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Review Article

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Recovery of Phosphorus by Acid Extraction from Incinerated Ash of Sewage Sludge

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ABSTRACT

Sewage sludge contains significant amounts of phosphorus, and in order to recover the phosphorus, some extraction method using acid or alkali are under way. The acidic extraction can recover the phosphorus with high recovery rate compared to the alkali method, and investigation of the phosphorus recovery using acid extraction was carried out. Almost all of the phosphorus was recovered from the ash, however, the recovered phosphorus is mainly composed of aluminum phosphate which has few usages, and much more reform of the method is needed, and some ideas for the matter are introduced.

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Introduction

High volumes of sewage sludge have been discharged in Japan, and these amounts are increasing every year (Figure 1) [1]. Almost all sludge has been disposed in landfill sites as waste. Recently, some of it tends to be incinerated for thermal recycle, and incinerated ash is used as a cement raw material. However, these ashes contain significant amounts of phosphorus as shown in Table 1, and these concentrations are increasing by improvement of phosphorus removal technique of sewage treatment. The phosphorus recovering technique from ash has not been developed, and most of the phosphorus is discharged in the environment without recycling.

Sludge amount (DS-10^3 Ton)

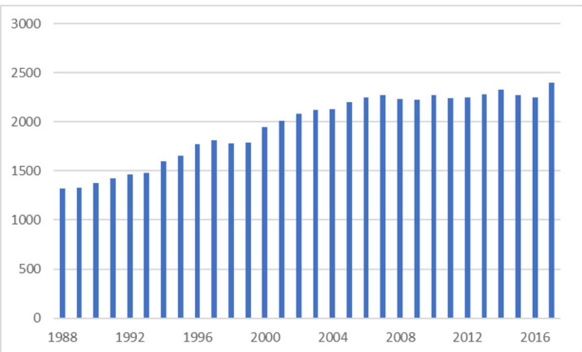


Figure 1: Trend of the Sewage Sludge in Japan

In order to solve the matter, many chemical extraction methods have been investigated using acid or alkali [2,3]. The acid treatment can extract almost all of the phosphorus compared with the alkali treatments, and is regarded to be a useful method. However, the recovered phosphorus contained significant amounts of aluminum, and some improvements of the method are needed, and to solve the matter, some studies were carried out. We introduce the outline of the method.

Basic Procedure of the Acidic Phosphorus Extraction Method

The Feature of the Raw Ash

The phosphorus concentration in the sewage ash differs depending on the discharge site, however, it is expected to usually contain 15% – 25% (w%, as a form of P_2O_5) of phosphorus. The incinerated ashes which were discharged from Yokkaichi city sewage treatment facility, were used in our experiment. Features of the ashes are shown in the Table 1.

Table 1: Elemental Composition of the Incinerated Ash of Sewage Sludge

Element	Ash-1	Ash-2
Al_2O_3	12.6	18.1
SiO_2	36.8	31.2
P_2O_5	17.2	18.1
SO_3	1.20	1.6
K2O	2.64	1.7
CaO	9.42	9.5
Fe_2O_3	12.0	12.3
others	10.8	7.5
Unit; W%		

Outline of the Basic Procedure

Basic procedure is shown as follows (shown in Figure 2). Phosphorus in the ash can be extracted easily by using strong acid like sulfuric acid or hydrochloric acid, and separated by solid/liquid separation. The extracted phosphorus is considered to be precipitated at the pH 4 or 5 by addition of the conventional alkali metal compounds or alkali earth metal compounds like NaOH, Na_2CO_3, Mg $(OH)_2$ or $CaCO_3$ (stated as alkali I in Figure 2), and recovered by the solid/liquid separation. Later, the phosphorus removed extract is neutralized using alkali substances like NaOH or Na_2CO_3 or Ca $(OH)_2$ (stated as alkali II in Figure 2). Through the treatment, all most all of the heavy metals are removed from treated water (processes water) as a residue, and the treated water can be discharged to the environment [4].

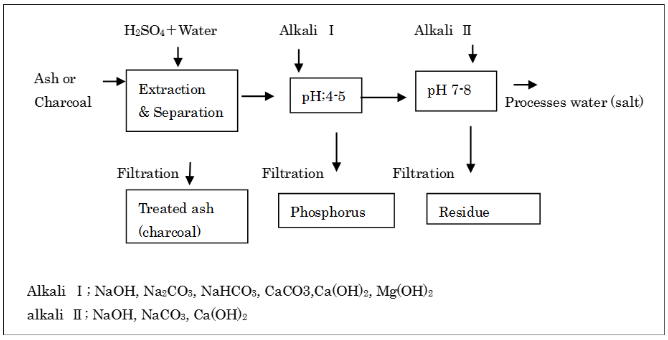


Figure 2: Basic Recovery Method

In the same way, phosphorus can be recovered from charcoal of sewage sludge [5].

The Acidic Phosphorus Extraction

Selection of the Acid

Strong acids are considered to extract phosphorus effectively. However, HCl contains high amounts of chlorine component which is not good for the usage of the recovered phosphorus. HNO_3 is expensive compared by H_2SO_4 or HCl, and high concentration of the nitrogen wastewater will be discharged, therefore, H_2SO_4 is considered to be the best acid for the phosphorus extraction.

Extraction Rate in Acidic Condition

The phosphorus extraction rate is expected to be high in strong acidic conditions, however, a minimum additional rate is needed for cost effective method. In order to confirm the proper additional rate, phosphorus extraction rates were investigated as follows.

100g of the ash was mixed with some amounts of H_2SO_4, and relation with the phosphorus concentration and pH of the extracts were investigated. The phosphorus concentrations tended to be high with the addition of the acid, and around pH 2.0 phosphorus concentration tends to be flat, and it is considered that most of the phosphorus in the ash was extracted in this pH [6,7].

Recovery of the Phosphorus from Acidic Extract

Alkali Material

In the acid treatment, phosphorus extracted from ash is precipitated as a form of phosphates through neutralization processes. As the alkali, usually NaOH, Na_2CO_3 or Ca $(OH)_2$ are used. Sodium compounds like NaOH or Na_2CO_3 are expensive compared to calcium compounds such as Ca $(OH)_2$, $CaCO_3$. On the contrary, phosphorus which is recovered by calcium compounds contains significant amount of $CaSO_4$ because of lower solubility of $CaSO_4$, and makes phosphorus of lower purity.

On the other hand, Mg $(OH)_2$ is regarded as a relatively less expensive reagent, and $MgSO_4$ formed by the reaction of Mg $(OH)_2$ and H_2SO_4, is soluble in water, therefore, a high quality of phosphorus is expected to be recovered in this method [8].

Phosphorus (g)

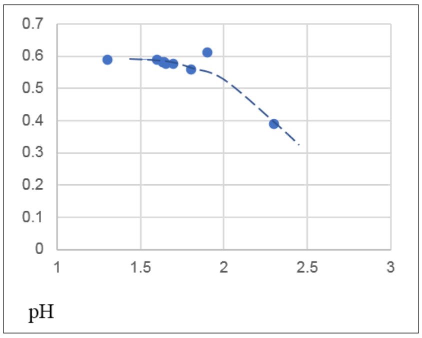


Figure 3: Relation with Extracted Phosphorus and Treated pH Ash; 100g

Phosphorus (g/L)

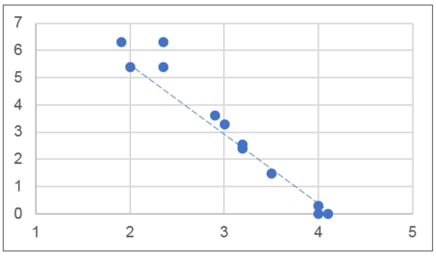


Figure 4: Relation with P Concentration and pH of the Processes Water

Neutralization Processes

In order to find the proper pH for recovering the phosphorus from extract, the relation with the phosphorus concentrations and the pH of the extracts were investigated using the extract as mentioned 3.2 (100g of the ash and H_2SO_4). The phosphorus concentrations of the extracts tended to low with addition of the alkali (Na_2CO_3), and around pH 4, most of the phosphorus was considered to be precipitated.

The Feature of the Residues

The phosphorus removed extract is considered to contain many heavy metals. These heavy metals can be precipitated by addition of NaOH or Na_2CO_3, resulting in forming a residue. The residue was investigated using X-ray analysis and chemical analysis. The residue was composed SiO_2, CaO, SO_3, MgO, and many heavy metals like Cu, Zn, Cd, Mn were confirmed [9]. Pb was not found because of low solubility of PbSO4 formed by the addition of H_2SO_4.

Treated Water

Phosphors and harmful heavy metals removed from treated water have to be discharged to environment. In order to confirm the discharging of the processes water, the processes water was investigated by chemical analysis, and also evaporated for the X-ray analysis.

The processed water is composed of some salt of sodium, calcium or magnesium, and the concentrations of the harmful heavy metals are lower than the Japanese environmental standard, and considered possible to discharge to the environment.

In the case of high concentrations of Na_2SO_4 or $MgSO_4$, recovering can be possible for one of the recycling methods.

Feature of the Recovered Phosphorus

Amount of the Recovered Substants

Recovering was carried out as follows.

Run1: 100g of ash was mixed with diluted H_2SO_4 (35g as H_2SO_4) for extraction, extracted phosphorus was recovered using Na_2CO_3, and treated as mentioned in chapter 2.2.

Run2: 100g of ash mixed with H_2SO_4 same way as run1, extracted phosphorus was recovered using $CaCO_3$, and treated the same way.

Run3: 100g of ash was mixed with H_2SO_4 same way, and extracted phosphorus was recovered using Mg $(OH)_2$, and treated the same way.

The amounts of the phosphorus and other substants are shown in Table 2.
The weight of the ash was degreased from 100g to 80g-81g by acid treatment as the result of acidic elution.

Table 2: Phosphorus Recovery Condition and the Amount of the Recovered Materials

Run	Raw material	Amount of raw material	Amount of acid	Alkali	Amount of alkali	Treated ash or charcoal	P	Residue	Salt
Run#1	Ash-2	100g	30g	Na2CO3	25g	80g-81g	57g	4g	67g
Run#2	Ash-2	100g	30g	CaCO3	15g	80g-81g	122g	4g	10g
Run#3	Ash-2	100g	31g	Mg (OH)2	13g	80g-81g	31g	5g	31g

T-ash: treated ash P: Recovered phosphorus Used amount of Ash: 100g

Composition of the Recovered Phosphorus

Raw ash, treated ash, recovered phosphorus and salt were investigated using an X-ray analyzer. Raw ash was mainly composed of SiO_2, Al_2O_3, Fe_2O_3, P_2O_5 and Al_2O_3.

P_2O_5 and Al_2O_3 in the treated ash were degreased by the elution of the phosphorus, contrary SO_3 component which was formed by the reaction of H_2SO_4, was increased. P_2O_5 and other component in the recovered phosphorus is shown in table 3 and Figure 5.

Table 3: Component of the Recovered Materials (Unit: %)

	Raw ash	T-ash	P1	P2	P3	R1	R3	S2	S3
SiO_2	31.2	32.3	0.9	1.2	1.1	43.5	5.0	1.1	3.4
Al_2O_3	18.1	10.9	35.2	20.4	29.4	1.4	1.6	0.2	0.0
CaO	9.5	11.7	0.2	20.5	0.8	4.4	1.9	17.3	0.8
P_2O_5	18.1	1.9	43.9	23.7	51.5	5.0	3.7	<0.1	1.4
Fe_2O_3	12.3	15.1	3.0	1.5	4.5	1.9	1.0	<0.1	0.1
MgO	2.6	1.1	0.1	<0.1	3.9	18.6	81.0	12.4	31.0
SO_3	1.6	21.8	13.0	31.7	4.7	9.8	2.4	57.8	61.5
Others	6.6	5.2	3.7	1.0	4.1	15.4	3.4	11.2	1.8

Ash: Raw ash (Ash 2) T-ash: Treated ash run 2 P1: Recovered phosphorus run 1
P2: Recovered phosphorus run 2 P3: Recovered phosphorus run 3 R1: Recovered residue run 1,
R3: Recovered residue run 3 S2: Salt run 2 S3: Salt run 3

Contents (%)

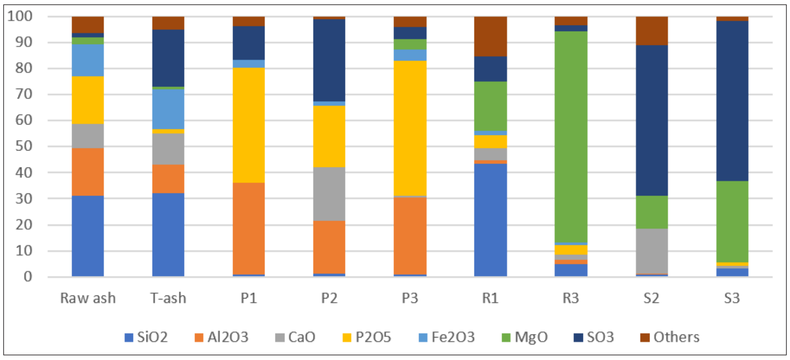


Figure 5: Component of the Recovered Materials

The recovered phosphorus in run 1 is mainly composed of Al_2O_3, P_2O_5, and is regarded to exist as a form of $AlPO_4$ by chemical composition and X-ray diffraction spectra (XRD)

Counts

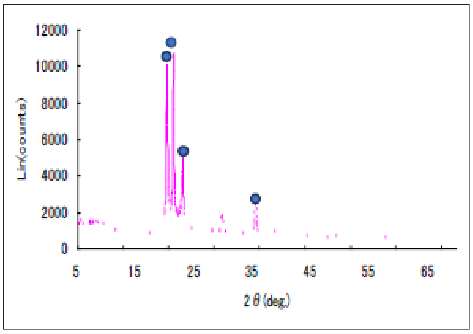


Figure 6: XRD chart of Recovered Phosphorus(•$AlPO_4$)
(The sample was treated at 600°C, 1 hour for analysis)

Phosphorus Recovering Rate

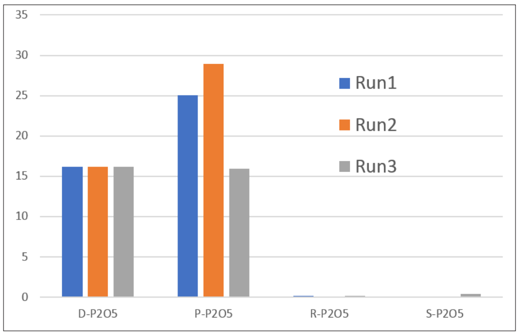
Phosphorus recovery rates are estimated by the transition of the phosphorus compositions and amount of the recovered materials. In order to evaluate the net amount of the phosphorus, amounts of the P_2O_5 in the raw ash and the recovered materials using the following formula.

Amount of the P_2O_5 = W ×P-r
W: Amount of the recovery materials
P-r: P_2O_5 (%) of the recovered materials

The amount of the phosphorus in some recovered materials are shown in Figure 7. Almost all of the phosphorus was recovered in the recovered phosphorus, and a very small amount of the phosphorus is contained in the residue or salt. The amount of the phosphorus in the recovered phosphorus exceeds the amount of the phosphorus in raw ash, which is considered to be due to the any analytical error or influences of the moisture which is contained in the recovered phosphorus.

The phosphorus extracted from raw ash (100g) by the acid treatment are estimated 16.2g from the transition of the P_2O_5 values (18.1% to 1.9%) and weight of the ash, and almost extracted phosphorus (about 90%) are recovered.

Phosphorus (g)



D-P_2O_5: Extracted Phosphorus from Raw ash (100g)
P-P_2O_5: Phosphorus in the Recovered Phosphorus
R-P_2O_5: Phosphorus in the Residue
S-P_2O_5: Phosphorus in the Salt
Figure 7: Transition of the Phosphorus Components (P_2O_5) Through Treatment

Usage of the Recovered Phosphorus and Remained ash or Waste Water

The recovered phosphorus is mainly composed of $AlPO_4$. On the contrary, the phosphorus recovered from livestock feces is mainly composed of $Ca_3(PO_4)_2$, and very small $AlPO_4$ content [10]. The matter is the usage of the recovered phosphorus which contains significant amounts of $AlPO_4$. $AlPO_4$ can be used as a raw material of ceramics, and as a Pb encapsulation agent or some uses like Fluorine stabilizer are under consideration [11-13]. However, these usages are very limited compared with the $Ca_3(PO_4)_2$, and expanding the usage of the $AlPO_4$ is needed.

Some Studies are Introduced as Follows

Conversion of the $AlPO_4$ to other Phosphates

The recovered phosphorus by the acidic treatment is mixed with aq. Solution of NaOH, and the $AlPO_4$ in the recovered phosphorus reacts with added Sodium Silicate, and forms Aluminum silicate gel. The formed Na_3PO_4 by the gelation can be recovered by solid-liquid separation from the gel (Figure 8) [14].

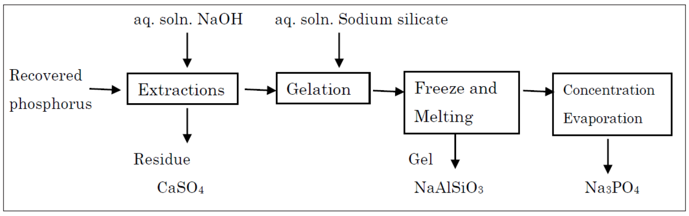


Figure 8: Conversion Method of $AlPO_4$ to Other Phosphates

Conversion of the AlPO4 to another Phosphates Salt through Crystallization

The recovered phosphorus was dissolved by the addition of H_2SO_4, and the phosphorus containing extract was mixed with Na_2SO_4 or $(NH_4)_2SO_4$, and cooled at a low temperature, and crystal of alum was formed. The alum has low solubility at low temperature, and easily be separated by crystallization. Result of the treatment, almost all of the aluminum component in the extract can be removed as alum, and the phosphorus can be recovered as a form of Na_2HPO_4 or $(NH_4)_2HPO_4$ (Figure 9) [15].

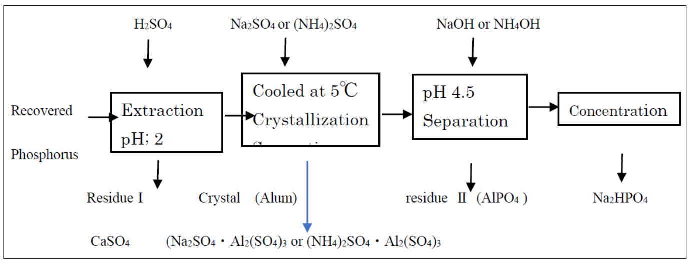


Figure 9: Conversion Method of the $AlPO_4$ to another Phosphates

Conclusion

In the recovery of the phosphorus from ash, acidic treatment can effectively extract the phosphorus, and recover the phosphorus using a cost-effective conventional alkali reagent. Phosphorus was recovered mainly as a form of $AlPO_4$ which has limited usage, and many investigations searching for the usages will be needed.

Incinerated ash is mainly used as a raw material of cement. The Phosphorus component in the ash is inconvenient for usage as a raw material of cement. The ash treated by this method has lower phosphorus concentrations compared to non-treated ones, and can be more useful for the raw material of cement.

Acknowledgement
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