

RECOVERY OF PHOSPHATE FROM UNUSED RESOURCES

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Abstract : The recovery of aqueous phosphate from a model solution consisting of NH_4^+ , NO_2^- and NO_3^- , which are contained in a surplus that phosphate in rivers in Tokushima Prefecture, Japan, using boehmite together with the elution behaviors of phosphate from dephosphorization slag using various eluates were examined. The recovery of aqueous phosphate using boehmite was not influenced by the coexistence of those nitrogen-containing contaminants under various pH conditions. For the elution behaviors of phosphate from dephosphorization slag, it was found that aqueous HNO_3 among various acidic and basic solutions was a suitable solution as an eluate. Present study suggests that the employment of the unused resources such as aqueous phosphate in rivers and phosphate in the dephosphorization slag can be used as a possible candidate as a new raw material for rare phosphate.

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INTRODUCTION

Since Japan does not have phosphorus ore, all phosphorus ore is imported from various countries. However, it is pointed out that phosphorus ore will disappear in the near future. Furthermore it should be noted that several countries have stopped the export of phosphorus ore. Therefore a development of a new raw materials containing phosphate is an urgent problem in Japan. It is generally known that a certain amount of phosphates are contained in various unused resources. For example, an amount of phosphate contained in sea and river and that contained in dephosphorization slag exhausted from steel plants are corresponding to that imported into Japan a year, respectively. In the present manuscript, the recovery of phosphate from these two unused resources was studied. For the former resources, the effect of the coexistence of NH_4^+ , NO_2^- and NO_3^- , which are contained in a surplus than phosphate in rivers in Tokushima Prefecture, Japan,¹ on the removal of aqueous phosphate using boehmite ($\text{Al}(\text{OH})\text{O}$) was examined.^{2,3} It had been already reported that boehmite showed a certain simultaneous removal of phosphate together with fluoride while no influence of the presence of carbonate, sulphate and chloride on the removal of phosphate by boehmite

was observed.³ It should be noted that rivers in Tokushima Prefecture contains the greatest amount of phosphates among all prefectures in Japan, due to the delay of the spread of a sewage institution. For the latter resources, the elution behaviors of phosphate from dephosphorization slag using various eluates were examined. As described above, it is possible to recover aqueous phosphate from sea and river. However it should be noted that the concentration of phosphate in sea and river is several ppm. Therefore it is necessary to concentrate those waters by approximately 100,000 times to equal to 13 % of the content of phosphorus in the phosphorus ore used as a resource. As another possible candidate for the phosphorus resource, dephosphorization slag has been sometimes suggested.⁴ Since the content in phosphate in dephosphorization slag is rather corresponded to that in phosphorus ore, the concentration, that is needed in the recovery of aqueous phosphate from sea and river, is not necessary. It should be noted that 80% phosphate, that Japan imports a year, is contained in the dephosphorization slag exhausted from the process of steel. However most of the slag cannot be used efficiently.⁴ In this section, the dephosphorization slag was considered as a new phosphorus resource. The elution of phosphate from the slag by various

eluates was examined.

MATERIALS AND METHODS

The removal of aqueous phosphate using boehmite was investigated according to the procedure shown in our previous papers.^{2,3} Boehmite was prepared from boehmite sol obtained by hydrolyzing aluminum isopropoxide. Boehmite sol thus prepared was evaporated and dried overnight under vacuum, followed by a milling treatment. The solid thus obtained was used in the present study. According to the data on river in Tokushima Prefecture,¹ a concentration of aqueous compound containing nitrogen in river is contained about ten times greater than that of aqueous phosphate.¹ Therefore, in order to examine the effect of aqueous compound containing nitrogen on the removal of aqueous phosphate, three possible compounds containing nitrogen such as NH_4^+ , NO_2^- and NO_3^- were employed as a contaminant. The aqueous sample solution was prepared from phosphate ($\text{NaHPO}_4 \cdot 12\text{H}_2\text{O}$; 4 mmol/L) in the presence and absence of ten times greater amount by weight of one of those contaminants. As NH_4^+ , NO_2^- and NO_3^- , NH_4Cl , NaNO_2 and NaNO_3 , respectively, were used. In order to examine the removal behavior of aqueous phosphate using boehmite, the aqueous sample solution (100 mL) was stirred at 120 rpm in a constant-temperature bath at 298 K for 10 min. Boehmite (0.4 g, 6.67 mmol) was then added into the solution. After a specific period, the solution was filtered and analyzed by inductively coupled plasma – atomic emission spectrometry (ICP-AES; PerkinElmer Japan, Optima 3000) for phosphate and by ion-chromatography for NH_4^+ , NO_2^- or NO_3^- . In order to examine the elution of phosphate immobilized onto boehmite (regeneration process), boehmite (0.2 g) employed for the removal of aqueous phosphate followed by dryness was kept for 24 h at 298 K in an eluate (10 mL). As an eluate, aqueous solutions of NH_3 and NaOH were employed.

The elution behaviors of phosphate from dephosphorization slag using various eluates were examined as follows. The dephosphorization slag was obtained directly from a steel plant. The composition of the slag was analyzed by using X-ray fluorescence (XRF; Shimadzu, EDX-800) and ICP-AES. In order to examine the elution behaviors of phosphate from dephosphorization slag, a distilled water together with various concentration of aq. HNO_3 , aq. HCl , aq. H_2SO_4 and aq. NH_3 were employed as an eluate. After 100 mL of one of these eluates was added in a flask, 2.0 g of the crushed slag was added into the flask. The mixture was stirred by 130 rpm in the constant temperature bath. The solution was filtered after a specific period, and analyzed by ICP-AES for phosphate. The solid thus separated was dried and analyzed by X-ray diffraction (XRD; Rigaku, RINT

2500X), X-ray photoelectron spectrometry (XPS; Shimadzu, ESCA-1000) and XRF. In XPS analysis, the binding energies were corrected using 285.0 eV for C 1s as an internal standard. Argon-ion etching of the samples in XPS analysis was carried out at 2 kV for 1 min with a sputtering rate estimated as approximately 2 nm/min for SiO_2 . In order to confirm the element distribution in the dephosphorization slag, a small amount of the slag was milled and calcined at 1173 K. The slag thus obtained was analyzed using electron probe micro analyzer (EPMA; EDAX, Phoenix).

RESULTS AND DISCUSSION

Removal of aqueous phosphate using boehmite

The removal behaviors of aqueous phosphate using boehmite from the aqueous sample solution in the presence and absence of NH_4^+ , NO_2^- and NO_3^- were described in FIGURE 1. Regardless of the presence and absence of these three contaminants, the removal rates showed similar values at the same pH conditions.

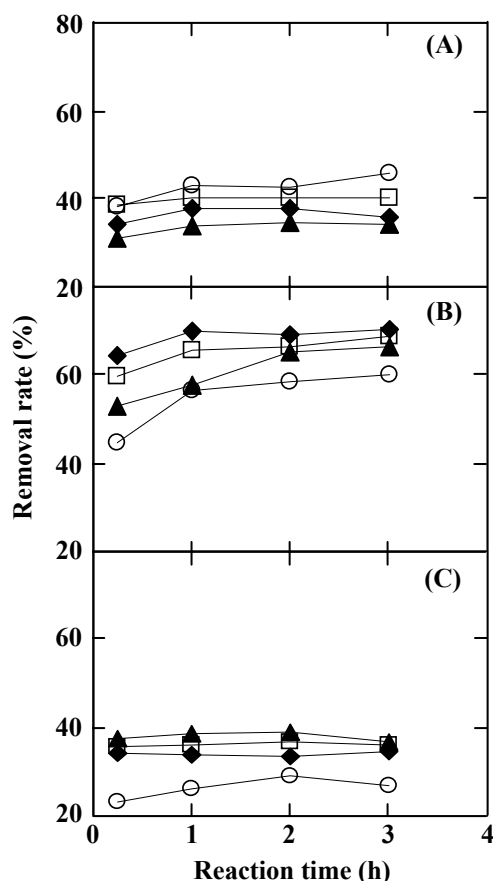
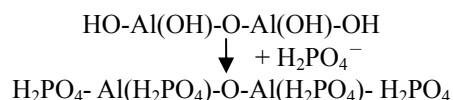


FIGURE 1. Removal rate of PO_4^{3-} from an aqueous solution in the absence (◆) and presence of NH_4^+ (○), NO_2^- (▲) and NO_3^- (□) at (A) pH uncontrolled, (B) pH = 4, and (C) pH = 10.

This indicates that the removal of aqueous phosphate from the aqueous sample solution using boehmite is not influenced by the presence of these three nitrogen-containing contaminants.

It should be noted that the removal rate in case of no control of pH and pH=10 (FIGURES 1 (A) and (C), respectively), approximately 30-40 % of the removal rate was observed while rather greater removal rate (40-60 %) was observed at pH=4 (FIGURE 1 (B)). It is generally known that phosphate species (H_2PO_4^- , HPO_4^{2-} and PO_4^{3-}) in aqueous solution are mainly formed in acidic-neutral, neutral-basic and strong basic conditions, respectively.⁵ Therefore the effect of the solution pH on the removal rate is due to such a pH-sensitive phosphate nature. Since H_2PO_4^- is favorably present at pH=4, it can be suggested that OH species in boehmite is ion-exchanged by H_2PO_4^- during the removal to form phosphate-containing aluminum compounds as shown below.



In order to check the presence of phosphates species in boehmite after the removal, boehmite previously used for the removal without control of solution pH (FIGURE 1 (A)) were analyzed by XRD and XPS. Unfortunately XRD of all samples previously employed to obtain the results shown in FIGURE 1 (A) except the sample used in the presence of NH_4^+ showed only the signal of Al(OH)O (JCPDS 49-0133) and no signals of other species could be detected (not shown). From the sample used in the presence of NH_4^+ , NH_4Cl (JCPDS 7-0007) was also detected together with Al(OH)O (not shown). However, as shown in our previous papers,^{2,3} phosphate species was certainly detected from these samples using XPS (TABLE 1). Signals due to P 2p were detected at approximately 134 eV from all samples previously employed to obtain the results shown in FIGURE 1 (A) regardless of argon-ion etching. Furthermore signal due to N 1s was also detected from the sample used in the presence of NH_4^+ as expected from XRD analysis. It should be noted that atomic ratios of P/Al near the surface region of all samples were rather similar regardless to the presence and absence of argon-ion etching, again indicating that the removal of phosphate using boehmite was not influenced by the presence of those three nitrogen-containing contaminants.

In order to regenerate phosphate from boehmite immobilized with aqueous phosphate, boehmite (0.2 g), which was previously employed for the removal of aqueous phosphate (2 mmol/L, 50 ml) at pH = 4 for 6 h, was kept in aq. NaOH solution (0.1 mol/L, 10 mL) and aq. NH_3 solution (1.0 mol/L, 10 mL) for 24 h at 298 K. It is confirmed that 32 and 43 %

phosphates were eluted from the immobilized boehmite by the treatment using aq. NaOH and NH_3 solutions, respectively. Therefore the present study shows that boehmite can be used for the removal of aqueous phosphate from the model solution for rivers in Tokushima Prefecture, in which phosphate, NH_4^+ , NO_2^- , and NO_3^- were present, followed by the regeneration of phosphate.

TABLE 1. XPS results of the samples previously employed to obtain the results shown in Fig. 1 (A).

In sample solution	Time* (min)	Binding energy (eV)			P/Al**
		Al 2p	P 2p	N 1s	
Before removal	0	74.3	-	-	-
	1	74.9	-	-	-
PO_4^{3-}	0	74.2	133.9	-	0.048
	1	74.3	134.0	-	0.054
$\text{PO}_4^{3-} + \text{NO}_2^-$	0	73.7	133.3	-	0.055
	1	74.2	134.3	-	0.041
$\text{PO}_4^{3-} + \text{NO}_3^-$	0	74.2	134.1	-	0.054
	1	74.8	134.8	-	0.039
$\text{PO}_4^{3-} + \text{NH}_4^+$	0	73.9	133.9	400.4	0.068
	1	74.7	134.4	401.1	0.047

* Etching time. ** Atomic ratio.

Elution of phosphate from dephosphorization slag using aqueous solution

At first, to confirm the composition in the dephosphorization slag, the slag was dissolved in aq. HNO_3 to be analyzed using ICP-AES. When the slag (2.0 g) was dissolved in 100 mL of 1 mol/L HNO_3 , the amount (1.7 g) of the slag dissolved showed to be maximum after 4 h. Therefore the solution thus obtained was analyzed by ICP-AES. When the indissoluble solid was analyzed by XRF, phosphorus, aluminum and magnesium was not detected since these were dissolved in the acidic solution. Based on the results obtained by ICP-AES for the dissolved species and XRF for the indissoluble species, the composition in the dephosphorization slag was confirmed as shown in TABLE 2.

TABLE 2. Composition in the slag.

Element	Content (mmol/g-slag)
P	0.4072
Al	0.2483
Si	4.7277
Ca	7.7141
Mn	0.9575
Fe	2.5210
Mg	0.4763

FIGURES 2 and 3 show the elution rate of phosphate from the dephosphorization slag using various acidic and basic solvents. It should be noted that the elution was not observed at 278, 298 and 338 K using a distilled water. As shown in FIGURE 2, 1 mol/L HNO_3 is a suitable solvent for the elution of phosphate from the dephosphorization slag while the elution was not observed using basic solution of 1 mol/L NH_3 .

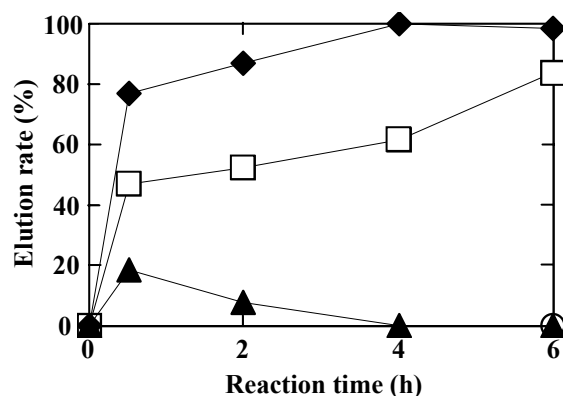


FIGURE 2. Elution rate of PO_4^{3-} from the slag using 1 (◆), 0.5 (□), and 0.2 mol/L HNO_3 (▲) together with 1 mol/L NH_3 (○).

Furthermore 1 mol/L HCl rather than 1 mol/L H_2SO_4 was also a suitable solvent (FIGURE 3). However this solvent cannot be recommended due to Green Chemistry.

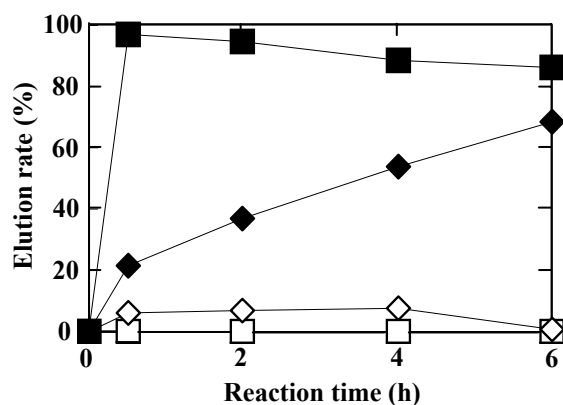


FIGURE 3. Elution rate of PO_4^{3-} from the slag using 0.1 (□) and 1 mol/L HCl (■) together with 0.1 (◇) and 1 mol/L H_2SO_4 (◆).

As shown in FIGURE 2, phosphorus can be easily eluted using 1 mol/L HNO_3 . Such an elution behaviors should be influenced by the situation of phosphorus species. Therefore, in order to check the situation of phosphorus species in the dephosphorization slag, the slag was analyzed by XRD and EPMA. From XRD analysis of the slag, the presence of calcium hydroxide was confirmed while

other species could not be detected (not shown). To detect other species, the slag was also analyzed by EPMA. From EPMA analysis, it was detected that oxide species were distributed widely over the slag. Since the slag was obtained from the steel plant, Fe-species were certainly detected. It should be noted that Fe-species co-existed with Mn-species while Fe-species did not co-exist with phosphorus species. Phosphorus species were detected together with calcium species. Furthermore calcium species was also co-present with oxygen, indicating that CaO was present in the slag. Based on these results, most of phosphorus species may be present as calcium phosphates in the slag. Together with SEM results, the situation described above for the dephosphorization slag was shown in FIGURE 4. If calcium phosphates are present in the slag, it is reasonable that phosphorus can be easily eluted from the slag using acidic solvents.

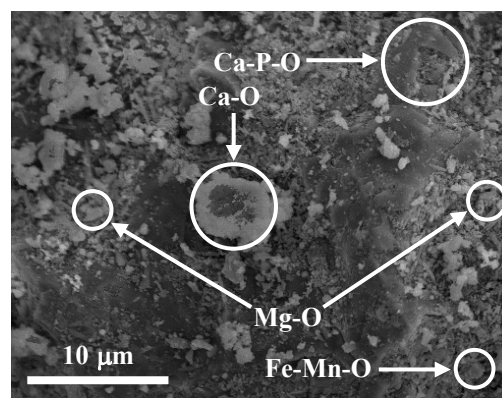


FIGURE 4. EPMA of the dephosphorization slag.

CONCLUSION

It was found that the effect of the nitrogen-containing compounds such as NH_4^+ , NO_2^- and NO_3^- on the removal of aqueous phosphate was rather negligible, indicating that the present removal procedure of aqueous phosphate can be possible for revival in Tokushima Prefecture. The present study also revealed that, from the dephosphorization slag, phosphorus species could be easily eluted using acidic solutions. Therefore it can be suggested that the dephosphorization slag is as another candidate of the new resources of phosphate.

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