research will study the performance of several kinds of paper sludge ashes based on the calcium content. Nine kinds of the paper sludge ashes will be tried into coal fly ash C, in order to analyse their performance during the leaching mechanisms. In addition, 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 effective in decreasing the As, Se and B leaching concentration simultaneously.

2. Methods

2.1 Materials

Fly ash sample which used in this research was Fly ash C (FA C). It derived from a pulverized coal-fired power plant unit 2 electrostatic precipitators number 1. This coal fly ash containing As 26.39 μg/L, Se 186.51 μg/L and B 7.85 mg/L based on ICP-AES analysis.

Paper sludge ash as the suppressing material has been tested for stabilized As, Se, and B in FA C. Inorganic Chemical composition of fly ash C and paper sludge ashes could be shown in Table 1.

Table 1. Chemical composition in FA C and paper sludge ashes based on XRF analysis

Samples		**FA C**	**PS Ash 3**	**PS Ash 4**	**PS Ash 5**	**PS Ash 6**	**PS Ash 7**	**PS Ash 8**	**PS Ash 9**	**PS Ash 10**	**PS Ash 11**
Ash composition [%]	SiO_2	64.3	31.47	44.21	42.36	26.03	32.39	28.76	37.82	40.6	26.2
	$Al2O_3$	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_2O_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_2O	1.20	0.24	0.95	0.41	-	0.26	0.02	0.41	0.71	0.16
	K_2O	0.80	0.20	2.09	1.99	0.93	0.53	0.15	1.87	2.34	0.07
	P_2O_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_2O_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

2.2 Leaching Test

2.2.1 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.

2.2.2 Ethylene glycol leaching method

CaO needs a high temperature (>1000^{o}C) to decompose, so it is difficult to measure with thermal gravimetric directly. In this research, determination of CaO in paper sludge ash with the combination of TG and ethylene glycol have been developed. At the beginning of this method 1 mg PS ash was weighed and added 25 ml warm ethylene glycol (T=80^{o}C). Then stirred at 200 rpm (temperature was keep at 80^{o}C) for one hour. After one hour, sample was filtered by 0.45 μm cellulose acetate membrane filter. The concentration of Ca in solution measured by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.3 Instrumentation
Some instruments have been used to analysis Calcium compound in paper sludge ashes. X-ray Diffraction (XRD) labX XRD6100, Shimazu, Kyoto, Japan has been used for qualitative analysis. The sample in powder form was pressed into a sample holder so that have a smooth flat surface. The sample was irradiated with Cu Kα-radiation between 10^o and 80^o (2θ). Scanning speed is 2^o/min, at an acceleration voltage of 40kV and tube hazard 30 mA. Software module "DDView and Sleve," database PDF－II release 2013 from the International Center for Diffraction Data (ICCD) was used to analysis diffraction pattern after measurement. PDF II means database which 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 $CaCO_3$. Paper sludge ashes sample (9-12mg) was heated with a measurement temperature from 30 to 1000^oC at a heating rate of 10^oC/min under a nitrogen atmosphere at a flow rate of 200ml/min. This instrument work based one measure of weight/mass change (loss weight) as a function of temperature, time and atmosphere. Percentage of CaO measured by combining ICP-TG through ethylene glycol leaching process because CaO needs the high temperature (>1000^oC) to decompose, so it is difficult 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. Results and Discussion

3.1 Effect of Suppressing Material
In order to know the effect of paper sludge ashes into trace element leaching concentration each paper sludge ash have been tested into FA C. The result shown that the addition of paper sludge ash can increase the pH value of leached and decreasing leaching concentration of trace elements in FA C as demonstrated in figure 1. It consentient with statement [4] that CaO in coal fly ash sample directly affects the mobility of trace elements by determining pH of the leaching medium. Figure 1(a) shows effect each paper sludge ashes in controlling leaching Arsenic (As). Arsenic leaching concentration in FA C without additive material was 17.55 μg/L, but after added paper sludge ashes it could be decreased. All of paper sludge ashes could be decreased As leaching concentration under environmental standard, but the most effective to decreasing Arsenic concentration in FA C was PS ash 11 followed by PS ash 3 and PS ash 6 (0.01 μg/L, 1.04 μg/L and 1.65 μg/L respectively). Then, pH also one of the most important 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. Selenium (Se) leaching concentration in FA C without additive material was 186.51 μg/L. Paper sludge ashes also could keep stabilization selenium in coal fly ash. It proves by figure 1b Selenium leaching concentration decreasing until 0.615 μg/L, 14.65 μg/L and 17.02 μg/L by PS ash 11, PS ash 5 and PS ash 9 respectively but only PS ash 11 addition could decrease until under environmental limit as display in figure 1(b). Boron leaching concentration also keep 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 1(c). 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 at controlling Boron, but no in arsenic and selenium. Different with PS ash 11, it good in three of trace elements: arsenic, selenium, and boron. PS ash 3 and PS ash 8 also keep stable to decreasing leaching concentration of three kinds trace elements in FA C. In order to know why some paper sludge ashes

give good effect but the others no, calcium qualitative and quantitative analysis in FA C have been done.

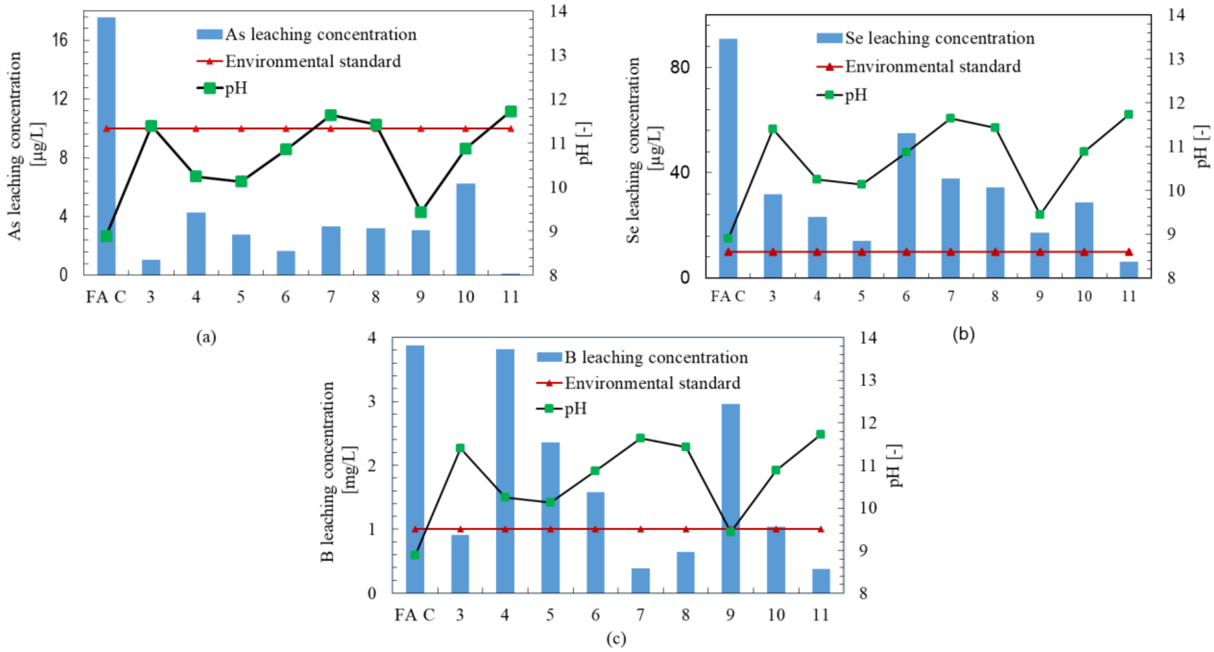
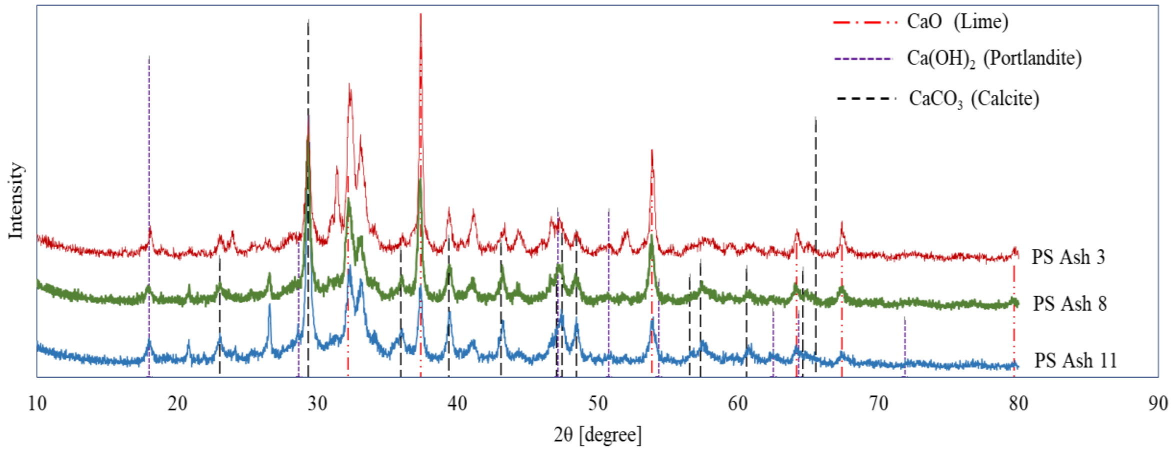


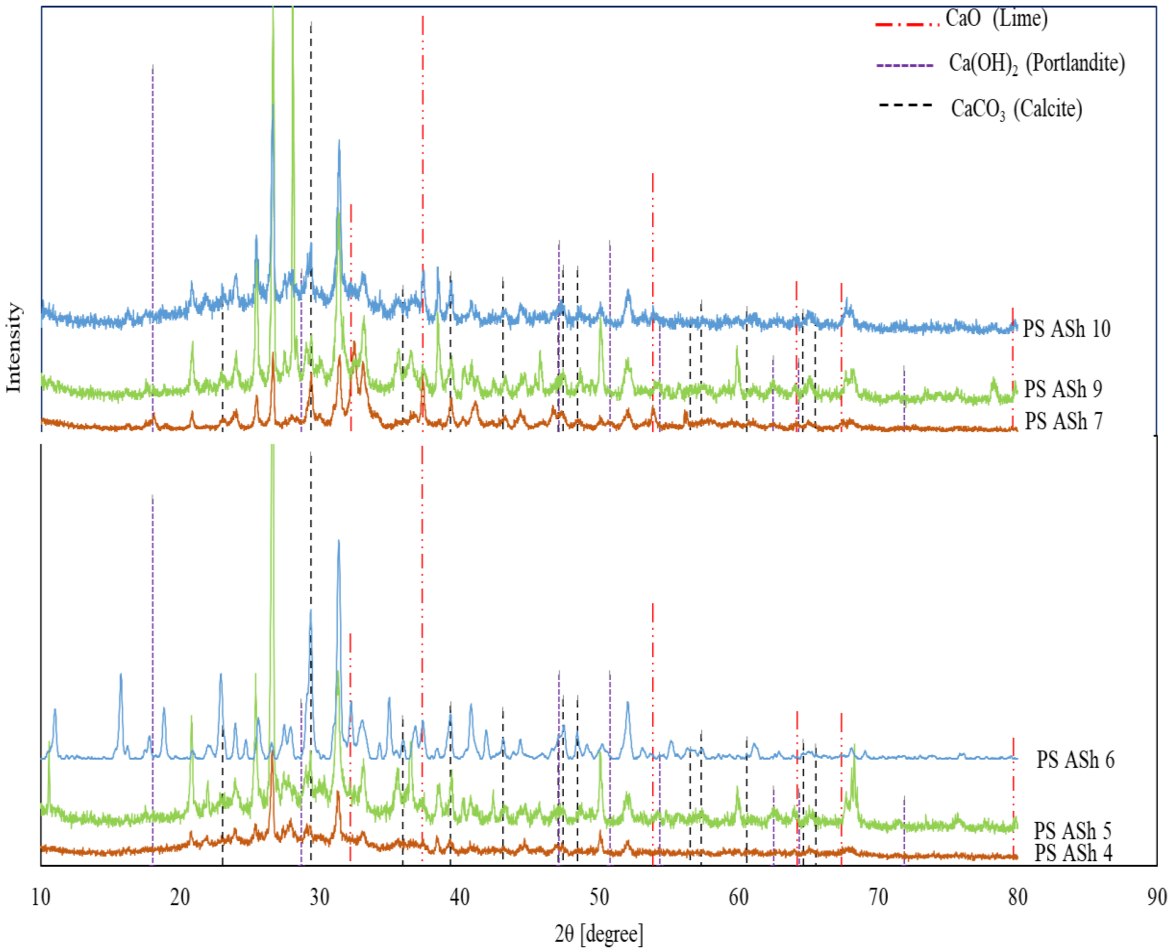
Figure 1. The effect of additive material in controlling trace elements leaching concentration (a) Arsenic, (b) Selenium, and (c) Boron

3.2 Qualitative Analysis by XRD

X-ray diffraction analysis was performed to analysis calcium compound in the paper sludge ashes. Calcium oxide (CaO), Calcium Hydroxide ($Ca(OH)_2$) and Calcium carbonate ($CaCO_3$) pure have been used as a standard to analysis calcium compound in paper sludge ashes. As can be seen from Figure 2 raw peak of each paper sludge ash have different intensity. Figure 2(a) indicate that peak of diffraction pattern from PS ash 3, 8 and 11 was detected as CaO, $Ca(OH)_2$ and $CaCO_3$. Based on figure 2(a), PS ash 3, 8 and 11 predicted have high calcium compound. Different with figure 2(b) the higher intensity of sample there are on different intensity of calcium standard. Only a small part of the diffraction peak detected as calcium compound. It predicted that PS ash 4, 5, 6, 7, 9 and 10 have low calcium compound. In order to make sure this hypothesis quantitative analysis has been done.



(a)



(b)

Figure 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.

3.3 Quantitative Analysis by TG and Ethylene Glycol Method

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 paper sludge ash. Figure 3 shows 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 $CaCO_3$ respectively. 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 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 $CaCO_3$ dissolved hardly. As shown in

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the Table 2, it became clear that CaO and $Ca(OH)_2$ can be completely extracted by the Ethylene Glycol method. Calcium compound extracted from paper sludge ash by the ethylene method was converted into CaO and the CaO content in the paper sludge ash was determined by subtracting the $Ca(OH)_2$ amount.

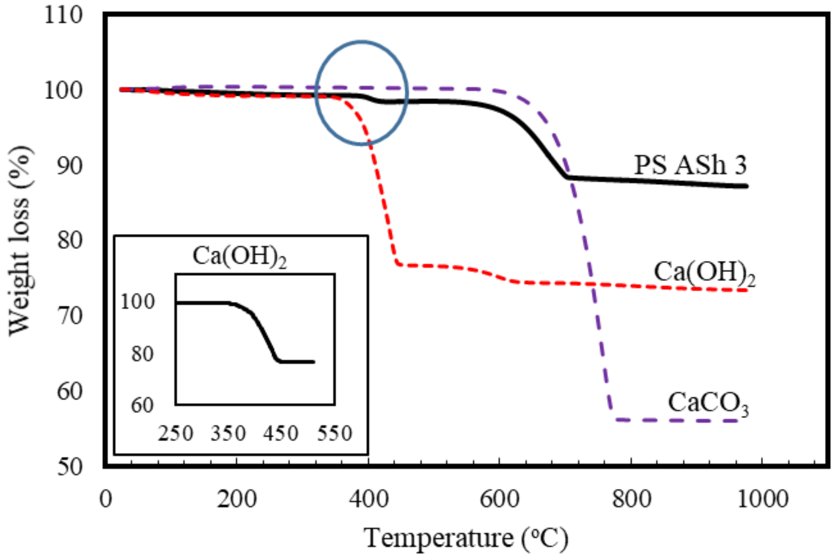

Figure 3. Thermal decomposition curves of PS ash 3, $Ca(OH)_2$ and $CaCO_3$

Table 2. Solubility of CaO, $Ca(OH)_2$ and $CaCO_3$ 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

3.4 Calcium Performance in Paper Sludge Ashes

It has been known that each paper sludge ashes give different effect to control leaching concentration of As, Se, and Boron in coal FA C. In aims to know the kind of calcium compound TG analysis and EG method has been done. Figure 4 shows the concentration of calcium compounds which contained in paper sludge ashes.

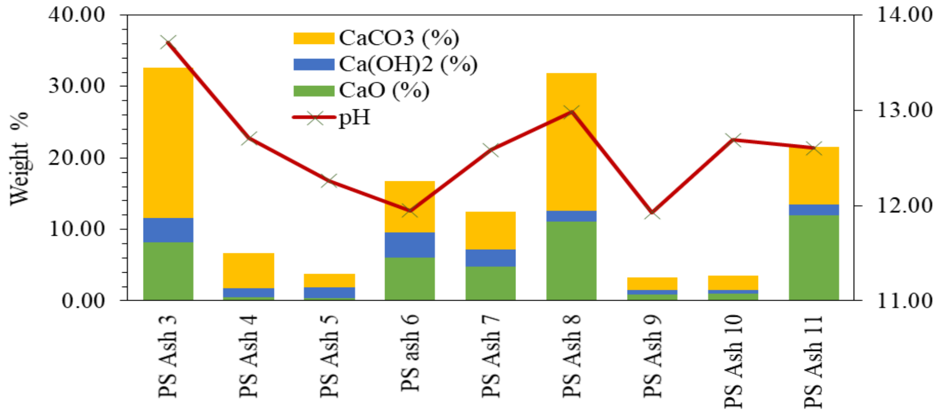

Figure 4. Calcium compounds content of paper sludge ashes and it relation with the alkalinity

$Ca(OH)_2$ and $CaCO_3$ were result from TG and CaO was result from 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, 8, 11 and 6 with the total 32.69%, 31.86%, 21.53%, and 16.81% respectively. The highest 21.12% $CaCO_3$, 3.55% $Ca(OH)_2$ and 12.03% CaO consecutively consist on PS ash 3, 6 and 11. The alkalinity of paper sludge ashes which could increasing pH value in leaching process of coal fly ashes also could be seen in figure 4. The highest alkalinity found in PS ash 3, 8 and 11 (13.72, 12.98 and 12.61 respectively).

Related to the result of additive material effect in controlling trace elements leaching concentration arsenic, selenium and boron can be known that the highest calcium compound not give the best effect in controlling leaching concentration simultaneously. Figure 5 shows which one is the best PS ashes in controlling As, Se and B simultaneously.

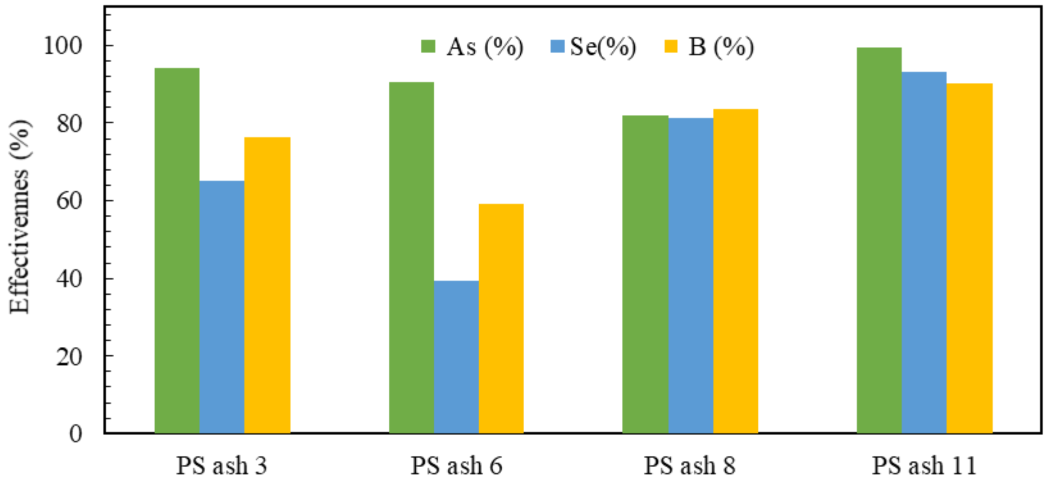

Figure 5. The capability of paper sludge ashes in decreasing trace elements

Percentage of effectiveness shows the capability of PS ashes which contain the highest calcium in decreasing leaching of trace elements. PS ash 3 which contains the highest calcium compound and consist of the highest $CaCO_3$ only can control leaching concentration As, Se and B were 94.07%, 65.13% and 76.42% respectively. PS ash 6 which contains the highest $Ca(OH)_2$ can control leaching

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concentration of 90.60% As, 39.48% Se, and 59.28% B. PS ash 8 which contains the second highest of calcium compound can control around 80% of As and B but only around 60% of Se and B. The most effective to control leaching three of As, Se and B is found in PS ash 11. PS ash which containing the highest CaO can control As, Se and B were 99.43%, 93.22% and 90.34% respectively. It means the kind of calcium which most affected is CaO and the most effective to control leaching concentration of As, Se, and B is PS ash 11.

4. Conclusion

Based on this research has been known that each PS ash give different effect in controlling leach out of trace elements in FA-C suitable with kind and total calcium which contained in each PS ash. In this research found that PS ash 11 is most effective for stabilization of trace elements in coal fly ash because it can control trace elements leaching more than 90% simultaneously.

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