The Role of Calcium Compound on Fluorine Leaching Concentration

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Abstract. The performance of calcium compound in leaching mechanisms has been known through the addition of high calcium compound material. The addition of those materials was proven that the additives could simultaneously inhibit the leaching of several trace elements such as arsenic, selenium, boron and fluorine. This study will be focused on the role of calcium compound onto fluorine leaching concentration. Fluorine is one of trace elements consisting in most of coals that has effect in environmental pollution. The application of mixture additives in leaching process was given a promising effect in inhibit the leaching of fluorine until less the environmental limit (0.8 mg/L). This researched will present the information about calcium compound related with fluorine leaching mechanism after the addition of mixture additives (Ca(OH)2, PS ash 8, and BF cement) into 14 different coal fly ashes (FA A, B, C, B, E, F, G, H, I, J, K, L, M, and N). This information will be important in the coal fly ash utilization to minimize the effect of fluorine leaching concentration into the environment.

1. Introduction
Coal has been predicted as the largest source of power generation in 2040 with a share almost 30 percent [1]. It is means that the production of coal fly ashes will still affected the environment because of the hazardous element containing in the coal fly ash [2]. One of the toxic trace elements consisting in coal fly ash is fluorine. Fluorine is the most reactive of all the chemical elements which including into hazardous trace elements in coal, and study was reported that about 10-40% of fluorine in coal entered into coal fly ash through the combustion process [3-5]. Therefore, the utilization of coal fly ash in various purposes needs to be awareing about the fluorine effect into the environment. Fluoride (the anion of fluorine) has been listed as one of the contamination in water by the WHO because could cause many problems in human health [6]. In plants, fluorine could be absorbed by plants under natural condition and it is bound into insoluble compounds such as CaF2 [7]. In the development of additives for inhibit the leaching of the trace element into the environment, previous study was found that calcium has positive effect in decreasing trace element leaching concentration [8]. Then, the application of mixture additives was given promising effect in inhibits the leaching of several trace elements, including the leaching of fluorine [9]. This study was purposed to investigate about the calcium compound which plays important role during the fluorine leaching mechanisms. This information will require in controlling the effect of fluorine into the environment.

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2. Methods

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

| Fly Ash (FA) | FA A | FA B | FA C | FA D | FA E | FA F | FA G | FA H | FA I | FA J | FA K | FA L | FA M | FA N |
|-------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Power station | Unit 2 | Unit 2 | Unit 2 | Unit 2 | Unit 1 | Unit 1 | Unit 1 | Unit 1 | Unit 1 | Unit 1 | Unit 1 | Unit 1 | Unit 1 | Unit 1 |
| Chamber of electrostatic precipitator | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 | EP1 |
| SiO₂ | 52.61 | 51.42 | 64.34 | 57.49 | 55.30 | 66.99 | 66.21 | 59.25 | 59.21 | 60.57 | 56.82 | 57.32 | 64.84 | 63.08 |
| Al₂O₃ | 31.35 | 22.39 | 22.79 | 16.68 | 30.84 | 26.40 | 26.65 | 25.63 | 26.32 | 21.83 | 21.06 | 20.68 | 23.28 | 22.73 |
| TiO₂ | 2.08 | 2.16 | 2.27 | 1.14 | 1.94 | 2.01 | 1.77 | 1.99 | 1.77 | 1.11 | 1.06 | 0.96 | 1.12 | 1.24 |
| Fe₂O₃ | 7.06 | 7.01 | 3.71 | 3.93 | 5.75 | 2.15 | 2.57 | 7.49 | 6.79 | 7.17 | 7.23 | 7.17 | 5.81 | 5.65 |
| CaO | 3.26 | 10.80 | 2.71 | 0.45 | 2.28 | 0.66 | 0.81 | 2.05 | 2.07 | 1.43 | 8.86 | 8.79 | 1.39 | 2.67 |
| MgO | 0.58 | 1.05 | 0.85 | 0.22 | 0.98 | 0.51 | 0.54 | 0.79 | 0.91 | 0.52 | 0.96 | 1.02 | 0.82 | 1.12 |
| Na₂O | 0.38 | 1.23 | 1.20 | 0.38 | 1.14 | 0.27 | 0.29 | 0.60 | 0.74 | 0.44 | 0.75 | 0.80 | 0.52 | 1.25 |
| K₂O | 0.96 | 1.19 | 0.80 | 1.43 | 1.20 | 0.58 | 0.54 | 1.56 | 1.44 | 1.76 | 1.67 | 1.67 | 1.97 | 1.67 |
| P₂O₅ | 0.61 | 0.22 | 0.07 | 0.10 | 0.19 | 0.04 | 0.06 | 0.18 | 0.18 | 0.16 | 0.28 | 0.27 | 0.13 | 0.20 |
| MnO | 0.09 | 0.18 | 0.06 | 0.04 | - | 0.12 | 0.11 | - | 0.10 | - | - | - | 0.00 | 0.07 |
| V₂O₅ | 0.00 | 0.00 | 0.00 | 0.03 | 0.01 | 0.01 | 0.02 | 0.03 | 0.03 | 0.15 | 0.17 | 0.17 | 0.08 | 0.04 |
| SO₃ | 0.27 | 1.22 | 0.35 | 0.28 | 0.28 | 0.26 | 0.44 | 0.42 | 0.50 | 0.35 | 0.84 | 0.87 | 0.35 | 0.53 |

2.2. Additives
An additive is used to elevate the calcium content in the coal fly ash sample. There are two kinds of mixture additives used in this researched: (1) The mixture of PS ash 8 and BF cement (2) The mixture of Ca(OH)₂, PS ash 8 and BF cement. The previous researched presented that these two mixtures were given promising effect in the leaching of several trace elements from coal fly ash with low calcium content (FA C and FA H). The calcium containing in PS ash 8 and BF cement respectively are 51.22% and 48.35% (Table 2). The coal fly ash samples mixed with the additives in the certain ratio before the leaching process. The ratio of the additives based on the total sample is 3% of calcium hydroxide (Ca(OH)₂), 10% of PS Ash 8, and 10% of BF Cement. Then, 1:10 of coal fly ashes and distilled water prepared for the 6 hours leaching in the room temperature.

2.3. Analysis and Instrumentations
Ion chromatography analysis (ION ANALYZER IA-300) was performed in order to determine the fluorine leaching concentration from the 14 different coal fly ashes for before and after the application of the additives. Then, the data of leachate alkalinity was provided by pH/ION METER D-53, HORIBA in order to probe the effect of pH into fluorine leaching concentration. In addition the data for thermal gravimetric analysis (TG/DTA6300 SII EXSTAR 6000, HITACHI), ethylene glycol analysis, ICP-AES (ULTIMA2, HORIBA Ltd) and XPS analysis was used to explain the role of calcium onto the fluorine leaching mechanisms.
### Table 2. Chemical composition for additives by XRF analysis

| Chemical composition | Additives          |
|----------------------|--------------------|
|                      | 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      |

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3. Results and Discussions

3.1. Effect of pH in fluorine leaching process

The different calcium compound on coal fly ashes also affected pH of the leachate. The pH of the leachate from the fourteen coal fly ashes before the application of mixture additives is linear with the calcium content on each coal fly ashes based on the XRF analysis (Table 1). After the application of the mixture additives, the pH of the leachate is become higher. The leachate pH from the mixture additives PS Ash 8 and BF cement is slightly lower than mixture additives Ca(OH)$_2$, PS Ash 8 and BF cement (pH around 12, Figure 1). This is proven the study that explained alkalinity is one of the factors which affected the trace element leaching concentration into the environment and the high alkaline pH is giving positive effect in decreasing the trace element leaching concentration [10-12].
3.2. Effect of additives into fluorine leaching concentration

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

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

**Figure 2.** Effect of the mixture additives into different coal fly ashes on fluorine leaching concentration
In addition, amongst the coal fly ashes which have fluorine leaching higher than the standard, the calcium content containing in those coal fly ashes is very various including the lowest (0.81%) and the highest (10.80%) once. This is proven that the amount of calcium consisting in the coal fly ash sample is not liner with the fluorine leaching concentration. Furthermore, this result also stated that calcium compound containing in the coal fly ashes are diverse and there is a specific calcium compound which affected the fluorine leaching concentration. Later, this study will inform the calcium compound which plays an important role during the fluorine leaching concentration.

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

3.3. The role of calcium in fluorine leaching process

The both of the mixture of the additives presented the promising effect in minimizing the effect of the fluorine leaching into the environment. Calcium compound consisting in the coal fly ashes and in the additives were believed to take important role during the leaching of the fluorine. Figure 3 showed the XRD analysis result of the PS ash 8 and BF Cement. This figure explained that CaO, Ca(OH)$_2$ and CaCO$_3$ were the main calcium containing on these additives.

![Figure 3. XRD patterns of (a) PS ash 8 and (b) Blast Furnace Cement (BFC)](image-url)
Meanwhile, thermal gravimetric analysis (TGA) and ethylene glycol analysis were carried out in order to find the amount of those calcium compounds in the both of PS ash 8 and BF cement (Table 3). This data explained that the most calcium compound which might affected the fluorine leaching concentration is calcium oxide (CaO) and calcium carbonate (CaCO₃). These calcium compounds will be reacting with other chemical composition which will stabilized the hazardous heavy metals consisting in coal fly ashes.

| Additives material | CaO (%) | Ca(OH)₂ (%) | CaCO₃ (%) |
|--------------------|---------|-------------|-----------|
| PS ash 8           | 11.1    | 1.44        | 19.32     |
| BF Cement          | 1.62    | 0.31        | 6.45      |

Several studies have been researched the calcium and fluorine bearing compound consisting in coal fly ashes which might be produced during the combustion process [13-15]. The study said that mainly fluorine compound in coal is insoluble fluorine such as CaF₂, MgF₂, FeF₃, and AlF₃. These fluorine compounds are the main occurrence state after coal combustion process and difficult to break down even at high temperature. Wang, et al explained that several oxide compounds inside the coal including CaO in the fly ashes were took part in the formation of insoluble fluorides. This is confirmed the previous result that CaO is one of the main calcium compound which plays role in fluorine leaching process.

![Figure 4. XPS analysis result on the mixed coal fly ash sample and additive (FA C and Ca(OH)₂)](image)

Other than that, based on the XRD analysis data and TG/EG analysis data, the amount of calcium hydroxide is a few. But, calcium hydroxide is native calcium compound to enrich the calcium content on the coal fly ash samples. Even though the amount that little amount of Ca(OH)₂, this compound have ability to decrease the fluorine leaching. The XPS analysis was did into one of the coal fly ash sample (FA C) which already mixed with Ca(OH)₂. The peak showed that after the mixing process, the estimated calcium compound consisting in the samples is CaF₂. This is 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 the increasing amount of CaF₂ or other insoluble compound of fluorine which may cause by the chemical stabilization during the leaching process.
4. Conclusion
The application of mixture additive in leaching process has shown promising effect into fluorine leaching concentration. The various kinds of coal fly ashes was treated with the mixture of Ca(OH)$_2$, PS Ash 8 and BF cement as the additives, then the results confirmed that these additive mixtures is appropriate to apply in fluorine leaching concentration. CaO and CaCO$_3$ was mainly the main calcium compound consist in the additives. These calcium compounds was took part in the chemical stabilization of fluorine during the leaching concentration to produce the insoluble fluoride compounds. CaF$_2$ believed to be the one of fluoride compound consisting in the mixture of coal fly ashes and additives which difficult to break down even with the high temperature.

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