

PHOSPHORUS RECOVERY FROM SEWAGE-SLUDGE MOLTEN SLAG USING A COMBINATION OF ACID-DISSOLUTION, ALKALI-PRECIPITATION, AND ION-EXCHANGE

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Keywords: Phosphorus recovery, Sewage sludge molten slag, Acid elution, Alkali precipitation, Ion-exchange

Abstract: We recently reported an efficient procedure for recovering phosphoric acid from dephosphorization slag. This recovery procedure consists of a combination of the following four processes: (1) A first dissolution process of slag in a nitric acid solution; (2) a precipitation process then adds ammonia to the obtained eluate; (3) a second dissolution process dissolves the precipitation from the nitric acid eluate; and, (4) the final process involves ion exchange in which the obtained eluate is passed through an ion exchange resin. In the present study, this recovery procedure was applied to concentrate and recover phosphorus from sewage-sludge molten slag, which is an unused resource that should be considered a new resource for phosphorus. As a result, our procedure for recovery from dephosphorization slag was viable following two revisions. Initially, the time for the first dissolution process was extended from 0.2 h to 1 h, but 0.2 h proved to be the optimum time for dephosphorization slag. Next, we discovered it was better to perform the filtration one day after adding the ammonia instead of immediately after adding it. The other two processes could be treated under substantially the same conditions as in the case of dephosphorization slag, and high-purity phosphorus was obtained.

(Received Dec 13, 2022; Accepted Feb 1, 2023)

INTRODUCTION

Steelmaking slag, animal manure, and sewage sludge are resources that typically unused. The previously overlooked value of these resources, however, is attracting attention for the recovery of phosphorus. And these new sources are now being regarded as a permanent phosphorus resources that could replace rapidly depleting natural phosphate rock.¹ Fertilizer is the main use for phosphorus from these unused resources. However, the use of the recovered phosphorus as cheap fertilizer reduces the added value of the recovered phosphorus and is the same as disposing of the phosphorus in soil. Furthermore, when the recovered phosphorus is used as fertilizer, it cannot be used as a raw material for the production of highly functional materials. Against this background, we have developed a technology to

recover calcium phosphate from chicken manure²⁻⁵ and phosphoric acid and calcium phosphate from dephosphorization slag.^{6,7} Our developed technology combines simple and easy processes such as acid dissolution, alkali-precipitation, and ion-exchange, which results in the recovery of phosphoric acid and calcium phosphate, both of which can be used as raw resources for highly functional materials with high added value. This markedly increases the added value of the recovered phosphorus.

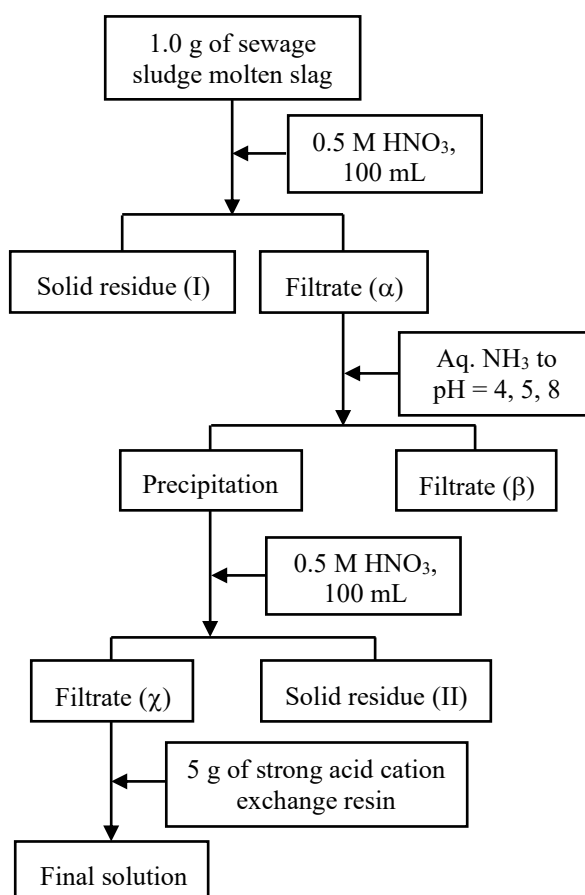
In the present study, we focus on phosphorus recovery from sewage-sludge molten slag instead of chicken manure and dephosphorization slag. In Japan, 56,000 tons of phosphorus is discharged as sewage-sludge every year, since it is reported that 1.4 g of phosphorus is discharged as domestic sewage per person per day.^{8,9} Various treatment processes are used to concentrate the phosphorus discharged into sewage-

sludge. If sewage sludge is safe, it can be directly used as fertilizer. Along with phosphorus, however, sewage-sludge could contain various heavy metals and pharmaceutical-derived antibiotic, and the direct use of these substances poses the risk of environmental pollution. Melting technology has been developed to separate such heavy metals and decompose harmful organic substances, and the obtained molten slag has been used as a civil engineering and construction material. However, since phosphorus is concentrated in the sewage-sludge molten slag, research and development for uses as a phosphorus fertilizer is also progressing.¹⁰ Under such circumstances, however, the phosphorus concentrated in the sewage-sludge molten slag cannot be used as a raw material for high value-added phosphorus-containing products. Therefore, in order to increase the added value of phosphorus in the sewage-sludge molten slag, we decided to apply our phosphorus recovery method consisting of the following four processes. (1) A process for dissolving the sewage sludge molten slag in an aqueous nitric acid solution (First acid elution process). (2) A process for the addition of an aqueous ammonia solution to the first acid eluate to precipitate crystals (Alkali precipitation process). (3) A dissolving process of the precipitated crystals in an aqueous nitric acid solution (Second acid elution process). (4) The process of passing the second acid eluate through an ion-exchange resin (Ion-exchange process). For Process (1), the elution amount of phosphorus is directly linked to that of the phosphoric acid obtained in the final recovered product. Furthermore, for Process (2), the precipitation rate is directly linked to the amount of phosphorus obtained in the final recovered product. On the other hand, Processes (3) and (4) showed little effect on the amount of phosphorus acquired.^{6,7} Therefore, the first acid elution process (Process (1)) and the alkali precipitation process (Process (2)) were examined in detail in order to adjust the entire process to suitable conditions, since these two processes show the most influence on how effectively the phosphorus in the sewage-sludge molten slag could be used. Then, the precipitation obtained via Processes (1) and (2) under suitable conditions was used for Processes (3) and (4).

MATERIALS AND METHODS

We obtained the sewage-sludge molten slag from an advanced sewage treatment facility in Japan. X-ray fluorescence (Supermini200WD (Rigaku)) was used to estimate the compositions for Mg, Al, Si, P, Ca, Cr, Fe, Cu, Ce, and others in this slag, which was found to be 29.53, 17.21, 20.14, 14.77, 5.65, 11.73, 0.06, 0.03, 0.43 and 0.45%, respectively. As a typical example, in the first acid-elution process (Process (1)), 1.0 g of the sewage-sludge molten slag (particles less than 74 μm) was dissolved in 100 mL of 0.5 M HNO_3 at 293 K. This aqueous solution was stirred at 80 rpm for a

prescribed amount of time. The resultant solution was filtered to obtain Solid residue (I) and Filtrate (α). In the alkali precipitation process (Process (2)), aqueous ammonium was added to Filtrate (α) at 300 rpm for adjustment to solution pH values = 4, 5, and 8. The solution was then let stand for an additional 0.5 h with stirring, followed by filtration to produce Precipitation and Filtrate (β). In Process (3), the Precipitation was dissolved in 100 mL of 0.5 M HNO_3 at 293 K with stirring at 300 rpm for 0.5 h. The resultant solution was filtered to obtain Solid residue (II) and Filtrate (χ). In process (4), Filtrate (χ) was passed through 5.0 g of a strong acid cation exchange resin (PK216LH (Mitsubishi Chemical Co.)) in a burette at a flow rate of 2.5 mL/min to obtain the final solution in the present study.



Scheme 1 Experimental flow in the present study

RESULTS AND DISCUSSION

A typical series of processes is summarized as Scheme 1. The solutions and the eluates were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, SPS3520UV (SII Nanotechnology Inc.)). Some solid samples were analyzed using X-ray diffraction (XRD,

SmartLab/R/INP/DX (Rigaku Co.)) with a Cu K α radiation monochromator at 45 kV and 150 mA. All chemicals were purchased from FUJIFILM Wako Pure Chemical Co. and used as supplied.

Process (1): First acid elution process for obtaining Filtrate (α)

When our recovering procedure shown in Scheme 1 was used for other phosphorus-containing unused resources such as chicken manure,²⁻⁵ dephosphorization slag,^{6,7} powder collected in a bag filter during the recycling of used fluorescence tubes,¹¹ and the slag released by a chemical factory,¹² 0.5 M of HNO₃ was generally used as an eluting acid. However, since the elution characteristics of sewage-sludge molten slag were unknown, the results under normal conditions as an elution experiment for 1 h using 0.5 M HNO₃ were compared with the results of an elution experiment for 168 h using 15 M HNO₃, and these results appear in Figure 1. The elution concentration of each constituent element was expected to increase as the concentration of nitric acid increased. However, as shown in Figure 1, although there was a large difference in nitric acid concentration, there was no significant difference in the elution concentration of each constituent element. Therefore, we decided to use 0.5 M of nitric acid. The concentration of HNO₃ was the same as that in the recovery of phosphorus from other phosphorus-containing sources.^{2-7,11,12}

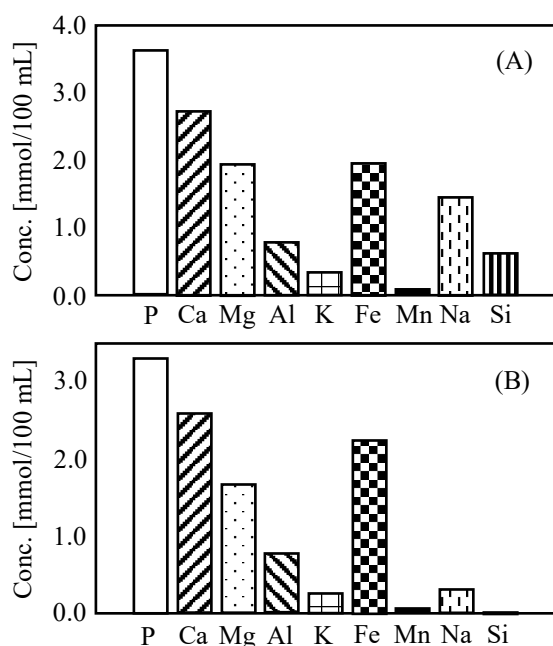


FIGURE 1. Elution behavior of each element from the sewage-sludge molten slag treated for 1 h using 0.5 M HNO₃ (A) and that for 168 h using 15 M HNO₃ (B).

Figure 2 shows the effect of the treatment time for the elution of the sewage sludge molten slag using 0.5

M HNO₃, although treatment times of less than 0.2-0.5 h are reported as suitable for the elution of phosphorus from various phosphorus-containing unused resources.^{2-7,11,12} However, as shown in Figure 2, when using sewage-sludge molten slag, a longer treatment time resulted in a slight increase in the elution of phosphorus from the slag, while the elution of calcium as a second main element seemed insensitive to the concentration of HNO₃. Since it seemed advantageous to avoid a long elution operation, 0.5 M nitric acid was used and the treatment time was set to 1.0 h for obtaining Filtrate (α).

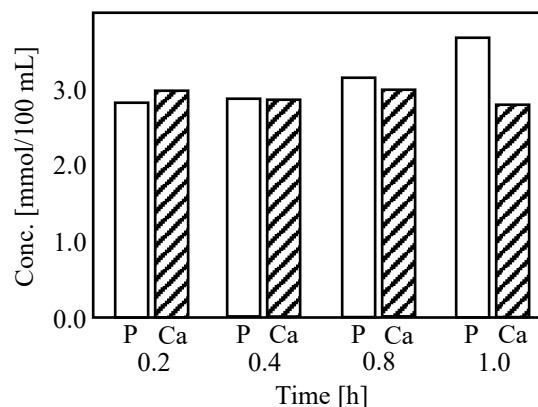


FIGURE 2. Elution behavior of P and Ca from the sewage-sludge molten slag treated for various treatment times using 0.5 M HNO₃.

Figure 3 compares the XRD of the sewage sludge molten slag and Solid residue (I) obtained after 1 h of elution. The sewage sludge molten slag contained Fe₂O₃ and many other components, which are not identified here, but Fe₂O₃ was detected as the main component in Solid residue (I), which indicated that Fe₂O₃ was separated to some extent in this process.

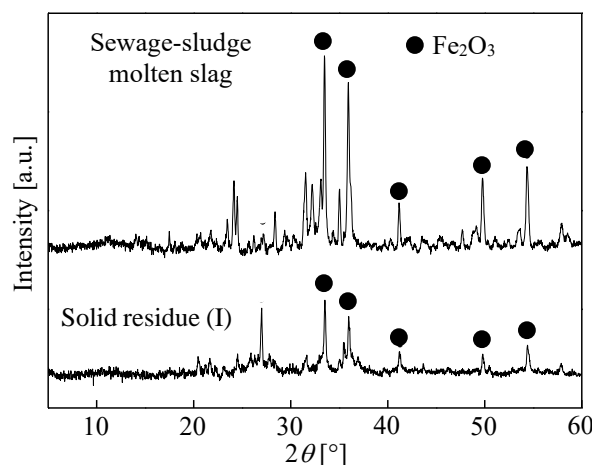


FIGURE 3. XRD of the sewage-sludge molten slag and Solid residue (I) obtained after 1 h of elution

Process (2): Alkali precipitation process for obtaining precipitation

In Process (2), aqueous NH_3 was added to Filtrate (α), which was obtained under the conditions determined above, in order to adjust the pH to values of pH = 4, 5, and 8, after which the solution was left stand for an additional 0.5 h with stirring. Then the solution was filtered to achieve Precipitation and Filtrate (β). In previous studies on various phosphorus-containing unused resources,^{2-7,11,12} Filtrate (β) was immediately obtained after the filtration and used in the subsequent Process (3). However, letting the Filtrate (β) that was obtained here stand for one day resulted in the formation of a greater amount of precipitation. Therefore, we examined the precipitation behavior for both cases.

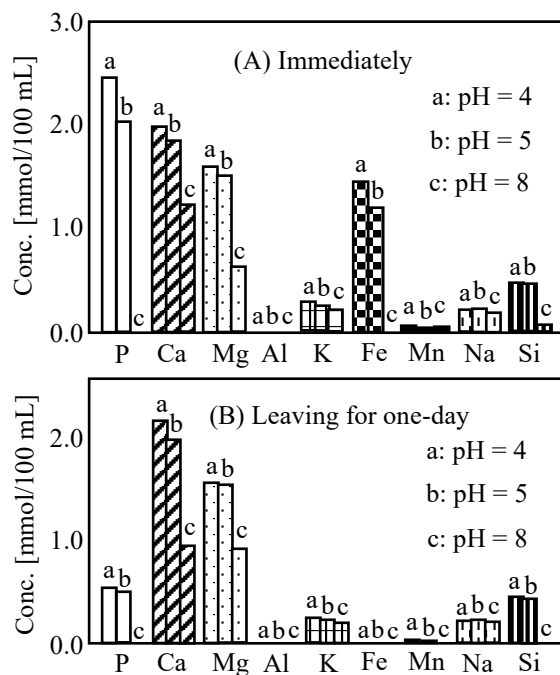


FIGURE 4. Concentration of each constituent element in Filtrate (β) detected immediately and one-day after the addition of aq. NH_3 to Filtrate (α)

Figures 4 (A) and (B) show the concentration of each constituent element in Filtrate (β) detected immediately and one-day after the previous treatment, respectively. As shown in Figure 4 (A), the complete precipitation of phosphorous was not achieved at values for pH = 4 and 5, while the more basic condition at pH = 8 resulted in complete precipitation. Similar behaviors were also detected for the precipitation behaviors of aluminum and iron. Furthermore, with the noted exceptions of potassium and sodium, the concentration in Filtrate (β) was greatly reduced at pH = 8, indicating that the separation of most of the potassium and sodium from other elements was achieved in this process. However, this situation was

changed greatly by letting Filtrate (β) stand for one day, as shown in Figure 4 (B). With the exceptions of calcium, magnesium, potassium, and sodium, the concentration in the solution was decreased significantly as the decreased elements made up the Precipitation, which then was employed in the following process. The lower or lack of phosphorous in Filtrate (β) was suitable. However, leaving Filtrate (β) for one-day also resulted in no detection of iron, which is an element that is one of the most inseparable from phosphorous.

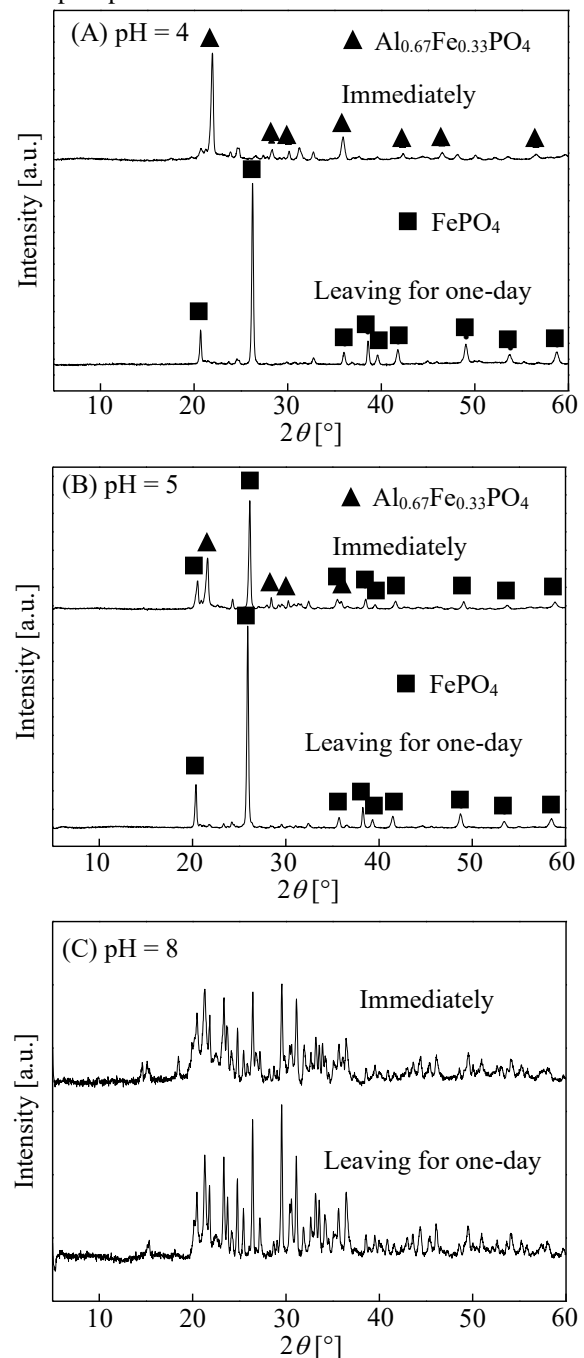


FIGURE 5. XRD of Precipitation simultaneously obtained with Filtrate (β) adjusted to values of pH = 4, 5, and 8

As expected, the components in the Precipitation immediately obtained when the pH values of Filtrate (β) were adjusted at pH = 4, 5, and 8, were completely different after the solution was left stand for one day. As shown in Figures 5 (A) and (B), the Precipitation obtained at values for pH of 4 and 5 consisted mainly of FePO_4 after one day. The Precipitation obtained at pH = 4 consisted mainly of $\text{Al}_{0.67}\text{Fe}_{0.33}\text{PO}_4$, but shifted to FePO_4 after one day. By contrast, the Precipitation obtained at pH = 4. In contrast, Precipitation obtained at pH = 8 showed a complex mixture of the sewage-sludge molten slag, regardless of the time it was left stand. These results revealed that Process (2) strongly contributed to the separations of phosphorus, aluminum, and iron from other elements in the slag. The following Process (3) used all the Precipitation shown in Figure 5.

Process (3): Second acid-elution process for obtaining Filtrate (χ)

In Process (3), Precipitation obtained in Process (2) was again dissolved into in 100 mL of 0.5 M HNO_3 followed by filtration to obtain Filtrate (χ).

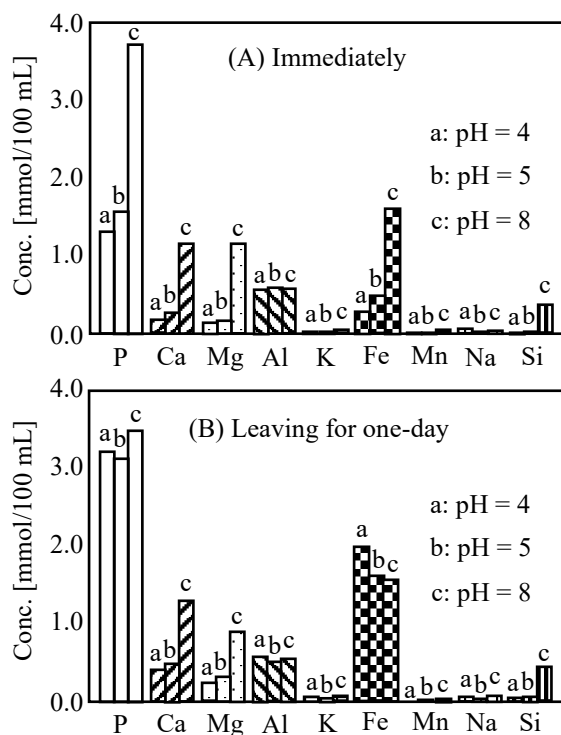


FIGURE 6. Concentration of each constituent element in Filtrate (χ) obtained after the dissolution of precipitation, obtained immediately and one day after in Process (2)

Figures 6 (A) and (B) show the concentrations of each of the constituent elements in Filtrate (χ) obtained after dissolution of the Precipitation obtained immediately and one day after Process (2), respectively. Figure 6 (A) shows Filtrate (χ) obtained

after the dissolution of precipitation via immediate treatment at pH = 8, which revealed greater concentrations of phosphorus, calcium, magnesium, iron, and silicon and indicated the need to separate phosphorus from other cations during Process (4). By contrast, the dissolutions of calcium, magnesium, iron, and silicon could be suppressed by using the precipitation obtained at a pH of either 4 or 5. This situation could be suitable for the following process. However, the concentrations of phosphorus at pH values of 4 and 5 were lower than those at pH = 8, which indicates poor phosphorus recovery. However, this situation was significantly improved with precipitation via Filtrate (χ), which was obtained after the dissolution of the Precipitation that was left stand for one day during in Process (2). As Figure 6 (B) shows, under the conditions at pH = 4 and 5, low concentrations of calcium, magnesium, and silicon were achieved while high concentrations of phosphorus and iron were maintained. Since iron can be removed in Process (4),⁶ its coexistences with phosphorus is not a problem at this stage. Furthermore, low concentrations of other elements, particularly silicon, can reduce the load in the following process. In order to check the separation of phosphorus from other cations, all of the constituents of Filtrate (χ) shown in Figure 6 were employed in Process (4).

Process (4): Ion-exchange process for obtaining the final solution

In Process (4), all the constituents of Filtrate (χ) shown in Figure 6 were passed through a strongly acidic cation exchange resin to obtain each final solution.

Figures 7 (A) and (B) show the concentrations of each constituent element in Final solution that use all of Filtrate (χ) via that gathered immediately or one day after Process (2), respectively. As shown in Figure 7 (A), Final solution obtained via Precipitation obtained at pH = 8 contained the highest concentration of phosphorus. Unfortunately, the concentrations of other constituent elements were also higher, indicating that Final solution contained various contaminant. However, as shown in Figure 7 (B), Final solutions obtained via Precipitation obtained at pH = 4, 5, and 8 contained similar high concentrations of phosphorus. Furthermore, in Final solution obtained via precipitation obtained at pH = 4, constituent elements other than phosphorus were scant. Therefore, the results of this study prove that an aqueous solution containing a high concentration of phosphorus could be obtained from sewage-sludge molten slag via the method developed by us to obtain phosphoric acid from dephosphorization slag.⁶

In the present study, the most suitable recovery was obtained when using Precipitation obtained at pH = 4, which the was let stand for one day, as shown in Table 1, where each recovery was calculated from the percentage of the molar number in Final solution

against that in Filtrate (α). In this case, the concentrations in Final solution for phosphorus, silicon, sodium, iron, and others were 2.52, 0.07, 0.04, 0.03, and 0.02 mmol/100 mL at pH = 4 in Figure 7 (B). Based on these concentrations, the compositions for phosphorus, silicon, sodium, iron, and others were calculated to be 94.0, 2.6, 1.5, 1.1, and 0.7%, respectively. This quantifies the efficiency of the present recovery for phosphorus from sewage-sludge molten slag. It should be noted that phosphorus was concentrated to 94.0% in Final solution, but as a total, only 56.2% of phosphorus was recovered from Filtrate (α) as shown in Table 1. Therefore, we would like to further improve the recovery rate.

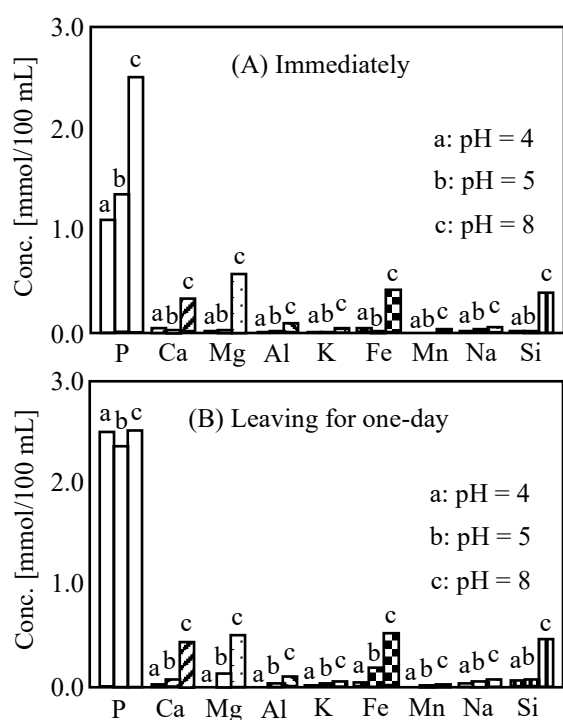


FIGURE 7. Concentration of Final solution using all of Filtrate (χ) gathered either immediately or one day after Process (2)

TABLE 1. Recoveries [%] of the constituent elements as calculated from the percentage of the molar number in Final solution against that in Filtrate (α).

pH	Immediately			Leaving for one-day		
	4	5	8	4	5	8
P	25.5	29.8	57.1	56.2	57.8	50.9
Ca	1.8	1.1	12.5	0.3	2.9	15.7
Mg	0.7	1.7	28.9	0.0	7.0	23.6
Al	2.6	2.4	15.5	0.1	4.5	14.0
K	3.9	5.5	15.5	4.2	13.7	16.1
Fe	2.1	1.0	22.0	1.3	10.1	23.1
Mn	4.2	2.9	35.6	0.0	10.8	39.8
Na	6.1	7.0	15.4	13.5	16.5	24.8
Si	2.5	4.9	64.0	8.9	12.9	69.1

The present recovery method is characterized by recovering phosphorus, which is an exhaustible resource, using nitrogen-derived nitric acid and ammonia, which are inexhaustible in the atmosphere. However, the reuse of nitric acid and ammonia must be considered in future technological developments. Since our ultimate goal is to obtain a nitric acid solution containing only phosphorus, we believe that nitric acid can be reused if phosphorus is removed from the nitric acid solution. Regarding the recovery of ammonia, our laboratory is developing continuous ammonia recovery technology, using absorption-desorption nature for ammonia between magnesium hydrogen phosphate and magnesium ammonium phosphate.¹³⁻¹⁶

CONCLUSIONS

Herein we describe our use of a previously developed process to recovering phosphoric acid from sewage-sludge molten slag. This process consists of four steps: Process (1) is a first acid elution; Process (2) involves alkali precipitation process; Process (3) is a second acid elution, and, Process (4) is accomplished via ion-exchange. The present study shows that a highly efficient enrichment of phosphorus is achieved by slightly modifying the recovery method for dephosphorization slag. The following two points were corrected. The optimum conditions for phosphorus recovery are as follows. In First acid elution process, the sewage-sludge molten slag was dissolved in 0.5 M HNO₃ for 1 h, while the treatment time was fixed at 0.2 h in the phosphorus recovery from dephosphorization slag.⁶ Furthermore, in order to significantly increase the amount of precipitation immediately obtained after the addition of aqueous ammonium to nitric acid eluate, the initial amount was let stand in solution for 1 day prior to filtration.

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