The Development of a Fluorine Removal Agent Using Incinerated Ash (II)

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Abstract: The compounds of aluminum phosphate are used to remove the fluorine compounds from wastewater. The fluorine removal agent using the ash of sewage sludge and the municipal waste in addition to sulfuric acid were investigated. The removal agent showed high removal performance, and the fluorine concentration of the treated water reached below 0.1 mg/L, and the noticeable elution of the harmful metals from the ashes were not found in this experiment.

Key words: Incinerated ash, fluorine removal, water treatment.

1. Introduction

Fluorine is widely distributed in the environment [1, 2] and is widely used as an important material especially in semiconductor industries. The removal of fluorine compounds is known as a difficult matter due to its solubility in water [3], and some pollution has been reported [4, 5]. To make an advanced removal technique, phosphorus containing materials are considered useful, and some studies have taken place [6, 7]. We found that the mixture of aluminum phosphate and the ash of municipal waste is effective [8, 9]. However, in order to make more low cost removal agents, cheap raw materials instead of aluminum phosphate are needed. The incinerated ash of sewage sludge contains significant amounts of phosphorus existing in a form of aluminum phosphate, and considered possible to be a new raw material [10, 11].

Another aspect is that increasing amounts of large amount of the ash of waste has become an important matter, and finding many usages is an important matter.

We expected that the mixture of the ash of sewage sludge and the ash of municipal waste is effective for the fluorine removal, and will promote the waste recycling. From this aspect, the experiments with the fluorine removal agent using these ashes were carried out.

2. Methods

2.1 Materials

As raw materials, the incinerated ash of municipal waste (referred to as EP-ash) and ash of sewage sludge (refer to sewage-ash) are used. The chemical components are shown in Table 1. The EP-ash is mainly composed of CaO, and SiO₂ and contains a significant amount of Al₂O₃ and Fe₂O₃. These components are considered to be derived from woody waste or garbage. The chemical composition of the sewage-ash is composed of SiO₂, CaO, Fe₂O₃ and significant amount of P₂O₅.

2.2 Test Water

The following test waters were prepared:

Test Water-I: Sodium fluoride reagent, diluted with pure water to adjust the fluorine concentration to about 5 mg/L.
Table 1  Composition of raw ash (using X-ray analyzer).

| Classification | SiO₂ | Al₂O₃ | CaO | P₂O₅ | Fe₂O₃ | SO₃ | Cl  | Other |
|----------------|------|-------|-----|-------|-------|-----|-----|-------|
| EP-ash         | 26.4 | 7.3   | 34.9| 1.0   | 9.7   | 4.4 | 4.6 | 11.7  |
| Sewage ash     | 32.1 | 7.2   | 14.1| 17.2  | 18.0  | 1.5 | 0.2 | 9.7   |

Unit: Wt %.

Fig. 1  Experimental procedure.

Test Water-II: Factory wastewater containing fluorine.

2.3 Experiment Procedure

In reference to the fluorine removal, the aluminum phosphate in the ash is expected to react with the fluorine compounds in a form of ionized state. The aluminum phosphate dissolves in water in acidic condition as phosphate ion. In order to dissolve the aluminum phosphate in the ash, a small amount of dilute sulfuric acid was added to the sewage-ash, and was kneaded with EP-ash to make a removal agent. This removal agent was put into Test Water-I, after stirring for several minutes, filtration was carried out using a filter paper (Toyo Roshi Kaisha, ADVANTEC, 5 A), and the fluorine concentrations of the filtrate (treated water) were analyzed. (Fig. 1).

2.4 Analysis Method

The analysis method is as follows:

pH: Glass electrode
Fluorine ion: Automatic Analyzer (Auto Analyzer, manufactured by Bertech Corp.)
Copper, zinc, cadmium, lead, arsenic, selenium: ICP-MS

3. Results and Discussions

3.1 Mixing Ratio of the Raw Materials

In order to find an optimal mixing ratio to make the removal agent, 2 mL of H₂SO₄ (98%) was added to 10 g of the sewage-ash with 100 mL of water (refer to acidic-mixture). And 5 g of EP-ash was mixed with 1 to 10 mL of the acidic-mixture respectively. Later, 100 mL of the Test Water-I was added to them respectively, and the fluorine removal test was carried out in the way as mentioned. The fluorine concentration and pH in the filtrate were shown in Fig. 2.

The fluorine concentration in the treated water became lower toward the high acidic-mixture addition rate, and the pH also became lower (about pH 6) because of the influence of H₂SO₄. From the result, we decided the optimal addition rate of the acidic-mixture was 10 mL.

In order to find an optical H₂SO₄ addition rate to make the acidic-mixture, some kinds of acidic-mixture which contains different amounts of H₂SO₄ were prepared. And 1 mL to 6 mL of the H₂SO₄ was mixed with 10 g of the sewage-ash respectively, and diluted to 100 mL by the addition of water, and using 10 mL of them, the fluorine removal test was carried
out as mentioned above.

Higher removal performance was found in higher H$_2$SO$_4$ addition rate toward addition rate 3 mL, but further, in higher addition rate (4 mL or 5 mL), then pH became acidic condition (pH lower than 5), and fluorine removal effect was decreased (shown in Fig. 3). Especially, in the case of the addition rate of 5 mL, fluorine concentration of the treated water became higher than that of Test Water-I, which is considered to be the elution of fluorine which is originally contained in the raw ash.

As a result, an appropriate blend rate to make the removal agent was judged as below.

EP-ash: 5 g, and acidic-mixture 10 mL

Acidic mixture is made by the addition of 2 mL H$_2$SO$_4$ to the 10 g of the sewage-ash with 100 mL of water.

3.2 Investigation on the Volume of Test Water

In order to confirm the removal ability to a large volume of the Test-Water-I, the investigation was carried out on the various volumes of the Test Water-I (100 mL to 900 mL). In the case of 100 mL, the fluorine concentration of the treated water reached about 0.1 mg/L, then, the fluorine concentration of the treated water became higher by increasing the volume of the Test-Water toward 900 mL. However, in the case of Test-Water 900 mL, the fluorine concentration of the treated water was confirmed to be lower than the Japanese environmental standard (Fig. 4).

3.3 Wastewater Treatment Experiment

The fluorine removal experiment was carried out on the agent of the optimal mixing rate as mentioned using 1000 mL of Test Water-II. The analytical results are shown in Table 2. Fluorine in the Test Water-II decreased from 1.4 mg/L to 0.4 mg/L and it was possible to keep it below the Japanese environmental standard.

Fig. 2 Relation between F concentration of the treated water and the mixing rate of the acidic-mixture.

Fig. 3 Comparison with the F concentration of the treated water and the H$_2$SO$_4$ addition rate.
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4. Summary

Using the incinerated ash of the municipal waste and sewage sludge, research on the removal method of the fluorine was carried out. The fluorine removal agent made from the ash has an ability to remove a low concentration of fluorine. It will possibly be an inexpensive removal agent, and be a way to recycle incinerated ash. However, the ash usually contains some salts and many harmful elements [12], so the influences of these materials should be taken into account, and many further studies are needed further.

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