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Research Article

Investigation of the Fluorine Insolubilizes Agent for Biomass Ash

Masaaki Takahashi[1]*, Yukimasa Takemoto[1], Tadaharu Kado[2], Atsushi Suzuki[3], Ayaka Oshima[3], Tomoyuki Ueno[3] and Kentaro Hosokawa[3]

[1]Yokkaichi University, Yokkaichi, Mie, Japan

[2]Okamoto Doseki Kougyou Ltd, Kiho-cho, Minami Muro Gun, Mie, Japan

[3]Mie, Environmental Conservation Agency, Kawage-cho , Tsu, Mie, Japan

***Corresponding Author:** Masaaki Takahashi, Yokkaichi University, Yokkaichi, Mie, Japan.

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Abstract

In order to develop a treatment agent that insolubilizes fluorine in biomass ash, various phosphates compounds like calcium phosphate and aluminum phosphate or incinerated ash of sewage sludge which is containing a large amount of phosphorus components, were added to the biomass ash. The fluorine elution properties were investigated, and the solubility was significantly lowered by adding sulfuric acid or phosphoric acid to the agent, and showed effectiveness as a fluorine elution inhibitor.

Keywords: Incinerated Ash; Fluorine; Insolubilizes; Calcium Phosphate; Sulfuric Acid

Introduction

As a part of decarbonization efforts, the use of biomass resources is progressing, but as a result, a large amount of incinerated ash is being emitted, which is increasing (Figure 1) [1]. Incineration ash contains large amounts of potassium and amorphous silicon [2], and its usefulness as a resource has been especially pointed out in Japan, which relies on most of them from overseas.

Biomass incinerated ash is made by incinerating natural wood, and normally incinerated ash is not considered to contain harmful heavy metals such as mercury or cadmium, but some ash contains hexavalent chromium, fluorine, etc. Cases have been reported [3] that had been an obstacle to promote the usage of the incinerated ash. For this reason, significant amount of the incinerated ash is disposed as a waste in landfill sites in Japan.

Regarding hexavalent chromium in the ash, some methods which reduce it to trivalent chromium using iron (II) sulfate or sodium sulfide [4] have already been put into practical use.

As the fluorine insolubilize methods, addition of a chelate resins or cement solidification methods are widely practiced [5], but there are some concerns that the organic chelating agents will decompose in nature, and make secondary pollutions [6,7]. For this reason, insolubilize treatment using inorganic reagents like phosphoric acid or alkali metal phosphates are studied [8]. The authors investigated the fluorine insolubilize effects of various phosphoric acid-based reagents in order to investigate cheaper fluorine elution inhibitors [9].

Ash amount 10^4 ton

Method

Raw ash

As the raw ash, a discharged ash from biomass power generation facility was used. Table 1 shows the moisture content and Ignission loss (treated at 600°C) of the raw ash. The elemental composition of the ash is shown in table 2. Since the fluorine concentration in the raw ash was low compared by the assumed ash, and as a test ash sodium fluoride reagent (Kanto Kagaku Co., Ltd.) was added to the raw ash in advance to make the fluorine concentration approximately 2.5 mg/L in the elution test.

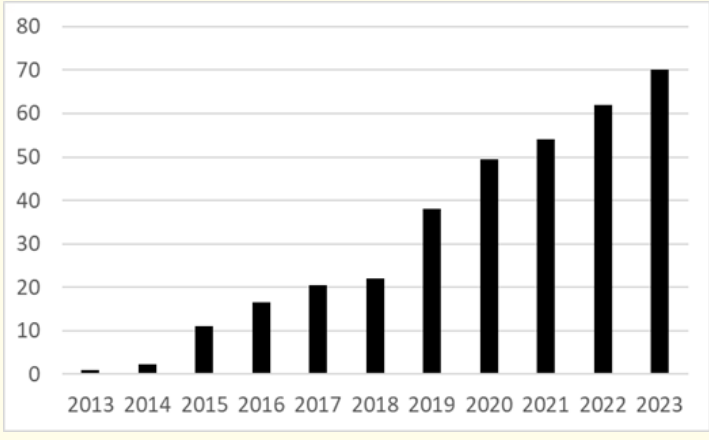

Figure 1: Estimated amount of the discharged ash in Japan [1].

Analytical method

As the simple elution test, 10g of the test ash was put into the beaker (volume 100mL), and water was added to the beaker to make total water 100mL, then the water was filtrated using filter paper (ADVANTEK 5A) after 1 minute of stirring. The filtrate was investigated using following analytical methods.

pH; glass electrode method

- **Fluorine:** The concentration of fluorine was analyzed by a simple test method (Pack Test, manufactured by Kyoritsu Rikagaku Co., Ltd.) or by the Alizarin-Complex colorimetric method. In this method, 5% of acetylacetone (Fuji Film - Wako Pure Chemical Industries, Ltd.) was added to prevent color development interference such as aluminum [10].

Insolubilize agents under consideration

Various phosphates (see below) and sewage ash [11] which contains large amounts of phosphorus were selected as a possible fluorine insolubilize reagent. Fluorine insolubilize agent considered to be needed water-soluble phosphate compounds, and aluminum phosphate or calcium hydrogen phosphate are considered ineffective which has lower solubility. However, these reagents can make effective by addition of an acid which make it water-soluble. In this study, effect of the addition of sulfuric acid or phosphoric acid was investigated.

<Reagents used>

- Calcium dihydrogen phosphate ($Ca(H_2PO_4)2H_2O$; (Kanto Chemical Co., Ltd.)
- Aluminum phosphate ($AlPO_4$); (Kanto Chemical Co., Ltd.)
- Calcium hydrogen phosphate ($CaHPO_4$); (Taihei Ceramics Pharmaceutical Co., Ltd.)
- Sewage sludge incineration ash: Yokkaichi City Hinaga Purification Center discharged, phosphorus content (P_2O_5: 18%)
- Sulfuric acid; (Kanto Chemical Co., Ltd.)
- Phosphoric acid; (Kanto Chemical Co., Ltd.)

Experimental method

Insolubilize treatment

To make the test ash, mentioned above, 10 g of the raw ash was put into a 100 mL beaker, and 5mL of aqueous sodium fluoride solution (0.1 mg/mL) was added.

As the insolubilize treatment, each possible insolubilize agent as mentioned were added to the test ash with 5 mL of supplemental water, and mixed 1 minute, followed by the simple elution test.

Simple elution test

Various insolubilize agent were added to the test ash mentioned above, and the elution properties of fluorine were compared according to the procedure shown in figure 2. Since conventional elution tests are conducted at a solid-liquid ratio of 1:10, therefore, 90 mL of water (total water volume of 100 mL take account of the water content in test ash) was added for the elution test. After stirring with a glass rod for 1 minute, sample were filtrated using filter paper (ADOVANTEC 5A), and the fluorine concentration of the filtrate was analyzed by the simple elution test. As a control, 10g of test ash was similarly put into a beaker, and 100mL of water (total volume) was added, and the treatment was performed (Figure 2).

	Raw ash 1
Water content	13
Ignission loss	7.6
Color	Dark gray

Table 1: Properties of raw ash.

Element	Content
Al_2O_3	6.3
SiO_2	44
P_2O5	2.3
SO_3	2.7
K_2O	6.7
CaO	24
Fe_2O_3	7.5
Others	6.5

Table 2: Chemical composition of the ashes.

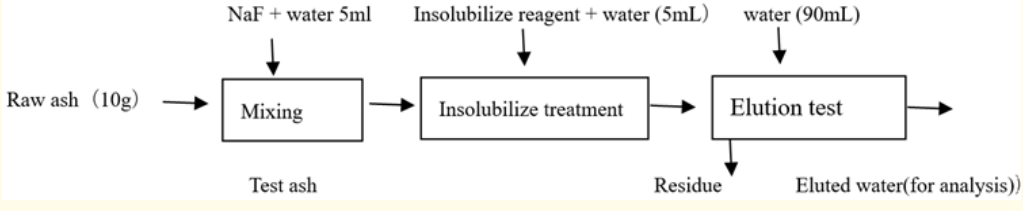

Figure 2: Procedure of the experiment.

Results

Preliminary test results

The fluorine insolubilize performance of the various phosphorus compounds or combinations of these compounds and an acid were investigated using the method as mentioned.

Calcium dihydrogen phosphate was found to be effective. No significant effect was observed on an aluminum phosphate and monocalcium phosphate or sewage sludge ash without acid addition. However, effect was confirmed by the addition of sulfuric acid or phosphoric acid to the compounds mentioned above (Table 3).

Fluorine elution trend with the reagent addition amount

We investigated the relationship between the added amount of the reagent and the fluorine concentration of the eluted water using some reagents considered to be effective (shown in the table 3), like calcium dihydrogen phosphate and the mixture of H_2SO_4 or H_3PO_4 and aluminum phosphate, monocalcium phosphate or sewage sludge ash.

The fluorine concentrations of the eluted water were decreased by the addition of the reagents shown in the figure 3 or figure 4.

Reagent in investigation	Additional reagent	Addition ratio	Effect	Reference
$AlPO_4$	None		×	
$AlPO_4$	H_2SO_4	Ratio (Mol.)1:1	○	Effective in pH>4
$AlPO_4$	H_3PO_4	Ratio (Mol.)1:1	○	Effective in pH>4
$Ca(H_2PO_4)_2$	None		○	
Sewage sludge ash	None		×	
Sewage sludge ash	H_2SO_4	Ash 10g: H_2SO_4 4g	○	Effective in pH>4
$CaHPO_4\,2H_2O$	H_2SO_4	Ratio (Mol.)1:1	○	Effective in pH>4
$CaHPO_4\,2H_2O$	None		△	slightly

Table 3: Outline of the effectiveness of the reagents.

○; Effective △; Effective (slow) ×; not effective

For 10g of the test ash, the eluted fluorine concentration was become lower than 0.8 mg/L (Japanese Environmental Standard) in the leaching test by addition of 0.05g of $AlPO_4$ (addition of H_2SO_4 or H_3PO_4). Also, the fluorine concentration became lower than 0.8 mg/L by the addition of 0.1g of calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$, calcium hydrogen phosphate ($CaHPO_4$+H_2SO_4) and the sewage ash (ash+H_2SO_4) as shown in figure 3 or figure 4.

Aluminum phosphate is highly effective but expensive. Calcium hydrogen phosphate is suitable from a cost standpoint. Sewage sludge incineration ash is cost-effective, but the route for obtaining incineration ash has not yet been established. It is also necessary to check the risk of harmful substances leaching from them.

pH change during fluorine elution prevention treatment.

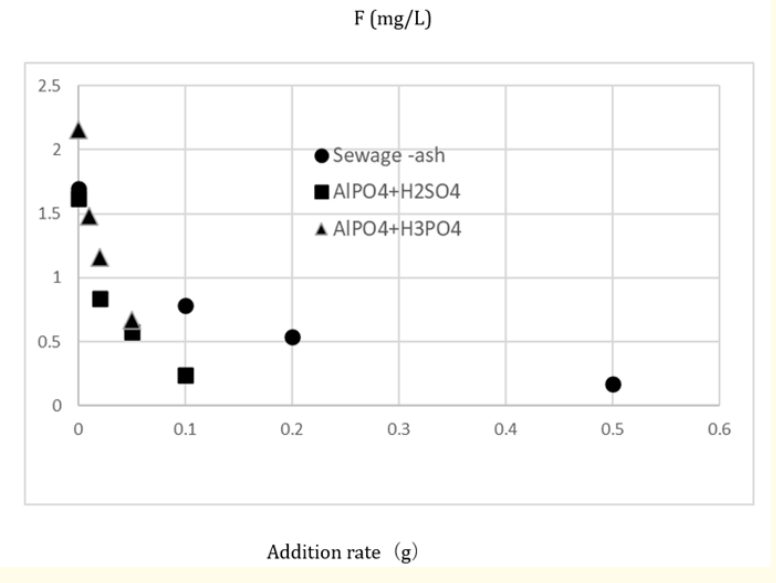

Figure 3: Relation with the reagent addition rate (ash: 10g) and eluted fluorine concentration (1).

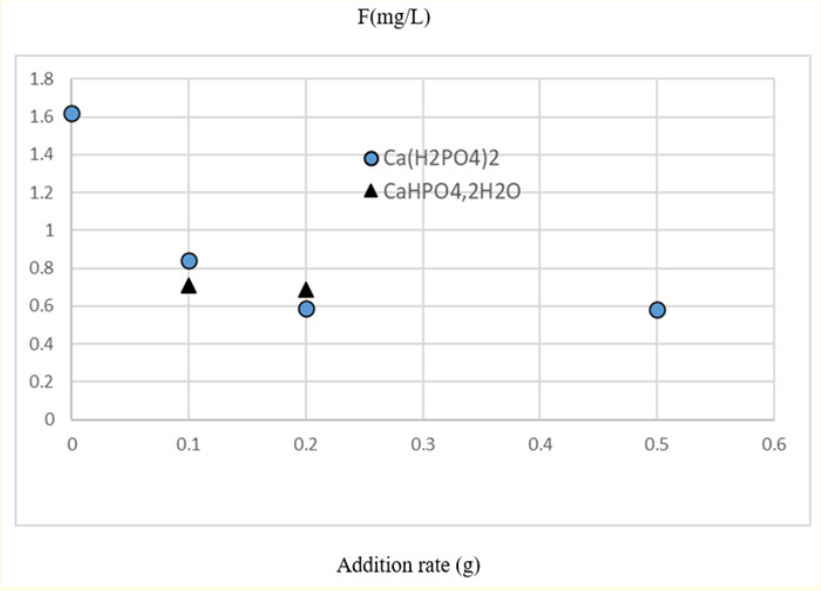

Figure 4: Relation with the reagent addition rate (ash: 10g) and eluted fluorine concentration (2).

Most of the incinerated ash is alkaline, but since the insolubilize agents are acidic, and be expected that the alkalinity of the ash will be weakened by the treatment. When we investigated the pH trend before and after the above treatment, we found that the pH of the eluate decreased from alkaline (around pH 10) due to the addition of the reagent, and decreased to around 7 when the amount added exceeded about 0.2 g per 10 g of ash. (Figure 5).

Consideration

Insolubilize effect of fluorine in incinerated ash was observed by combination of sulfuric acid or phosphoric acid and aluminum phosphate, or calcium phosphate, etc. The formation of a calcium phosphate apatite is assumed to be the function of this [12].

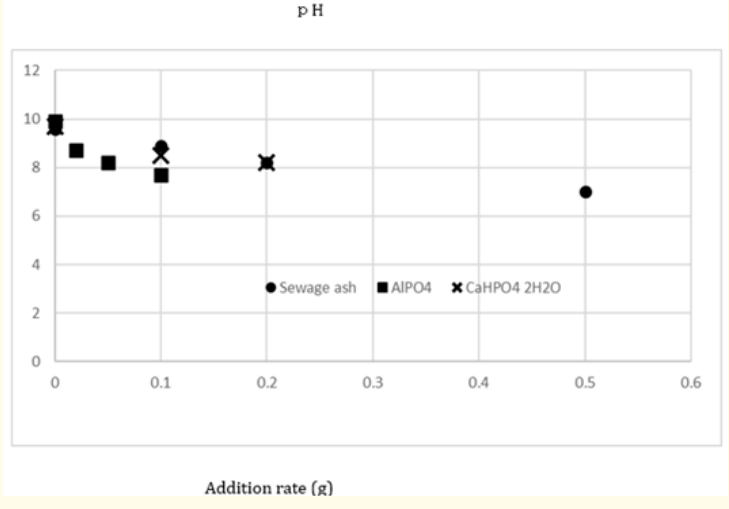

Figure 5: Relation with the reagent addition rate (ash: 10g) and pH of the eluted water.

Phosphoric ion combines with calcium ion to form calcium phosphate apatite [13]. It has been reported that this apatite compound binds with various ions and becomes insolubilized according to Reaction Formula I and Reaction Formula II [14].

$10Ca(OH)_2 + 6PO_4^- = Ca_{10}(PO_4)_6.(OH)_2$----------(I)

$Ca_{10}(PO_4)_6.(OH)_2 + 2F^- = Ca_{10}(PO_4)_6.F_2 + 2(OH)^-$----------(II)

To form calcium phosphate apatite, water-soluble phosphorous compounds such as phosphoric acid, ammonium phosphate, and sodium phosphate are used as phosphates ion sources. Since calcium is normally contained in large amounts in incinerated ash, it is thought that the apatite compound can be easily formed by adding phosphoric acid or a water-soluble phosphorous compound. Calcium phosphates ($Ca_3(PO_4)_2$, $CaHPO_4$) or aluminum phosphate have low water solubility, but they can be effective by increasing the solubility of phosphorous by adding sulfuric acid to make them acidic.

In this experiment, control the elution of the fluorine from incinerated ash is considered to effective by adding sulfuric acid to various phosphates compounds to make them acidic. In addition, incinerated ash is usually alkaline, and the addition of these agents are expected to have a neutralizing effect.

Aluminum phosphate is highly effective but relatively expensive, on the other hand, calcium phosphate-based chemicals are generally used as fertilizers and are relatively inexpensive, so they are considered to be low-cost treatment agents.

From the perspective of reducing reagent costs, it is desirable to use sewage incinerated ash, but there is no established route to obtain the sewage ash, and investigation of the other hazardous substances in the sewage ash should be needed. Other possible sources, include chicken manure which contains a large amount of calcium phosphate will be possible.

The main component of insolubilize agent used this method is phosphate compounds, and it is thought that this reagent can also be used as a fertilizer.

Many heavy metal phosphates are insoluble in water, furthermore has been reported that the apatite compounds combine with boron to make it insolubilize [15], so it is expected that it may also be used as an insolubilize reagent for harmful substances other than fluorine.

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