

ELUTION BEHAVIOR OF DEPHOSPHORAZATION SLAG TO VARIOUS ACIDS AND EFFECT OF ADDITION OF AQUEOUS ALKALI TO ACID ELUATE

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Abstract: We recently developed a method for efficiently recovering phosphoric acid from dephosphorization slag. The most important processes in this recovery technique involve elution of the dephosphorization slag into an acid solution (acid-elution process) and the addition of an alkali to the acid eluate to form a precipitate (alkali-precipitation process). Ultimately, we settled the use of an aqueous nitric acid solution for the acid-elution step, while an aqueous ammonia solution proved to be the optimal choice to accomplish alkali precipitation. Herein, we describe the procedures used to compare the utility of nitric acid with that of hydrochloric acid, sulfuric acid, and citric acid in the acid-elution process, and describe our comparison of an aqueous sodium hydroxide with that of an aqueous ammonia in the alkali-precipitation process. Finally, we summarize our findings on the acids and alkalis that proved to be suitable for this technology.

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INTRODUCTION

Phosphorus produced from phosphate rock is indispensable as a fertilizer for food production and is also used for the synthesis of precursors of various important chemical products.¹ Since phosphate rock is not a natural resource in Japan, this country must rely on imports from abroad.² However, countries that produce phosphate rock, such as the United States and China, have upgraded the status of phosphate rock to that of strategic material and placed restrictions on exports in an attempt to forestall the future depletion of phosphate.³ Based on this situation, the country could find itself unable to procure sufficient amounts and would be forced to pay escalating prices. Unlike fossil fuels, which are lost when burned, phosphorus resources, once imported into Japan, change shape and remain in the country semi-permanently. For example, dephosphorization slag discharged from the steelmaking process,^{4,5,6} as well as from chicken manure^{7,8,9} and sewage sludge,¹⁰ contains phosphorus that has utility as a substitute for phosphate rock. Japan is a world leader in the development of

technology for recovering phosphorus from these unused phosphorus-containing resources. However, most of the technology is geared toward using the recovered phosphorus as fertilizer. This is tantamount to discarding the recovered phosphorus in the soil again, whereupon it cannot be used as a raw material for manufacturing important chemical products.

Against this backdrop, our laboratory is developing phosphorus-recovery technology that can be used for industrial production from unused resources. Recently, we developed technology to recover high-purity calcium phosphate from composted chicken manure⁷ as well as from the incineration ash of chicken manure,^{8,9} and also to recover high-purity phosphoric acid from dephosphorization slag.^{5,6} Herein, we describe the results of a detailed examination of the key processes in the technology for obtaining phosphoric acid from dephosphorization slag, which is believed to contain phosphorus comparable to that imported by Japan. The technology we have developed consists of the following four processes. (1) A process for dissolving dephosphorization slag in acid, which is the first acid-elution process. (2) A process for the addition of

an alkali solution to the acid eluate to precipitate crystals, which the alkali precipitation process. (3) The second process of dissolving the precipitated crystals in acid. (4) The process of passing the second acid eluate through an ion-exchange resin.

For Process (1), how to dissolve phosphorus is directly linked to the amount of phosphoric acid obtained in the final recovered product. Furthermore, for Process (2), how phosphorus is precipitated is directly linked to the amount of phosphorus obtained in the final recovered product. On the other hand, Processes (3) and (4) have been shown to have little effect on the amount of phosphorus acquired.⁵ Therefore, the first acid elution process (Process (1)) and the alkali precipitation process (Process (2)) were examined in detail, since these two processes have the most influence on how effectively the phosphorus in the dephosphorization slag can be used.

MATERIALS AND METHODS

We obtained dephosphorization slag from a steel plant in Japan. The composition estimated using X-ray fluorescence for Mg, Al, Si, P, Ca, Ti, Mn, and Fe in this slag was 1.69, 1.39, 15.8, 2.72, 49.5, 2.37, 7.89, and 18.6%, respectively.⁵ As a typical example, we treated 1.0 g of dephosphorization slag with 100 mL of 0.5 M aqueous nitric acid solution.^{5,6} In the first acid elution process, 1.0 g of the dephosphorization slag (particles less than 355 μm) was dissolved in 100 mL of 0.5 M HNO_3 at 293 K. This aqueous solution was stirred at 130 rpm for a prescribed amount of time, although the solution was stirred for only 0.2 h, in our previous study.^{5,6} Furthermore, various concentrations of aqueous hydrochloric acid, sulfuric acid, and citric acid were used in the first acid elution process to compare the efficiency with that of nitric acid.^{5,6} The resultant solution was filtered to obtain the residue and the filtrate. In the alkali precipitation process, aqueous ammonia was added to the filtrate at 200 rpm for adjustment to a solution pH = 4.^{5,6} The solution was then let stand for an additional 0.5 h without stirring to allow a precipitate to form. In the present study, aqueous sodium hydroxide was used together with ammonia and the pH setting were varied at 4, 5, 6, and 7. The solutions obtained via the first elution process and the alkali precipitation process were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, SPS3520UV, SII Nanotechnology Inc.). Dephosphorization slag was supplied by a steel plant in Japan. All chemicals were purchased from FUJIFILM Wako Pure Chemical Co. and used as supplied.

RESULTS AND DISCUSSION

Figure 1 shows the elution behavior of phosphorus from the dephosphorization slag using 0.3, 0.4, and

0.5 M of nitric acid. As expected, the use of higher concentrations of nitric acid was suitable, and the use of 0.5 M of nitric acid resulted in an almost complete elution of phosphorus from the slag after only 0.2 h of acid-treatment. In our previous studies, we decided to use 0.5 M of nitric acid and to avoid the use of higher concentrations.

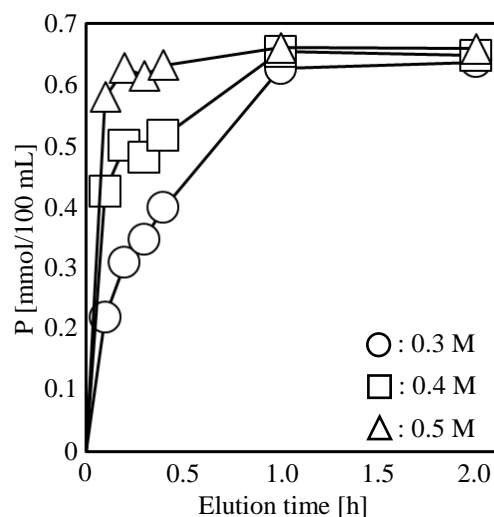


FIGURE 1. Elution behavior of phosphorus using 0.3, 0.4, and 0.5 M of HNO_3 .

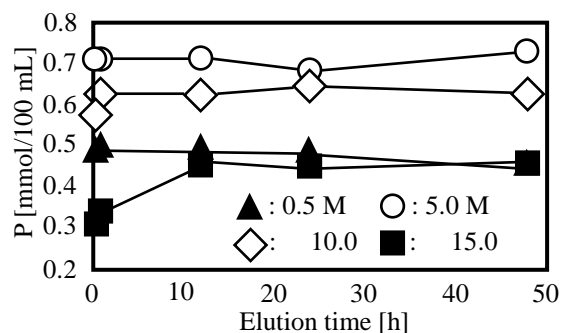


FIGURE 2. Elution behavior of phosphorus using 0.5, 5.0, 10.0, and 15.0 M of HNO_3 .

To reduce the amount of waste liquid in the subsequent filtration processes, however, we decided that the use of a higher concentration of nitric acid should be considered. Therefore, results from the use of 5.0, 10.0, and 15.0 M of nitric acid were compared with the results from using 0.5 M in the elution of dephosphorization slag for up to 48 h. At the time of practical use, when this method was implemented in a large plant, there was a problem of whether it could be handled in a short processing time of 0.2 h. It is expected that it will be difficult to mass-process in too short a time. It is also necessary to clarify what will happen if there is a problem with the plant and the processing time in this process is long. Therefore, the processing time was extended to 48 h. As shown in Figure 2, the elution of phosphorus was increased with a concentration of nitric acid of 10.0 M,

followed by a decrease in the elution when using 15.0 M of the acid. In the case of the highest concentration of 15.0 M of nitric acid, the elution of phosphorus was suppressed, since the surface of the slag was covered with the passive film produced by the use of highly concentrated nitric acid.¹¹ It should be noted that a short elution time of around 0.2 h was suitable for the elution of phosphorus from the dephosphorization slag.

Since there could be a more suitable acid than nitric acid for the elution of dephosphorization slag, the elution behavior was investigated using hydrochloric acid, sulfuric acid, and citric acid.

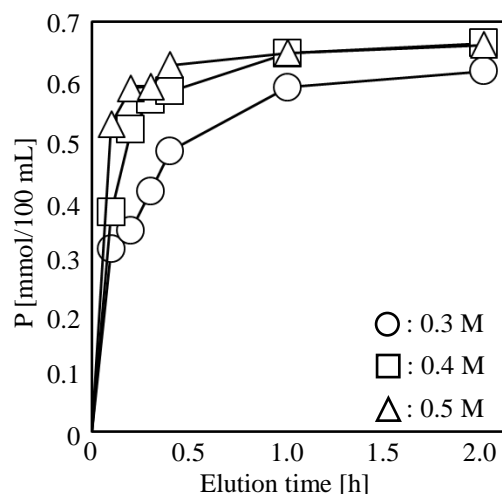


FIGURE 3. Elution behavior of phosphorus using 0.3, 0.4, and 0.5 M of HCl.

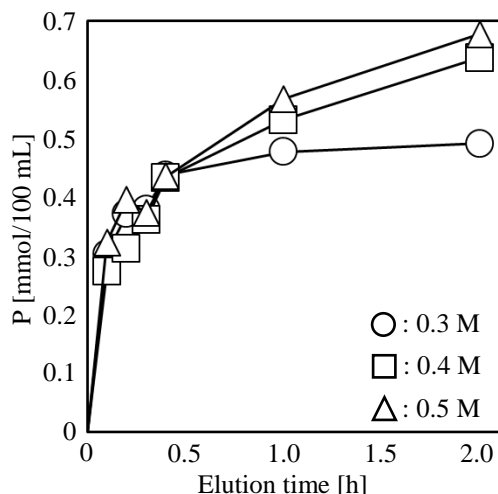


FIGURE 4. Elution behavior of phosphorus using 0.3, 0.4, and 0.5 M of H₂SO₄.

Figure 3 shows the elution behavior of phosphorus from dephosphorization slag using 0.3, 0.4, and 0.5 M of hydrochloric acid. The elution behavior using hydrochloric acid was similar to that using nitric acid. However, paying attention to the elution behavior up

to an elution time of 1 h using 0.5 M of hydrochloric acid demonstrated that the elution amount of phosphorus tended to gradually increase with elution time when compared with the use of nitric acid. Further, as will be described later, the amount of elution of phosphorus using hydrochloric acid seemed to be inferior to that of nitric acid.

On the other hand, when sulfuric acid was used, the elution behavior of phosphorus was different from when either nitric acid or hydrochloric acid was used. As shown in Figure 4, the elution amount of phosphorus did not depend on the concentration of sulfuric acid up to an elution time of 0.5 h, and was considerably lower than the results when using either of nitric acid or hydrochloric acid. However, when the elution time exceeded 0.5 h, the eluted amount of phosphorus increased according to the concentration of sulfuric acid. This is because calcium phosphate, which has low solubility and is produced via a reaction between calcium and phosphorus, covered the slag, which suppressed the elution of various components until the elution time reached 0.5 h.⁹ After 0.5 h, calcium phosphate also began to dissolve, and the dissolution of phosphorus proceeded when the slag finally came into direct contact with the acid.

Figure 5 compares the elution behavior of phosphorus up to an elution time of 48 h when using nitric acid, hydrochloric acid, or sulfuric acid, and when the pH was adjusted to levels used for 5.0 M nitric acid. The elution amount of phosphorus was on the order of nitric acid > hydrochloric acid > sulfuric acid, and an elution time of 0.2 h was deemed sufficient for nitric acid in this case as well.

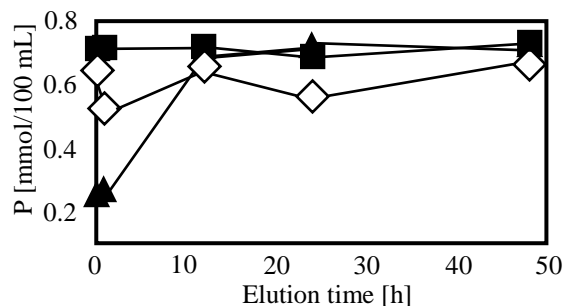


FIGURE 5. Elution behavior of phosphorus using aqueous HNO₃ (■), HCl (◇), and H₂SO₄ (▲).

Above, we describe the elution behavior of phosphorus from dephosphorization slag using an inorganic acid, while the elution behavior of phosphorus by an organic acid was also examined by using aqueous citric acid. If dephosphorization slag can be dissolved in an organic acid and the concentration of phosphorus in the acid elution is high, the acid eluate can be introduced into a special furnace and converted into yellow phosphorus; the furnace is described in its patent.¹² A temperature of 563 to 883 K in this special furnace is sufficient.

Since the acid eluate contains an organic acid, the exothermic reaction associated with the burning of the organic substance in the furnace would be advantageous for the production of yellow phosphorus using high temperature. In the production of yellow phosphorus from phosphate rock, an electric furnace is usually used with the temperature adjusted between 1,673 and 1,773 K.¹² However, this method would not be applicable in Japan due to the high cost of energy that it required. Therefore, the application of the acid eluate to the above-patented method is appropriate.

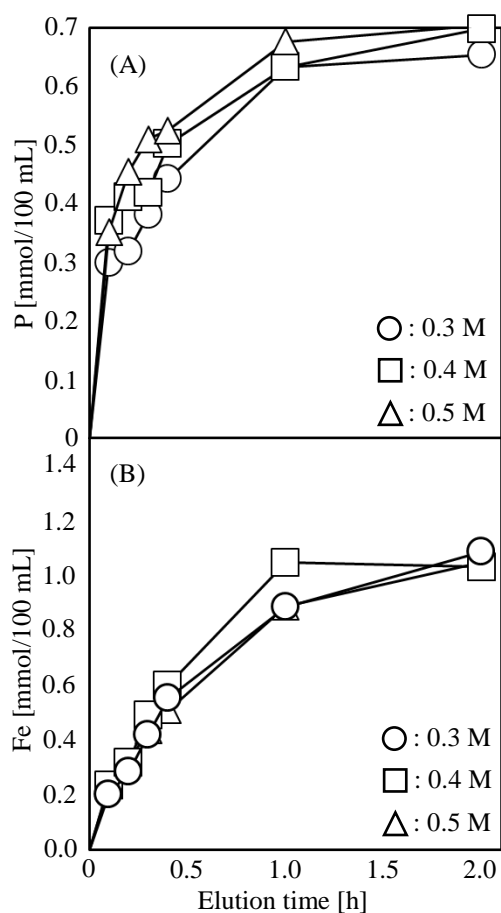


FIGURE 6. Elution behavior of (A) phosphorus and (B) iron using 0.3, 0.4, and 0.5 M of citric acid.

As shown in Figure 6 (A), the elution of phosphorus for 0.5 h was insensitive to the concentration of citric acid and, compared with the use of inorganic acids, the phosphorus elution rate was rather suppressed. After 0.5 h, however, the elution of phosphorus became more remarkable as the acid concentration increased, and the amount of phosphorus elution after 2 h was comparable to that when using an inorganic acid. The fact that phosphorus elutes from dephosphorization slag in organic acids is very important. Unfortunately, along

with the elution of phosphorus, the elution of iron was also remarkable, as shown in Figure 6 (B). Therefore, it was difficult to concentrate the phosphorus in the acid eluate using the first acid elution process alone.

Next, we examined the alkali precipitation process to precipitate crystals by adding an alkali to the filtrate obtained by filtering the solution obtained in the first acid-elution process. In the present study, filtrate was obtained as described in the Methods

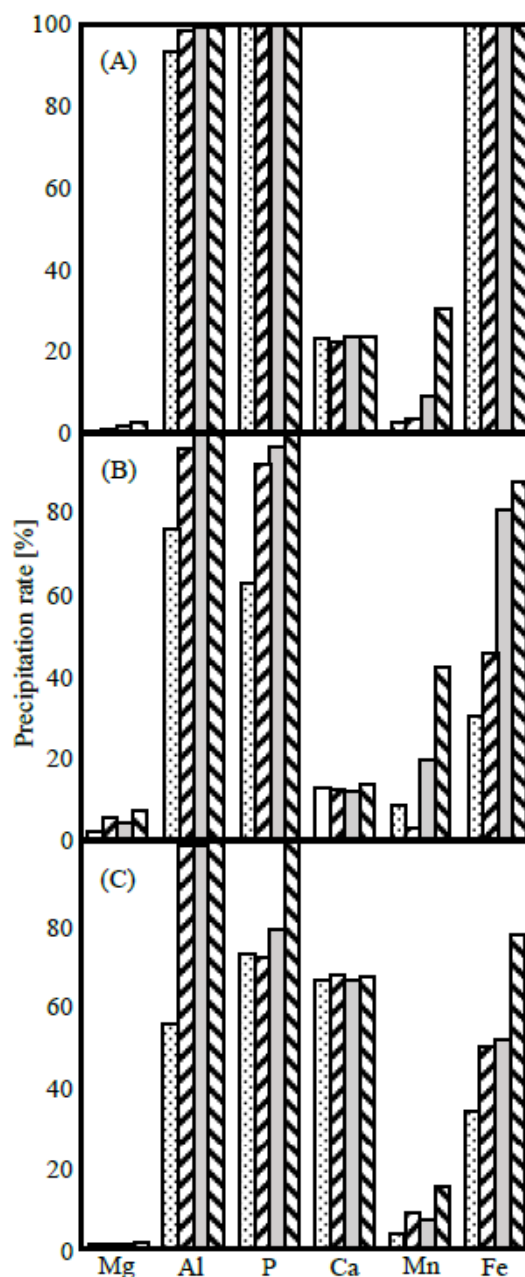


FIGURE 7. Precipitation rate of various cations after the addition of aqueous ammonia into acid eluate using (A) nitric acid, (B) hydrochloric acid, and (C) sulfuric acid to reach pH 4 (□), 5 (▨), 6 (▩), and 7 (▧).

section. Furthermore, filtrates obtained via the use of hydrochloric and sulfuric acids were also examined. In the Methods section, we describe how the precipitate was formed at pH = 4 by the addition of aqueous ammonia, and here the results are expanded to pH = 4, 5, 6, and 7.

Figure 7 (A) lists the precipitation rates of various cations when using an acid filtrate of nitric acid. These were calculated from the ICP results of the corresponding filtrates. The precipitation rates of phosphorus and iron reached 100% even after an adjustment to pH = 4. At pH = 4, however, the precipitation rates for magnesium, aluminum, calcium, and manganese did not reach 100%, which indicated that phosphorus was enriched in the precipitation. In particular, magnesium, calcium, and manganese all were favorably removed by the precipitation. In using an acid filtrate of hydrochloric acid, as shown in Figure 7 (B), the precipitation rate of phosphorus was 100% only when pH = 7 due to the addition of a large amount of aqueous ammonia. Comparing Figures 7 (A) and 7 (B), in the case of Figure 7 (B), the precipitation rate of each metal was small unless a large amount of ammonia was added to raise the pH. When a small amount of ammonia was added, each metal element became a highly soluble chloride and was not precipitated. On the other hand, when the pH was raised, it was converted

to hydroxide, resulting in the evident precipitation formation.

When using an acid filtrate of sulfuric acid, as shown in Figure 7 (C), the precipitation rate of phosphorus was suppressed further than that using an acid filtrate of hydrochloric acid. The method described in our previous papers^{5,6} for adding aqueous ammonia to the nitric acid filtrate to reach a pH = 4 was validated by these results.

In the alkali precipitation process, it is common to use an aqueous sodium hydroxide together with aqueous ammonia. Therefore, we examined the addition of aqueous sodium hydroxide into the filtrate of acid eluate to form a precipitate. Here, we focused on the precipitation rate of iron together with phosphorus, which was calculated using the concentration of these elements in the corresponding solution before and after the addition of each form of aqueous alkali. In the present study, filtrate was obtained through the Methods section described above, while nitric acid was used in the first acid elution process.

When using aqueous ammonia, the lowest pH (= 3) was insufficient for the formation of precipitation containing phosphorus and iron, as shown in Figures 8 (A) and 8 (B), respectively, even if the time from the addition of water-soluble ammonium to filtration (precipitation time) was as short as 0.1 h. At pH = 4

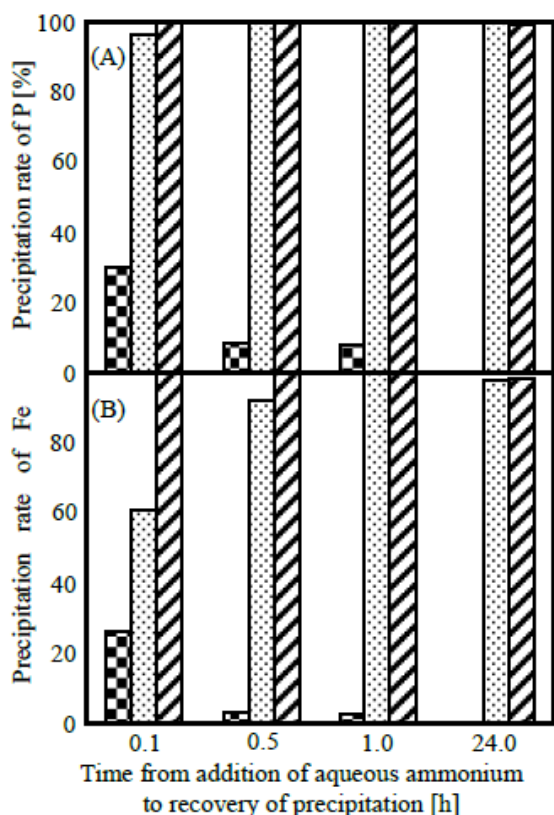


FIGURE 8. Precipitation rate of (A) phosphorus and (B) iron after the addition of aqueous ammonia into an acid eluate using nitric acid to reach pH = 3 (■), 4 (▣), and 5 (▤).

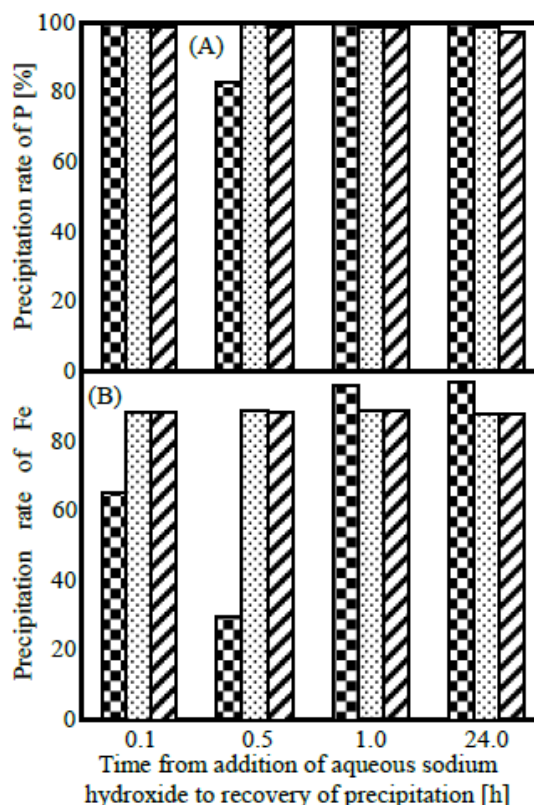


FIGURE 9. Precipitation rate of (A) phosphorus and (B) iron after the addition of aqueous sodium hydroxide into acid eluate using nitric acid to reach pH = 3 (■), 4 (▣), and 5 (▤).

and 5, most phosphorus and iron were precipitated when the precipitation time was 0.5 hours or longer. On the other hand, when the precipitation time was 0.1 h at pH = 4, most of the phosphorus precipitated, but only about 60% of the iron was detected. Therefore, the concentration of phosphorus in the precipitate could have been enriched.

When using aqueous sodium hydroxide, as shown in Figure 9, at pH = 4 and 5, the precipitation rates of phosphorus and iron were about 100 and 90%, respectively, regardless of the precipitation time, and it was difficult to concentrate phosphorus in the corresponding precipitate. At pH = 3 with the precipitation times of 0.1 and 0.5 h, an evident difference in the precipitation rates of phosphorus and iron was detected. However, in this case, a large amount of sodium remained in the precipitation and in the filtrate excluding the precipitation. Obviously, if a large amount of sodium remains in the precipitation, it would be difficult to remove it in the subsequent steps for the second acid-elution and the ion-exchange processes.

As shown in our previous paper,⁵ the structure of the precipitated crystals obtained here are different from that in the dephosphorization slag. However, the structure of the phosphorus compounds has not been identified by XRD due to the low phosphorus content. It has also been clarified that if phosphorus can be completely dissolved from the crystals by Process (3), cations other than phosphorus will be removed by the following Process (4), since phosphorus exists in the form of phosphate anions. Therefore, the crystal morphology obtained in Process (2) does not affect Processes (3) and (4) and is not considered in the present study.

CONCLUSIONS

Using the process we previously developed for described of recovering phosphoric acid from dephosphorization slag, we examined in detail a first acid-elution process and an alkali precipitation process, both of which greatly affected the recovery rate of phosphorus. The use of various concentrations of nitric acid, hydrochloric acid, sulfuric acid, and citric acid in this acid-elution process validated our established treatment of dephosphorization slag using 0.5 M of nitric acid for times as short as 0.2 h. In the alkali precipitation process, the pH used for precipitation was examined using typical forms of alkali such as aqueous ammonia and aqueous sodium hydroxide. The result showed that suitable precipitation could be obtained at pH = 4 via the use of aqueous ammonia with a precipitation time of approximately 0.5 h.

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