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A Technique for recovering Sodium phosphate from incinerated ash of sewage treatment sludge by Hydrothermal Synthesis

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Many studies on the phosphorus recovering technology from incinerated ashes of sewage treatment sludge are going under way. Incinerated ashes contain Si, Al, Ca and P as major components, therefore, phosphorus recovering method by zeolite forming processes is expected to be an effective method. As a test study, recovering of phosphoric salt by using hydrothermal technique was carried out. Incinerated ash of sewage treatment sludge was mixed with NaOH aq. solution, and the mixture was treated at high temperature. Sodium phosphate formed with this reaction was recovered by filtration followed by evaporation. To find out the optimal condition, various concentration of NaOH solution (solid/liquid = 1:1 to 1:4) was added to the ash, this mixture was treated at 20℃ to 180 ℃, for 1 hour to 24 hours, and phosphorus recovering rate of each run was observed. The highest phosphorus recovering rate (46%) was achieved at 100℃, with 8 hours of heating. The phosphorus removed ash was composed of SiO_2, Al_2O_3, Na_2O and had indicated methylene blue adsorption ability and higher specific surface area than untreated ash. The result indicated that there was formation of zeolite in the ash. Sodium phosphate recovered in this procedure was considered to be consisted of Na_3PO_4 and excess NaOH which can be recycled as hydrothermal processes.

Keywords : Sewage treatment sludge, Ash, Phosphorus, Zeolite, Recovering technology

1. INTRODUCTION

Incinerated ashes of sewage treatment sludge contain significant amount of phosphorus, and it seems to be an important phosphorus resource in future. However, recovering technology of phosphorus has not been highly developed, and the phosphorus in the ash is not effectively utilized as industrial raw materials. In order to establish the phosphorus recovering technology from these ashes, studies on the processes of acidification followed by alkalization are now in progress[2,3,4]. For promotion of the utilization of the recovered phosphorus, studies on recovering of phosphate salts such as sodium phosphate or calcium phosphate seem to be required.

Incinerated ashes contain large quantities of metals such as Si, Al and Ca, therefore, hydrothermal synthesis of zeolite was expected as one of the methods for the utilization of the ash such as fly-ash[1]. Phosphorus is expected to be combined with aluminum or calcium in the ash, therefore, sodium phosphate can be recovered by a hydrothermal synthesis of zeolite gel in the same way as shown in Scheme 1. Based on this reaction, we proposed sodium phosphate recovering processes by using hydrothermal synthesis as shown in Fig. 1. In these processes, ash is heated with an aqueous solution of NaOH, phosphorus can be separated from the ash accompanied by the zeolite formation, forms sodium phosphate, elute in the process water. The eluted sodium phosphate is recovered by crystallization. The residual process water contains excess NaOH, therefore, it can be recycled as a hydrothermal synthesis process water. For a test study, some experiments related to phosphorus salts recovering from incinerated ash were carried out.

Scheme 1

$(SiO_2, CaO, Al_2O_3, P_2O_5)$ + NaOH ⟶ $Na_2O \cdot Al_2O_3 \cdot xSiO_2$ + Na_3PO_4

Major components of incinerated ash of sewage treatment sludge

(CaO)

2. METHOD AND MATERIALS

2-1. Case studies on treating conditions

An ash of incinerated sewage treatment sludge coming from the Yokkaichi City Municipal Water Treatment Facility was used. The incinerated ash of sewage treatment sludge (12.5g) was mixed with an aqueous sodium hydroxide solution in a vessel made of fluoride resin. After sealing the vessel by a container made of stainless steel, the vessel was heated at 40-180℃. The hydrothermal synthesized ash was washed with 1.5 liter of distilled water, and it was recovered as materials like zeolite after drying process at 105℃. Sodium phosphate formed in this reaction remained in the washing water, and recovered by evaporation for analysis instead of crystallization process. Various conditions were studied by changing each parameter such as concentration of sodium hydroxide solution, liquid/solid(L/S) ratio, heating temperature and heating time. These treated ashes were analyzed by X-ray florescent analyzer. The phosphorus recovering rate was estimated by the difference of P_2O_5 concentration between incinerated ash and hydrothermal synthesized ash.

2-2. Recovery of Sodium phosphate at the optimal condition

Hydrothermal synthesis used the incinerated ash (50g) was carried out at the optimal condition which was obtained the highest recovering rate of the phosphorus. The amounts and compositions of recovered materials were investigated. Also, the recovered zeolite was estimated by the methylene blue adsorption capacity, specific surface area and pore volume.

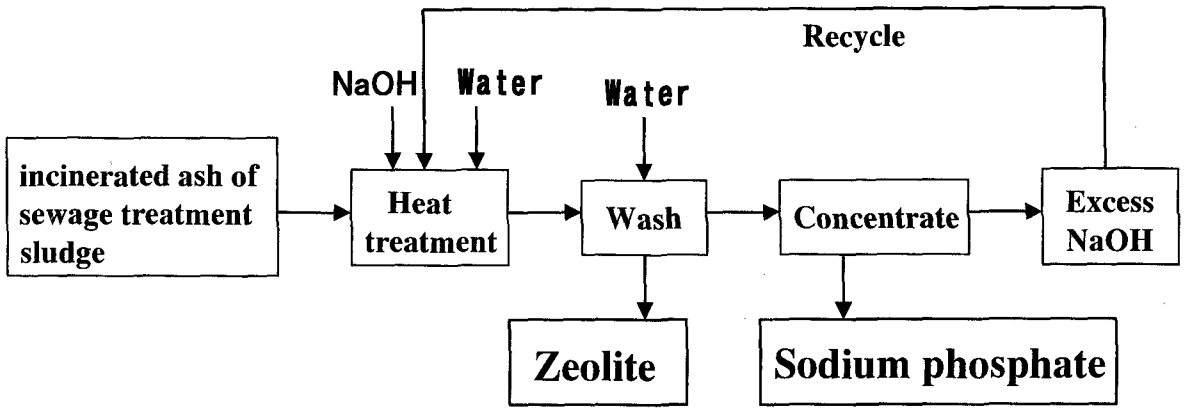

Fig.1 Sodium phosphate recovering processes from incinerated ash of sewage treatment sludge

3. RESULTS

3-1. Case studies on treating conditions

In case 1, L/S ratio dependence of phosphorus recovering rate in hydrothermal treatment of the incinerated ash was examined under the following conditions : L/S, 0.5-3.4; concn. of NaOH, 14g/25ml; heating temp., 180 ℃ ; heating time, 2hours. The recovering rate of phosphorus was about 45% with more than L/S=2 (Fig.2). In case 2, heating temperature dependence of phosphorus recovering rate in hydrothermal treatment of the incinerated ash was examined under the following conditions : heating temperature, 20-180 ℃ ; L/S, 2; concn. of NaOH, 12.5g/25ml; heating time, 2hours. The recovering rate of phosphorus was very high at 100℃ (Fig.3). In case 3, concentration of NaOH dependence of phosphorus recovering rate in hydrothermal treatment of the incinerated ash was examined under the following conditions : concn. of NaOH, 0-12.5g/25ml; L/S, 2; heating temperature, 100℃; heating time, 2hours. The phosphorus recovering rate was increased with the concentration of sodium hydroxide (Fig.4). In case 4, heating time dependence of phosphorus recovering rate in hydrothermal treatment of the incinerated ash was examined under the following conditions : heating time, 1-24hours; L/S, 2; concn. of NaOH, 12.5g/25ml; heating temperature, 100℃. The recovering rate of phosphorus was about 45% for the run of the heating time more than 2hours (Fig.4). From those results, the highest phosphorus recovering rate (46%) was observed under the condition of L/S=2, concn. of NaOH 12.5g/25ml, 100℃ and 8hours. Furthermore studies are required to design for achievement of higher phosphorus recovering rate since the obtained value was not sufficient for practical use.

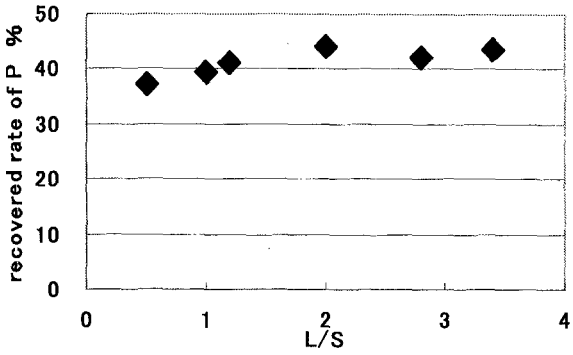

Fig.2 P recovering rate with relation to L/S

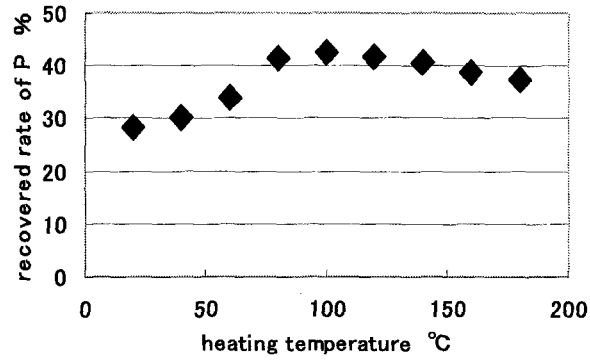

Fig.3 P recovering rate with relation to heating temperature

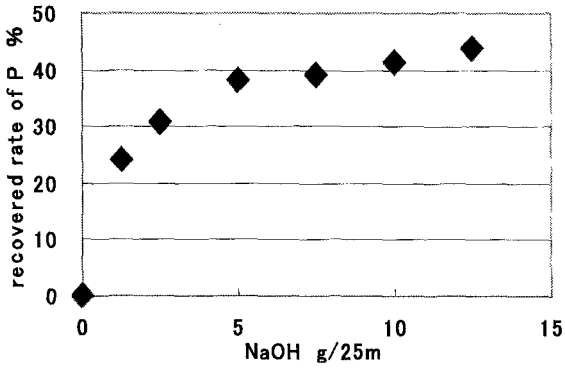

Fig.4 P recovering rate with relation to the NaOH concn.

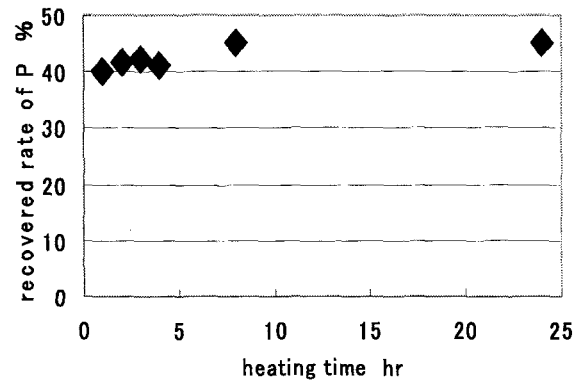

Fig.5 P recovering rate with relation to heating time

3-2. Recovery of Sodium phosphate at the optimal condition

The incinerated ash of sewage treatment sludge (50g) was mixed with 50% aqueous sodium hydroxide solution (100ml), and hydrothermal treatment was carried out at 100℃ for 8 hours. The hydrothermal synthesized ash was washed with 3 liters of distilled water. The treated ash was recovered as zeolite with drying process at 105℃ after filtration. Generally, Sodium phosphate formed in this reaction could be recovered by concentrating and crystallization procedure on this synthesis. However, in this experiment, recovered sodium phosphate contained excessive amount of NaOH used on the hydrothermal reaction. This NaOH has hygroscopicity which interferes X-ray florescent analysis, therefore to make the analysis easier, sulfuric acid was added to the recovered phosphorus for converting the excess NaOH to Na_2SO_4.

The amounts of these recovered materials are shown in Table.1. The recovered materials were analyzed by X-ray florescent analyzer, the compositions are shown in Table 2. The results showed that the phosphorus in the ash was decreased, on the other hand, SiO_2 and Al_2O_3 are almost the same, Na_2O was increased. Therefore, this was showed that only phosphorus in ash was dissolved in the process water, and suggested that Na_2O was combined with inorganic component in ash, and material like zeolite has formed. Recovered sodium phosphate contained Na_2O, SiO_2, which was considered sodium silicate derived from silica component dissolved with NaOH, and excess NaOH. The excess NaOH was estimated 58% (29g) of the initial amount, these NaOH can be recycled as alkali in the hydrothermal synthesis process. Sodium phosphate was estimated as the form of $Na_3PO_412H_2O$ by the ignition loss and recovering pH (>10).

The properties of recovered zeolite was evaluated by the methylene blue adsorption capacity, specific surface area by BET and pore volume. The results are shown in Table 3. The adsorption capacity of the recovered zeolite was about 5 times as much as raw ash. Specific surface area of it was 9 times as much as raw ash. The pore volume of it showed 14 times as much as raw ash, and showed effective as adsorbents.

Table 1. The amount of these recovered materials

Incinerated ash	NaOH	Recovered zeolite	excess NaOH	Recovered Na_3PO_4
50g	50g	49.6g	29.3g	24.9g

Excess NaOH and recovered Na_3PO_4 was estimated by mass balance

Table 2. The composition of recovered materials

	Incinerated ash	Recovered zeolite	Recovered Na_3PO_4
SiO_2	26.4	26.1	35.0
Al_2O_3	11.8	13.2	1.0
CaO	13.9	15.8	0.1
P_2O_5	18.6	11.6	25.9
SO_3	1.4	1.0	0.0
Fe_2O_3	16.8	19.3	0.0
Na_2O	1.3	3.7	27.2
K_2O	2.8	1.2	7.6
Others	7.1	8.1	3.2

The composition of recovered Na_3PO_4 was corrected by mass balance

Table 3. The characteristics of recovered zeolite

	Incinerated ash	Recovered zeolite
MB adsorption ability (mg/g)	0.3	1.3
specific surface area (m^2/g)	4	36
pore volume (cc/g)	0.02	0.28

4. CONCLUSIONS

In order to find the sodium phosphate recovering method, as in the basic study, hydrothermal treatment was carried out on the incinerated ash of sewage treatment sludge using sodium hydroxide. In the hydrothermal treatment, aluminum and silica in incinerated ash reacted with added sodium hydroxide, formed substance like zeolite, and generated sodium phosphate. The hydrothermal treatment was done under many experimental conditions, and condition of L/S=2, NaOH 12.5g/25ml, 100℃, 8 hours enabled the highest recovering rate (46%). The zeolite recovered on this experiment was considered to be the materials as like zeolite by it's composition and characteristics. The recovered sodium phosphate was presumed to be mainly consisted with sodium phosphate, however contained sodium silicate formed by-reaction.

This experimental results showed some possibilities that can directly recover phosphate salts like sodium phosphate from incinerated ash of sewage treatment sludge and synthesize material like zeolite. However, a lot of experiments in improving experimental conditions for higher recovering rate and purity are needed. Furthermore semi-plant level test is also needed for practical use.

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