Experiment on Phosphorus Recovery from Digested Sludge Using Struvite Crystallization Method

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1. Introduction

The Osaka City Government has been promoting a project of centralized sewage sludge treatment. Anaerobically digested sludge generated at each sewage treatment plant is conveyed to Maishima Sludge Center through the sludge-conveying conduit. Those plants adopt a high-solids and thermophilic digestion process to ensure the efficiency and stability of sludge treatment. The digested sludge generated from the process contains highly concentrated NH_4^+, HPO_4^{2-} and Mg^{2+}. Therefore there is concern that they may cause significant damage to the sludge treatment by precipitating struvite scale on inner walls of the latter facilities such as piping, reservoir tank for digested sludge or sludge-conveying conduit. Currently, in order to prevent generation of struvite scale, ferric salt is added into the digested sludge. HPO_4^{2-}, which is one of struvite components, is fixed as ferric phosphate. However, ferric salt might give a bad influence on the melting furnace in Maishima Sludge Center, or running cost would be expensive if keeping on using ferric-salt reagent continuously.

Recently, a new method to recover phosphorus has been developed. It is a struvite crystallization method from the digested sludge directly. This paper reports the result of the pilot-plant experiment.

2. Experiment plant

Schematic diagram of the experimental plant for struvite recovery is shown in Fig. 1 and the specification of the plant is summarized in Table 1. It consisted of a struvite crystallization and granulation unit, a struvite concentration unit and a struvite recovery unit.

At the struvite crystallization and granulation unit, the digested sludge was supplied to the struvite reactor, and reagents ($MgCl_2$ or $Mg(OH)_2$, and NaOH) were injected in order to remove PO_4-P from the digested sludge by crystallizing struvite. Then the reactor-treated sludge flowed out from the struvite reactor. At the struvite concentration unit, minute struvite crystals were collected from the reactor-treated sludge by the liquid cyclone, and they were returned to the reactor as seed crystals. Thus, minute crystals grew into granules and then accumulated in the struvite reactor while going and returning the struvite reactor and the liquid cyclone.

The accumulated granules in the struvite reactor need to be occasionally removed. The mixtures of the granules and sludge in the struvite reactor were withdrawn from the bottom. Then the struvite granules were separated from the mixtures at the struvite recovery unit.

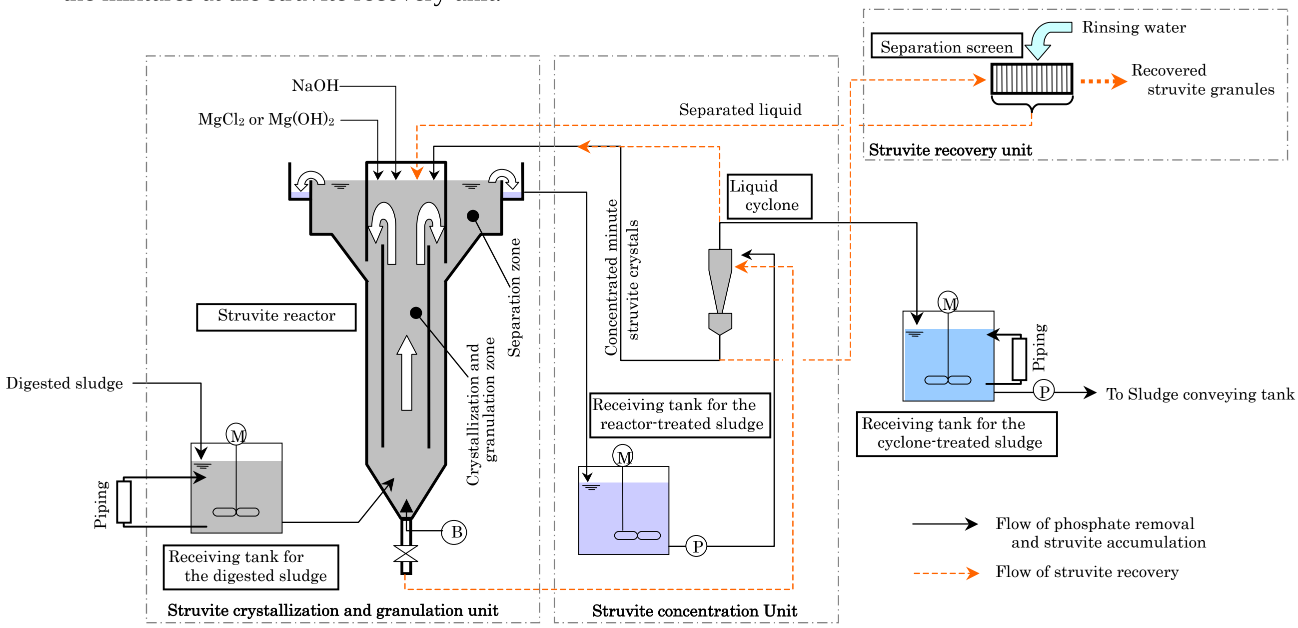

Fig. 1 Schematic diagram of struvite recovery experimental plant

3. Results

(1) Review of Mg reagent

The pH of the digested sludge was around 8 when it was supplied into the struvite reactor. The digested sludge contained about 100 to 140 mg/L of PO_4-P, about 1,000 mg/L of NH_4-N and about 10 mg/L of Soluble-Mg, which were the main components of struvite.

Fig. 2 shows the relationship between the molar ratio of added Mg to PO_4-P in the digested sludge and the PO_4-P in the reactor-treated sludge.

When $MgCl_2$ was added (see ●and ○), the PO_4-P concentrations in the reactor-treated sludge were mostly equal to or less than 20 mg/L, which was the target value for this experiment. On the other hand, when $Mg(OH)_2$ was added without pH adjustment (see △), the PO_4-P concentrations in the reactor-treated sludge were influenced by the molar ratio of added Mg. In order to achieve 20mg/L or less of PO_4-P, 1.5 or more ratio of added-Mg/PO_4-P was needed. These results suggest that it takes more time to complete the reaction of struvite generation by using $Mg(OH)_2$ than $MgCl_2$ since the solubility of $Mg(OH)_2$ is lower than that of $MgCl_2$. Furthermore, the solubility of $Mg(OH)_2$ is lowered in the digested sludge, as its pH was already around 8 before these treatment. In the case of $Mg(OH)_2$ with pH adjustment (see ▲), the solubility was much more lowered because pH was raised to 8.5 by adding NaOH, and the PO_4-P concentration was almost at the same level as that of the digested sludge. This suggests that it is unnecessary to adjust pH by adding NaOH in the case of using $Mg(OH)_2$ as the Mg reagent.

These results conclude that $MgCl_2$ would be more appropriate as the Mg reagent. However, $MgCl_2$ is four times expensive than $Mg(OH)_2$ in Japanese market and $Mg(OH)_2$ is also useful as long as it is correctly used. Therefore $Mg(OH)_2$ was selected as the Mg reagent, taking into account of the required amount not only in the experiment plant but also in full-scale plants.

Table 1　Specification of experiment plant

Treatment capacity of struvite reactor	5 m^3/day
Hydraulic retention time of struvite reactor	Crystallization and granulation zone : 25 min
	Separation zone : 20min
Overflow rate of separation zone	30 m^3/m^2/day
Agitation air to struvite reactor	30 m^3/m^2/hr
Treatment capacity of liquid cyclone	100 to 1400 m^3/day
Separation screen	Mesh size: 0.3 mm

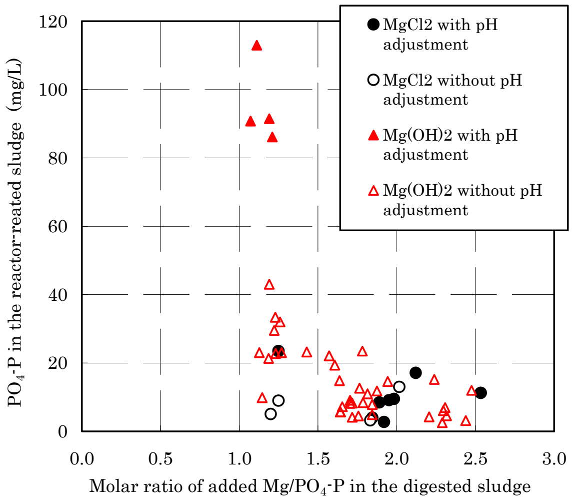

Fig. 2　Relationship between the molar ratio of added Mg/ PO_4-P in the digested sludge and the reactor-treated sludge PO_4-P (Mg reagent: $MgCl_2$ and $Mg(OH)_2$)

(2) Quantity of Soluble-Mg in the reactor-treated sludge

Fig. 3 shows the relationship between PO_4-P and remaining Soluble-Mg (S-Mg) in the reactor-treated sludge. The shapes of the dots express the molar ratio of added Mg to PO_4-P in the digested sludge.

In the case the molar ratio of added Mg/digested sludge PO_4-P was 1.5 or more (see ◆ and ×), remaining S-Mg in the reactor-treated sludge was more than 15mg/L while PO_4-P was less than 20mg/L. If the reactor-treated sludge contains high concentration of remaining S-Mg and it is mixed with untreated digested sludge, struvite scale would possibly precipitate. Therefore, it is necessary to pay attention to how to reduce remaining S-Mg such as extending the reaction time.

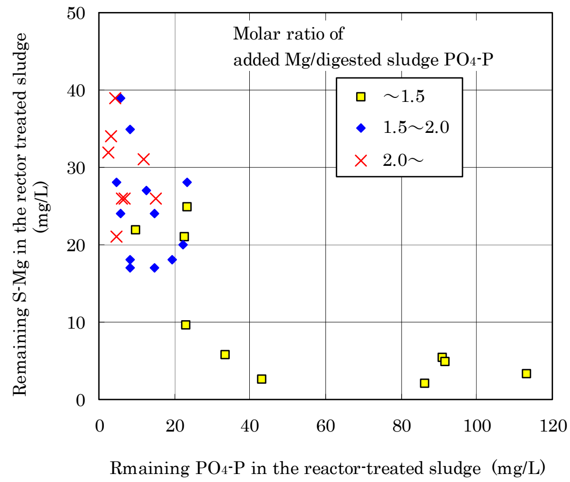

Fig. 3　Relationship between PO_4-P and S-Mg in the reactor-treated sludge (Mg reagent: $Mg(OH)_2$)

(3) Properties and particle sizes of the recovered struvite

For separation and recovery of the particles from the treated sludge, a screen with mesh size of 0.3mm was used in the struvite recovery unit. The withdrawn interval had to be set at one to two weeks because the diameter of the granules had to be kept larger than the mesh size. Setting this withdrawn interval ensured the diameter size of the recovered struvite particles to be maintained at 0.3 to 2mm. About 60% or more of these particles were 425 to 800μm in diameter by volume percentage.

(4) Applicability of the recovered particles for fertilizer

Table 2 summarizes the contents of major components and hazardous components of the recovered particles from the experimental plant. The recovered particles contained nitrogen, phosphorus and magnesium. The percentages of them are approximately equal to those of pure struvite. And the results of X-ray diffraction also revealed that the recovered particles were struvite.

The values of hazardous components were much less than the official permit of the Fertilizer Control Act in Japan. All the information above verifies that the recovered particles are available for one of raw materials of compound fertilizer.

Table 2 Contents of major components and hazardous components

Analysis parameters		Unit	**Content in the recovered particles**	**Content in pure struvite**
Ammonia nitrogen	(as N)	(%)	5.40	5.71
Citric acid-soluble phosphate	(as P_2O_5)	(%)	27.98	28.91
Citric acid-soluble Magnesium	(as MgO)	(%)	15.00	16.42
Major components, total	*	(%)	33.38	34.62
Thiocyanate	(as SCN)	(%)	<0.02	
Nitrite	(as NO_2)	(%)	<0.01	
Biuret nitrogen	(as $(CO{\bullet}NH_2)_2NH$)	(%)	<0.01	
Sulfamic acid	(as NH_2SO_3H)	(%)	<0.01	
Titan	(as Ti)	(%)	0.0028	
Total mercury	(as T-Hg)	(%)	<0.000001	
Cadmium	(as Cd)	(%)	<0.00001	
Lead	(as Pb)	(%)	0.0003	
Chromium	(as Cr)	(%)	0.0001	
Arsenic	(as As)	(%)	0.00028	
Nickel	(as Ni)	(%)	0.0029	

* Total percentage of Ammonia nitrogen and Citric acid-soluble phosphate

(5) Results of simulated experiment of sludge conveyance

As shown in Fig.1, each of the receiving tanks for the digested sludge and the cyclone-treated sludge was connected with the piping. Each piping was made of SUS304 and had a diameter of 25 mm. The inner surface of it had be scratched intentionally. The sludge in each tank was continuously circulated through the pipe at the flow rate of 100 L/min in order to confirm whether struvite scale formation would occur on inner wall of the pipe or not.

125 days after beginning of circulation, struvite scale that had a thickness of about 2.5mm was observed on the piping in which digested sludge had been circulated, whereas no scale was detected on the piping in which the cyclone-treated sludge had been circulated (Fig. 4). In addition, a large amount of scale formation was observed on the agitation blades used in the receiving tank for the digested sludge, whereas no scale formation was found on the agitation blades of the receiving tank for the reactor-treated sludge (Fig. 5).

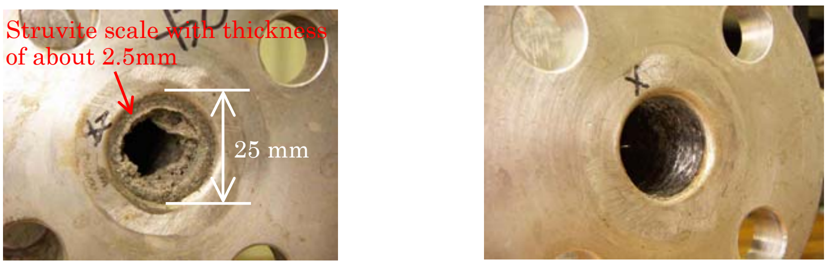

Fig. 4 Digested sludge circulated pipe (left)
Cyclone-treated sludge circulated pipe (right)

Fig.5 Agitation blade used in the receiving tank for the digested sludge (left)
and in the receiving tank for the reactor-treated sludge (right)