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Ammonium Phosphate Recovery from Incinerated Ash of Sewage Sludge

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Abstract: In order to establish a phosphorus recovery method, some phosphorus recovery methods from incinerated ash of sewage sludge were investigated. The phosphorus which is recovered from ash with acidic treatment, is mainly composed of aluminum phosphate. In order to remove aluminum component from aluminum phosphate, alum formation processes was investigated. The phosphorus extracted from ash was mixed with ammonium sulfate in existence of sulfuric acid, and formed alum (aluminum ammonium sulfate), and was separated by crystallization. The phosphorus which had aluminum removed, was recovered by addition of ammonium hydroxide. The recovered phosphorus was considered ammonium phosphate by X-ray analysis and XRD.

Key words: Incinerated ash, sewage sludge, acid treatment, ammonium phosphate, alum.

1. Introduction

Sewage sludge contains significant amounts of phosphorus, and in order to recover the phosphorus from it, many investigations have been carried out [1-5].

The phosphorus in the sludge is regarded as existing mainly as a form of aluminum phosphate [6], which has few uses, and the existence of aluminum component is not good for fertilizer and is a bad influence on many plants, therefore, some recovery methods which can recover phosphorus with low aluminum content are recommended. In acidic treatments, almost of all phosphorus in the ash can be extracted from the ash, however, the extracted phosphorus consists mainly of aluminum phosphate [7]. On the contrary, in alkali treatments, low aluminum contents of phosphorus can be recovered [8], however, the recovery rate is low compared to acidic treatments, and in order to attain higher extraction rates, hydrothermal processes are considered useful compared to conventional alkali extraction [9].

Aluminum ions react with monovalent cations like NH_4^+, K^+, Na^+ under existence of H_2SO_4, and form alum, it is widely known. Some alum like $AlNH_4(SO_4)_2$ or $AlK(SO_4)_2$ has low solubility in water at low temperature. As mentioned, phosphorus is thought to exist mainly as a form of aluminum phosphate, aluminum element is considered to react with these cations, and formed alum which can be separate by crystallization resulting in formation of H_3PO_4 as shown in Eq.(1) [10-12].

$$AlPO_4 + H_2SO_4 + (NH_4)_2SO_4 \rightarrow AlNH_4(SO_4)_2 + H_3PO_4 \quad (1)$$

The formed phosphoric acid is expected to contain significant amounts of non-reacted H_2SO_4, and separation of these contaminants is thought not easy. In order to confirm the reaction, neutralization of the phosphoric acid using NH_4OH is considered easy, and we investigated the basic condition of the method.

2. Method

2.1 Ash

The incinerated ash which was discharged from Yokkaichi municipal waste water treatment facility

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was used in the experiment. The ash is made from sewage sludge which is incinerated in a fluidized bed incinerator at 850 °C. Chemical components of the ash is shown in Table 1.

2.2 Phosphorus recovery Method

The outline of the phosphorus recovery method is shown in Fig. 1. Phosphorus in the ash is extracted using an aqueous solution of H_2SO_4. In order to complete alum formation, further, small amounts of H_2SO_4 was added to the extract. Later, powder of ammonium sulfate was dissolved to the extract at room temperature, and the mixture is cooled below 5 °C.

After one day, crystal of alum is formed, and separated by filtration. Aq. solution of ammonium hydroxide is added to the extract to adjust the pH 4 ~ 5 which is considered to be best for the separation of non-reacted phosphorus ($AlPO_4$ or $FePO_4$) [13]. Non-reacted aluminum phosphate is precipitated, and removed by filtration as residue, and the aluminum removed phosphorus can be recovered by vaporization of the filtrate.

3. Result and Discussion

3.1 Aluminum Phosphate Preparation

Aluminum ammonium sulfate ($AlNH_4(SO_4)_2{\cdot}12{\cdot}H_2O$) has low solubility in water at low temperature (4 g in 100 mL water at 0 °C) [14]. In order to make crystallization of the alum, concentration, about 100 g/L of the aluminum phosphate is considered to be needed. However, in consideration of the usual extraction rate (solid-liquid ratio 1:10), aluminum phosphate concentration in the extract is expected to be low, and further concentration will be needed. In order to solve the matter, we adopted a high solid- liquid ratio and counter current extraction method [15, 16], and possible aluminum phosphate concentration (about 80 g $AlPO_4$/L) can be attained by adoption of solid-liquid ratio 1:3.

Raw ash and treated ash was analyzed using X-ray analyzer followed by dehydration. Phosphorus and aluminum in the ash was degreased by acid treatment, and SO_3 component was increased depending on the reaction of H_2SO_4 and calcium component in the ash (Table 1). The phosphorus extraction rate was calculated from the elemental composition, and considered about 80%.

3.2 Addition Rate of the Ammonium Sulfate

In order to find the optimal addition rate of ammonium sulfate, 100 mL of aluminum phosphate solution (P: 1.6%, H_2SO_4: 7%) which was extracted from ash was mixed with sulfuric acid (9 g), and 3 g to

Table 1 Elemental composition of the ash.

Element	Raw ash	Treated ash
Al_2O_3	18.1	7.6
SiO_2	31.2	44.3
P_2O_5	18.1	3.4
SO_3	1.6	14.6
K_2O	1.7	1.8
CaO	9.5	10.5
Fe_2O_3	12.3	13.4
Others	7.5	4.6

Unit: wt %.

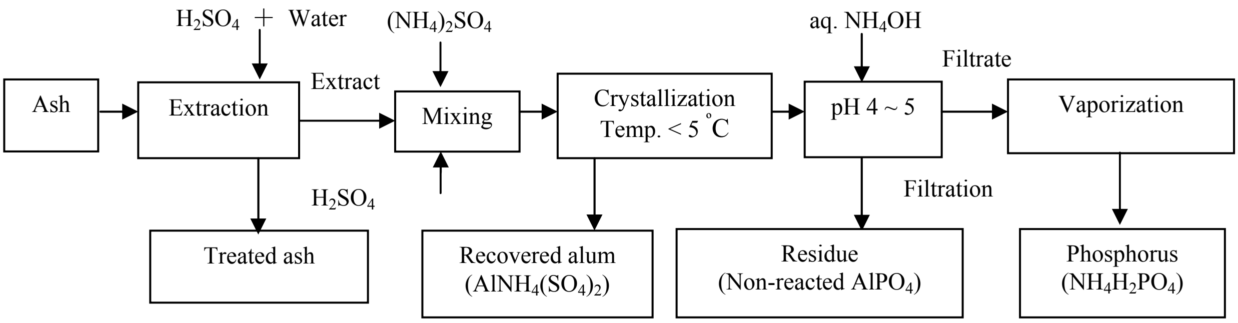

Fig. 1 Recovery method.

15 g of ammonium sulfate powder was added, and dissolved at room temperature. Later, the mixture was cooled to 3 °C, 24 h later, formed crystal (which expected to be alum) was recovered. The amount of the formed crystal has increased by the addition of ammonium sulfate toward the equivalent ratio, when the addition rate reaches 7 g larger than the chemical equivalent amount, increasing rate of the formed crystal tend to be plateau (Fig. 2). The most suitable addition rate is considered to be 7 g more than equivalent (surplus).

3.3 Addition rate of Sulfuric Acid

In order to find the optimal addition rate of sulfuric acid, 100 mL of aluminum phosphate solution (P: 2.3%, H_2SO_4: 8.6%) which was extracted from ash was mixed with ammonium sulfate (12 g), and 7 g to 24 g of sulfuric acid was added at room temperature. Later, the mixture was cooled at 3 °C, 24 h later, formed crystal (which expected to be alum) was recovered. The amount of the formed crystal has also increased by the addition of sulfuric acid toward the equivalent ratio, when the addition rate reaches 10g larger than the chemical equivalent amount, increasing rate of the crystal tend to be plateau (Fig. 3). The most suitable addition rate is considered to be 10g more than equivalent (surplus).

3.4 Composition of the Recovered Phosphorus

In order to confirm the formation of the ammonium phosphate, phosphorus containing water (300 mL) which was extracted from ash using H_2SO_4 was prepared. The phosphorus and H_2SO_4 concentration of the phosphorus containing water is estimated to be P: 3%, H_2SO_4: 7%. Later, 43 g of H_2SO_4 and 34 g of $(NH_4)_2SO_4$ was added to the phosphorus containing water, and dissolved at room temperature. The mixture was cooled for 24 h at 3 °C, and formed crystal (108 g) was separated using filter paper (Toyo Roshi Kaisha, Ltd. ADVANTEC).

The crystal formed by cooling was expected to be alum, and dehydrated at 180 °C for analysis, and analyzed using chemical mass balance, and the result (shown in Fig. 4) indicates the formation of alum. Small amount of P_2O_5 is found, which is considered to be derived from formed phosphoric acid, and remained in the crystal.

In order to recover phosphorus, 58mL of ammonium hydroxide solution (NH_3: 28%) was added to the filtrate, and adjusted at the pH 4 ~ 5. Light charcoal precipitate was formed which was expected as non-reacted phosphate, and removed by filtration using filter paper as a residue, and dried at 105 °C (amount: 48 g). The phosphorus which was expected to be ammonium phosphate (64 g), was recovered by evaporation of the filtrate, and analyzed using XRD and X-ray analyzer followed by drying (105 °C).

The residue was mainly composed of P_2O_5, SO_3, Fe_2O_3 and NH_3 (estimated by chemical composition), and most of the aluminum component was removed.

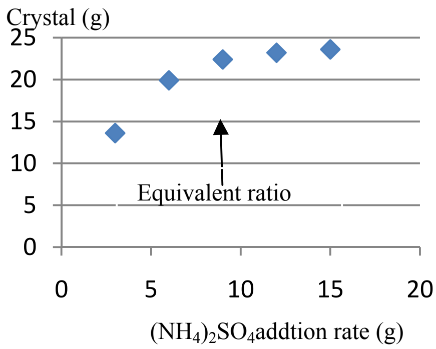

Fig. 2 Relation with formed crystal and ammonium sulfate.

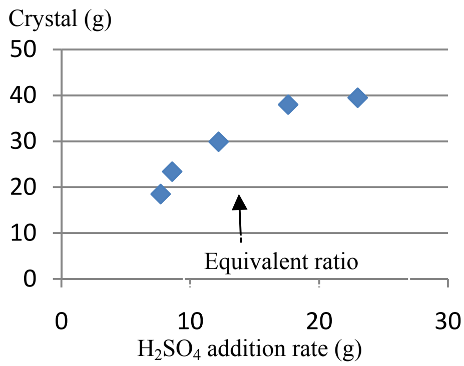

Fig. 3 Relation with formed crystal and sulfuric acid

The residue is considered to consist of ferric phosphate and ammonium sulfate which remained in the residue. Aluminum component was almost removed by the crystallization, however, significant amounts of phosphorus was remained in the residue as ferric phosphate. The ash contains significant amounts of iron [17]. The iron component in the extract forms ferric aluminum sulfite ($FeNH_4(SO_4)_2$) which is soluble in water, and is considered to be remained in the residue.

The recovered phosphorus was also analyzed using an X-ray analyzer, and is mainly composed of P_2O_5 and SO_3. As mentioned, X-ray analyzer used on this experiment cannot detect nitrogen element, modified composition is shown in Fig. 4. We concluded that the recovered crystal is alum ($AlNH_4\ (SO_4)_2 \cdot 12H_2O$) by the composition and XRD data (Fig. 5). The recovered phosphorus is also considered to be a mixture of ammonium phosphate ($NH_4H_2PO_4$) and ammonium sulfate (Fig. 6).

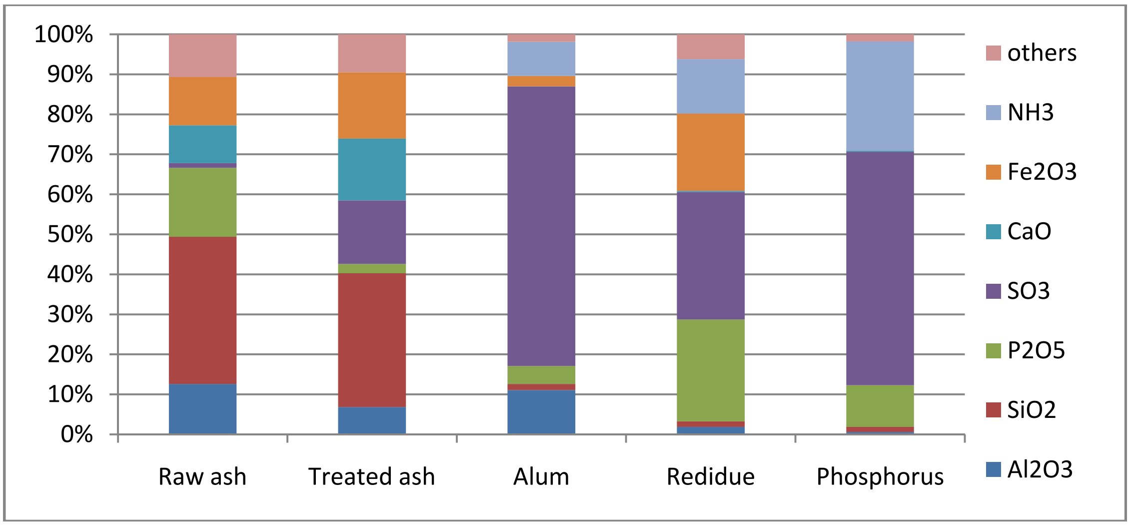

Fig. 4 Chemical composition of the recovered materials.

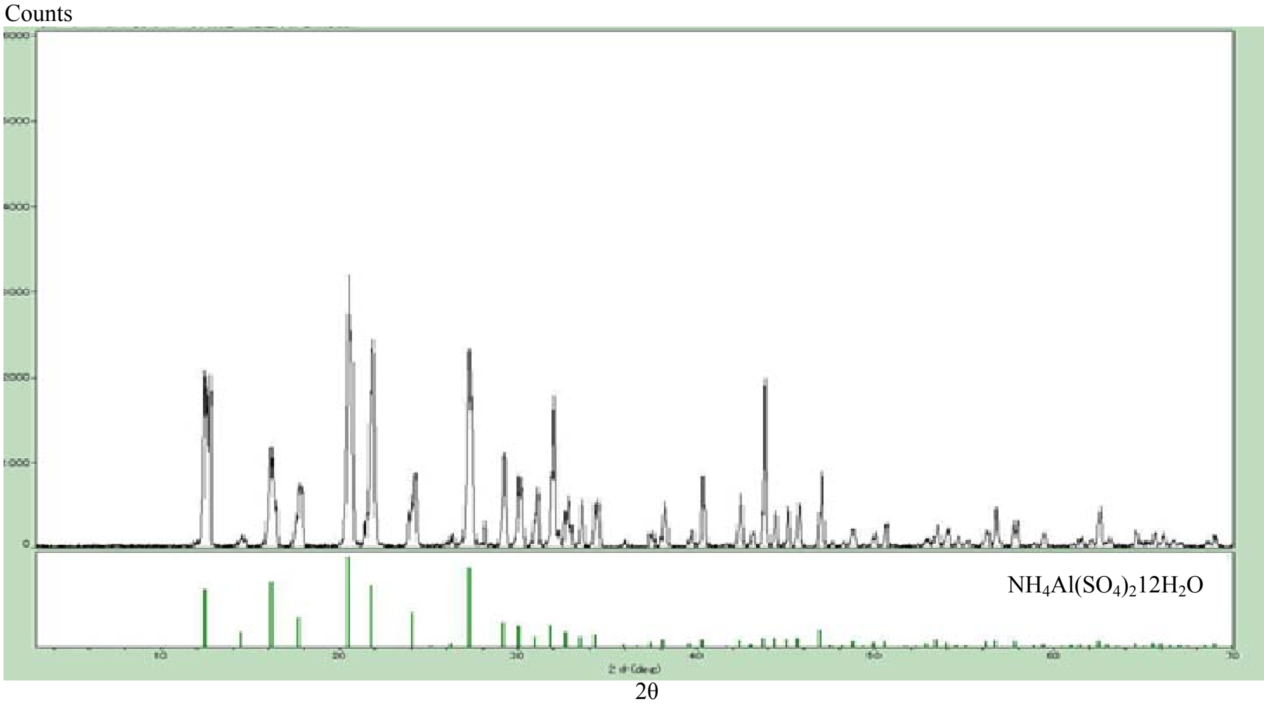

Fig. 5 XRD of the recovered crystal.

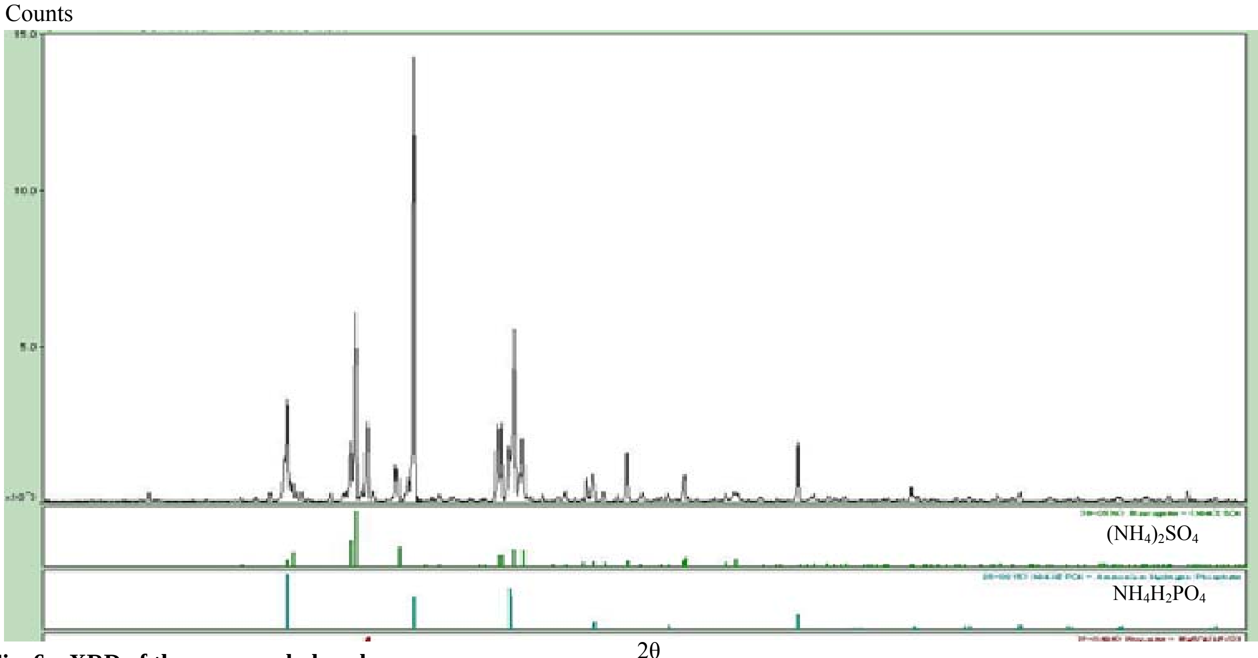

Fig. 6 XRD of the recovered phosphorus.

4. Conclusions

In order to recover phosphorus with low aluminum content, a recovery method by alum formation was investigated. The aluminum component in the phosphorus formed alum by addition of $(NH_4)_2SO_4$, and was separated from phosphorus, and ammonium phosphate was recovered.

Alum can be used in food additives and also many industrial raw materials, The recovered ammonium phosphate contains ammonium sulfate, and the separation of the mixture is considered to be difficult. Ammonium phosphate and ammonium sulfate can be used as fertilizer [18], therefore, this mixture is expected to be a fertilizer.

However, significant amounts of phosphorus remains in the residue, and a high phosphorus recovery rate will be needed.

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