

Recovery and Enrichment of Phosphorus from the Nitric Acid Extract of Dephosphorization Slag

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Abstract

A method for the recovery and enrichment of the phosphate from dephosphorization slag was examined. First, the elution of aqueous phosphate from dephosphorization slag using aqueous HNO₃ was examined using both the batch and flow methods. With the batch method, 82% of the dephosphorization slag could be dissolved within 30 min using 1.0 mol/L HNO₃, indicating that the batch method could be used for mass processing to extract phosphorus in the bulk phase, but all components contained in the slag were unselectively dissolved. In contrast, by using 0.05 mol/L HNO₃ via the flow method, 22% of the slag was dissolved in 100 min giving a more selective dissolution of phosphate from the slag compared with the batch method, which indicated that this method would be incompatible with mass processing for the purpose of extracting phosphorus in the bulk phase. In order to remove the Fe-species in the aqueous solution obtained by the batch method using 1.0 mol/L HNO₃, which has been referred to as the “slag solution,” it was necessary to add calcium hydroxyapatite (CaHAp) to the slag solution. The optimal conditions for the removal of Fe-species using CaHAp were observed at a solution pH of ca. 1.5, which resulted in 100% removal of the Fe-species after 4 h. When the pH of the slag solution was adjusted to 7.0 after removing the Fe species, a pale pink solid sample was precipitated. The amounts of phosphate in the slag solution and in the pink solid were 3.5 and 42.0 mol%, respectively, indicating that the treatment suggested in the present study could be used for the recovery and enrichment of phosphate, that is, phosphorous, from dephosphorization slag.

Introduction

Phosphorus is an essential element for plant growth and has no substitute in food production. Phosphate rock as a raw material of phosphorus is a finite, non-renewable resource. Therefore, phosphorus is an important strategic resource for agricultural and food production. In the chemical industry, it is used in fire retardants, glues, food additives, detergents, etc. (Matsubae-Yokoyama, *et al.*, 2009). Furthermore, phosphorous is one of the three most important elements in fertilizers together with nitrogen and potassium (Kubo *et al.*, 2010). Since phosphate rock is not indigenous to Japan, it must be imported. It has been pointed out that phosphate rock resources will disappear in the near future (Abelson, 1999). However, according to the recent data from United States Geological Survey (USGS), the supply of phosphate rock will likely be available for approximately 370 years. However, it should be noted that it is becoming more and more difficult to secure high-quality phosphate rock due to its increased demand worldwide. Therefore, the United States stopped exporting phosphate rock in 1997 to conserve its own resources. Other exporting countries followed the lead of the United State (Yokoyama *et al.*, 2007). Therefore, the development of new raw

materials containing phosphorus is an urgent issue in Japan. It is noteworthy that phosphorus is contained in the dephosphorization slag that is released from steel processing in Japan, amounting to ca. 80% of the phosphorus that is imported in the form of phosphate rock by Japan, but most of the slag cannot be efficiently used (Kubo *et al.*, 2010). This slag may represent a new source of phosphorus that can replace phosphate rock.

However, since the dephosphorization slag itself is too difficult to use as a resource for phosphorus, we have attempted to dissolve the slag to form aqueous phosphate, which can be easily used as a raw material for various phosphate-containing compounds. As shown in our previous papers (Sugiyama *et al.*, 2011, 2012), phosphate can be dissolved from the slag using an aqueous HNO₃ solution, while other components are simultaneously dissolved to form an aqueous complex mixture containing phosphate. Therefore, in order to use the aqueous phosphate, the enrichment of phosphate would be required. It should be noted that any enrichment procedure must be simple and inexpensive.

In the present study, the improvement in the phosphate content was examined for both the solid and the solution forms that are obtained after the treatment of dephosphorization slag. Specifically, the following three treatments were examined: (1) the dissolution of

the dephosphorization slag to form an aqueous complex mixture containing phosphate, which is referred to as a “slag solution” in the present study; (2) the removal of Fe-species from the slag solution using calcium hydroxyapatite (CaHAp) to form a Fe-free solution; and (3) the formation of precipitation containing a greater content of phosphate from the Fe-free solution.

1. Experimental

The elution behaviors of phosphate from the dephosphorization slag using various concentrations of aq. HNO₃ (Wako Pure Chemical Industries, Ltd.) as an eluate were examined using batch or flow methods. The slag was obtained directly from a steel plant. The composition of the slag was analyzed using X-ray fluorescence (XRF; EDX-800, Shimadzu Corp.) and inductively coupled plasma-atomic emission spectrometry (ICP-AES; Optima 3000, PerkinElmer Japan). The composition of the dephosphorization slag is described in **Table 1** (Sugiyama *et al.*, 2011). It should be noted that phosphate is referred to as P in the present paper.

Table 1 Composition of the dephosphorization slag

Element	Content [mmol/g-slag]
P	0.407
Al	0.248
Si	4.73
Ca	7.71
Mn	0.958
Fe	2.52
Mg	0.476

The elution behaviors of phosphate were examined using the batch method, which began with the addition of 100 mL of aq. HNO₃ to a flask (200 mL), followed by the addition of 1.0 g of the slag (particles of 0.425–2.0 mm). The mixture was stirred at 130 rpm and 298 K in a constant-temperature bath. The solution was filtered after 100 min using filter paper (4 μm of pore size) and a membrane filter (0.45 μm of pore size), and analyzed by ICP-AES. To examine the elution behaviors of phosphate in the flow method, the slag (1.0 g and particles of 0.425–2.0 mm) was placed in a burette (7 mm of diameter and 10 mL of the total volume), the bottom of which was packed using glass wool. From the top of the burette, 100 mL of aq. HNO₃ was dropped at 1.0 mL/min. Every 20 min, 20 mL of the dropped solution was analyzed by ICP-AES, and the process was repeated 5 times.

The removal of the aqueous Fe-species using CaHAp was examined as follows. CaHAp was prepared from Ca(NO₃)₂·4H₂O (Wako Pure Chemical Industries, Ltd.) and (NH₄)₂HPO₄ (Wako Pure Chemical

Industries, Ltd.) in an aqueous solution at pH 11 under a N₂ atmosphere (Sugiyama *et al.*, 2001). The XRD pattern of CaHAp matched the reference data for Ca₁₀(PO₄)₆(OH)₂ (JCPDS 9-0423) (**Figure 1**). To examine the removal of the aqueous Fe-species with CaHAp, the pH of the slag solution obtained from the batch method using 1.0 mol/L HNO₃ for 4 h was adjusted using aq. NH₃, and then 1.0 g of CaHAp (particles < 0.85 mm) was added to the pH-adjusted solution. The solution was stirred at 130 rpm and 298 K in a constant-temperature bath for 4 h and then analyzed using ICP-AES.

In order to precipitate the solid, which contained the phosphate, from the solution treated using CaHAp, the pH of the treated solution was adjusted to 7.0 to form a pale pink solid. The solid samples were dried and analyzed using X-ray diffraction (XRD; RINT 2500X, Rigaku Corp.) and/or XRF.

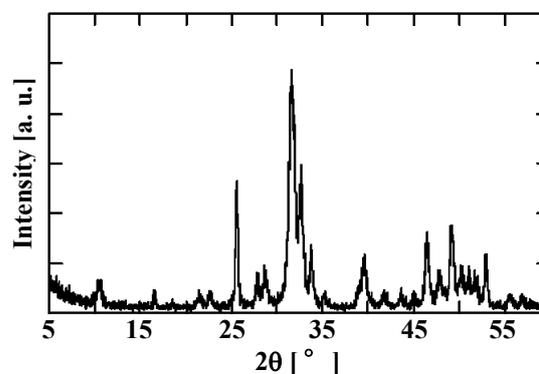


Fig. 1 XRD pattern of CaHAp

2. Results and Discussion

2.1 Comparison of the elution behavior from dephosphorization slag using batch and flow methods

As shown in our previous paper (Sugiyama *et al.*, 2011), the elution of aqueous phosphate from the dephosphorization slag using aq. HNO₃ was examined using the batch method with 1.0 mol/L HNO₃. With 82% of the slag dissolved, ca. 80% of the phosphate was eluted within 30 min (Sugiyama *et al.*, 2011), indicating that the selective elution of phosphate from the slag did not proceed using the batch method. Therefore, we examined the effect of the use of the flow method on the selective elution of phosphate from the slag. Two main factors differentiate the flow system from the batch system. One is the elution solution and the other is the sample. In the batch system, the concentrations of various species dissolved from the slag in the elution solution increase with the time of treatment, while a fresh elution solution is always supplied to the slag in the flow system. Furthermore, the dissolution from the slag occurs mainly from the surface of the slag in the flow system due to the maintenance of the slag particles during dissolution, while dissolution comes from both

the surface and the bulk of the slag in the batch system due to the collapse of the slag particles during stirring.

In the present study, the duration of one run was 20 min, and after every run, 20 mL of the eluted solution was analyzed. When 1.0 mol/L aq. HNO₃ was used in this method, the exit of the burette was occluded due to rapid dissolution followed by the formation of a fine precipitate on the glass wool. Therefore, 0.5, 0.2, 0.1, and 0.05 mol/L HNO₃ were used as an eluate to examine the elution behavior of phosphate from the dephosphorization slag.

When 0.01 mol/L HNO₃ was used, the elution of the phosphate could no longer be detected. As shown in **Figure 2**, the elution behaviors of phosphate strongly depended on the concentration of the aq. HNO₃. When 0.5 mol/L HNO₃ was used, a greater amount of phosphate was eluted during the first run, followed by a decrease with run times. When 0.2 mol/L HNO₃ was used, the maximum elution of phosphate was detected at around 2-3 runs. In contrast, when lower concentrations of HNO₃ solutions (0.1 and 0.05 mol/L) were used, the elution of phosphate was more constant during all runs.

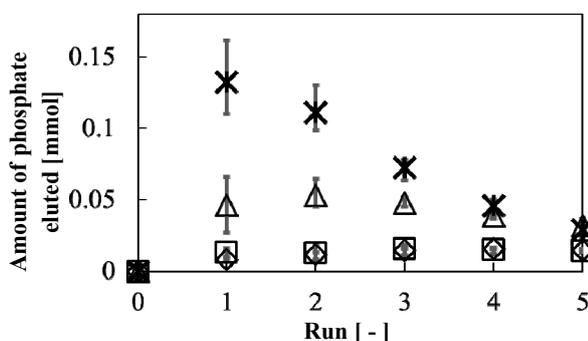


Fig. 2 Elution behavior of phosphate from the dephosphorization slag using various concentrations of HNO₃. Symbols: *, Δ, ◇, and □ = 0.5, 0.2, 0.1, and 0.05 mol/L HNO₃ as an eluate

This consistency may indicate that the elution behaviors of compounds other than phosphate may depend on the concentration of aq. HNO₃. Furthermore, elution behavior may be influenced by the batch and flow methods. Therefore the amounts of various elements eluted from the dephosphorization slag for 100 min using batch and flow methods were compared (**Table 2**). As described in Table 2, with the exception of the elution of P and Al, the amount of each element eluted using the batch method was greater than that using the flow method, regardless of the concentration of HNO₃. During the elution of Al, using 0.05 mol/L HNO₃, a slightly greater amount was eluted than when using the batch method. A greater and more selective elution of P (phosphate) was evident using the flow method with 0.05 mol/L HNO₃. A slight advantageous effect of the use of the flow method on the selective elution of phosphate was observed at 0.1 mol/L HNO₃, while it

was no longer observed at 0.2 mol/L HNO₃. Although these results indicate that the flow method is advantageous for the selective elution of phosphate, particularly when using dilute HNO₃, the amount eluted against the elution time was certainly lower.

Table 2 The amounts (mmol) of each element eluted from the dephosphorization slag (1.0 g) using batch and flow methods

	0.05 mol/L HNO ₃		0.1 mol/L HNO ₃		0.2 mol/L HNO ₃	
	Batch	Flow	Batch	Flow	Batch	Flow
P	0.034	0.065	0.066	0.069	0.284	0.185
Al	0.079	0.088	0.157	0.111	0.257	0.204
Si	0.458	0.185	0.788	0.653	1.610	0.818
Ca	2.000	1.890	3.220	2.050	5.280	4.090
Mn	0.167	0.149	0.235	0.164	0.562	0.392
Fe	0.160	0.142	0.316	0.302	1.120	0.556
Mg	0.000	0.000	0.000	0.000	0.224	0.129

Estimated deviation: less than 8, 7, 8, 5, 3, 11, 6 and 6% for P, Al, Si, Ca, Mn, Fe, Mg, and K, respectively

2.2 The removal of aqueous Fe-species using CaHAp

As described in Table 2, the Fe-species was extensively eluted from the dephosphorization slag together with the target phosphate, the content of which was enriched. XRD showed that Fe-species seemed to be present as complex oxides such as FeSiO₃ rather than single oxides or phosphates of Fe in the dephosphorization slag. Previous reports have established that aqueous Fe³⁺ can be efficiently removed using CaHAp (Moriguchi *et al.*, 2008, 2009), even with the coexistence of Ca²⁺ and PO₄³⁻ (Sugiyama *et al.*, 2012), as shown in Table 2. During the removal of aqueous metallic cations, CaHAp dissolves to form Ca²⁺ and PO₄³⁻ (Xu and Schwartz, 1994; Lower *et al.*, 1998). Then, PO₄³⁻ reacts with the aqueous metallic cations to form an insoluble precipitation. Therefore, care should be taken to maintain the concentration of phosphate during removal since an excess amount of phosphate due to the excess dissolution of CaHAp is possible. However, if this process is properly executed, CaHAp can be repeatedly employed for the removal of the Fe-species (Fe-CaHAp). When Fe-CaHAp is treated using aq. Ca(NO₃)₂, the regeneration of CaHAp is possible (Sugiyama *et al.*, 2006, 2009). In some cases, the regeneration results in the formation of a calcium phosphate species rather than CaHAp (Sugiyama *et al.*, 2003). The regenerated CaHAp or calcium phosphate species can be reused for the removal of aqueous cations (Sugiyama *et al.*, 2002, 2003). In the present study, the slag solution obtained after elution in the batch method was used for the removal of aqueous Fe-species using CaHAp. The removal behaviors of Fe-species together with the elution behaviors of phosphate from CaHAp are described in **Figure 3**. It should be noted that phosphate from the slag was contained in the slag solution (0.48 mmol), which is emphasized by the

horizontal dash line shown in Figure 3. When removal proceeds with neither an increase nor a decrease in the concentration of phosphate due to the dissolution of CaHAp, the precipitation of phosphate-containing compounds should be efficiently accomplished.

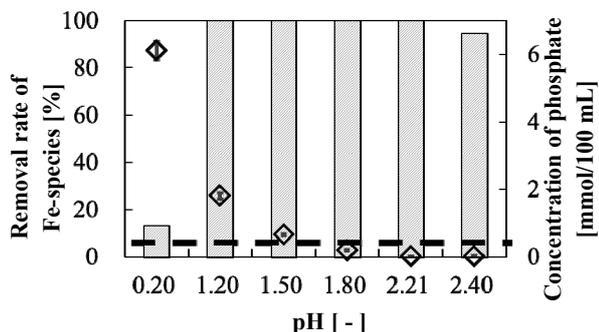


Fig. 3 Removal rate of Fe-species and the concentration of phosphate during CaHAp treatment; bar: removal rate of Fe-species; \diamond : concentration of phosphate

As described in Figure 3, when the solution pH was between 1.2 and 2.2, the complete removal of Fe-species was achieved. However, concentrations of phosphate that were both greater and lower than 0.48 mmol/100 mL were detected in the solution where the pH was adjusted to less than 1.2 and greater than 1.8, respectively. When the solution pH was less than 1.2, the concentration of aqueous phosphate that was formed via the dissolution of CaHAp was beyond that used for the precipitation of Fe-containing phosphate. In contrast, when the solution pH was greater than 1.8, the concentration of aqueous phosphate used for the precipitation of Fe-containing phosphate was beyond that formed via the dissolution of CaHAp. Therefore, these conditions were inefficient for the present purpose. At a solution pH from ca.1.5 to ca.1.8, and with no evident change in phosphate concentration, complete removal of the Fe-species from the slag solution can proceed using CaHAp.

2.3. Enrichment of phosphate using the slag solution treated with CaHAp

In the solution obtained via the removal of the Fe-species from the slag solution (referred to as the Fe-free solution), elements other than phosphorus were still present, and the separation of these elements should be done to enrich the phosphate content in the final product. In adjusting the solution pH to 7.0 for the Fe-free solution using aqueous NH_3 , a pale pink solid sample was precipitated. The molar ratios of various elements in the precipitated sample together with the slag solution and the Fe-free solution are summarized in **Figure 4**. As expected, the Fe-species in Sample 1 (slag solution) was completely eliminated from the solution (Sample 2). It is noteworthy that elements other than P, Ca and Mn were separated from the final solid samples. The molar ratio of P in Sample 1 was 3.5 mol% while that in Sample 3 was extensively improved to 42.0

mol%. The results shown in Figure 4 indicate that the combination of three processes used in the present study (the elution of aqueous phosphate from dephosphorization slag, the removal of Fe-species, and precipitation) is one of the most viable candidates for the recovery and enrichment of phosphate in dephosphorization slag.

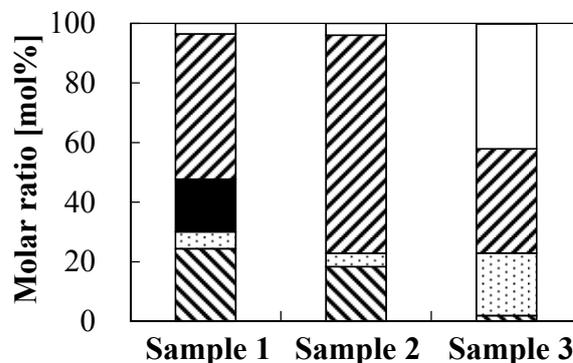


Fig. 4 Molar ratios of each element contained in the various samples; Sample 1, slag solution; Sample 2, the Fe-free solution; Sample 3, precipitated sample. Bars: \square , /// , \blacksquare , □ , and ▨ were P, Ca, Fe, Mn,

If calcium phosphates are formed in the final solid sample (Sample 3), this final solid can be used in place of phosphate rock, which also consists of various calcium phosphates. Unfortunately, XRD results of the final solid sample showed an amorphous phase and afforded no information of the Mn species even after the calcination at 1,073 K (not shown). Therefore, the final solid sample may be a mixture of an un-crystallized phosphate species of calcium and manganese. Based on the color (pale pink) of the final solid and the precipitation procedure of Sample 3 using aqueous NH_3 , the final solid seemed to contain ammonium manganese phosphate (MnNH_4PO_4). In order to remove manganese from Sample 3, the procedures described in the present study (a combination of dissolution, removal of Mn using CaHAp, and precipitation) were conducted under various conditions. However, we could not remove the Mn from Sample 3. Therefore, we concluded that manganese should be removed during an initial stage of the steel processing (Nakato and Taguchi, 1994).

Conclusions

The present study showed that dephosphorization slag can be used in a combination process that consists of elution, Fe-removal and precipitation that resulted in a simple method for the recovery and enrichment of phosphate. Approximately 80% of the phosphorus imported in Japan is contained in dephosphorization slag, the bulk of which cannot be used efficiently. Therefore, the proposed combination process could amount to a productive technique. The application of the combination to other candidates is now in progress.

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Literature Cited

- Abelson, P. H.; "A Potential Phosphate Crisis," *Science*, **283**, 2015 (1999)
- Kubo, H., K. Matsubae-Yokoyama and T. Nagasaka; "Magnetic Separation of Phosphorus Enriched Phase from Multiphase Dephosphorization Slag," *ISIJ Int.*, **50**, 59-64 (2010)
- Lower, S. K., P. A. Maurice, S. J. Traina and E. H. Carlson; "Aqueous Pd Sorption by Hydroxyapatite: Applications of Atomic Force Microscopy to Dissolution, Nucleation, and Growth Studies," *Am. Mineral.*, **83**, 147-158 (1998)
- Matsubae-Yokoyama, K., H. Kubo, K. Nakajima and T. Nagasaka; "A Material Flow Analysis of Phosphorus in Japan," *J. Indust. Eco.*, **13**, 687-705 (2009)
- Moriguchi, T., S. Nakagawa and F. Kaji; "Reaction of Ca-Deficient Hydroxyapatite with Heavy Metal Ions along with Metal Substitution," *Phosphorus Res. Bull.*, **22**, 54-60 (2008)
- Moriguchi, T., S. Nakagawa and F. Kaji; "Adsorbability of Alizarin Red S on Fe(III)- and Pb(II)-Treated Hydroxyapatite in Water," *Phosphorus Res. Bull.*, **24**, 62-72 (2010)
- Nakato, S. and S. Taguchi; "Method for Removing Manganese in Molten Iron and Production of Pure Iron for Industrial Purpose," JP-A-H06-145767 (1994)
- Sugiyama, S., T. Moriga, H. Hayashi and J. B. Moffat; "Characterization of Calcium, Strontium, Barium and Lead Hydroxyapatites: X-ray Diffraction, Photoelectron, Extended X-ray Absorption Fine Structure and MAS NMR Spectroscopies," *Bull. Chem. Soc. Jpn.*, **74**, 187-192 (2001)
- Sugiyama, S., T. Ichii, H. Hayashi and T. Tomida; "Lead Immobilization by Non-Apatite-Type Calcium Phosphates in Aqueous Solution," *Inorg. Chem. Commun.*, **5**, 156-158 (2002)
- Sugiyama, S., M. Fujisawa, T. Koizumi, S. Tanimoto, K. Kawashiro, T. Tomida and H. Hayashi; "Immobilization of Aqueous Heavy Metals with Phosphates and Sulphates," *Bull. Chem. Soc. Jpn.*, **76**, 2419-2422 (2003)
- Sugiyama, S., K. Fukuta and K.-I. Sotowa; "Formation of Hydroxyapatite-Layer on Glass-Plate and Its Removal-Regeneration Properties of Aqueous Cadmium," *J. Colloid Interface Sci.*, **299**, 270-273 (2006)
- Sugiyama, S., Y. Shimizu, T. Manabe, K. Nakagawa and K.-I. Sotowa; "Preparation of Hydroxyapatite Film and Its Application in the Removal and Regeneration of Aqueous Cations," *J. Colloid Interface Sci.*, **332**, 439-443 (2009)
- Sugiyama, S., D. Ioka, T. Hayashi, M. Noguchi, K. Nakagawa, K.-I. Sotowa and K. Takashima; "Recovery of Phosphate from Unused Resources," *Phosphorus Res. Bull.*, **25**, 18-22 (2011)
- Sugiyama, S., T. Hayashi, I. Shinomiya, K. Nakagawa and K.-I. Sotowa; "Recovery and Enrichment of Aqueous Phosphate from the Slag Released by a Chemical Factory," *Phosphorus Res. Bull.*, **27**, 23-27 (2012)
- Xu, Y. and F. W. Schwartz; "Lead Immobilization by Hydroxyapatite in aqueous solution," *J. Contam. Hydrol.*, **15**, 187-206 (1994)
- Yokoyama, K., H. Kubo, K. Mori, H. Okada, S. Takeuchi and T. Nagasaka; "Separation and Recovery of Phosphorus from Steelmaking Slags with the Aid of a Strong Magnetic Field," *ISIJ Int.*, **47**, 1541-1548 (2007)