Efforts to Phosphorus Recovery by Separation Treatment System of Sewage Sludge

Keiichi Sone: Senior Reservcher of R&D Div., Tokyo Metropolitan Sewerage Service Corp.,
Yukitoshi Iwasa: Chief Resercher of Institute of Sewerage Technology, Tokyo Metropolitan Sewerage Service Corp.,
Makoto Muto: Director for Planning Div., Bureau of Sewerage Tokyo Metropolitan Government,
Hiroaki Mitamura: Director for R/D Div.,Bureau of Sewerage Tokyo Metropolitan Government,
Masaki Fujie: Deputy Director for R/D Div., Bureau of Sewerage Tokyo Metropolitan Government,
Hiroyuki Kato: Project Assoc. Prof., The University of Tokyo, Department of Urban Engineering,

1. Introduction

The sewerage system in Tokyo is almost completed and all sludge generated during the sewage treatment process is incinerated after being thickened and dehydrated.

The sludge generated in the sewage treatment process is classified into primary sludge formed in the primary clarifier and excess sludge formed in the final clarifier. They are generally mixed, thickened, dewatered, and incinerated.

Due to differences in the removal mechanism in the wastewater treatment, the composition of primary sludge and of excess sludge differ greatly.

The incinerator ash is recycled by being used as raw material for cement and light aggregate materials and secondary concrete products, and the other is landfilled.

Phosphorus resources in Japan are heavily dependent on imports. While doing so, the drastic increase in the price of phosphate rock in the Financial Crisis in 2008 highlighted the urgent need to secure resources, thus driving efforts to recover phosphorus contained in sewage sludge.

The authors' payed attention to the phosphorus concentration in excess sludge is high, and developed a method of separating primary and excess sludge, and concentrating, dehydrating, incinerating them separately and supply excess sludge incinerator ash as phosphorus resources.

Key words: sewage sludge, phosphorus recovery, reformulation of sludge component, separate incineration,

2. Outline of sewage treatment in Tokyo

2.1 Sewage treatment in Tokyo

The sewerage system in Tokyo cover the 23 wards of the central city area and the surrounding residential Tama area.

The combined sewer system is served in 80% in the 23 wards area and 25% in the Tama area. The rest is served by a separate sewer system. Since it is difficult to secure landfill sites in Tokyo, so that the sludge cake must be incinerated for volume reduction and stabilization, and effective use of incinerator ash has been promoted. It became possible to incinerate all sludge in 2003. Table1 shows the situation of sewage treatment (2020).[(1)] The total population of Tokyo in 2020 is 14 million inhabitants. A total of 5,460,000 m3 of sewage water is treated every day for the 23 wards and the Tama area. The daily amounts of sewage sludge, dewatered sludge, and incinerator ash, which is formed at the end of treatment, are 208,000 m^3, 3,200 t, and 88 t, respectively.

	Area (ha)	Population (persons)	Sewage treatment amount (m^3/day)	Sludge treatment amount (m^3/day)	Dewatered sludge amount (t/day)	Incinerator ash generation (t/day)	Number of STPs
Ward Area	628	9,653,112	4,446,840	174,670	2,450	72.1	13
Tama Area	1,940	4,298,524	1,015,150	33,210	742	16.2	7
Total	2,568	13,951,636	5,461,990	207,880	3,192	88.3	20

Table－1 Sewage treatment in Tokyo (2020)[(1)]

The sewage is treated by the conventional activated sludge process in Tokyo in principle. To improve the water quality in rivers and sea areas to which the effluent is discharged, advanced treatment processes, such as the anaerobic-oxic (AO) process and the anaerobic-anoxic-oxic (A_2O) process, for enhancing phosphorus removal have been steadily introduced.

As a result, the phosphorus content in the sludge is gradually increasing, as described in 2.3.

2.2 Recycling of incinerator ash in Tokyo

Tokyo has reduced the volume and stabilized sludge by total incineration. Furthermore, the generated incinerator ash is recycled as a raw material for cement, lightweight aggregate, raw material for secondary concrete products, and carbide. (Fig.1)

However, the higher the phosphorus content in the incinerator ash, the more difficult it becomes to maintain the strength of the cement or concrete secondary products, which impedes the recycling in this field.

Fig.1 Recycle and Disposal of incineration Ash in Tokyo, 2016

2.3 Annual change of the phosphorus concentration in the incinerator ash

The phosphorus concentration (P_2O_5) in the incinerator ash generated at the Tokyo sewage treatment plant has been increasing over the years, as shown in Figure 2. A, B, and C show the P_2O_5 concentration in the incinerator ash at the ward treatment plants that receive the combined sewage. D, E, and F are sewage treatment plants in the Tama area, which receive separate sewage and mainly treat domestic wastewater. Especially in recent years, the concentration of P_2O_5 in the Tama area has exceeded 30%.

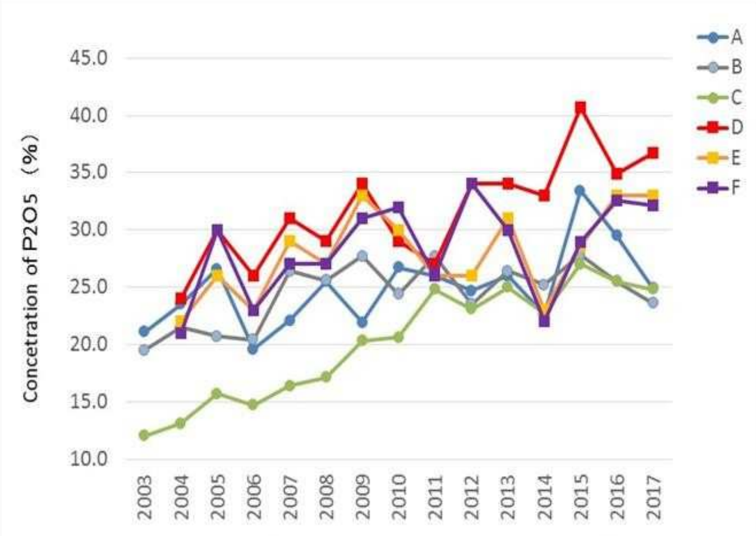

Fig.2 Annual change of P_2O_5 concentration in incineration ash of each plant

The increase in phosphorus concentration in the incinerator ash is considered to be due to the introduction of advanced treatment as mentioned above and changes in the lifestyle (eating habits) of residents.

3. Trend of phosphorus resources in Japan (2), (3)

Phosphorus resources in Japan are heavily dependent on imports. Countries that produce rock phosphate are concentrated in limited areas and some of these countries restrict its export. Figure 3 shows the change in the countries from which Japan imports rock phosphate, the amount imported, and the price of rock phosphate. Japan imports rock phosphate mainly from China, South Africa, Jordan, and Morocco.

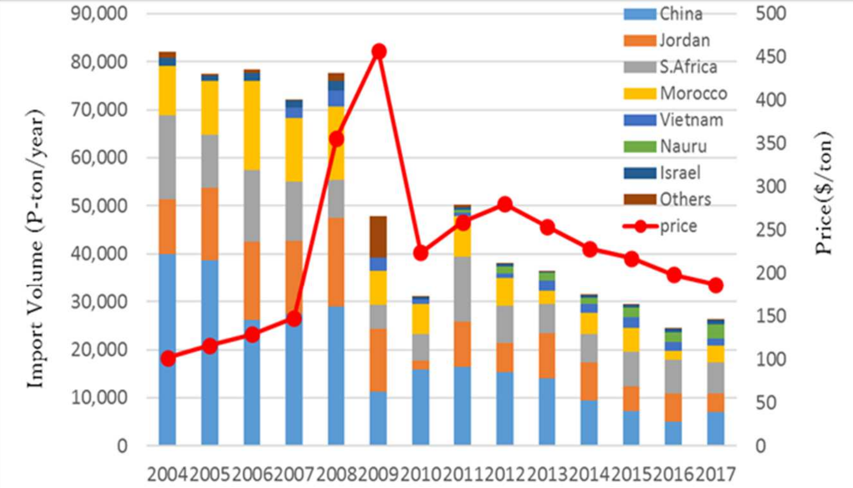

Fig. 3 Annual changes in imports by country and price
(Ministry of Finance trade statistics)

As shown in Figure 3, following the price increase of resources such as rare metals during the Financial Crisis in 2008, the price of phosphate rock also skyrocketed, triggering a sense of crisis and urgency of securing phosphorous resources in Japan.

Although the price of rock phosphate has now almost returned to normal and the import volume has decreased.

However phosphorous recovery from sewage sludge is attracting attention as a domestic source of phosphorus.

4. Comparison of compositions of primary and excess sludge

4.1 Behavior of metals and nutrient salts in sewage treatment

As shown in Figure 4, the sludge in the primary sedimentation tank is mainly produced by the precipitation of particulate substances in the influent, and heavy metals are in hydroxide forms and are mostly transferred to the primary sludge.

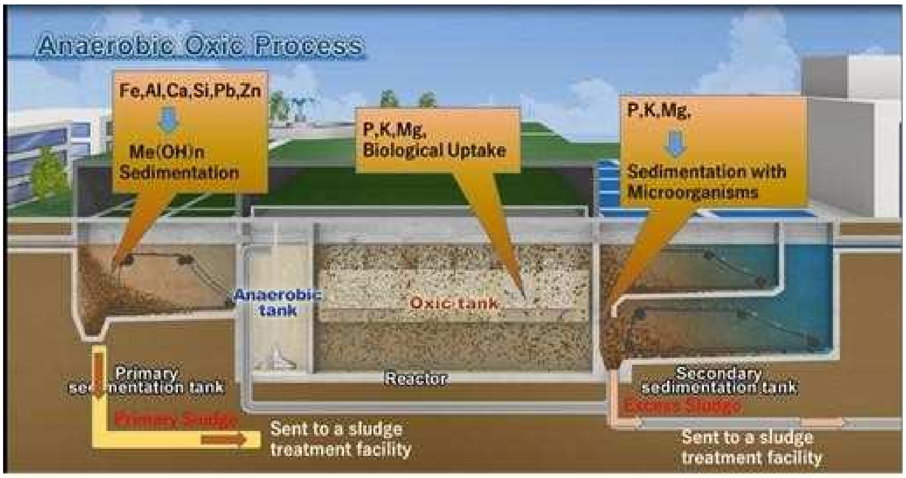

Fig. 4 Behavior of metals and nutrient salts in sewage treatment

Meanwhile, most of the phosphorus in sewage is dissolved as phosphate ions and flows into the reactor as it is without settling in the primary sedimentation tank. The soluble phosphate ions are absorbed together with potassium and magnesium, as an essential nutrient for microorganisms in the activated sludge, and transferred to the excess sludge in secondary sedimentation tank.

4.2 Comparison of compositions of incinerator ash from primary and excess sludge

We collected 9 samples from each of primary sludge and excess sludge at 4 centers (separate system) in the Tama area and 1 center (combined system) in the Ward area, and we performed a component analysis to prove the 4-1 reasoning after.

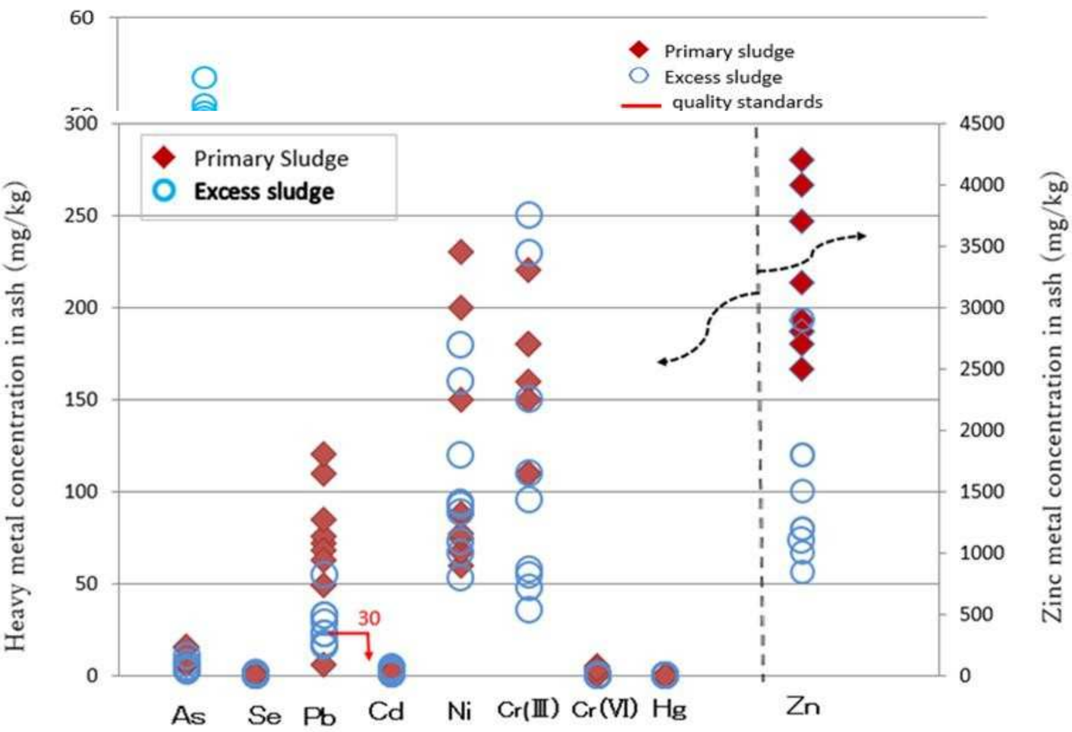

Fig. 6 Distribution of Heavy metals in primary and excess sludge ash

The preparation method of ash was to evaporate the water content of the sludge, and to incinerate at the temperature of 850 ° C in an electric furnace.

The components of the obtained incinerator ash were analyzed, and the distribution of each component element is shown in Fig. 5 for the main component and Fig.6 shows for the heavy metals component. Looking at these, it was confirmed that there was a large difference in the component ratios of primary and excess sludge ash. Comparing the content ratios of P, K, and Mg for the main components in Fig.5, these are existed more in excess sludge ash. On the other hand, it was confirmed that Ca, Si, Al, and Fe are existed more in primary sludge ash.

Looking at the heavy metals in Fig. 6, it was confirmed that Pb and Zn were more distributed in the primary sludge ash.

Table 2 shows the average values of the component of 9 samples of primary and excess sludge ash, and the tendency to shift to excess sludge, and the content of phosphate rock in China and Morocco, and it also shows the gypsum board quality standards required for the recycling of phosphorus.

Table 2 Comparison of compositions of incinerator ash from primary and excess sludge, Quality standards, and rock phosphate composition

	Primary Sludge Ash(A)	Excess Sludge Ash(B)	B/A	Required Level (4)	Phosphorus Rock (5)	
	Average of 5center 9samples				China	S.Africa
P_2O_5 (wt%)	26.7	48.9	↗	33 ↑	34.4	36.8
CaO (wt%)	17.3	11.0	↘		50.1	52
SiO_2 (wt%)	25.7	9.3	↘	14 ↓	3.3	1.5
Al_2O_3 (wt%)	11.0	4.9	↘	Total 13 ↓	1.1	0.3
Fe_2O_3 (wt%)	6.2	5.0	→		2.6	0.4
MgO (wt%)	2.6	6.7	↗		0.9	0.1
Na_2O (wt%)	1.3	3.0	↗		—	—
K_2O (wt%)	2.3	9.7	↗	3 ↓	—	—
SO_3 (wt%)	2.3	0.4	↘		—	—
F (wt%)	—	—			2.8	3.8
As (mg/kg)	8.9	4.8	↘		—	—
Se (mg/kg)	0.9	1.2	↘		—	—
Pb (mg/kg)	72.0	27.0	↘	30 ↓	—	—
Cd (mg/kg)	2.6	1.7	↘		—	—
Hg (mg/kg)	ND	ND	—		—	—
Ni (mg/kg)	115	103	→		—	—
Zn (mg/kg)	3200	1480	↘		—	—
Cr(Ⅲ)(mg/kg)	212	115	↘		—	—
Cr(Ⅵ)(mg/kg)	1.9	ND	—		—	—

From Fig. 5, Fig. 6, and Table-2, they were found that the phosphorus content in the excess sludge ash has reached nearly 50%, which exceeds the phosphorus content of the phosphate rock of around 35%. In addition, K and Mg are also contained in a large amount in excess sludge ash.

This indicates that these elements are incorporated into activated sludge microorganisms as essential substances for living organisms.

On the other hand, the concentration of Ca, Si, Al, Fe, in excess sludge incinerator ash is about half that of raw sludge incinerator ash. Next, we looked at the concentration of trace heavy metals. In order to effectively utilize incinerator ash, further reduction of these trace heavy metals is necessary. Figure 5 and Table 2 show that As, Pb, Cr(III), Cd, and Zn in excess sludge ash are reduced to 1/2 to 1/3 of raw sludge incinerator ash. From this, it was confirmed that the excess sludge incinerator ash has a composition close to that of phosphate rock that are advantageous for phosphorus recovery.

4-3 Amount of phosphorus distributed to primary sludge and excess sludge

From the phosphorus content ratio in the primary and excess sludge obtained in the survey of 4-2, the distribution ratio of phosphorus to each is calculated.

Based on the operation results of the treatment plants, which is less affected by recycle flow in Tokyo. Assuming that the total amount of dry sludge matter generated at the STP is 1WDS , the amount of primary sludge dry matter generated at the primary settling tank is 0.58 WDS. The amount of excess sludge dry matter is 0.42 WDS.

The organic content of sludge in Tokyo tends to increase year by year, but here both are set at 85%, so inorganic content is 15%.

From the survey of 4-2, the P2O5 contents in the primary and the excess sludge incinerator ash are 26.7% and 48.9%, respectively.

The amount of phosphorus in primary and excess sludge ash is as follows.

(1) Amount of P2O5 in primary sludge incinerator ash:

(0.15 x 0.58 x 0.267) WDS = 0.0232 WDS

(2) Amount of P2O5 in excess sludge incinerator ash:

(0.15 x 0.42 x 0.489) WDS = 0.0308 WDS

As a results, it is estimated that phosphorus generated in sewage treatment (inflow water phosphorus amount-discharged water phosphorus amount) will be transferred to primary sludge incinerator ash at a rate of 43% and excess sludge incinerator ash at a rate of 57%.

In the future, if the advanced treatment more introduce at the sewage treatment plant and the phosphorus removal rate is improved and the load of sludge recycle flow is reduced, the amount of phosphorus in the excess sludge incinerator ash is expected to increase.

5. Process of manufacturing phosphoric acid and gypsum boards in a phosphoric acid manufacturing plant (An example of reuse in Japan)

Figure 7 shows the method of manufacturing phosphoric acid from rock phosphate in Japan. (5)

The composition of phosphate rock is expressed as Ca5(PO4)3F for the sake of convenience. In phosphoric acid manufacturing plants, sulfuric acid is added to the rock phosphate, and the phosphorus dissolves in the solution as phosphoric acid, and the calcium in the rock phosphate reacts with the sulfuric acid to form calcium sulfate dihydrate (gypsum dihydrate: CaSO4•2H2O), and precipitates.

The phosphoric acid solution is supplied as a raw material for fertilizers, etc. The precipitated gypsum is separated, washed, and supplied to gypsum board manufacturing plants as a raw material such as wall panels and ceiling boards of houses.

Since phosphoric acid manufacturing plants use all of rock phosphate, so little waste is generated from the manufacturing.

Gypsum boards are excellent in fire resistance and sound insulation, and since it may be touched by humans from its usage form, safety and aesthetics are required. Therefore, when using the incinerator ash of sludge as the raw material of gypsum boards, the strict quality standards shown in Table 2 are required.

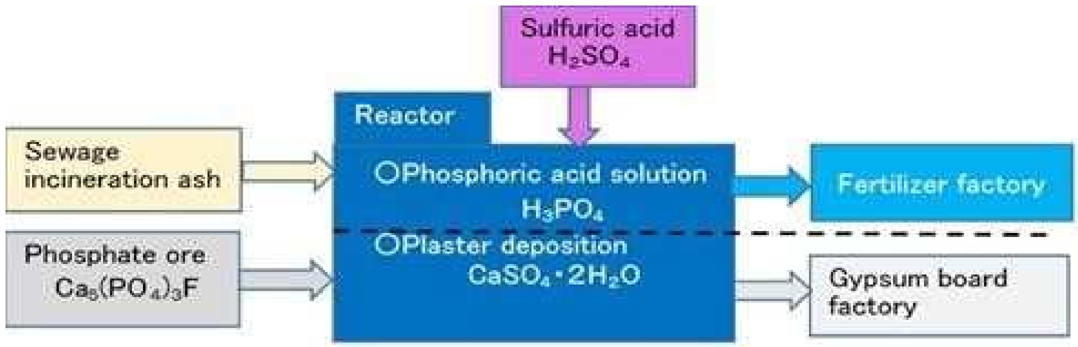

Fig-7 9 Manufacturing process of phosphoric acid and gypsum board

6. Improvement in composition of incinerator ash from excess sludge by addition of slaked lime

It has been verified that the incinerator ash of excess sludge has a high phosphorus content and small amounts of heavy metals. However, if the incinerator ash is to be used as a replacement for phosphate rock, it is necessary to reduce further the heavy metals, silica, and potassium content to control the quality of phosphoric acid solution and gypsum boards.

To reform the incinerator ash from excess sludge and make its composition close to that of phosphate rock as inexpensively as possible. We studied the use of slaked lime $Ca(OH)_2$ as a calcium additive and found that it has excellent effects of diluting heavy metals and removing potassium and magnesium.

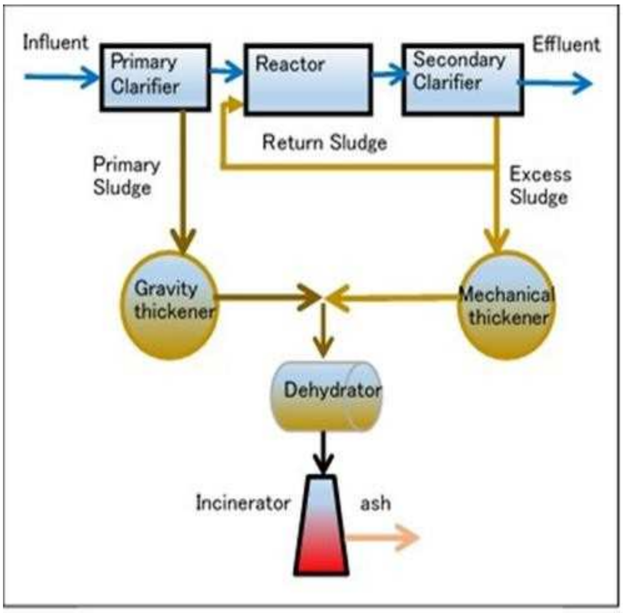

Fig-8 Traditional sludge treatment flow

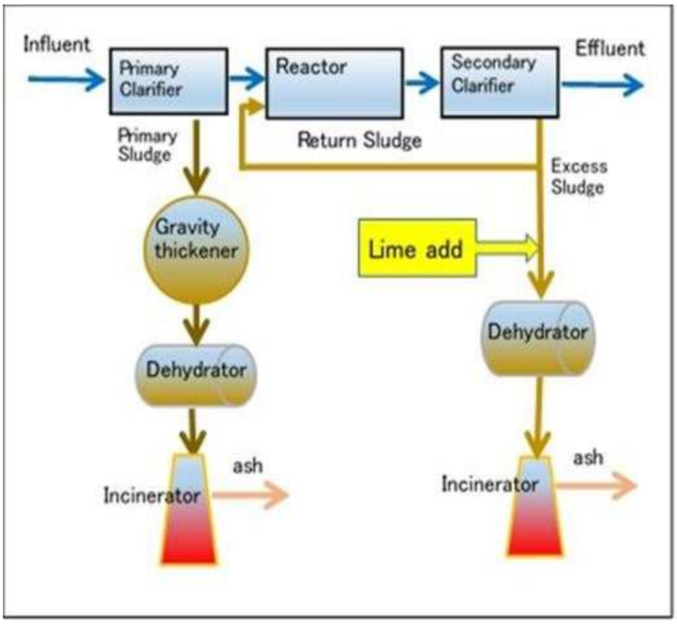

Fig-9 Fig.8 New Separate incineration flow

6.1 Flows for conventional and separated sludge treatments

Figure 8 shows the conventional sludge treatment flow, and Figure 9 shows the separation treatment flow studied this time. The conventional sludge treatment flow mixes the primary sludge with the excess sludge.

This mixture is then concentrated, dehydrated, and incinerated.

In the separation treatment, the primary and excess sludge are dehydrated and incinerated separately without mixing with each other. In addition, slaked lime is added to the excess sludge to improve the properties of the incinerator ash of the sludge

7. Slaked lime addition test [6]

7-1 Test conditions

Table3 Sludge properties and dehydration conditions

Sludge properties	Target sludge		Excess sludge
	Sludge conc.		0.3 ～ 1.0 （%）
	Organic content		85(%） or less
Dehydrate conditions	polymer	Kinds	Cationic
		Injection rate	2.0%or less
	Quality improving drug		Slaked lime
	Moisture content of dehydrated sludge		82 or less （%）
	Dehydration function		15～60 m3/h

Table-3 shows the properties of excess sludge to be tested and the target performance for dehydration.

We installed a high-efficiency centrifugal dehydrator with a treatment capacity of 15 to 60 m3 / h at the F Water reclamation center in the Tama area, and added lime to the excess sludge generated locally to evaluate dehydration performance and to analyze the properties of the cake obtained dehydration.

The properties of excess sludge were solid matter concentration 0.3-1.0%, and organic content ratio was to 85% or less, a high cationic polymer flocculants was used, and the injection rate was 2.0% or less.

Themoisture content of dehydrated sludge was 82% or less.

Lime addition rate （mg/L）		0	300	450	600
Excess Sludge	pH （−）	6.5	7.3	7.6	8.0
	MLSS （mg/L）	5600	6580	4870	4900
Dewatered Sludge	Moisture （%）	81.8	81.8	80.0	79.4
	Organic （%）	86.0	83.6	81.2	78.3
Changes in component content in incinerator ash due to addition of slaked lime	P_2O_5 （%）	49	41	39	35
	CaO （%）	9.6	26	33	39

	SiO_2 (%)	12	10	8.4	6.9
	Al_2O_3 (%)	7.1	6.4	4.4	3.8
	Fe_2O_3 (%)	5.3	4.8	3.9	3.4
	MgO (%)	7.6	5.8	5.9	6.2
	Na_2O (%)	1	0.9	0.9	1
	K_2O (%)	7.0	3.4	2.6	1.3
	SO_3 (%)	−	−	0.7	2.3
	Pb (mg/kg)	48	41	32	30
	As (mg/kg)	4.7	5.5	4.9	4.5
	Se (mg/kg)	−	−	−	2.9
	Cd (mg/kg)	3	3	1	1
	Hg (mg/kg)	ND	ND	ND	ND
	Ni (mg/kg)	130	110	88	73
	Zn (mg/kg)	2200	1900	1500	1400
	CrIII (mg/kg)	57	53	44	36

Table-4 Changes in slaked lime addition rate, sludge properties, and component content

7-2 Improvement of quality of incinerator ash by adding slaked lime

The amount of slaked lime to be added was 0, 300, 450 and 600 mg/L as Ca(OH) 2 with respect to excess sludge in order to determine the amount necessary for phosphorus to react with calcium.

Table 4 shows the component ratios when the amount of slaked lime added to the excess sludge was changed. From Table 4, the pH of excess sludge gradually increased from 6.5 before the addition of lime to 8.0 at lime addition amount 600 mg / L.

Similarly, the water content of dehydrated sludge decreased from 81.8% before addition to 79.4%, and the organic content decreased from 86.0% to 78.3%.

Fig-10 shows the changes in the main components. The P2O5 concentration in the incinerator ash before the addition of slaked lime was 49%, but it apparently decreased to 41, 39, 35% as the amount of slaked lime added increased to 300, 450, 600 mg / L.

The CaO content was 9.6% before the addition of slaked lime, but as the amount added increased, and with the addition of 600 mg / L, it increased to 39%.

On the other hand, SiO2, Al2O3 and Fe2O3 are decreased due to the dilution effect of CaO.

It was observed that K2O specifically decreased significantly from 7.0% to 1.3%.

Fig11 shows heavy metals decreasing in Pb, Zn, Cr(III), and Ni was observed, and the dilution effect of slaked lime was confirmed.

From this survey, it was confirmed that heavy metals is decreased by the diluting effect of slaked lime.

Especially potassium can be significantly decreased by adding slaked lime.

By doing so, it was confirmed that excess sludge incinerator ash approach the composition of phosphate rock [Ca5(PO4)3F]

It seems that the amount of slaked lime added depends on the purpose of using the incinerator ash, but it was found that the purpose of this study could be achieved with an amount of about 300 mg / L.

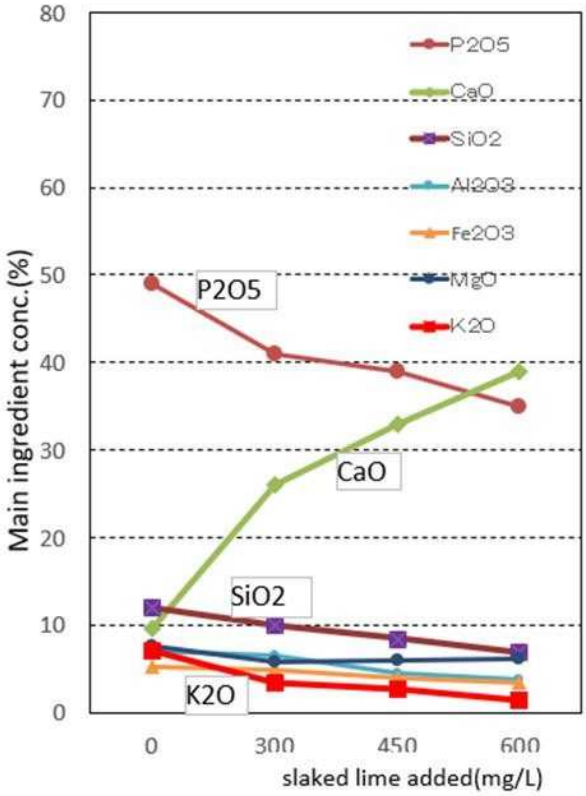

Fig-10 Change in conc. of major substances addition of slaked lime

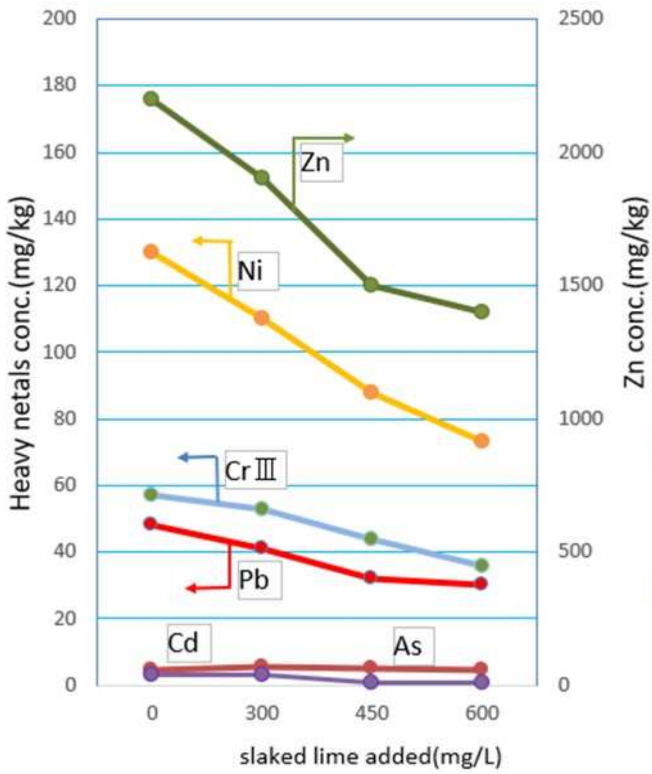

Fig-11 Change in conc. of heavy metals to addition of slaked lime

7-4 Detailed analysis of the effect of adding slaked lime

The apparent change in the concentration of each component in the incinerator ash with slaked lime addition to the excess sludge and it will be considered.

Fig.12 shows the apparent concentration ratio (residual ratio) by adding slaked lime when the concentration of each component before adding slaked lime is assumed to be 1.

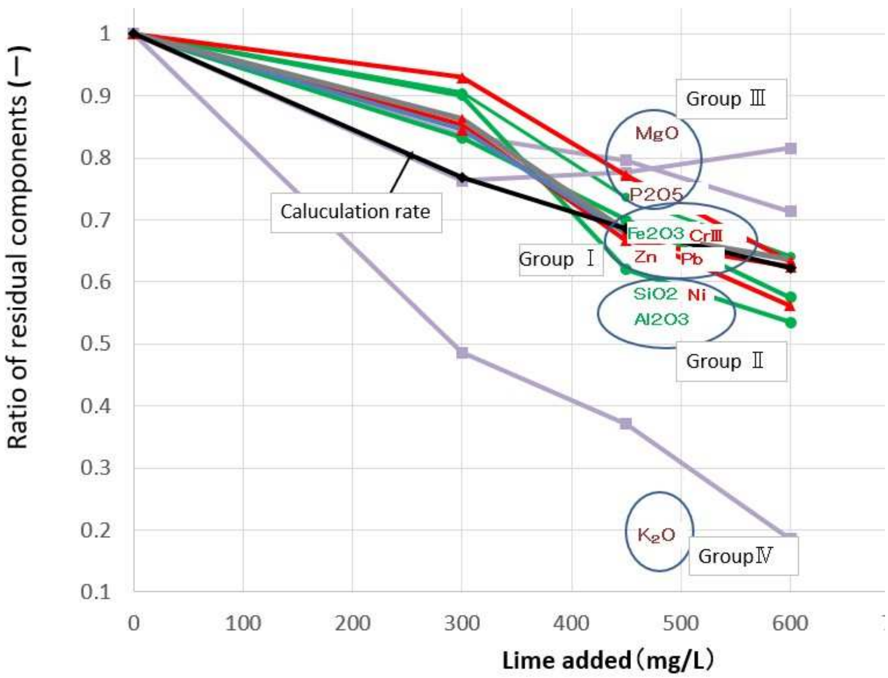

Fig-12 Ratio of residual components when lime is added

The calculated residual rate assumes that all slaked limeCa(OH)2 remains in the incinerator ash as CaO. In other words, it is simply diluted by CaO, and the calculated residual ratio of each component in the incinerator ash is 0.77, 0.69, and 0.62 for slaked lime addition amounts of 300, 450, and 600 mg/L, respectively.

The following 4 groups were considered as the behavior of each component due to the addition of slaked lime in the sludge treatment process.

Group I : Originally contained in the solid content of sludge, diluted as it is by CaO, and remains in incinerator ash. (Fe2O3,Zn,Pb,CrIII)

Group II : Component in the solid content are not completely fixed by CaO, but are slightly transferred to the dehydration filtrate side. (SiO2, Al2O3, Ni)

Group III : Solids of sludge and component distributed in the liquid phase are captured by Ca and transferred to incinerator ash. (P2O5, MgO)

Group IV : Component that exist in the sludge in some form replace Ca and move to the filtrate side. (K2O)

The actual residual rate of each component shown in Fig.12 is dispersed and decreased in groups I to IV as the amount of slaked lime added is increased. When the addition amount is 600 mg / L, Fe2O3, Cr(III), Pb,and Zn as group I are almost the same as the calculated residual rate. The residual rates of Ni, SiO2, and Al2O3 in Group II were slightly low at 0.54 to 0.57, and the residual rates of P2O5 and MgO in Group III were high at 0.71 and 0.82.

In the case of K2O in group IV, the residual rate was 0.18, which was particularly low.

From the results of the slaked lime addition experiment, it was assumed that each component showed the composition of incinerator ash through its own reaction form.

In any case, it was confirmed that adding slaked lime to excess sludge improves the quality of incinerator ash and works favorably as a phosphorus resource.

8. Conclusion

① As phosphorus resources in Japan are heavily dependent on imports, it is necessary to extract phosphorus from sewage sludge, which is a new method, in order to secure a stable supply of phosphorus within Japan.

② As the concentration of phosphorus in incinerator ash is increasing over time, it has become easier to utilize it as a phosphorous resource.

③ Primary and excess sludge are formed during sewage treatment. Because of the differences in the removal mechanism, heavy metals accumulate in the primary sludge, and phosphorus, potassium, and magnesium accumulate in the excess sludge.

④ By adding slaked lime to the excess sludge, dehydrating and incinerating it, high-quality incinerator ash close to phosphate rock was obtained. This has paved the way for providing excess sludge ash in a form that is easy to use as a phosphorus resource.

⑤ Based on the results of this research, Tokyo Metropolitan Government plans to build a sludge separation system and promote the effective use of incinerator ash.

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