# Phosphorus Removal from Hoggery Sewage Using Natural Calcium Carbonate

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#### Abstract

For the treatment of hoggery sewage, an attempt was made to develop a phosphorus removal technique by using natural calcareous materials whose products can be restored to farmland as phosphate materials with minimal waste, at a low cost and with easy management. The results of tests on packed materials passing through a water column under the same conditions reveled that the efficiency of phosphorus removal characteristics was in the order of Sakhalin surf clam > oyster seashell, scallop seashell > coral sand > fossilized seashell > dolomite for twice the daily amount of passed water. In brief, young calcareous sources originating from marine Conchifera were superior as dephosphorization materials. The mechanism involved in phosphorus removal of natural calcareous materials was neither absorption to materials nor crystallization but a direct replacement reaction from carbonates to phosphates. Since the produced salts were CaHCO3 and Ca4H (PO4) 3 with low Ca/P and OH/P ratios, highly valuable phosphates for fertilizer were obtained. Since the pH of effluents was 8.5 at the maximum and lies within the legal standard range, the dissolution of carbonates and the production of phosphates prevent clogging and the total cost is low. If the TOC and TIC concentrations of influents are high, the TIP concentration in the effluents easily increases. However, it was demonstrated that 24 h aeration in the presence of sludge results in a decrease of the pH due to accelerated nitrification and that the release of supersaturated CO<sub>2</sub> into the atmosphere can lower the TIC significantly.

Discipline: Agricultural environment Additional key words: oyster seashell, Sakhalin surf clam, scallop seashell, coral sand, calcareous material

# Introduction

It is generally recognized that nutrient salts of nitrogen, phosphorus, etc. substantially affect the eutrophication of a water body. The effluent standard for nitrogen and phosphorus according to the Japanese Water Pollution Control Law has decreased based on examinations at intervals of 5 years. As a result, the development of techniques for the disposal of livestock excreta is essential to preserve the growth of stock breeding.

For the removal of nitrogen, removal of active sludge with intermittent aeration<sup>3,4,7</sup> and soil column method<sup>1,4</sup> through biological denitrification have been developed. However these methods cannot be easily applied for the removal of high concentrations of nitrogen and phosphorus in hoggery sewage. In addition, the removal of phosphorus by soil absorp-

tion is limited by the absorption capacity<sup>4)</sup>. Furthermore, physico-chemical methods of phosphorus removal such as lime coagulation method<sup>6)</sup> and crystallizing dephosphorization method<sup>2,5,6)</sup> are costly and since the generated amount of sludge is large and the pH of sludge is high, their application is unsuitable from the standpoint of farmland restoration. Therefore, a phosphorus removal method using natural calcareous materials whose products can be restored to farmland as phosphate materials with limited waste, at a low cost and with easy management was developed for the treatment of hoggery sewage.

# Materials and methods

#### 1) Experiment 1

The dephosphorization capacity of natural materials mainly consisting of calcium carbonate was

examined based on water passage tests. The dephosphorization reaction occurring in a column was examined stoichiometrically by chemical component analysis of influents and effluents.

(1) Column packing materials

Materials mainly consisting of natural calcium carbonate, dolomite, fossilized seashell, coral sand, oyster seashell (Ostracea), Sakhalin surf clam (Spisula syballae) and scallop seashell (patinopecten) were selected and crushed into fragments. The crushed fragments 1.0-1.7 mm in grain size were employed as packing materials.

(2) Composition of synthesized sewage

In general, the nitrogen concentration of hoggery sewage is several thousands mg/L and the phosphorus concentration is several hundreds mg/L<sup>3,4)</sup>. Sewage is treated after the completion of intermittent aeration treatment and the corresponding concentration of nitrogen is 100 mg/L and lower while 25 mg/L and higher for phosphorus. Table 1 shows the composition of the synthesized sewage used in Experiment 1. The pH and Ca/P mole ratio of sewage were set at 7.0 and about 0.7, respectively, for the physico-chemical removal of phosphorus.

(3) Water passage testing method

Fig. 1 shows a testing device. This is a simple device which allows sewage to pass through a peristaltic pump and a column packed with test materials. The passing speed of water is fixed at twice or 6 times the column capacity/day and the adjustment

Table	1.	Composition	of	synthesized	influents
1.244			_	a at measures	

CaCl <sub>2</sub>	1.9 mmol/L
MgCl <sub>2</sub>	1.8
NaNO <sub>3</sub>	7.1
NaCl	1.5
K <sub>2</sub> HPO <sub>4</sub>	1.6
KH <sub>2</sub> PO <sub>4</sub>	1.6
KCl	2.5
KHCO <sub>3</sub>	1.0
K <sub>2</sub> SO <sub>4</sub>	0.5

was carried out by adjusting the rotating speed of a pump itself and the ON/OFF switching of the power source for the pump with a timer, where the continuous inflow was set at less than 1/20 of the column capacity. The synthesized sewage was renewed every day, the receptacle for effluents was covered with parafilm to avoid the discharge of CO2 to the atmosphere and measurements of the pH, acidity and alkalinity were performed within a day.

(4) Method for measuring the water quality components

The pH, TIP (total inorganic phosphoric acid) concentration, alkalinity (4.8 Bx), acidity (8.3 Ax), and the Ca and Mg concentrations were measured for the effluents and influents. The colorimetric method after reduction with ascorbic acid was applied for the measurement of the TIP concentration. The titration method using 0.05 mol/L H<sub>2</sub>SO<sub>4</sub> and 0.10 mol/L NaOH was applied for 4.8 Bx alkalinity



Fig. 1. Apparatus used

and 8.3 Ax acidity, respectively. After the addition of  $SrCl_2$ , the concentrations of Ca and Mg were measured by atomic absorption spectrophotometry.

#### 2) Experiment 2

Oyster seashell was selected as a high dephosphorization-rate material and dephosphorization was examined in terms of the stability to thermal treatment, the difference in grain size of crushed fragments, the daily amount of passing water, and variation of the load.

# (1) Column packing materials

Air-dried oyster seashell was crushed in a stainless steel mortar and separated according to the grain size by using a square mesh sieve. Groups of small size, middle size and large size particles were defined in the range of 1.0-1.7, 1.7-2.8 and 2.8-5.0 mm, respectively. In addition, the fine grain fraction of oyster seashell was heated at 200, 600 and 800°C for 30 min in a muffle.

#### (2) Influents

Secondary treated hoggery water is a solution obtained by treating a mixture of swine feces and urine using the intermittent aeration active sludge method for dephosphorization. This raw water was mixed for 8-12 days and lots stored in a refrigerator were employed as influents for the water-passing test with daily renewal.

(3) Water-passing test method

The same method as that used in Experiment 1 was employed. However, the water-passing speed was set at twice and 6 times the column capacity for each fraction of raw material grain size and 6 times the column capacity for each fraction of heattreated samples.

(4) Method for measuring the water quality components

In addition to the components measured in Experiment 1, TOC, TIC, TP, NH<sub>4</sub>-N, NO<sub>2</sub>-N, NO<sub>3</sub>-N, Na, K, Cl and SO<sub>4</sub> were determined. Measurements were performed by the heating method (Shimadzu TOC5000) for TOC and TIC, by the potassium peroxodisulfate ( $K_2S_2O_8$ ) decomposition method for T-P, by the indophenol method for NH<sub>4</sub>-N, by ion chromatography (Yokogawa IC-7000) for NO<sub>2</sub>-N, NO<sub>3</sub>-N, Cl, SO<sub>4</sub> and TIP, by atomic



Fig. 2. Changes in phosphorus concentrations of effluents depending on material used

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absorption spectrophotometry after the addition of CsCl for Na and K.

#### **Results and discussion**

#### 1) Experiment 1

Fig. 2 shows the results of the water passage test. Although the grain size was uniform for each raw material, there was a great difference in the TIP concentration. The TIP concentration decreased in the order of oyster seashell < Sakhalin surf clam < coral sand < scallop seashell < fossilized seashell < dolomite for 6 times the daily amount of passed water and in the order of Sakhalin surf clam < oyster seashell, scallop seashell < coral sand < fossilized seashell < dolomite for twice the daily amount of passed water. Based on these results, it was concluded that a young calcareous source originating from marine Conchifere was an optimum dephosphorization material. In addition, the TIP concentrations in the effluent were unexpectedly high several days after the beginning of water passage except for fossilized seashell and Sakhalin surf clam.

Table 2 presents stoichiometric simultaneous equations for calculating the Ca/P and OH/P ratios of phosphates generated in a packed material column from the respective values of pH, 4.8 Bx, 8.3 Ax, Ca, Mg and TIP in influents and effluents.

For the dissolution of CaCO<sub>3</sub> and MgCO<sub>3</sub> in the materials, since the primary dissociation constant  $pK_1$  of  $H_2CO_3$  is 6.3 and the secondary constant  $pK_2$  is 10.3, the reactions of CaCO<sub>3</sub> +  $H_2O \rightarrow Ca^{2+}$  +  $HCO_3^- + OH^-$  and MgCO<sub>3</sub> +  $H_2O \rightarrow Mg^{2+}$  +  $HCO_3^- + OH^-$  proceeded when the pH of the measured solution was within the range of 6.3–10.3<sup>80</sup> The molarity of Ca<sup>2+</sup> + Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> and OH<sup>-</sup> in effluents was different, although the same molarity

# Table 2. Estimation methods of OH/P, Ca/P of phosphate salts formed in the column

dP	=	P <sub>in</sub> - P <sub>out</sub>
dCa	=	Ca <sub>in</sub> - Ca <sub>out</sub>
dMg	=	Mg <sub>in</sub> - Mg <sub>out</sub>
TIC	=	4.8  Bx + 8.3  Ax - P
dTIC	=	TIC <sub>out</sub> - TIC <sub>in</sub>
Casalt	=	dCa + dTIC + dMg
Psalt	-	dP
OHsalt	=	$dTIC - (H_2PO_4^- out - H_2PO_4^- in)$
		- (H <sub>2</sub> CO <sub>3out</sub> - H <sub>2</sub> CO <sub>3in</sub> )
H <sub>2</sub> PO <sub>4</sub> <sup></sup>	=	P/(10 (pH - pKc) + 1); pKc = 6.85
$H_2CO_3$	=	TIC/(10 (pH - pKc) + 1); pKc = 6.28

was observed at the time of dissolution and release into the liquid phase, because subsequent reactions for phosphate production and their accompanying change in pH led to a change in the dissociation states of the dissolved carbonic acid, hydration dissociation ion species and phosphate ion species. However, the quantity of dissolved mole of a material can be calculated from the difference in the concentration of  $H_2CO_3 + HCO_3^-$  between the effluent and the influent. Here, since the sum of measured alkalinity and acidity, i.e. the quantity of acids and alkalis required for change from 4.8 to 8.3 in pH was physico-chemically equal to the total mole quantity of H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> and the concentration of phosphoric acid measured by the colorimetric method was equal to that of  $H_2PO_4^- + HPO_4^{2-}$ , the mole quantities of  $H_2CO_3$ + HCO3<sup>-</sup> in the influent and effluent were respectively evaluated and the mole quantity for material dissolution was calculated from the difference.

The mole quantity of Ca<sup>2+</sup> taken in the salt produced was determined by subtracting the mole quantity originating in the dissolution of MgCO3 from the sum of the dissolution mole quantity obtained by the above method and the difference in Ca<sup>2+</sup> concentration between the influent and the effluent. As for OH<sup>-</sup>, the greater part of the OH<sup>-</sup> quantity released into the liquid phase in the above equation was consumed for incorporation in the salt produced and the reaction of  $H_2PO_4^- \rightarrow HPO_4^{2-}$ ,  $H_2CO_3$  $\rightarrow$  HCO<sub>3</sub><sup>-</sup> in the liquid phase. As a result, the quantity remaining unchanged in the OHliquid phase was negligible. The OH- quantity consumed in the liquid phase can be deduced from the difference in the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub> concentration between the influent and the effluent based on a conversion formula from the TIP, TIC and pH to the H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, H<sub>2</sub>CO<sub>3</sub>. The respective values of pK used in the formula were set at 7.3 and 6.38), but varied with the ionic strength. Here, since the dissolution mole ratio of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> to HPO<sub>4</sub><sup>2-</sup> was 1, the pH of an influent regulated without KHCO3 alone was 6.85, and the pH of an influent regulated with 0.05 mmol of Na2CO3 and NaHCO3 at respective concentrations without phosphorus ion species alone was 6.28, these values were adopted for the reactions.

Fig. 3 shows the dissociation state of phosphoric acid with the Ca/P and OH/P ratios of various salts including phosphate, calcium and hydroxyl groups calculated relative to  $HPO_4^{2-}$ . Based on the



Fig. 3. Mole ratio Ca/P, OH/P of each calcium phosphate complex (assuming the initial deionized status of phosphate is HPO<sub>4</sub><sup>2-</sup>)

principle of electric neutrality in salts, the salts were distributed on a straight line as shown in Fig. 3.

Salts containing greater amounts of Ca and OH relative to P cannot be easily dissolved and CaHPO<sub>4</sub> and Ca<sub>4</sub>H(PO<sub>4</sub>)<sub>3</sub> are more suitable from the standpoint of collection and utilization of phosphorus from sewage.

Table 3 shows the results of analysis of various materials and quantities of water passed as well as the mole ratios of Ca/P and OH/P of phosphates in the column calculated by the above formulae. Generally, the pH of treated liquid-waste is considered to be about 10.5 based on the lime coagulation method<sup>2,6)</sup> and around 9.5 based on the crystallizing dephosphorization method<sup>5,6)</sup>. The

upper limit of the pH of effluents in this test was very similar to that of the Japanese standard waste water value (not higher than 8.5) and can be used practically. The ratios of Ca/P and OH/P were in the range of  $0.91 \sim 1.34$  and  $-0.24 \sim 0.66$ . Comparison of these values and those in Fig. 2 suggests that CaHPO4 and Ca4H(PO4)3 were produced. In dolomite and fossilized seashell with a low removal ratio, the dissolution mole quantity was smaller than that of others. Generally, the produced salts are considered to be Ca2(OH)PO4, Ca3(PO4)2 for the lime coagulation method<sup>2,6)</sup> and Ca<sub>5</sub>(OH)(PO<sub>4</sub>)<sub>3</sub> for the crystallizing dephosphorization method<sup>5,6)</sup>. In contrast to conventional methods, highly valuable products for fertilizer can be obtained based on this test. In Fig. 2, dTIC and dP denote the dissolution mole quantity of carbonate salts and the mole quantity of phosphorus produced, and clogging is more likely to occur when the value of dP/dTIC increases. Since this value was about 1 or greater for dolomite and fossilized seashell and approximately 1 or smaller for other materials, clogging along the passage of water was unlikely to occur. Generally, in the crystallizing dephosphorization method for achieving dephosphorization by using rock phosphate and bone charcoal as seed crystals and growing a crystal as Ca<sub>5</sub>OH(PO<sub>4</sub>)<sub>3</sub> on the surface, clogging is a major problem in practice<sup>5,6)</sup>. However in this test, since the dissolution reaction of the material is further added, clogging does not occur, hence the advantage of the method.

Treatment	Y V	nH	4.8 Bx	8.3 Ax	T – P	Ca	Mg	dTIC	dP	Casalt	OH <sub>salt</sub>	Р	salt
Treatment	~	pri		(1	nmol/L	.)		(mm	ol/L)	(mmol/L)		Ca/P	OH/P
Effluent													
Coral sand	6	8.26	4.73	0.00	0.63	1.28	1.84	2.90	2.62	3.40	1.33	1.30	0.51
	2	8.41	4.22	-0.25	0.48	1.16	1.81	2.29	2.77	2.94	0.69	1.06	0.25
Fossilized	6	7.95	3.55	0.34	1.34	1.26	1.66	1.35	1.91	2.05	-0.12	1.07	-0.06
seashell	2	8.36	3.45	-0.17	0.61	1.05	1.63	1.47	2.64	2.41	-0.12	0.91	-0.05
Dolomite	6	7.83	3.53	0.43	1.73	1.07	2.00	1.03	1.52	1.58	-0.36	1.04	-0.24
	2	8.19	4.02	0.04	0.94	1.02	2.13	1.92	2.31	2.39	0.37	1.03	0.16
Oyster	6	8.00	4.89	-0.12	0.32	1.41	1.72	3.25	2.93	3.74	1.72	1.28	0.59
seashell	2	8.51	5.14	-0.42	0.28	1.41	1.75	3.24	2.97	3.70	1.64	1.25	0.55
Scallop	6	7.82	4.12	0.02	0.77	1.29	1.70	2.17	2.48	2.80	0.71	1.13	0.29
seashell	2	8.58	4.92	-0.46	0.23	1.42	1.71	3.03	3.02	3.52	1.42	1.17	0.47
Sakhalin	6	8.03	4.72	-0.10	0.35	1.42	1.66	3.07	2.90	3.61	1.53	1.24	0.53
surf clam	2	8.10	5.10	-0.19	0.02	1.36	1.62	3.69	3.23	4.33	2.12	1.34	0.66
Influent		7.01	2.60	1.85	3.25	1.88	1.74						

Table 3. Concentration of the influent and effluent and characteristics of phosphate salts formed

Based on the calculations, Fig. 4 shows the input and yield of individual components, the dissolution of carbonate salts and the quantitative relation of the salts produced with coral sand employed as a material for 6 times the daily quantity of passed water. The width of an arrow in Fig. 4 is proportional to the mole quantity. It appears that, 1) although part of Ca in the influent was also incorporated in the phosphate salts produced, Ca present in the dissolution of a material was also incorporated to a greater extent, 2) that the consumption of  $OH^-$  produced with the dissolution of a



- Fig. 4. Budget of each element in the packed coral sand column system of v=6 times/day Thickness of arrow indicates the amount of each element.
  - \*1: OH<sup>-</sup> consumption with reaction of  $H_2PO_4^ \rightarrow HPO_4^{2-}$
  - \*2: OH<sup>-</sup> consumption with reaction of PHO<sub>4</sub><sup>2-</sup>  $\rightarrow$  PO<sub>4</sub><sup>3-</sup>
  - \*3 : OH<sup>-</sup> consumption with reaction of H<sub>2</sub>CO<sub>3</sub>  $\rightarrow$  HCO<sub>3</sub><sup>-</sup>

material was higher in the reaction of  $H_2PO_4^- \rightarrow HPO_4^{2-}$  in the liquid phase and salts produced than in the reaction of  $H_2CO_3 \rightarrow HCO_3^-$  and 3) that the concentration of TIC increased by an amount nearly equal to the significant decrease in the TIP of the effluent in the relation between input and yield. The dephosphorization mechanism in this method consisted of a replacement reaction from calcium carbonate to calcium phosphate, and not simple adsorption onto the material nor crystallization reaction.

# 2) Experiment 2

Table 4 shows the concentrations of representative components after aeration for 24 h for each lot of the original liquid brought in. These original liquids were effluents in the biological dephosphorization test of hoggery sewage produced by the intermittent aeration active sludge method. With the biological treatment of hoggery sewage, TIP concentration cannot be lower than 20 mg/L<sup>7)</sup> and was in the range of 22.1–117 mg/L. In addition, Lot nos. 1–5 showed a gradual decrease in TIP concentration which may correspond to the logarithmic phase of microorganisms, while in Lot nos. 5–10 the value of TIP was nearly constant, 30 mg/L and only in Lot no. 12, 2.5 times concentrated original treated liquid was used.

The results of Experiment 1 showed that the dephosphorization characteristics deteriorated when the quantities of dissolved material were small but that the quantity of dissolved materials could only increase by decreasing the  $Ca^{2+}$ ,  $OH^-$  and  $HCO_3^-$  concentrations in the liquid phase based on the mass action law. For dephosphorization, however, a

Table 4. Change in chemical components of influents before and after (values in parenthesis) aeration (24 h) (Unit: mg/L except pH)

Lot no.	F	н	Т	ос		ГIC	NI	H4-N	N	O <sub>2</sub> -N	N	D <sub>3</sub> -N	Г	ΊP	С	Ca	1	Mg
31	6.21		25.5		0.50	5	2.6		0.0		62.0		45.3		63.0		24.0	
2	6.44		24.1		2.22		0.3		0.0		56.8		43.9		61.8		29.3	
3	7.16		23.7		11.07		0.0		0.0		42.0		38.5		56.2		27.9	
4	7.32		26.4		26.54		5.8		5.6		27.6		34.2		51.3		28.3	
5	7.82	(7.56)	30.8	(27.2)	59.40	(24.77) <sup>a)</sup>	27.3	(1.6)	1.3	(14.8)	9.6	( 27.7)	28.2	(29.0)	48.9	( 46.7)	25.0	(26.3)
6	7.65	(7.70)	31.6	(25.1)	59.10	(10.47)	27.6	( 0.0)	1.0	( 0.0)	14.3	(43.1)	29.3	(27.0)	49.3	( 43.5)	25.6	(25.6)
7	7.74	(7.64)	28.2	(21.6)	61.13	(15.60)	24.5	( 0.1)	0.5	( 0.0)	11.6	( 39.4)	30.3	( 26.0)	51.9	( 44.7)	30.1	(30.0)
8	7.85	(8.00)	55.1	(46.7)	76.97	(53.23) <sup>a)</sup>	40.7	(18.2)	1.1	(19.7)	12.5	(17.0)	28.2	( 20.0)	56.0	(44.1)	32.5	(33.8)
9	7.72	(7.44)	58.5	(41.5)	97.33	( 9.70)	30.5	(1.4)	0.0	(4.1)	23.7	(48.3)	31.3	( 30.2)	53.9	( 50.9)	32.9	(37.7)
10	7.66	(7.50)	31.4	(24.6)	60.00	(10.50)	27.1	( 1.0)	0.0	( 0.0)	14.0	( 32.0)	30.0	(27.6)	47.0	( 43.2)	33.0	(34.5)
11	7.63	(7.58)	14.6	(14.6)	45.27	(32.13) <sup>a)</sup>	37.4	(28.6)	1.3	( 6.4)	19.4	( 20.9)	22.1	( 20.1)	31.1	(27.3)	26.2	(26.3)
12	5.66	(5.56)	31.5	(33.9)	1.33	( 0.82)	29.0	(28.3)	0.8	( 2.1)	137.2	(149.9)	105.0	(116.8)	156.1	(169.7)	65.1	(67.3)

a): Without initial sludge.

decrease in the  $Ca^{2+}$  and  $OH^-$  concentrations become unsuitable based on this law. Thus, it is important that the  $HCO_3^-$  concentration remain low in influents and the effect of aeration was examined.

Generally, the concentration of dissolved TIC depends on the pH<sup>8)</sup>. Based on the mass action law, because the speed at which the  $H_2CO_3 = HCO_3^-$ + H<sup>+</sup> reaction in the solution reaches an equilibrium is high enough<sup>8)</sup>, the HCO<sub>3</sub><sup>-</sup>/H<sub>2</sub>CO<sub>3</sub> ratio increases 10 times for 1 unit increase in pH. On the other hand, since the concentration ratio of H<sub>2</sub>CO<sub>3</sub> in the liquid phase to CO2 in the atmosphere has a fixed value based on Henry constant, when the equilibrium relation is reached, in a solution with a pH range within the primary dissociation constant of 6.3 and the secondary dissociation constant of 10.3, in open system atmosphere, the dissolution potential of CO<sub>2</sub> and its ionic species increases 10 times for 1 unit increase in pH. However, there is often an oversaturation of carbonate species caused by the decomposition of organic materials in sewage. Accordingly, the concentration of CO2 and its ionic species in the liquid phase is not completely determined by pH, but when the system is allowed to stand at the atmospheric pressure, the potential of release of CO2 into the atmosphere increases with the oversaturation rate. As shown in Table 4, the pH fluctuated due to aeration. The increase of pH was due to the reaction in which oversaturated CO<sub>2</sub> in the liquid was released into the atmosphere and the equilibrium relation recovered when HCO3<sup>-</sup> +  $H_2O \rightarrow H_2CO_3 + OH^-$  in the liquid phase and NH4<sup>+</sup> was generated by the decomposition of organic materials. The decrease of pH was due to

the nitrification reaction by microorganisms. The sign and size of a pH variation were determined by the size of the respective factors. As shown in Table 4, the TIC concentration decreased by the aeration treatment and this effect was enhanced in the presence of sludge. As a result, in Lot nos. 5, 8 and 11 there were a considerably high concentration of TIC and high ratio of NH4<sup>+</sup>/NO3<sup>-</sup> after the aeration because aeration was conducted without initial sludge. The above results show that the nitrification reaction proceeded in the presence of sludge and the oversaturation rate of CO2 increased due to the decrease in pH caused by nitrification. In addition, the breakup of the atmosphere-water interface by aeration results in a rapid release of CO<sub>2</sub> into the atmosphere8).

Decrease of both TIP and Ca concentrations due to aeration was observed. Since these phenomena were particularly conspicuous when the pH was high after the aeration (Lot nos. 8, 6 and 7) and the decrease in the TIP and Ca concentrations coexisted, they were considered to be due to the removal by the production of calcium phosphate rather than to the biological incorporation of phosphorus. Since the biological dephosphorization in the effluent was limited, an increase in pH due to the residual NH<sub>4</sub><sup>+</sup> was required to achieve further dephosphorization by a physico-chemical reaction, so that the aeration became insufficient and high concentrations of TOC and TIC remained.

Table 5 shows the TIP concentration in liquids before and after the passage through each column. Lot no. 12 with a high concentration of TIP (117 mg/L) showed a slight increase in concentration in

Table 5. PO<sub>4</sub>-P concentrations (mg/L) in influent and effluent in each column

Lot no.	•	<b>v</b> =	=6 (times/c	lay)	V =	=2 (times/c	lay)	v =	6 (times/c	lay)
	Influent	Fine <sup>a)</sup>	Middle <sup>a)</sup>	Coarse <sup>a)</sup>	Fine	Middle	Coarse	200°Cb)	600°C <sup>b)</sup>	lay) 800°C <sup>b)</sup> 0.0 0.0 0.0 0.0 3.9 9.1 10.2 10.7 10.2 4.7 7.3
Ĩ	45.3	7.4	5.8	16.7	6.0	4.4	3.4	3.7	2.4	0.0
2	43.9	5.7	6.5	19.2	5.2	4.6	4.4	4.5	3.6	0.0
3	38.5	6.7	7.1	17.2	4.9	5.4	4.5	6.1	4.8	0.0
4	34.2	8.4	10.8	18.7	6.4	6.4	5.9	7.0	9.1	0.0
5	29.0	9.7	10.8	16.4	8.2	7.8	7.2	7.0	8.8	3.9
6	27.0	8.0	10.1	16.1	5.6	5.2	5.9	4.7	6.6	9.1
7	26.0	7.4	10.0	15.5	6.2	5.6	6.2	5.6	8.1	10.2
8	20.0	10.9	11.0	12.9	10.5	9.7	10.1	12.2	11.1	10.7
9	30.2	10.7	15.0	22.5	7.9	8.0	9.0	7.8	10.5	10.2
10	27.6	9.1	9.0	12.8	7.5	6.1	7.6	5.5	4.2	4.7
11	20.1	6.3	8.7	13.0	5.1	5.0	4.9	4.6	5.4	7.3
12	116.8	9.0	16.9	37.0	7.4	7.3	9.1	5.4	7.5	8.7

a): Grain radius; Fine: 1.0-1.7 mm, Middle: 1.7-2.8 mm, Coarse: 2.8-5.0 mm.

b): Heat treatment; 30 min before packing to the column.

effluents than other Lots, but for a large daily quantity of water passed and a large grain size, the TIP concentration was high from the first period after the start of water passage. Comparison of TIP concentrations of v=2 and v=6 (coarse grain of a crushed material) in Table 5 reveals that even when the grain size was large, dephosphorization improved when the time of contact between influents and the material was sufficiently long. The concentration ratio (difference in TIP concentration between large and small grain size in case of large daily quantity/ TIP concentration of influent) was  $26.1 \pm 8.3\%$  in all the Lots and 24.0% in Lot no. 12 and therefore independent of the TIP concentration in influents. The above difference may be caused by the fall of the column tube wall without contact with materials at high speed passage.

Comparison of Tables 4 and 5 reveals that the TIP concentration in the effluents increased when the TOC and TIC concentrations in the influent increased. As in Experiment 1, quantities of dissolved moles of individual column material were calculated, and the values were +1.5 to 2.8 mmol/L in most of the Lots. However in Lot no. 12, the values were especially high (2.5 to 4.0 mmol/L) because the TIP concentration in the influents was high, whereas in Lot nos. 5, 8 and 9, the values were low (-4 to +0.8, minus values indicate the production of CaCO<sub>3</sub> in the column) because the TOC and TIC concentrations in the influent were high. In order to remove phosphorus efficiently from hoggery sewage using this method, the concentration of TIP in the influent

should be high and those of TOC and TIC in the influent low.

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