

# Struvite recovery from wastewater having low phosphate concentration

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## Abstract

Liquid-solid two-phase fluidized bed type reactor was operated for struvite recovery for the purpose of developing the reactor that can be applied to wastewater having low  $\text{PO}_4\text{-P}$  concentrations. In area-wide sewage sludge treatment plant, the reactor was examined to recover struvite from thickener effluent, whose  $\text{PO}_4\text{-P}$  concentration was around 40 mg/L. When the thickener effluent was treated by the reactor without the addition of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  affected struvite recovery and the Ca contents of the recovery particles increased. In batch tests, it was confirmed that the condition where struvite precipitates prior to calcium phosphate in wastewater requires the condition of  $[\text{Ca}^{2+}]/[\text{Mg}^{2+}] < 0.25$  in the influent. The inorganic SS flowing into the reactor was also found to affect the recovery in column tests. To prevent this effect by the inorganic SS, the reactor was operated without the influent of fine suspended solids in the wastewater from the melting furnace. The only influent processed was the thickener effluent, and  $\text{MgCl}_2$  aq. was added using a magnesium resource. Consequently, the recovery rate improved to 62%. In the case that struvite is recovered from wastewater including low  $\text{PO}_4\text{-P}$  concentration, the recovery rate of struvite was affected by the coexistent substances in the influent. But if this effect was controlled, this reactor could recover struvite particles passably.

Keywords Struvite; fluidized bed; calcium phosphate; melting furnace

## Introduction

Increasing demand for methods of preventing eutrophication in closed water bodies in Japan, combined with a nationwide shortage of phosphorus resources, has recently stimulated extensive studies on several kinds of phosphate recovery processes. Struvite (magnesium ammonium phosphate:  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) recovery is one of the most promising of these processes because struvite has a high utility value and is easy to handle when recovered in granular form. Until recently, six full-scale plants using struvite crystallizers have been operating in Japan, and the recovered struvite granules have been used mostly as fertilizer (Katsuura et al., 1998, Tomoda, 1999). However, the application of this recovery process is limited to the supernatant of anaerobically digested sludge and some industrial wastewater having high phosphorus concentrations. This is because the effluent from a struvite crystallizer normally has a rather high phosphate concentration, and the efficiency of the struvite recovery process tends to deteriorate in applications involving low phosphate concentrations.

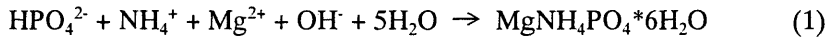
Therefore the authors have developed a new type of struvite crystallizer that can be applied to wastewater having low phosphate concentrations. In this article, the experimental results of this reactor are reported.

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## Theoretical Considerations

### Struvite reaction

In wastewater containing both soluble  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$ , struvite crystallizes if  $\text{Mg}^{2+}$  and alkali are added.



The equilibrium of Eq. (1) is expressed as a solubility product, KSP. Tsuno et al. demonstrated this equilibrium in an experiment (Tsuno et al., 1991), where  $\log\text{KSP}(\text{struvite}) = -14.1$ :

$$\text{KSP} = r_1[\text{Mg}^{2+}] \cdot r_2[\text{HPO}_4^{2-}] \cdot r_3[\text{NH}_4^+] \cdot r_4[\text{OH}^-] = 7.8 \times 10^{-15} \text{ (mol/L)}^4 \quad (2)$$

$r$  : activity coefficient of individual ions

Equation (2) shows that a high pH level is required to treat wastewater having a low  $\text{PO}_4\text{-P}$  concentration. A high pH level is necessary because the running costs of a reactor would increase if too much  $\text{Mg}^{2+}$  were added.

Table 1 lists the dissociation constant for each ion (Stumm et al., 1981). Each ion in Eq. (2) has a different form depending on the pH condition of the water. Furthermore, each ion has a short reaction time in a struvite reactor and, thus, the reaction does not quite attain equilibrium. If this difference from equilibrium for a single ion is given as  $s$ , the concentration product of four ions in effluent KSP is expressed by:

$$\begin{aligned} \text{KSP} &= r_1 s_1 [\text{Mg}^{2+}] \cdot r_2 s_2 [\text{HPO}_4^{2-}] \cdot r_3 s_3 [\text{NH}_4^+] \cdot r_4 s_4 [\text{OH}^-] \\ &= \text{KSP} \cdot S^4 \end{aligned} \quad (3)$$

$$S = (s_1 s_2 s_3 s_4)^{0.25} \quad (4)$$

Table 1 Dissociation constants

$\log^* \text{K}_1(\text{hydrolysis of } \text{Mg}^{2+})$	-11.4
$\log \text{K}_1(\text{NH}_4^+)$	-9.24
$\log \text{K}_1(\text{HPO}_4^{2-})$	-12.1
$\log \text{K}_2(\text{H}_2\text{PO}_4^{2-})$	-7.2
$\log \text{K}_3(\text{H}_3\text{PO}_4)$	-2.1

### Phosphate removal

In a reactor, struvite crystallizes on the surface of seeds instead of in wastewater. Accordingly, the recovered struvite is granular. However, if there is excessive crystallization in any particular volume of wastewater, struvite first crystallizes in the wastewater before crystallizing on seeds. Consequently, the reaction conditions must be controlled, such as by circulating treated water to the lower section of a reactor.

## Materials and Methods

### Pilot plant

The reactor is a liquid-solid two-phase fluidized bed reactor, which has seeds of struvite particles (see Figure 1). Table 2 lists the size and the operating specifications of the reactor. The reactor is 5.3 m high, its reaction section has a diameter of 0.6 m, and its separation section has an overflow rate of 20 m/hr. Past struvite reactors in Japan had large separation sections whose top overflow rates were around 50 m/day. The structure of these separation sections was based on the following concepts:

- The large separation section holds the fine particles momentarily. This is to prevent the fine struvite particles from flowing out into the effluent and being lost.

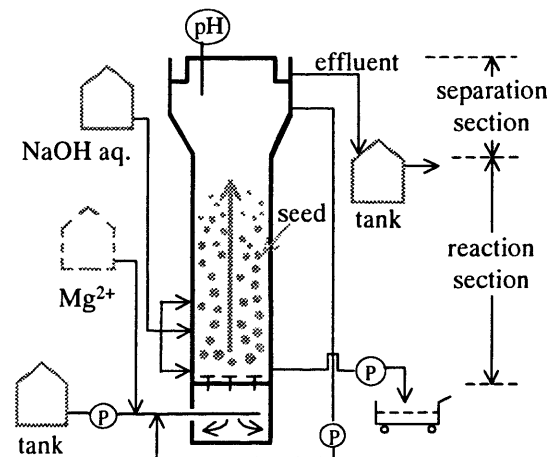


Fig.1 Scheme of pilot scale reactor

b. The fine particles remain in the separation section until they grow to the extent that they are not lost in the effluent from the reaction section. These grown particles are subsequently recovered.

However, these reactors require set-up areas for large separation sections. Accordingly, these reactors cannot be easily scaled up to treat large volumes of wastewater. Since the purpose was to develop a reactor that can be easily scaled up, the authors first determined the appropriate particle size of seeds for the reactor and then designed the reactor structure. Namely, fluidization of the seeds was firstly considered and then settleability of the seeds arrived at the reactor structure.

Table 3 lists the formulas and the conditions related to fluidization of the seeds (The Society of Chemical Engineers, Japan, 1999). Given a particle size of 1 mm for every single seed and a superficial upflow velocity of 60 m/hr (based on an empty vessel) in the reaction section, the height of the fluidized bed was calculated as 135% of the height required for the previous fluidization. Since a bed built in accordance with this calculation was found to be sufficiently high to fluidize the seeds, this particle size was adopted as the standard. The overflow rate in the separation section was set up to be half of that in the reaction section. This was done to prevent seed outflow in the event of excessive expansion of the fluidized bed. Because the authors considered separation for only particles of around 1 mm, the separation section is smaller than that used in past reactors. Therefore, production using this type of reactor is easy to scale up.

Because the reactor was not equipped to handle aeration mixing, the alkali injection nozzles were set up for use verti-

Table 2 Pilot scale reactor

Treated quantity		266 m <sup>3</sup> /day
circulating quantity of effluent		133 m <sup>3</sup> /day
Reaction part	diameter	0.6 m $\phi$
	LV(sum of influent and circulating water of effluent)	60 m/hr
Separation part	Diameter	0.85 m $\phi$
	Overflow rate	20 m/hr
Height		5.3 mH
Aeration		-
Operating pH		8.8

Table 3 Calculation of fluidization

$Re_t = D_p U_i Y_F / Z_F$	(1)
$U_i = \{(4/225)(Y_P - Y_F)2g^2 / Z_F Y_F\}^{1/3} D_p$ $10 < Re_t < 500$	(2)
$U_0 / U_i = \epsilon^N$ $N = (4.45 + 18D_p / D_F) Re_t^{-0.1}$ $1 < Re_t < 200$	(3)

Case

$$D_p = 1.0 \times 10^{-3}, D_F = 0.6, g = 9.8, U_0 = 1.67 \times 10^{-2}$$

$$Y_P = 1.7 \times 10^3, Y_F = 1.0 \times 10^3, Z_F = 1.0 \times 10^{-3}$$

$$Re_t = 94.2, U_i = 9.4 \times 10^{-2}, \epsilon = 0.54$$

$$0.54 / 0.4 \times 100 = 135 (\%)$$

Table 4 Operation condition

	Run 1	Run 2
Influent	thickener effluent and wastewater from melting	thickener effluent
Magnesium	—	MgCl <sub>2</sub> aq.
Alkali injection	two steps	three steps

cally in three steps. It was confirmed that the rate of crystallization could be controlled by varying the circulation of effluent in column tests, where the reactor was operated using volumes 266 m<sup>3</sup>/day for influent, with half of this volume circulated. For this study, the reactor was operated in accordance with the conditions listed in Table 4.

Table 5 Content of wastewater

	thickener effluent	filtrate	wet type E.P.	exhausted gas treatment tower	influent of struvite reactor
pH	6.41	6.33	5.77	7.13	
T-P mg/L	54.5	57.5	118.7	90.5	58.2
PO <sub>4</sub> -P mg/L	40.3	47.6	67.2	54.5	41.8
NH <sub>4</sub> -N mg/L	59.1	66.5	1.5	1.6	55.3
SS mg/L	668	260	1129	4773	766
Ca <sup>2+</sup> mg/L	45.7	57.3	32.0	42.8	45.0
Mg <sup>2+</sup> mg/L	60.0	67.9	545	3166	141

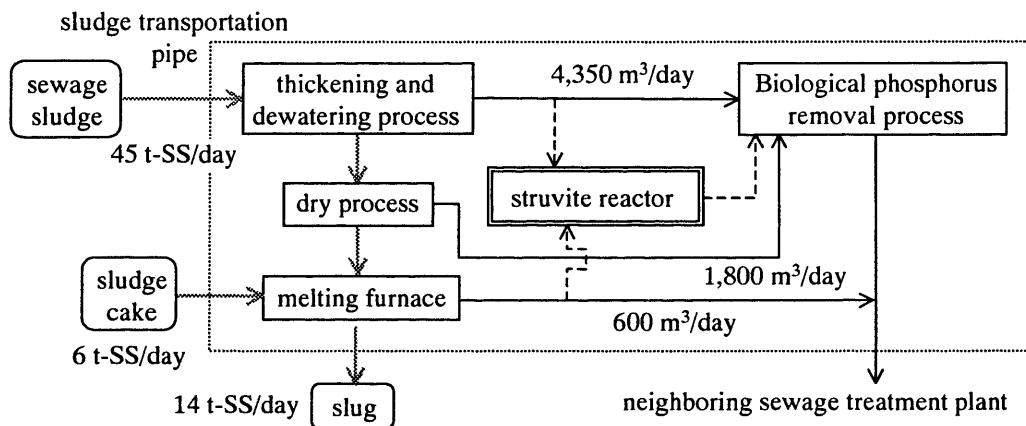


Fig. 2 Treatment process of Osaka-Minami ACE center and influent of pilot scale reactor

### Osaka-Minami ACE center

Osaka-Minami ACE center was selected as the examination site (Mishina et al.,1999). This ACE center is an area-wide sewage treatment plant for Southern Osaka. In fiscal 1998, its three melting furnaces treated 51 t/day (dry solid basis) of sewage sludge (see Figure 2).

In the sludge treatment process, the pilot scale reactor for struvite recovery treated three kinds of wastewater, thickener effluent, and wastewater from the E.P. and from the exhausted gas treatment tower. The thickener effluent included soluble PO<sub>4</sub>-P and NH<sub>4</sub>-N to crystallize struvite, and the wastewater from the tower included plenty of Mg<sup>2+</sup> (see Table 5). The reactor influent was adjusted to match the physical conditions at the ACE center.

### Column test

The column test was carried out to examine the scale-down capability of the pilot scale reactor.

The conditions of the test are as follows: diameter of reaction section: 30 mm; diameter of separation section: 43 mm; bed height: 2,000 mm; seeds of struvite (particle size of 0.5 to 1 mm): 500 g; influent a) is the influent filtrating through polypropylene membrane to the pilot reactor; influent b) is the mixture of SS in wastewater from the melting furnace with influent a); pore size of the membrane: 0.2\*10<sup>-6</sup> m; volume of the influent and circulation of the effluent during operation: 360 ml/min; operating pH level: 8.8

### Batch test

KH<sub>2</sub>PO<sub>4</sub>, NH<sub>4</sub>Cl, MgCl<sub>2</sub>·6H<sub>2</sub>O and CaCl<sub>2</sub>·2H<sub>2</sub>O are soluble in pure water, and each tested sample of water was 300 ml (Table 6). The concentration of each sample was set up based on the model of influent for the pilot reactor. Two-gram

seeds of struvite were added to each test sample of water, and each sample was adjusted to a pH of 8.8 by 0.5 mol/L

Table 6 Conditions of batch tests

PO <sub>4</sub> -P	30 mg/L	70 mg/L
NH <sub>4</sub> -N	60 mg/L	60 mg/L
Mg <sup>2+</sup>	50 mg/L	50 mg/L
	75 mg/L	75 mg/L
	100 mg/L	100 mg/L
Ca <sup>2+</sup>	[Ca <sup>2+</sup> ]/[Mg <sup>2+</sup> ] (mol/mol): 0.15, 0.3, 0.5, 0.75, 1	

their PO<sub>4</sub>-P, NH<sub>4</sub>-N, Ca<sup>2+</sup> and Mg<sup>2+</sup> concentration.

NaOH aq. The reaction time for all tests was two hours. The supernatants of treated water were filtrated through the membrane, which has a pore size of 0.45\*10<sup>-6</sup> m, and these filtrates were analyzed for

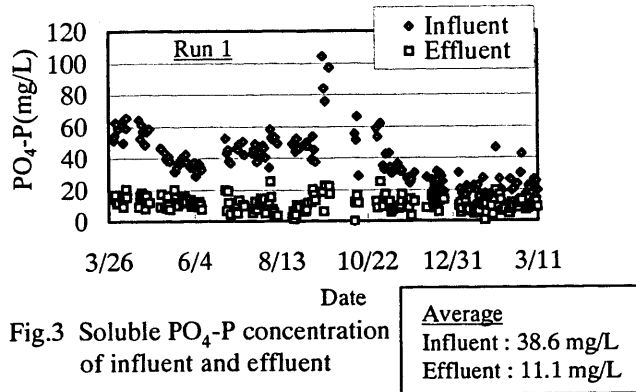


Fig.3 Soluble PO<sub>4</sub>-P concentration of influent and effluent

## Results and Discussion

### Phosphate removal by reactor

Figure 3 shows the influent and effluent soluble PO<sub>4</sub>-P concentrations at the pilot plant. Regardless of any slight changes in the influent concentration, the effluent PO<sub>4</sub>-P concentration was stable at around 10 mg/L.

Struvite particles had an average diameter of 2 mm, which was larger than the estimated standard. However, the fluidization of the seeds was sufficient for operating the reactor. When Mg<sup>2+</sup> was added from the gas scrubber of the melting furnace and alkali was injected in two steps during operation of the reactor, the relationship between the recovered struvite and the amount of soluble PO<sub>4</sub>-P that was precipitated in the reactor is that shown in Figure 4. The slope of the line in Fig. 4 indicates the proportion of struvite recovered, and the recovery rate was about 50% (for Run 1).

To compare the water quality of the effluent with the reaction equilibrium of struvite, the difference between the solubility product of struvite and the ion products of the effluent was calculated using Eq. (3), (4), and the values listed in Table 1.

Figure 5 shows the results of the calculation, revealing the relationship between S and the effluent soluble PO<sub>4</sub>-P concentration. S had a distribution of around 1.23. When the effluent PO<sub>4</sub>-P concentration was low, S dropped to 1.00. If each s

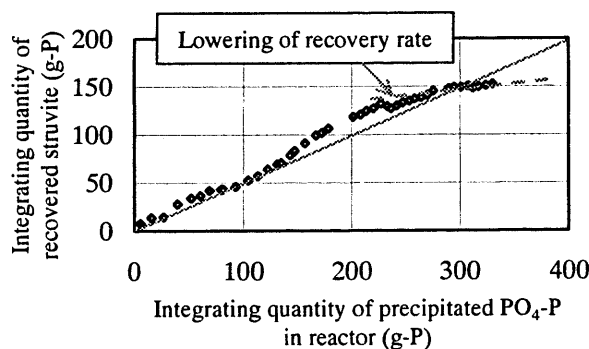


Fig.4 Recovery rate of struvite

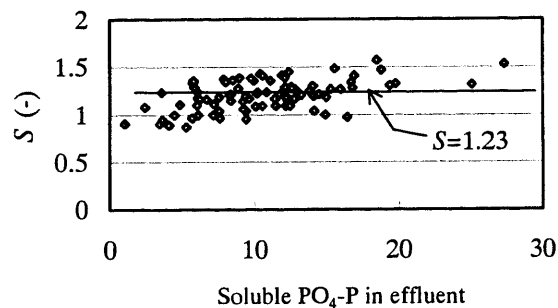


Fig.5 The relation between soluble PO<sub>4</sub>-P and S

is 1.00, the struvite reaction reaches its equilibrium. Therefore, when the effluent PO<sub>4</sub>-P concentration was low, the soluble PO<sub>4</sub>-P was considered to be precipitated by a secondary reaction with another substance in the influent. As a result of these findings, it was confirmed that a soluble PO<sub>4</sub>-P concentration can be ex-

Table 7 Content of recovered particle

	theoretical contents	recovered particles	recovered particles
		<u>1</u>	<u>2</u>
N	5.7	4.3	2.5
P <sub>2</sub> O <sub>5</sub>	28.9	30.1	26.4
MgO	16.4	15.2	10.3
CaO	—	3.4	10.8

(%)

- 1 : They were recovered just before the maintenance of melting furnace.  
2 : They were recovered among the maintenance of melting furnace.

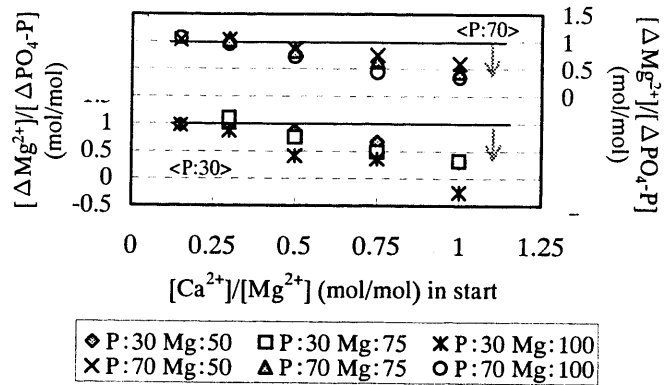


Fig.6 Results of batch tests

pected in the effluent from the reactor if the solubility product of struvite is corrected by  $S = 1.23$ .

### Effect of Calcium ions

Later in the process shown in Figure 4, the melting furnace entered a maintenance period and Mg<sup>2+</sup> was not added to the reactor influent. Therefore, the magnesium ion concentration in the reactor influent decreased to around 50 mg/L, and the Ca contents of the recovery particles increased (see Table 7).

As for the effect of calcium ions, Battistoni et al. reported the eutectoid reaction to struvite and calcium hydroxyapatite from the supernatant of digested sludge (Battistoni et al., 1998). They reported the results under the experimental conditions where  $[Ca^{2+}]/[Mg^{2+}] > 1.6$ , which is the molar ratio in influent. Their article does not describe how this phenomenon affects the recovery of phosphates.

In this work, influent was included in  $[Ca^{2+}]/[Mg^{2+}] < 1$ . The NH<sub>4</sub>-N concentration of the thickener effluent in the ACE center is one order of magnitude weaker than that in the supernatant of digested sludge. Therefore, struvite is difficult to precipitate compared with the supernatant of digested sludge.

Batch tests were implemented on the assumption that struvite formation can be affected by the coexistence of calcium ions. The resulting conclusion was that the condition where struvite precipitates prior to calcium phosphate in wastewater requires the condition of  $[Ca^{2+}]/[Mg^{2+}] < 0.25$  in the influent (see Figure 6). In the experiments at the ACE center, the wastewater from the gas scrubber had a high concentration of magnesium ions, an average of 3,165 mg/L. This wastewater mixed with the thickener effluent, and this mixture, which is the struvite reactor influent, had the  $[Ca^{2+}]/[Mg^{2+}]$  molar ratio of below 0.4. When the melting furnace was being repaired, the  $[Ca^{2+}]/[Mg^{2+}]$  molar ratio was about 0.6. Therefore it was supposed that calcium phosphate partly was co-crystallized with struvite for the coexistence of Ca<sup>2+</sup> at the ACE center.

### Effect of suspended solids from melting furnace

The wastewater used in the gas treatment process of the melting furnace contained fine inorganic solid substances. Figure 7 shows an X-ray diffraction spectrum of suspended solids in the gas scrubber. The diffraction peaks of Mg(OH)<sub>2</sub> and Ca<sub>7</sub>Mg<sub>2</sub>P<sub>6</sub>O<sub>24</sub> were confirmed. Depending on the operating conditions in the melting furnace, CaHPO<sub>3</sub> and Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> were detected and the amorphous substances were intermixed.

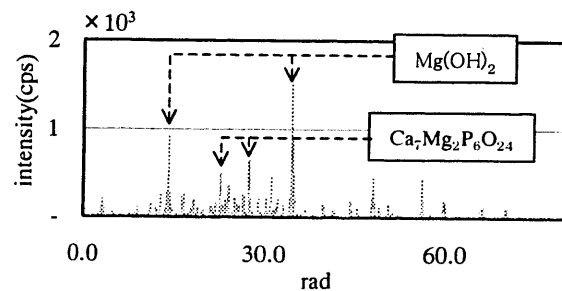


Fig.7 X-ray diffraction of suspended solids in the wastewater from the gas scrubber

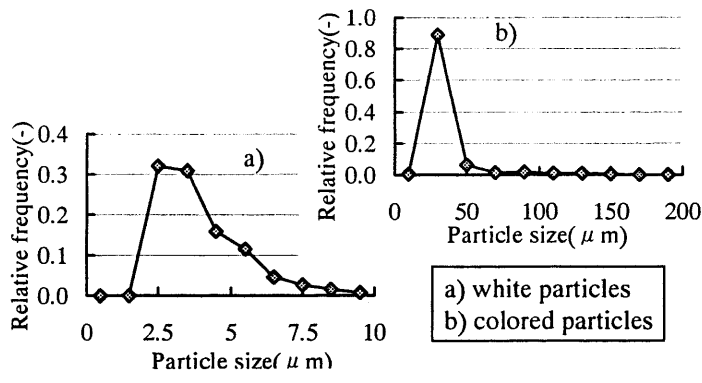


Fig.8 Particle size distribution of suspended solid in wastewater of the gas scrubber

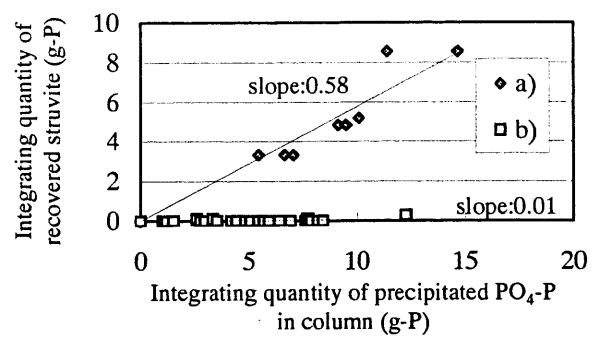


Fig. 9 Results of column tests

Figure 8 shows the particle size distribution of these suspended solids. These can be classified into two distributions by color. The relative frequency of the particle size distribution is biased near  $30 \times 10^{-6}$  m. The upflow of 20 m/hr in the separation section of the reactor suggests that this upflow was larger than the terminal velocity of a  $30 \times 10^{-6}$  m lead particle (lead density:  $1.13 \times 10^4$  kg/m<sup>3</sup>;  $U_{t,Pb} = (Y_{P,Pb} - Y_F)gDP_{Pb}^2/18ZF = 5.1 \times 10^{-3}$  m/s by Stokes's formula).

Therefore, irrespective of the operating conditions for the melting furnace, it was presumed that SS from the melting furnace is usually effluent without accumulating.

Using the column test, it was examined whether the fine particles affect on struvite recovery. Figure 9 shows the test results. Struvite was seldom recovered when inorganic SS flowed into the column at an average of 412 mg/L. Accordingly, inorganic SS is considered to be capable of affecting struvite recovery if a large volume of SS flows into the reactor.

To reduce this effect, the reactor was operated without wastewater from the melting furnace. Instead of wastewater, MgCl<sub>2</sub> aq. was added and alkali injection was done over three steps in Run 2.

In Figure 10, the authors added magnesium in the gas scrubber process during the period shown on the left side of the center line, and injected the alkali vertically in two steps. In the period shown on the right side of the center line, MgCl<sub>2</sub> aq. was added and alkali was injected in three steps (for the second run). The figure shows the improvement in the struvite recovery rate from 50% to 62% before and after this change in the operating method. This confirms that the influent containing suspended solids to the reactor must be considered in the recovery of struvite. Accordingly, it was confirmed that this reactor could recover struvite particles passably if it was controlled that the coexistent substances in the influent affected the recovery rate of struvite.

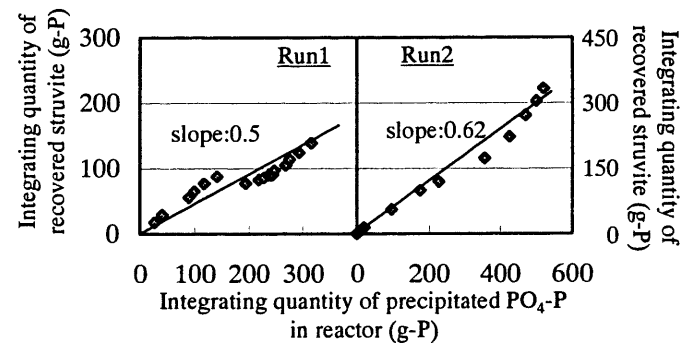


Fig.10 Recovery rate of struvite

**Conclusion**

The authors have examined a liquid-solid two-phase fluidized bed reactor for the purpose of developing the reactor that can be applied to wastewater having low phosphate concentrations and Osaka-Minami ACE center was selected as the examination site. As a result, it was found that struvite particles can be recovered, and that the reactor effluent can be expected to have the soluble PO<sub>4</sub>-P concentration if the solubility product of struvite is corrected. When the thickener

effluent was treated by the reactor without the addition of  $Mg^{2+}$ ,  $Ca^{2+}$  affected struvite recovery and the Ca contents of the recovery particles increased. In batch tests, it was confirmed that the condition where struvite precipitates prior to calcium phosphate in wastewater requires the condition of  $[Ca^{2+}]/[Mg^{2+}] < 0.25$  in the influent. The inorganic SS flowing into the reactor was also found to affect the recovery in column tests. To prevent this effect by the inorganic SS, the reactor was operated without the influent of fine suspended solids in the wastewater from the melting furnace. The only influent processed was the thickener effluent, and  $MgCl_2$  aq. was added using a magnesium resource. Consequently, the recovery rate improved to 62% and it was confirmed that this reactor could recover struvite particles passably.

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## Numencleture

DP : diameter of solid particle [m]	Ut : terminal falling velocity of a particle [ $m \cdot s^{-1}$ ]
DF : diameter of vessel [m]	
$\epsilon$ : bed voidage [-]	U0 : superficial velocity of liquid based upon empty vessel [ $m \cdot s^{-1}$ ]
g : acceleration due to gravity [ $m \cdot s^{-2}$ ]	
Ret : particle Reynolds number based on terminal falling [-]	YP : density of solid particle [ $kg \cdot m^{-3}$ ]
ZF : viscosity of liquid [ $kg \cdot m^{-1} \cdot s^{-1}$ ]	YF : density of liquid [ $kg \cdot m^{-3}$ ]