

Recovery of the Phosphorus from the Nitric Acid Extract of Powder Collected in a Bag Filter during the Recycling of Used Fluorescence Tubes

Shigeru SUGIYAMA^{1,2*}, Haruka KINOSHITA³, Ippei SHINOMIYA³, Ryuta KITORA³, Keizo NAKAGAWA^{1,2}, Masahiro KATOH¹ and Kohei MASUMOTO⁴

¹Department of Advanced Materials, Institute of Technology and Science, The University of Tokushima, Minamijosanjima, Tokushima-shi, Tokushima 770-8506, Japan

²Department of Resource Circulation Engineering, Center for Frontier Research of Engineering, The University of Tokushima, Minamijosanjima, Tokushima-shi, Tokushima 770-8506, Japan

³Department of Chemical Science and Technology, The University of Tokushima, Minamijosanjima, Tokushima-shi, Tokushima 770-8506, Japan

⁴Japan Recycling Light Technology & System, 1-62-17, Hibiki-machi, Wakamatsu-ku, Kitakyushu-shi, Fukuoka, Japan

Keywords: Used Fluorescence Tube, Recovery of Phosphate, Enrichment of Rare Earth Elements

Abstract

During the recovery of phosphorus from the powder collected in a bag filter during the recycling of used fluorescence tubes (bag-powder), the batch method with aqueous HNO₃ was used to examine the elution behavior of aqueous phosphate contained in the bag-powder. The main components of the bag-powder included Ca²⁺, PO₄³⁻ and Y³⁺ along with Si⁴⁺, Sr²⁺ and lanthanide cations such as La³⁺ and Ce⁴⁺. Therefore, it seemed possible that, with the selective dissolution of Ca²⁺ and PO₄³⁻ from the bag-powder, these lanthanide cations in the residue could be enriched. With the batch method, most of the phosphate in the bag-powder was dissolved within 0.2 min using 1.0 mol/L HNO₃. The dissolution behavior of calcium cation was similar to that of the phosphate. In contrast, the dissolution of yttrium, the content of which was the highest among the lanthanide cations in the bag-powder, was increased with the dissolution times, reaching complete dissolution after 24 h. The Sr²⁺, La³⁺ and Si⁴⁺ in the bag-powder, however, did not dissolve under the same conditions. Although Ca²⁺, PO₄³⁻ and Y³⁺ were the main components in the nitric acid extract, Y³⁺ was separated as YPO₄ at pH = 4.0, while Ca²⁺ and PO₄³⁻ were separated as calcium phosphates at pH = 7.0. These results revealed that the separation of calcium phosphates, YPO₄ and some residue was possible, and resulted in the enrichment of lanthanide cations along with the recovery of phosphorus from the bag-powder. Using the present technique, 91% of the P in the bag-powder was recovered.

Introduction

As shown in our previous paper (Sugiyama *et al.*, 2014), the development of new sources of phosphorus other than phosphate rock has recently become desirable since it is understood that phosphate rock as a raw material for phosphorus will disappear in the near future (Abelson, 1999). Therefore, some reports on the extraction of phosphate from sludge and from steel-making slag using acidic and alkaline solutions have been published (Takahashi *et al.*, 2001; Sano *et al.*, 2012; Teratomo *et al.*, 2012). Extraction of phosphate from iron ore using an acidic solution has also been reported (Zhang and Muhammed, 1989; Patrick and Lovel, 2001). In our laboratory, we have used slag released from the processing of steel (Sugiyama *et al.*, 2011, 2014) and that from chemical factories (Sugiyama *et al.*, 2012) as new sources of phosphorus. We have been able to dissolve aqueous phosphate from both types of slag using nitric acid, while a phosphate-containing solid could be precipitated from the nitric acid extract of the slag released from steel processing,

simply by adjusting the solution pH to 7.0 (Sugiyama *et al.*, 2014). Unfortunately, the precipitation was not calcium phosphates. If calcium phosphates are formed, the precipitation can be used in place of phosphate rock, which also consists of various calcium phosphates. It should be noted that any procedure for the recovery of phosphorus must be simple and inexpensive since the price of phosphorus is still low. Otherwise, it must be possible to use the by-products that are simultaneously produced to pay the cost for the recovery of the phosphorus.

In the present study, powder collected using a bag filter for the recycling of used fluorescence tubes (bag-powder) was employed as a new source of phosphorus. According to data from the Japan Lighting Manufactures Association and the Japan Recycling Light Technology & System, approximately 0.7–6 g of bag powder can be obtained from one fluorescence tube depending on the type of tube. From the Japan Recycling Light Technology & System, approximately 20 tons of bag-powder is produced per year and is estimated that 200 tons of the powder is produced per

Correspondence concerning this article should be addressed to
S. Sugiyama (E-mail address: sugiyama@chem.tokushima-u.ac.jp)

year in Japan. In the bag-powder, Ca^{2+} , PO_4^{3-} and Y^{3+} are the main contents, together with Si^{4+} , Sr^{2+} and lanthanide cations such as La^{3+} and Ce^{4+} while mercury compounds are completely removed. Therefore, if Ca^{2+} and PO_4^{3-} can be separated from the bag-powder as calcium phosphates, the enrichment of lanthanide cations such as Y^{3+} , La^{3+} , and Ce^{4+} together with the recovery of calcium phosphates is possible. This indicates that the enrichment of the concentration of those lanthanide cations could underwrite the cost for the recovery of the phosphates.

In the present study, the elution behavior of the bag-powder using nitric acid to form an aqueous complex mixture containing phosphate was first examined using a batch system, in order to confirm the most favorable dissolution of Ca^{2+} and PO_4^{3-} rather than other cations. The aqueous mixture is referred to herein as a nitric acid extract. Then, we examined the stepwise separation of YPO_4 followed by that of calcium phosphates from the nitric acid extract.

1. Experimental

We examined the elution behaviors of phosphate and various cations from the bag-powder using various concentrations of aq. HNO_3 (Wako Pure Chemical Industries, Ltd.) as an eluate using a batch method. The bag-powder was obtained directly from a collection supplier of used fluorescence tubes. The composition of the bag-powder 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 bag-powder used in the present study is described in **Table 1**. The homogeneity of the bag powder was not very good due to the characteristics of the waste disposal treatment. The deviation of the contents in the present lot is also described in Table 1. Furthermore, the composition was dependent on the types of fluorescence tubes as shown in data reported by the Japan Lighting Manufactures Association. It should be noted that phosphate will hereafter be referred to as P. The present study was focused mainly on cations with a composition greater than 3 mol%.

Table 1 Composition of the bag-powder

| Composition [mol%] | | | | | | |
|--------------------|----|----|-----|-----|-----|--------|
| P | Ca | Y | La | Si | Sr | Others |
| 23 | 34 | 17 | 3.8 | 3.0 | 4.5 | 14.7 |

Estimated deviation, less than 10, 16, 19, 23, 20, and 23% for P, Ca, Y, La, Si, and Sr, respectively.

The elution behaviors of phosphate were examined using the batch method, which began with the addition of 100 mL of aq. HNO_3 to a flask (200 mL), followed by the addition of 1.0 g of the bag-powder (particle size smaller than 100 μm). The mixture was stirred at 130

rpm and 298 K in a constant-temperature bath. The solution was filtered after a scheduled time of stirring using filter paper (4 μm pore size) and a membrane filter (0.45 μm pore size), and then was analyzed by ICP-AES.

In order to precipitate the solid from the nitric acid extract, which contained mainly Ca, P and Y, the pH of the nitric acid extract was increased using an aq. NH_3 solution. The solid samples thus obtained were dried and analyzed using X-ray diffraction (XRD; RINT 2500X, Rigaku Corp.).

2. Results and Discussion

2.1 Elution behavior from the bag-powder using various concentrations of HNO_3

Tables 2 and **3** show the elution behaviors of various cations from the bag-powder using 0.5 and 1.0 mol/L, respectively, for various stirring times. The eluates of P and Ca were detected even after a short stirring time of 0.1 h using both HNO_3 solutions, and the elution behaviors of these two cations were similar after 6.0 h of stirring. Furthermore, the effect of the concentration of HNO_3 on the elutions of La and Sr was not detected and the concentrations of these two cations were independent of the stirring times, although the elution of Si using 1.0 mol/L HNO_3 was evidently greater than that using 0.5 mol/L HNO_3 . It is interesting to note that the concentration of Y was increased with an increase in the stirring time. These results indicate that the selective separation of Ca and P from other cations may be possible with shorter stirring times using 0.5 or 1.0 mol/L HNO_3 .

Table 2 Elution behavior of various cations from the bag-powder using 0.5 mol/L HNO_3

| Stirring Time [h] | Concentration Eluted [mmol/100 mL] | | | | | |
|-------------------|------------------------------------|------|--------|---------|--------|--------|
| | P | Ca | Y | La | Si | Sr |
| 0.1 | 1.98 | 2.29 | 0.0283 | 0 | 0 | 0.0413 |
| 0.2 | 2.02 | 2.34 | 0.0365 | 0 | 0 | 0.0416 |
| 0.3 | 2.25 | 2.61 | 0.0604 | 0 | 0 | 0.0412 |
| 0.4 | 2.35 | 2.78 | 0.0735 | 0 | 0 | 0.0421 |
| 0.5 | 2.54 | 3.17 | 0.0813 | 0.00811 | 0.0276 | 0.0380 |
| 2.0 | 2.57 | 3.22 | 0.196 | 0.00848 | 0.0302 | 0.0378 |
| 4.0 | 2.58 | 3.22 | 0.340 | 0.00890 | 0.0302 | 0.0379 |
| 6.0 | 2.59 | 3.27 | 0.476 | 0.00930 | 0.0361 | 0.0387 |

When using 0.1 mol/L HNO_3 , a low concentration of P and Ca (1.40 and 1.41 mmol/100 mL, respectively) was detected after a stirring time of 0.3 h, indicating that the low concentration of HNO_3 was insufficient for the elution of these two cations from the bag-powder. In contrast, when using a higher concentration of HNO_3 , the concentrations of P and Ca eluted at 0.3 h were 2.25 and 3.08 mmol/100 mL using 2.0 mol/L HNO_3 , while the concentrations were 2.32 and 3.09 mmol/100 mL when using 5.0 mol/L HNO_3 , respectively. In

particular, the concentrations of P eluted using 2.0 and 5.0 mol/L HNO₃ were essentially identical to those shown in Tables 2 and 3. As described, the first purpose of the present study was the suitable elution of P and Ca from the bag-powder. Therefore, it was concluded that a suitable separation of P and Ca from the bag-powder would be possible using 1.0 mol/L HNO₃ and a shorter stirring time.

Table 3 Elution behavior of various cations from the bag-powder using 1.0 mol/L HNO₃

| Stirring Time [h] | Concentration Eluted [mmol/100 mL] | | | | | |
|-------------------|------------------------------------|------|--------|---------|--------|--------|
| | P | Ca | Y | La | Si | Sr |
| 0.1 | 1.83 | 2.12 | 0.0429 | 0.00816 | 0.0195 | 0.0370 |
| 0.2 | 2.39 | 2.84 | 0.0655 | 0.00952 | 0.0470 | 0.0370 |
| 0.3 | 2.43 | 2.94 | 0.0772 | 0.00978 | 0.0300 | 0.0378 |
| 0.4 | 2.55 | 3.08 | 0.0950 | 0.0101 | 0.0370 | 0.0381 |
| 0.5 | 2.41 | 3.21 | 0.143 | 0.0115 | 0.0758 | 0.0385 |
| 2.0 | 2.24 | 3.19 | 0.402 | 0.0118 | 0.0688 | 0.0388 |
| 4.0 | 2.34 | 3.35 | 0.816 | 0.0123 | 0.0783 | 0.0403 |
| 6.0 | 2.37 | 3.40 | 1.10 | 0.0125 | 0.0754 | 0.0407 |

In Tables 2 and 3, the eluates of various cations are evident, while no information was afforded from the solid residue. Therefore, the solid residue obtained after stirring using 1.0 mol/L HNO₃ for a given amount of time was analyzed using XRF.

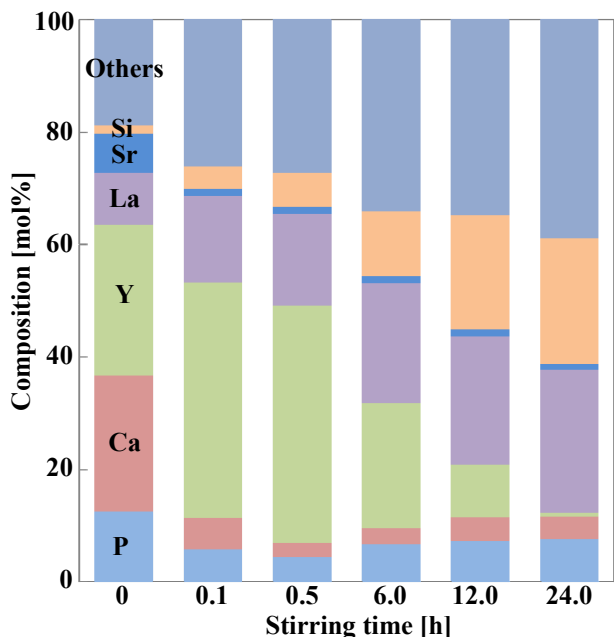


Fig. 1 Composition of cations in the solid residue obtained after the elution for given stirred times of the bag-powder using 1.0 mol/L HNO₃

As shown in **Figure 1**, Ca and P were evidently removed from the solid residue, while the compositions of other cations in the solid residue were increased as the stirring times were increased to 0.5 h. However, more stirring resulted in a decrease in the composition of Y in the solid residue and reached complete

dissolution after 24 h, as suggested in Tables 2 and 3 for the examples of nitric acid extract. Figure 1 shows that shorter stirring times presented an advantage toward the preferential elution of P and Ca, while longer stirring times resulted in the elution of Y together with P and Ca from the bag-powder. Therefore, in order to separate P and Ca from other cations, stirring times shorter than 0.5 h seemed to be suitable, and resulted in the enrichment of lanthanide cations in the powder.

2.2 Recovery of calcium phosphate and yttrium phosphate from nitric acid extract

As described above, most of the P and Ca in the bag-powder together with some Y were eluted in the nitric acid extract. The separation of P and Ca from Y should be established in order to reuse these eluted species. As shown in our previous report on the recovery of phosphate from the dephosphorization slag (Sugiyama *et al.*, 2014), the adjustment of the solution pH of the nitric acid extract resulted in the separation of precipitation containing phosphate from the extract. Therefore, the removal behavior of P, Ca and Y from the nitric acid extract using pH-adjustment was examined (**Figure 2**). As with the extract, the aqueous solution obtained after 1 h stirring of the bag-powder (1.0 g) in 1.0 mol/L HNO₃ was employed. The solution pH of the aqueous solution began at 0.34, and was increased using aqueous NH₃. As shown in Figure 2, the initial concentrations of P, Ca and Y in the aqueous solution were all set at 100%, and Y was completely removed from the aqueous solution at pH = 2.48, while more than 80% of P and Ca was still present in the aqueous solution at pH = 2.48–5.60. This indicated that Y can be separated as a solid precipitation from the solution at pH = 2.48–5.60.

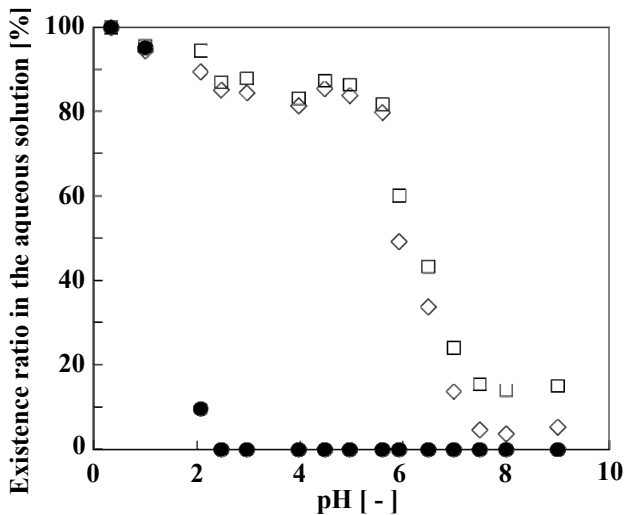


Fig. 2 Existence ratio of P (◇), Ca (□) and Y (●) in the aqueous solution at various pH

After calcination at 1073 K for 5 h, most of the XRD peaks for the solid precipitate obtained at pH = 4.0 matched the reference peaks of YPO₄ (JCPDS 110254) (**Figure 3**). Therefore, after the separation of YPO₄ was

obtained following the pH adjustment to 4, the remaining aqueous solution mainly consisted of P and Ca.

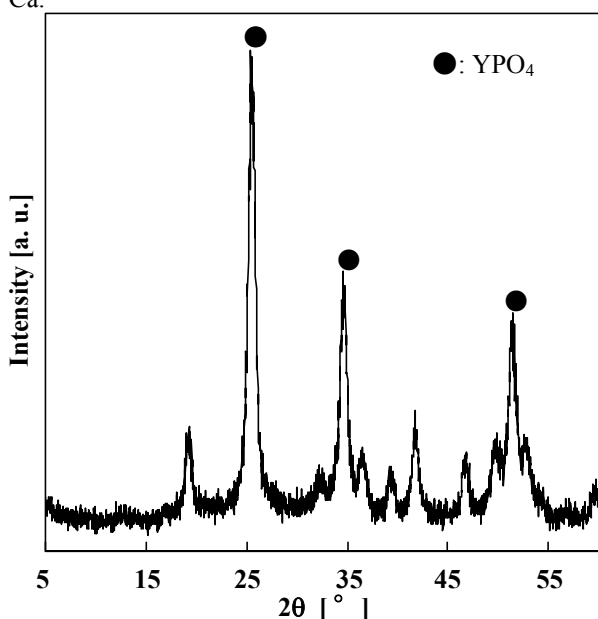


Fig. 3 XRD patterns of the solid precipitate obtained at pH = 4.0, but after the calcination at 1073 K for 5 h

Following further increases in the solution pH to 9.01, most of the P and Ca were also removed from the solution (Figure 2). In analyzing the solid precipitation obtained after the adjustment to pH = 7.0, the presence and absence of the separation at pH = 4.0 were strongly influenced by the content in the solid precipitation (Figure 4). In the absence of the separation of the first precipitation at pH = 4.0, Y was evidently contained in the final precipitation (Figure 4 (B)). However Y was completely eliminated from the final precipitation in the presence of the first separation (Figure 4 (C)).

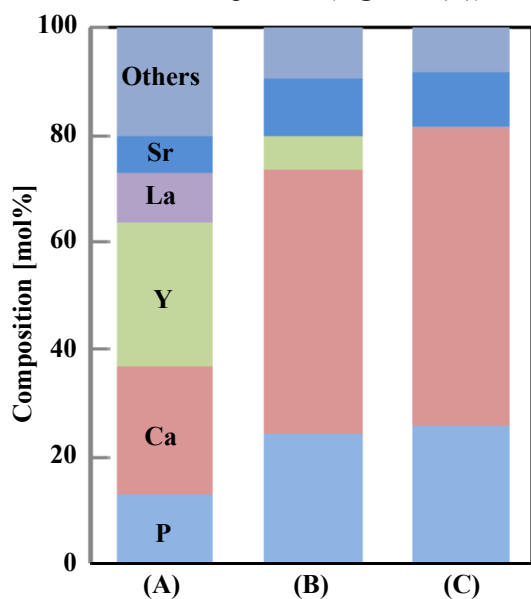


Fig. 4 Composition of cations in the bag-powder (A) and the solid precipitation obtained after the adjustment of pH = 7.0 in the absence (B) and presence (C) of the separation of the first precipitation at pH = 4.0

It was evident that the final precipitations shown in Figures 4 (B) and (C), contained P and Ca, respectively, as the main components. The XRD patterns of Figures 4 (B) and (C), albeit without calcination, roughly matched the reference patterns for calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; JCPDS 721243) (Figure 5). After the calcination at 1073 K for 5 h, the hydroxyapatite was completely converted to $\text{Ca}_3(\text{PO}_4)_2$ (JCPDS 90169) (Figure 5). Since it is well-known that $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is converted to $\text{Ca}_3(\text{PO}_4)_2$ under high temperature (Sugiyama *et al.*, 1998), the formation of the hydroxyapatite before the calcination was reasonable. Therefore, it was confirmed that a rather high purity of calcium phosphates together with yttrium phosphate could be separated from the nitric acid extract of the bag-powder.

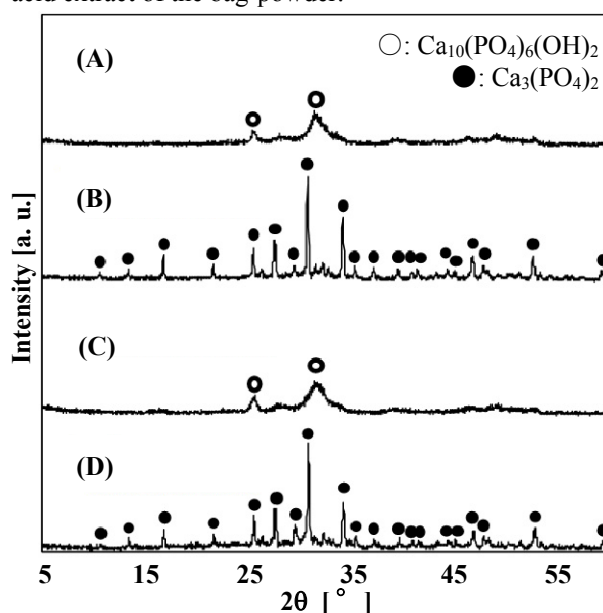


Fig. 5 XRD patterns of the solid precipitate obtained at pH = 7.0: (A) and (B); without the separation of the first precipitation at pH = 4.0 before and after the calcination at 1073 K for 5 h. (C) and (D); with the separation of the first precipitation at pH = 4.0 before and after the calcination at 1073 K for 5 h

Conclusions

The present study showed that powder collected using a bag filter for the recycling of used fluorescence tubes can be used for the recovery and enrichment of phosphate and lanthanide cations. Elution using nitric acid followed by precipitation using aq. NH_3 resulted in the separation of calcium phosphate and yttrium phosphate from the powder. Due to the separation of these phosphates, the contents of lanthanide cations such as La^{3+} and Ce^{4+} in the powder were enriched. The proposed recovery and enrichment procedure could amount to a productive technique. It should be noted that 91% of the P in the bag-powder was recovered

using the present technique. The application of the combination to other candidates is now in progress.

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