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A Technique for Recovering Phosphorus Salt from Incinerated Ash of Sewage Treatment Sludge

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Incinerated ashes of sewage treatment sludge contain a significant amount of phosphorus. Since phosphorus is one of the inevitable materials for us, many studies on recovering phosphorus from the ash are going under way. However, the phosphorus recovered from the sludge is mainly in the form of aluminum phosphate. In order to promote the utilization of them, aluminum ammonium sulfate formation processes was studied. Aluminum phosphorus recovered from incinerated ash of sewage treatment sludge by using H_2SO_4 and $CaCO_3$ was treated with H_2SO_4 for dissolving phosphorus. Dissolved phosphorus was mixed with ammonium sulfate, and the resulted aluminum ammonium sulfate was recovered at 3℃ in acidic condition. Phosphorus removed from aluminum phosphate was recovered as sodium phosphate by addition of sodium bicarbonate and sodium hydroxide followed by vaporization. As another processes, ammonium phosphate was recovered by addition of ammonium hydroxide solution as the same way of sodium phosphate.

Keywords : Sewage treatment sludge, ash, phosphate salt, recovering technology

1. INTRODUCTION

Incinerated ashes of sewage treatment sludge contain a significant amount of phosphorus. However, it's recovering technology has not been well established, and these ashes are not used as phosphorus resources. Since the retrieval of phosphorus is limited to a relatively small geographical area on earth, Japan is importing almost all of them from other nations. In order to establish the phosphorus recovering technology from these ashes, studies on the processes of acidification followed by alkalization are going under way [1]. However these recovered phosphorus were mainly in the form of aluminum phosphate [2-3] which has very limited applications for practical uses. In order to promote the utilization of them, some methods, changing the recovered aluminum phosphate to phosphoric acid [4] or another phosphate salts such as sodium phosphate or calcium phosphate are going under way [5-7]. Aluminum phosphate is expected to react with ammonium ion under strong acidic condition to form aluminum ammonium sulfate. Aluminum ammonium sulfate has low solubility at low temperature, therefore, aluminum component in the aluminum phosphate can be separated as shown in Eq.1. Consequently, aluminum free phosphorus reacts with alkali metals or ammonium ion to form sodium phosphate or ammonium phosphate (Eq.2,3). Based on this reaction, aluminum ammonium sulfate-forming process was studied for converting aluminum phosphate to other phosphate compounds in this research.

$$2AlPO_4 + (NH_4)_2SO_4 + 3H_2SO_4 = (NH_4)_2SO_4 \cdot Al_2(SO_4)_3 + 2H_3PO_4 \quad (1)$$

$$H_3PO_4 + 2NaHCO_3 = Na_2HPO_4 + H_2O + 2CO_2 \quad (2)$$

$$H_3PO_4 + 2NH_4OH = (NH_4)_2HPO_4 + 2H_2O \quad (3)$$

2. METHOD AND MATERIALS

2.1 Raw Materials

An ash of incinerated sewage treatment sludge associated with the Yokkaichi City Municipal Water Treatment Facility was used. This ash was incinerated in a fluidization-type incinerator at 850℃ and it was a brown colored fine powder [8]. Main components of the ash and recovered phosphorus were shown in Table 1.

2.2 Experimental Method

First of all, procedures A and B (Fig. 1) were thought as the basic recovering processes of phosphorus. In the procedure A, incinerated ash of sewage treatment sludge is mixed with sulfuric acid solution for dissolving phosphorus. The acidic solution which contains phosphorus from the ash needs to be concentrated to the maximum concentration available for crystallize aluminum ammonium sulfate. Concentrated acidic solution run to the aluminum ammonium formation processes directly as shown in Fig.1. In the procedure B, phosphorus in the ash can be recovered as a mixture of $AlPO_4$ and $CaSO_4$ by addition of calcium carbonate powder at pH 4 as shown in Fig.1. Using sulfuric acid, the recovered phosphorus is dissolved to make optimal concentration for crystallization of aluminum ammonium sulfate. The dissolved phosphorus can be run to the aluminum ammonium forming processes without concentration. However, procedure A was found difficult to operate under this experimental condition because of precipitation of SiO_2 and $CaSO_4$ eluted with phosphorus on the evaporation processes, and iron which also contained in the acidic water caused inadequate crystallization of aluminum ammonium sulfate. Therefore, procedure B was adopted in this study.

In the run 1, recovered phosphorus ($AlPO_4$ +$CaSO_4$) from ash (procedure B) was treated with sulfuric acid. The acidic water which contains phosphorus ($AlPO_4$) was added ammonium sulfate, and kept at low temperature to crystallized aluminum ammonium sulfate, aluminum phosphate was changed to phosphoric acid. The processes water was treated with sodium bicarbonate, and non-reacted aluminum phosphate remained in the processes water was removed at pH 4.5. Sodium phosphate formed with this reaction was recovered by addition of sodium hydroxide at pH 9 followed by evaporation procedure.

In the run 2, aluminum ammonium sulfate formation processes were carried out by using ammonium hydroxide instead of sodium hydroxide (Fig. 2). Aluminum ammonium sulfate was recovered as run 1, Aluminum removed acidic solution was treated with ammonium hydroxide, and the formed ammonium phosphate was recovered at pH 4.5 by vaporization.

3. Results

In the run 1, 200g of phosphorus recovered from incinerated ash of sewage treatment sludge by using sulfuric acid and calcium carbonate was used. This phosphorus (Table 1) was treated with 1000mL of sulfuric acid solution (135g(H_2SO_4)+1000mLH_2O) to dissolve aluminum phosphate. Then, the aluminum phosphate reacted with 65g of ammonium sulfate to form ammonium aluminum sulfate at low temperature. In this reaction, 257 g of ammonium aluminum sulfate was recovered by crystallization followed by cooling at 3℃. Sodium phosphate was recovered after removal of non-reacted aluminum phosphate with addition of sodium bicarbonate (165g) followed by neutralization with sodium hydroxide (20g). The converting rate of aluminum phosphate to sodium phosphate was estimated 65%, and this rate is expected to be much higher by selecting the lower crystallization temperature.

In the run 2, 200g of phosphorus was dissolved with H_2SO_4 in the same way as the run 1. Dissolved aluminum phosphate reacted with ammonium sulfate, and no-reacted aluminum phosphorus was removed by addition of ammonium hydroxide solution (100g NH_3 28%). As the result of this reaction, ammonium phosphate (95g) was recovered by vaporization.

The recovered ammonium aluminum sulfate was analyzed by a X-ray diffraction analyzer, and confirmed the production of $(NH_4)_2SO_4Al_2(SO_4)_3$ $24H_2O$ with its spectra and ignition loss (52%). The composition of these recovered materials was analyzed by using a X-ray florescent analyzer. Results are shown in Table 3. The residue of acid treatment in the run1 consisted of SO_3 and CaO, therefore, the residue was thought to be calcium sulfate derived from the phosphorus ($AlPO_4$ +$CaSO_4$). The recovered aluminum ammonium sulfate consisted of Al_2O_3 and SO_3, and was considered almost to be aluminum ammonium sulfate, agreeing with the result of X-ray diffraction analysis well. Recovered sodium phosphate mainly consisted of Na_2O and P_2O_5, and was considered to be $Na_2HPO_412H_2O$ as evidenced by heating loss and recovering condition (pH9). However it also contained a large amount of

SO_3, suggesting the existence of $Na_2SO_4 10H_2O$ derived from by-reaction of sodium bicarbonate and sulfuric acid, and small amount of remaining $(NH_4)_2SO_4$.

Recovered ammonium phosphate (in the run2) consisted of SO_3 and P_2O_5, was considered to be a mixture of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ as evidenced by the mass balance and recovering condition.

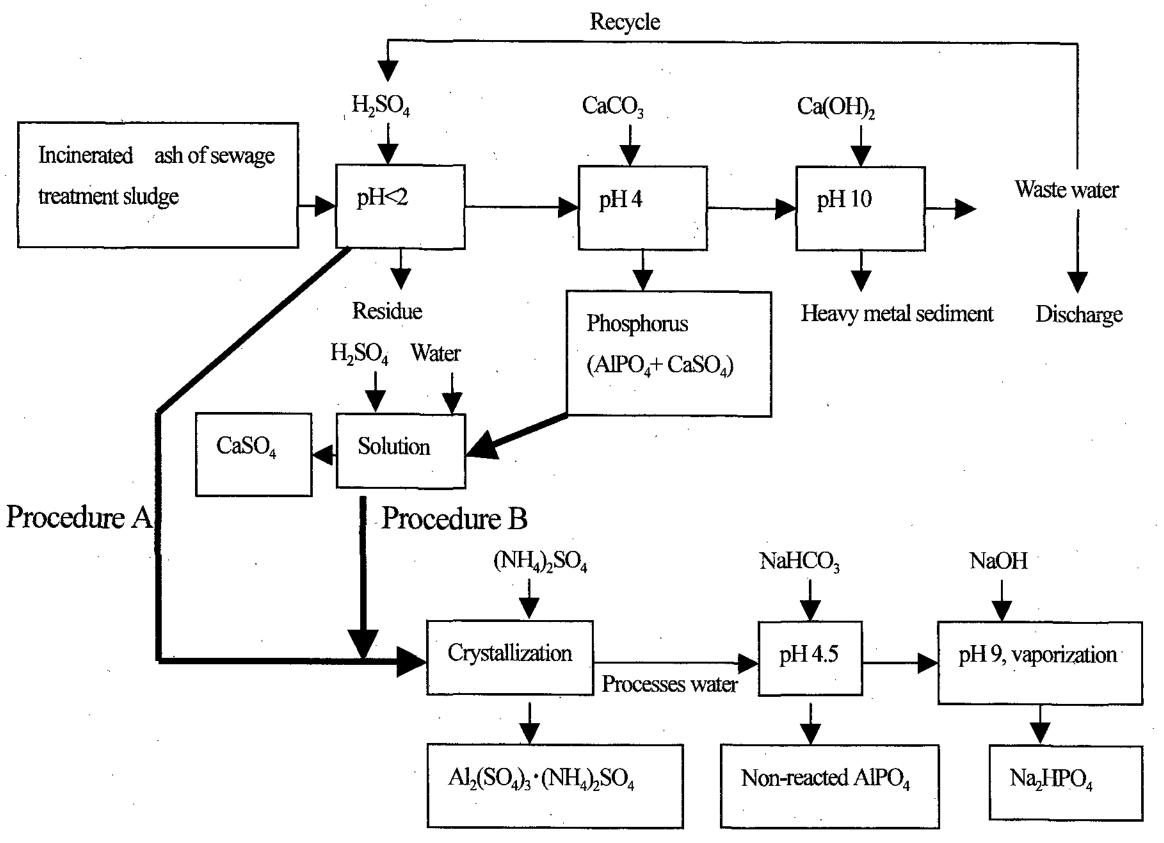

Fig. 1. Sodium phosphate recovering processes from incinerated ash of sewage treatment sludge (run 1)

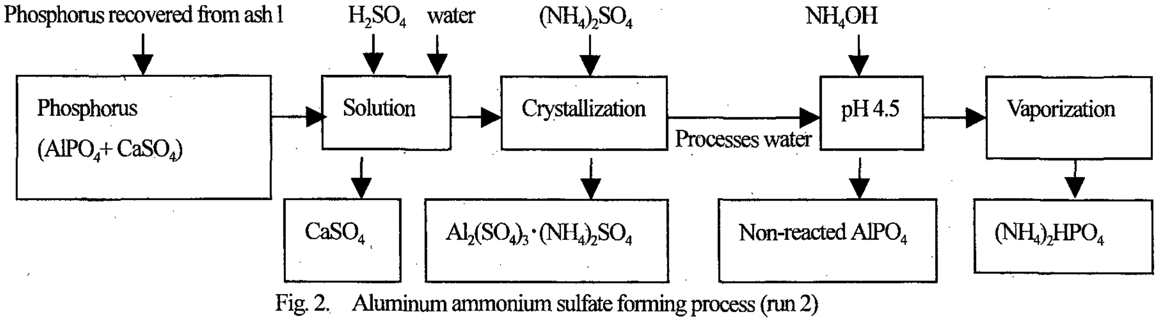

Fig. 2. Aluminum ammonium sulfate forming process (run 2)

Table 1. Composition of raw ash and phosphorus used in this experiment

Composition (%)	SiO_2	Al_2O_3	CaO	P_2O_5	SO_3	Fe_2O_3	Na_2O	Others
Ash	31.2	18.1	9.5	18.1	1.6	12.3	1.8	7.4
Phosphorus recovered from ash	0.09	12.7	31	21.8	31.4	2.6	<0.01	0.41

Table 2. Amount of recovered materials

	Residue of acid treatment ($CaSO_4$)	Recovered $Al_2(SO_4)_3(NH_4)_2SO_4 24H_2O$	Non-react $AlPO_4$	Recovered Phosphorus salt (Na_2HPO_4 $12H_2O$)	Recovered Phosphorus salt $(NH_4)_2HPO_4$
Run 1	95	253	32	310	—
Run 2	90	248	22	—	95

Unit: g. Phosphorus recovered from ash (200g) was used as for raw material in both run 1 or run 2.

Table 3. Composition of recovered materials

	Residue of acid treatment	Recovered aluminum ammonium sulfate	Non reacted $AlPO_4$	Recovered Na_2HPO_4 (Run1)	Recovered $(NH_4)_2HPO_4$ (Run 2)
Al_2O_3	0.07	17.2	5.0	<0.01	0.11
CaO	51.3	< 0.01	0.08	<0.01	<0.01
P_2O_5	0.04	0.56	30.0	24.7	26.6
SO_3	48.1	66.8	28.9	19.3	51.7
Fe_2O_3	0.01	0.10	11.3	<0.01	<0/01
Na_2O	0.06	< 0.01	0.05	52.1	<0.01
NH_3	<0.01	14.5	23.5	3.6	20.5
Others	0.42	0.84	1.17	0.30	1.09

NH_3 amount was calculated by mass balance

Fig. 3 X-ray diffraction pattern of the recovered aluminum ammonium sulfate

4. CONCLUSION

In order to establish the technology of recovering sodium phosphate or ammonium phosphate from incinerated ash of sewage treatment sludge, aluminum ammonium sulfate formation process has been carried out for the basic study. From experimental results, sodium phosphate or ammonium phosphate was recovered in the processes of aluminum ammonium sulfate formation. Therefore it can be concluded that this technology allows achieving the way for recovering phosphate salts from incinerated ash of sewage treatment sludge which contains a significant amount of phosphorus. However, recovered phosphate in this method contains other salts generated from by-reaction, and it needs much more study to find optimal condition of recovering phosphorus salts. Further more, middle-sized plant level test is needed to make this on practical use.

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