KEY FACTORS FOR THE SEPARATION OF SILICON AND IRON DURING PHOSPHORUS RECOVERY FROM SLAG DISCHARGED FROM THE DOUBLE-SLAG REFINING PROCESS

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Abstract: In the present study, we developed a technology for concentrating and recovering phosphorus from slag-like phosphorus-containing unused resources and applied it to slag discharged during the latest steelmaking process, that is, double-slag refining process (DRP). The technology we developed consists of the following four processes: Process (1) is the initial acid elution; Process (2) involves alkali precipitation; Process (3) is the second acid elution; and, Process (4) utilizes ion-exchange. In Process (1), the addition of DPR slag to 0.5 M of a nitric acid solution for 24 min resulted in sufficient phosphorus dissolution. In Process (2), ammonia was added to the dissolved solution, and phosphorus was precipitated with high efficiency. The timing of the addition of ammonia significantly influenced the removal of silicon and iron, which would have been inconvenient to accomplish in subsequent processes. In Process (3), the precipitation obtained in Process (2) was re-dissolved in a nitric acid solution. The dissolution of phosphorus together with other elements progressed sufficiently, and we confirmed that silicon could be completely separated as silica by using high-concentration nitric acid at this stage. The fact that silicon could be removed during Process (3) was an important finding, since silicon could not have been separated in the Process (4). In Process (4), by passing the phosphorus-containing solution obtained in Process (3) through an ion exchange resin, elements other than phosphorus and silicon could be removed, which confirms that the range of applications for this technology could be expanded.

INTRODUCTION

Phosphorus recovery is typically intended as a remediation for environmental pollution to insure water quality.[1-4] Recovering phosphorus from water systems that contain small amounts has improved the environment,[5-7] but reuse of the recovered phosphorus has not been considered. Recovery of phosphorus from water systems containing high concentrations, however, such as those contaminated with untreated sewage[8] or phosphorus-containing detergents,[9] has led to the use of the recovered phosphorus as a fertilizer. Thus, the recovery of phosphorus from water systems was initially focused on improving the environment.

The recovery of phosphorus from water systems has undoubtedly been effective in improving the environment, but rivers and seas are so large that the concentration of phosphorus is low. Therefore, in terms of recovering a large amount of phosphorus resources in a short period of time, the recovery of phosphorus from many water systems has not received much attention.

The situation changed, however, after it was pointed out that natural phosphorus resources could soon be depleted.[10] From the viewpoint of new phosphorus resource development, phosphorus has been recovered from solid unused resources that have the possibility of producing a large amount of this scarce natural element in a short period of time. Even today, the main focus of phosphorus recovery is use as a fertilizer. However, our laboratory aims to recover phosphorus in a form that could be used as a raw material for manufacturing foods, pharmaceuticals, and advanced materials. Thus far, our laboratory has investigated the recovery of phosphorus from slag released by a chemical factory,[11] dephosphorization slag,[12-14] solid

unused resource collected in a filter bags during the recycling of used fluorescence tubes,[15] composted chicken manure,[16] incineration ash of chicken manure,[17,18] and sewage-sludge molten slag.[19]

As part of a series focused on this study, this paper reports the results of phosphorus recovery from the double-slag refining process slag discharged from a modern steelmaking process. In particular, we discuss the results of studies on improving the efficiency of removing silica and iron, which are present in large amounts in the slag.

MATERIALS AND METHODS

Double-slag refining process produces slag, (DRP slag) that is a by-product of a new resource-saving and environmentally friendly steelmaking process used by a Japanese steel company. Compared with the processes used by conventional plants, this new approach reduces the amount of CO_2 generated by increasing the amount of scrap used in converters.[20]

The method of recovering phosphorus from DRP slag is similar to that from dephosphorization slag[12-14] and sewage-sludge molten slag,[19] and is a technique that combines acid-dissolution, alkali-precipitation, and ion-exchange. As a typical example, in the first acid-elution process (Process (1)), 1.0 g of DRP slag (particles less than 74 μm) was dissolved in 100 mL of 0.5 M HNO_3 at 298 K. This aqueous solution was stirred at 130 rpm for 24 min, which was determined to be optimal processing in the present study. The resultant solution was filtered to obtain 'Solid residue (I)' and 'Solution (a)'. In the alkali precipitation process (Process (2)), aqueous ammonia was added to 'Solution (a)' at 300 rpm to adjust the solution to pH 4. The solution was then let stand for an additional 0.5 h with stirring, followed by filtration to produce 'Precipitation' and 'Solution (b)'. In Process (3), the 'Precipitation' was dissolved in 100 mL of 0.5 M HNO_3 at 298 K with stirring at 300 rpm for 0.5 h. The resultant solution was filtered to obtain 'Solid residue (II)' and 'Solution (c)'. In process (4), 'Solution (c)' 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 (d)' in the present study. Inductively coupled plasma atomic emission spectrometry (ICP-AES, SPS3520UV (SII Nanotechnology Inc.)) was employed to analyze the solutions. X-ray diffraction (XRD, SmartLab/R/INP/DX (Rigaku Co.)) with a Cu Kα radiation monochromator at 45 kV and 150 mA was employed to analyze the solid samples. All chemicals were purchased from FUJIFILM Wako Pure Chemical Co. and used as supplied.

RESULTS AND DISCUSSION

Properties of DRP slag

Figure 1 displays the XRD patterns of DRP slag.

XRD signals due to Fe_2O_3 (JCPDF 01-084-0309) and $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ (JCPDF 00-026-1056) were detected, and these indicate that the main elements in DRP slag were iron, calcium, and phosphorus. ICP results of the slag are listed in Table 1. These were obtained using 0.1g of the slag that was completely dissolved in 100 mL of a 0.5 M HNO_3 solution for 24 h. It should be noted that slags discharged from steel processes, including DPR slag, are completely soluble in various inorganic and organic acids. In this paper, we used nitric acid, which does not remain in the final product. In Table 1, the concentration of each element has been corrected to 1.0 g of this slag dissolved in a 100 mL solution to serve as a reference for the purpose of this paper. Comparing Figure 1 and Table 1 shows a certain amount of silicon in Table 1, that is not listed in Figure 1. Therefore, the DPR slag is considered to contain compounds related to silicon in an amorphous state.
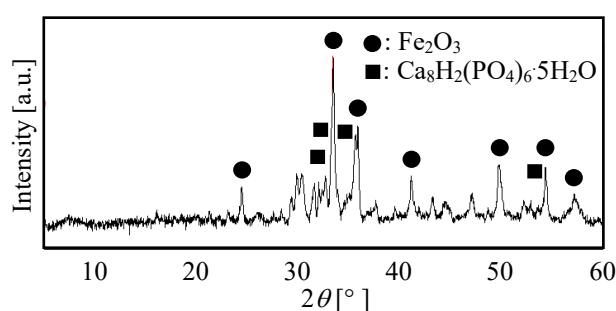

FIGURE 1. XRD of DRP slag

TABLE 1. Composition (mmol/100 mL) of DRP slag

P	Al	Fe	Si	Ca	Mg	Mn
0.558	0.381	2.154	2.286	5.674	0.659	0.405

Optimizing the time of acid dissolution for DRP slag in Process 1

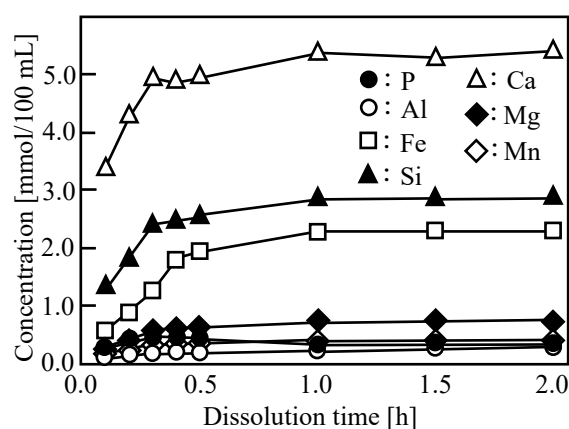In order to confirm the dissolution time of DRP

FIGURE 2. The dissolution behaviors of DRP slag using 0.5 M HNO_3

slag in 0.5 M of HNO_3 in Process (1), the dissolution behaviors of constituent elements in the slag were examined. As shown in Figure 2, the concentration of each element increased up to approximately 24 min and remained almost constant thereafter.

Therefore, in the present study, the dissolution time was fixed at 24 min.

Comparing the elution behavior in Process (1) with the precipitation behavior in Process (2)

Figure 3 shows the concentrations of each of the element in Solutions (a) and (b) obtained in Processes (1) and (2), respectively. The concentrations in Solution (a) in Figure 3 and Table 1 show that the dissolution rates of phosphorus, aluminum, iron, silicon, calcium, magnesium and manganese from DRP slag reached 89, 65, 68, 100, 82, 91, and 90%, respectively. This indicates, however, the non-selective dissolution of each element, and that specific elements were not separated in Process (1). However, comparing the concentrations of each element in Solution (a) with those in Solution (b) shows that most of the calcium, magnesium, and manganese was present in Solution (b) and had hardly migrated to the Precipitation that was used for process (3). In addition, since 59 and 69% of the iron and silicon in Solution (a) remained in Solution (b), the concentrations of these elements in the Precipitate could be lowered.

Unfortunately, 84% of the aluminum in Solution (a) was shifted to the Precipitation, and the concentration of the aluminum in the Precipitation could not be lowered. The focused element, phosphorus, was transferred at a rate of 90% in Solution (a) to the Precipitation. Figure 4 showed XRD of Precipitation obtained after the calcination at 1073 K for 5 h, since amorphous phase was detected form the solid before the calcination. According to the discussion above, XRD peaks due to $Ca_8H_2(PO_4)_6$ had
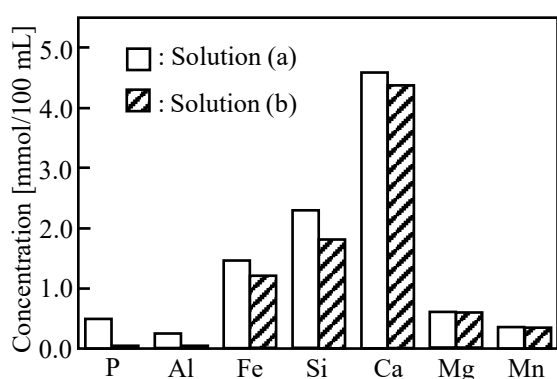
FIGURE 3. The concentrations of each element in Solutions (a) and (b)

disappeared, but those due to $AlPO_4$ (JCPDS 01-072-7638) and Fe_2O_3, the latter of which was converted from $Fe(OH)_3$ (JCPDS 33-0664) during the calcination, were evident. In Figure 4, phosphorus was detected as aluminum phosphate. However, according to the

results in Table 1 and Figure 3, phosphorus may be combined with another element and not detected by XRD. It is generally known that, phosphorus along with aluminum,[21] easily combines with iron.[22] Therefore, iron phosphate with low crystallinity may also be produced in the present step.

Comparing the elution behavior in Process (3) with the ion-exchange behavior in Process (4)

Figure 5 lists the concentration of each element in Solutions (c) and (d) obtained in Processes (3) and (4), respectively. The dissolution rates from the Precipitation of phosphorus, aluminum, iron, silicon, calcium, magnesium and manganese were 89, 95, 100, 31, 2, 100, and 75%, respectively, as estimated using the data from Solution (b) in Figure 3 and from Solution (c) in Figure 5. Therefore, separation of silicon and calcium from the phosphorus-containing solution proceeded favorably in Process (3). Comparing the concentration of each element in Solutions (c) and (d) in Figure 5 shows that all elements except phosphorus and silicon were almost completely removed from the solution through Process (4), in which Solution (c) was passed through 5.0 g of ion-exchange resins.
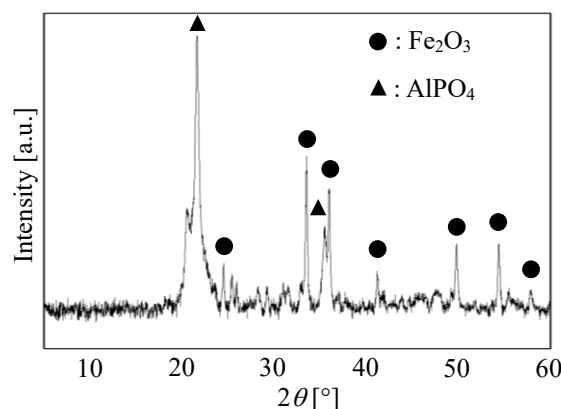
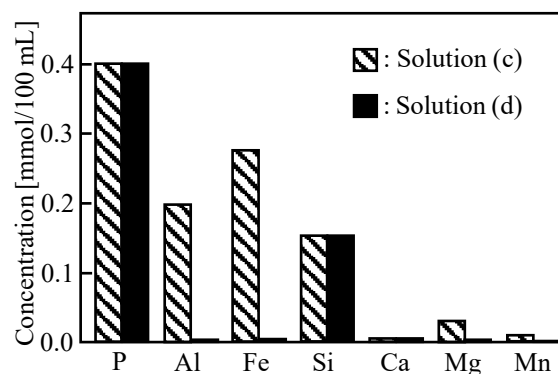FIGURE 4. XRD of Precipitation calcined at 1073 K for 5 h

FIGURE 5. The concentration of each element in Solutions (c) and (d)

Attempts to remove elements other than phosphorus

As these results show, the recovery rates of phosphorus in Processes (1), (2), (3), and (4) were acceptable at 89, 90, 89, and 100%, respectively, resulting in 71% of total recovery of phosphorus during the present recovery method. On the other hand, problems remained in the separation of elements other than phosphorus, particularly with regards to silicon. During the present research, we noticed that the amount of the Precipitation changed greatly depending on the timing of the addition of ammonia after dissolving the DRP slag in the nitric acid solution. This indicated the possibility of selectively separating some elements by controlling the timing. Furthermore, Solution (d) obtained in Process (4) contained a considerable amount of silicon together with phosphorus. Therefore, it became necessary to find conditions under which this silicon could be largely removed during Processes (1) and (4). Therefore, the above two items were additionally examined.

Figure 6 shows the precipitation ratios of various elements in Process (2), in which the timings of adding ammonia after dissolving the DRP slag in the nitric acid solution was adjusted to occur immediately (0 h), 1 h later, 4 h later, or 24 h later, after Process (1). When the timing of adding ammonia was delayed, the amount of precipitation obtained increased to 0.354, 0.309, 0.691, and 0.828 g, respectively. Therefore, it proved advantageous to delay the timing in order to recover greater amounts of precipitation. However, as shown in Figure 6, at 0 h, the precipitation ratio of phosphorus was 96 %, while those of silicon and iron were 20 and 25%, respectively. By contrast, the precipitation ratio of phosphorus was kept higher, 96% at 24 h, while those of silicone and iron were also higher, 100 and 94% at 24 h.
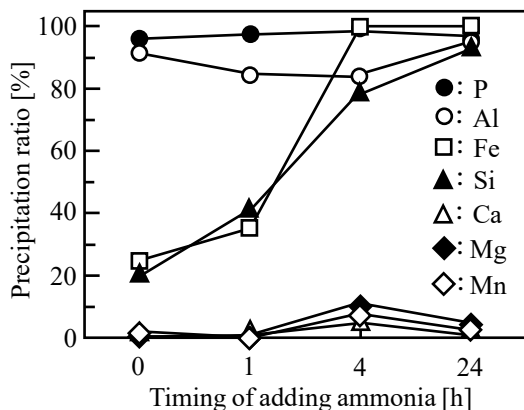
FIGURE 6. Precipitation ratios during Process (2) at various timepoints for the addition of ammonia

As shown in Figure 7, the intensity of XRD peaks due to Fe_2O_3 in samples of the Precipitation obtained after 0, 1, 4, and 24 h had increased at later timepoints. Silicon was not detected in Figure 7, since it was in an amorphous state as SiO_2. These results indicate that a shorter timepoints for the addition of ammonia must require for the separation of silicon and iron from the phosphorus-containing solution.

For the separation of silicon, we focused on the effect that pH exerts on silica in precipitation when zeolites were dissolved in a solution of hydrochloric acid.[23] In the present study, as the pH decreased, i.e. became more acidic, the number of dissolved silicon species in the hydrochloric acid solution was decreased, which led to the formation of silica crystals. As shown above, in our phosphorus recovery processes, the process in which silicon was most separated from the solution containing phosphorus was Process (3), in which the Precipitation obtained in process (2) was dissolved in a 0.5 M nitric acid solution for 0.5 h. Therefore, under the experimental conditions of Process (3) described above, Precipitation obtained in Process (2) was added to 0.5 M and 13.5 M nitric acid solutions and stirred for 18 h. After filtration of the stirred solution, we obtained the filtrate and the precipitation, which corresponded to Solution (c) and Solid residue (II) under the present conditions.
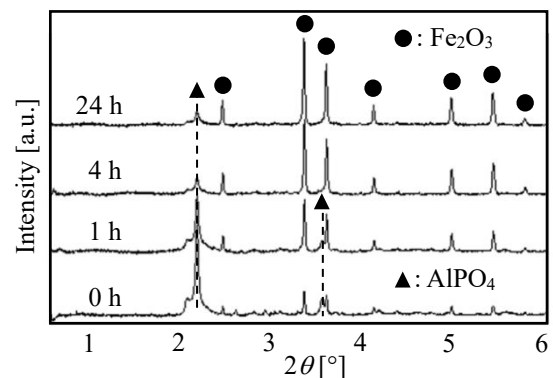
FIGURE 7. XRD of the Precipitations obtained at the timepoints of 0, 1, 4, and 24 h

Figure 8 compares the concentrations of elements present in Solution (c) using 0.5 M and 13.5 M nitric acid. Except for silicon, the concentration of each
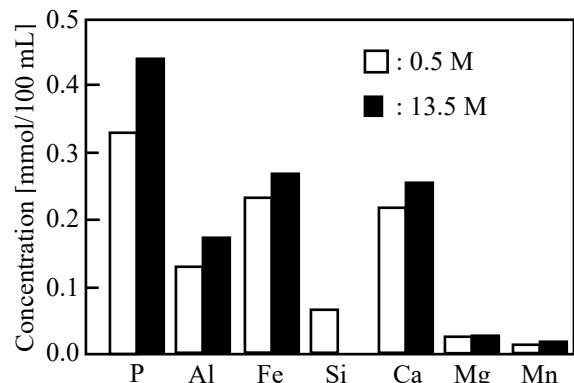
FIGURE 8. The concentration of each element in Solution (c) obtained with 0.5 and 13.5 M HNO_3

element tended to be higher in 13.5M nitric acid than that in 0.5 M, which is a normally expected phenomenon. Exceptionally, when the nitric acid concentration was 13.5 M, silicon became undetectable from the solution (C), indicating that silicon was precipitated as a solid.

Therefore, the precipitation containing Solid residue (II) was analyzed by XRD. As shown in Figure 9, the XRD of Solid residue (II) was matched to that characteristic of amorphous silica, indicating that the silicon was completely removed from Solution (C). The results of this study show that the problem of insufficient separation of silicon under our usual separation conditions could be solved.
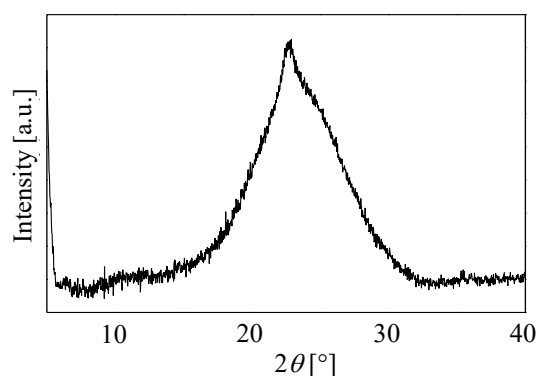

FIGURE 9. XRD of Solid residue (II) obtained with 13.5 M HNO_3

CONCLUSIONS

In the present study, we applied concentration technology to the recovery of phosphorus from solid unused resources that are treated as slag by-product in a modern double-slag refining process. This process consists of four steps: Process (1) is the first acid elution; Process (2) involves alkali precipitation; Process (3) is the second acid elution; and, Process (4) is accomplished via ion-exchange. The migration rates of phosphorus in those four processes were 89, 90, 89, and 100%, which are suitable levels for the concentration and recovery of phosphorus. Initially, the final solution obtained from Process (4) contained silicon along with phosphorus. It became clear that this silicon had to be removed in Process (2) by adjusting the timing of the addition of ammonia to be shortened as much as possible. Further, in Process (3), nitric acid with a high concentration should be used. In addition, since this slag is obtained from the steelmaking process, a large amount of iron may remain in the later process. As with silicon, however, if the addition of ammonia is timed correctly (shortened as much as possible) in Process (2), a considerable amount of iron could be separated.

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