Effect of Slag Composition on the Dissolution of Phosphorus from Steelmaking Slag by Selective Leaching

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Steelmaking slag is considered a potential source of P because of its huge production. In steelmaking slag, P is mainly distributed in the C_2S – C_3P solid solution which is more water-soluble than other phases. In order to recover P and recycle steelmaking slag, we have proposed the selective leaching of the P-concentrated solid solution. To clarify the applicability of this process to steelmaking slags with various compositions, the effects of P_2O_5 content, Fe_2O_3 content, and slag basicity on the dissolution behavior of the slag modified with the addition of Na_2O were investigated in this study. It was determined that the dissolution ratio of P reached approximately 76% regardless of the P_2O_5 content in slag, while the dissolution of Fe and Mg was poor. In the case of high P_2O_5 content, a leachate with higher P concentration and lower Ca and Si concentrations was obtained, exhibiting excellent selective leaching of P. Increasing the Fe_2O_3 content in slag not only promoted the dissolution of P but also decreased the dissolution ratios of other elements. With the increase in slag basicity, the dissolution ratios of Ca, Si, and P all increased. Most of the solid solution was dissolved from each slag without a large dissolution of other phases at pH 6, indicating that selective leaching of the solid solution was achieved over a wide range of slag compositions. After leaching, a residue with low P_2O_5 content and high Fe_2O_3 content was obtained.

KEY WORDS: steelmaking slag; slag composition; dephosphorization; selective leaching; P recovery.

1. Introduction

The recycling of industrial by-product has attracted widespread attention because of resource exhaustion and environmental protection. Steelmaking slag, a major by-product of the steelmaking process, is produced in an enormous quantity annually. Although steelmaking slag contains many valuable components, such as Fe_2O_3 , MnO , and P_2O_5 , it is mainly used as a roadbed and civil engineering material.¹⁾ The value of these elements in slag has not been exploited well. It would be desirable to recycle the steelmaking slag inside the ironmaking and steelmaking process, and to recover some valuable elements. However, the presence of P_2O_5 restricts the recycling of steelmaking slag, because it will result in high phosphorus (P) content in hot metal and increase dephosphorization burden. Therefore, a method for efficient separation and removal of P_2O_5 from slag would facilitate its utilization. Although P is a detrimental impurity in steel, it is an essential element in fertilizer, and plays a significant role in agriculture. Because the supply of phosphate ores is currently becoming very tight, and Japan has no domestic phosphate resources, the P separated from steelmaking slag is considered a potential sustainable source of phosphate.²⁾

Steelmaking slag, especially dephosphorization slag, is generally within the CaO – SiO_2 – Fe_2O_3 – P_2O_5 system, and after solidification, it mainly consists of calcium ferrite, wustite, and dicalcium silicate. The majority of the P_2O_5 in slag is distributed in the dicalcium silicate in the form of $2CaO \cdot SiO_2 \cdot 3CaO \cdot P_2O_5$ (C_2S – C_3P) solid solution.³⁾ On the basis of the difference in properties between the P_2O_5 or P-concentrated phase and other components, a great deal of effort has been made to recover P from slag by physical or chemical separation. A summary of the major technologies is presented in **Table 1**. Selective leaching of P is based on the fact that the P-concentrated solid solution dissolves more readily into the aqueous solution at a constant pH than do the other phases;⁹⁾ after leaching, the leachate containing soluble P can be used to produce phosphate fertilizer via precipitation. Because it is energy-saving and similar to the production of phosphate fertilizer via hydrometallurgical treatment,¹¹⁾ selective leaching shows an advantage in the recovery of P from steelmaking slag compared with other methods. However, in past work, the dissolution ratio of P from steelmaking slag was not high.¹²⁾ To promote the dissolution of P and achieve selective leaching of the solid solution, a series of improvements and innovations were adopted in our previous studies.^{13–15)} It has been shown that a better selective leaching of P could be realized when a slag with high P_2O_5 content was modified by the addition of Na_2O , cooled slowly, and leached in a citric acid

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Table 1. Proposed technology to separate and recover P from steelmaking slag.

Method	Researchers	Process Summary
Floatation separation	Ono <i>et al.</i> ⁴⁾	Slag was separated into two layers by floatation of dicalcium silicate with low density.
Reduction of dephosphorization slag	Li and Suito; ⁵⁾ Ishikawa <i>et al.</i> ⁶⁾	Dephosphorization slag was reduced by hot metal in a regenerator; the reduced P in hot metal was further dephosphorized to produce fertilizer.
Magnetic separation	Yokoyama and Nagasaka <i>et al.</i> ⁷⁾	C ₂ S–C ₃ P solid solution was separated from Fe ₂ O ₃ -containing matrix phase with the aid of a magnetic field.
Capillary action	Miki <i>et al.</i> ⁸⁾	The FeO-rich liquid phase was drawn into sintered CaO by capillary action, separating it from C ₂ S–C ₃ P solid solution.
Selective leaching of P	Teratoko and Kitamura <i>et al.</i> ⁹⁾	In steelmaking slag, C ₂ S–C ₃ P solid solution was selectively dissolved in acid solution at a constant pH.
Super gravity	Li and Guo <i>et al.</i> ¹⁰⁾	Super gravity was applied to separate C ₂ S–C ₃ P solid solution from slag based on density difference.

(H₃C₆H₅O₇) solution at pH 6.

To clarify the applicability of selective leaching of P to steelmaking slags with various compositions, it is necessary to study the influence of slag composition on the dissolution behavior of P under the above-mentioned conditions. It is well known that the Fe₂O₃ content and slag basicity ($R = (\text{mass\% CaO})/(\text{mass\% SiO}_2)$) have a significant influence on the dephosphorization of hot metal; the P₂O₅ content in dephosphorization slag is gradually increasing with the deterioration in the quality of iron ores and the improvement in dephosphorization.¹⁶⁾ Consequently, in this study, the effects of P₂O₅ content, Fe₂O₃ content, and slag basicity on the dissolution behavior of the slag modified with the addition of Na₂O were investigated.

2. Experimental Method

The experimental method is almost the same as that described in the previous papers.^{13–15)} **Table 2** lists the compositions of slags used in this study. Because the slag containing Fe₂O₃ exhibited a higher dissolution ratio of P,⁹⁾ Fe₂O₃ was used as the iron oxide in these slags. For Slags A–D, the P₂O₅ content varied from 3.0 to 10.0 mass%. The effect of Fe₂O₃ content was investigated in the case of slags with 3.0 mass% of P₂O₅. When the effect of slag basicity was studied, the existence of MnO and Al₂O₃ was taken into consideration, and the P₂O₅ content was set as 7.0 mass%. Synthetic slag was prepared by mixing reagent-grade CaO (obtained by the calcination of CaCO₃ at 1 273 K), SiO₂, Fe₂O₃, Ca₃(PO₄), MgO, MnO, Al₂O₃, and Na₂SiO₃, and then heating in an electric resistance furnace to 1 823 K under air atmosphere. After holding at this temperature for 1 h, the molten slag in a Pt crucible was first cooled to 1 623 K and kept at this temperature for 20 min to precipitate solid solution. Finally, the slag was cooled to 1 323 K at a speed of 5 K/min until it was taken out of the furnace.

Following slag synthesis, leaching experiments were carried out in a Teflon container, which was placed in an isothermal water bath at 298 K. The schematic of leaching apparatus is shown in **Fig. 1**. As mentioned in a previous study,¹⁵⁾ 1 g of the ground slag (with particles smaller than 53 μm) was added to 400 ml of distilled water and stirred with an agitation speed of 200 rpm; to maintain a constant pH during leaching, the leaching agent (citric acid,

Table 2. Compositions of slags with different P₂O₅, Fe₂O₃ contents, and basicities (R) (mass%).

Sample	CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	MgO	Na ₂ O	MnO	Al ₂ O ₃
Slag A	36.5	22.7	30.6	3.0	3.2	4.0	–	–
Slag B	35.5	22.1	29.8	5.5	3.1	4.0	–	–
Slag C	34.5	21.5	29.0	8.0	3.0	4.0	–	–
Slag D	33.7	21.0	28.3	10.0	2.9	4.0	–	–
Slag E	40.3	25.1	24.0	3.0	3.5	4.0	–	–
Slag F	33.3	20.8	36.0	3.0	2.9	4.0	–	–
Slag G (R=1.4)	31.3	22.2	28.0	7.0	4.0	3.5	3.0	1.0
Slag H (R=1.7)	33.7	19.8	28.0	7.0	4.0	3.5	3.0	1.0
Slag I (R=2.0)	35.7	17.8	28.0	7.0	4.0	3.5	3.0	1.0

Fig. 1. Schematic of leaching apparatus.

0.1 mol/L) was automatically added to the aqueous solution using a PC control system. Because the optimum pH for selective leaching of P was determined as 6 in a previous study,¹⁷⁾ each slag was leached at pH 6, respectively, in this study. The aqueous solution was sampled at adequate intervals during leaching and filtered by a syringe filter (< 0.45 μm). The slurry was filtered to collect residue after 120 min. The concentrations of each element in the aqueous solution

were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The mineralogical compositions of each slag and their residues after leaching were analyzed by electron probe microanalysis (EPMA) and X-ray diffraction (XRD) analysis.

3. Results

3.1. Mineralogical Composition

Figure 2 shows micrographs of the typical slags observed by EPMA. The chemical compositions of each phase in slags with different P_2O_5 and Fe_2O_3 contents, and basicity are listed in **Tables 3** and **4**. In each slag, three domains corresponding to three phases were clearly identified. The white-color phase with high Fe_2O_3 and MgO contents was magnesioferrite; the grey-color phase was considered the matrix phase because it mainly consisted of the CaO–SiO₂– Fe_2O_3 system; the black-color phase rich in P_2O_5 was the solid solution. With the increase in the P_2O_5 content in slag, the P_2O_5 content in the solid solution and in the matrix phase both increased. Increasing the Fe_2O_3 content in slag also resulted in a higher P_2O_5 content in the solid solution. These results were in good agreement with the results reported by Shimauchi *et al.*¹⁸⁾ In regard to Na₂O, it was mainly distributed in the solid solution and matrix phase; a higher P_2O_5 content in the solid solution matched with a higher Na₂O content in it. For the slags with different basicities, the P_2O_5 content in the solid solution and in the matrix phase both decreased with the increase in slag basicity; the Na₂O content in the solid solution was almost the same. The composition of magnesioferrite had no dependence on the P_2O_5 and Fe_2O_3 contents, or slag basicity.

The distribution ratios of P_2O_5 and Na₂O between solid solution and matrix phase were calculated as follows:

$$L_{P_2O_5} = \frac{(\%P_2O_5)_{SS}}{(\%P_2O_5)_{Matrix}} \dots\dots\dots (1)$$

Table 3. Compositions of each phase in slags with various P_2O_5 and Fe_2O_3 contents (mass%).

		CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	MgO	Na ₂ O
Magnesio-ferrite	Slag A (3.0%P ₂ O ₅)	2.3	0.0	86.1	0.0	10.4	1.2
	Slag B (5.5%P ₂ O ₅)	2.0	0.0	86.0	0.0	11.3	0.8
	Slag C (8.0%P ₂ O ₅)	1.8	0.0	86.8	0.0	11.1	0.3
	Slag D (10.0%P ₂ O ₅)	1.2	0.0	87.4	0.0	11.0	0.3
Matrix phase	Slag A (3.0%P ₂ O ₅)	27.2	29.9	33.5	0.3	0.9	8.1
	Slag B (5.5%P ₂ O ₅)	32.9	34.7	24.9	0.6	1.4	5.6
	Slag C (8.0%P ₂ O ₅)	34.4	33.1	25.9	1.1	1.5	3.9
	Slag D (10.0%P ₂ O ₅)	36.0	34.9	22.0	2.1	1.7	3.4
Solid solution	Slag A (3.0%P ₂ O ₅)	56.5	27.6	1.9	9.4	0.4	4.2
	Slag B (5.5%P ₂ O ₅)	53.4	21.4	1.3	17.5	0.5	6.0
	Slag C (8.0%P ₂ O ₅)	51.4	15.6	0.9	25.4	0.3	6.4
	Slag D (10.0%P ₂ O ₅)	50.7	10.6	0.6	31.0	0.3	6.8
Magnesio-ferrite	Slag E (24.0%Fe ₂ O ₃)	2.4	0.2	83.6	0.0	12.8	1.0
	Slag A (30.6%Fe ₂ O ₃)	2.3	0.0	86.1	0.0	10.4	1.2
	Slag F (36.0%Fe ₂ O ₃)	2.3	0.1	86.4	0.0	9.9	1.3
Matrix phase	Slag E (24.0%Fe ₂ O ₃)	26.8	30.2	33.0	0.3	1.2	8.5
	Slag A (30.6%Fe ₂ O ₃)	27.2	29.9	33.5	0.3	0.9	8.1
	Slag F (36.0%Fe ₂ O ₃)	25.6	30.4	33.6	0.3	0.8	9.3
Solid solution	Slag E (24.0%Fe ₂ O ₃)	57.5	29.1	1.8	7.3	0.7	3.7
	Slag A (30.6%Fe ₂ O ₃)	56.5	27.6	1.9	9.4	0.4	4.2
	Slag F (36.0%Fe ₂ O ₃)	55.2	25.9	1.6	11.8	0.3	5.1

Fig. 2. Micrographs of the typical slags observed by EPMA (R denotes slag basicity).

Table 4. Compositions of each phase in slags with different basicities (R) (mass%).

		CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	MgO	MnO	Al ₂ O ₃	Na ₂ O
Magnesio-ferrite	Slag G (R=1.4)	1.1	0.0	76.6	0.0	12.0	9.5	0.7	0.1
	Slag H (R=1.7)	1.5	0.0	75.7	0.0	12.3	9.2	1.0	0.2
	Slag I (R=2.0)	2.1	0.1	77.0	0.0	10.3	8.3	1.4	0.8
Matrix phase	Slag G (R=1.4)	34.1	38.6	15.7	2.3	2.4	1.4	1.9	3.8
	Slag H (R=1.7)	32.8	37.4	19.2	0.8	1.7	1.3	2.8	4.1
	Slag I (R=2.0)	27.6	33.3	25.1	0.4	0.9	0.9	4.7	7.1
Solid solution	Slag G (R=1.4)	47.9	13.6	0.8	30.5	0.5	0.4	0.0	6.5
	Slag H (R=1.7)	50.3	17.6	0.7	24.3	0.4	0.3	0.0	6.4
	Slag I (R=2.0)	50.8	22.2	0.9	18.9	0.2	0.2	0.0	6.7

$$L_{\text{Na}_2\text{O}} = \frac{(\%\text{Na}_2\text{O})_{\text{SS}}}{(\%\text{Na}_2\text{O})_{\text{Matrix}}} \dots\dots\dots (2)$$

where (%P₂O₅) and (%Na₂O) represent the P₂O₅ and Na₂O contents of each phase in mass%; and subscripts SS and Matrix denote the solid solution and matrix phase, respectively. **Figure 3** shows the influence of slag composition on the distribution ratios of P₂O₅ and Na₂O between solid solution and matrix phase. Comparing with the distribution ratio of P₂O₅ in the quenched slag,¹⁸⁾ the values of the present slags, which were cooled slowly, were far higher, indicating that the enrichment of P₂O₅ in the solid solution was promoted. Increasing the P₂O₅ content in slag led to a decrease in the distribution ratio of P₂O₅, while increasing the Fe₂O₃ content and slag basicity had an opposite effect. The distribution ratio of Na₂O increased with the P₂O₅ and Fe₂O₃ contents in slag; in the case of high P₂O₅ content, its value was more than 1.5, indicating that Na₂O preferred to combine with P₂O₅. With the increase in slag basicity, the distribution ratio of Na₂O decreased.

3.2. Dissolution Behavior of Various Slags

The changes in the concentrations of Ca, P, and Fe under various P₂O₅ contents in slag are shown in **Fig. 4**. The concentrations of each element in the aqueous solution increased with leaching time. The dissolution rate of each element was high in the initial stage because of the high concentration gradient between reaction interface and bulk solution, but their concentrations increased slowly after 60 min. Ca concentration was the highest among all the elements, and nearly two orders of magnitudes higher than that of Fe. P concentration was in a direct proportion to the P₂O₅ content in slag; in the case of slag containing 10 mass% of P₂O₅, it reached approximately 90 mg/L. In contrast, the concentrations of Ca and Fe decreased with the increase in the P₂O₅ content in slag. When the P₂O₅ content changed from 3 to 10 mass%, Ca concentration decreased

Fig. 3. Distribution ratios of P₂O₅ and Na₂O between solid solution and matrix phase (A) effect of P₂O₅ content; (B) effect of Fe₂O₃ content; (C) effect of slag basicity.

from about 460 to 280 mg/L, and Fe concentration was less than 4 mg/L.

On the basis of the concentrations of each element in the leachate after 120 min, the dissolution ratios of each element from slag were calculated by the following equation:

$$R_M = \frac{C_M \cdot V}{m_M} \dots\dots\dots (3)$$

where R_M is the dissolution ratio of element M; V is the final volume of the leachate (considering the volumes of the sampled solution and the added acid solution); C_M is the

Fig. 4. Changes in the concentrations of Ca, P, and Fe under various P_2O_5 contents.

concentration of element M in the leachate (mg/L); m_M is the original mass of element M in the slag (mg). **Figure 5** shows the calculated dissolution ratios of each element from slags with various P_2O_5 contents. The dissolution ratio of P was the highest in each case, reaching approximately 76% regardless of the P_2O_5 content in the slag. The dissolution ratios of Fe and Mg were far lower than those of other elements, especially Fe (less than 2%). This result indicates

Fig. 5. Dissolution ratios of each element from slags with various P_2O_5 contents.

that the matrix phase and magnesioferrite in which Fe and Mg were mainly distributed were resistant to dissolution. With the increase in the P_2O_5 content, the amount of the dissolved slag reduced because of a significant decrease in the dissolution ratios of Ca and Si. In the case of high P_2O_5 content, most of the P was dissolved, and the dissolution ratios of Ca and Si were less than 50% and 30%, respectively, exhibiting a better selective leaching of P.

The dissolution ratios of each element from slags with various Fe_2O_3 contents calculated by the above method are shown in **Fig. 6**. The major ions dissolved from the slags were those of Ca, Si, and P; the dissolution of Fe was minimal. Because of the lower P_2O_5 content in each slag, the dissolution of slag was significant, resulting in higher dissolution ratios of Ca and Si. With the increase in the Fe_2O_3 content in slag, the dissolution ratio of P increased, while those of other elements decreased. In particular, the dissolution ratio of Mg decreased several times when the Fe_2O_3 content increased from 24.0 to 30.6 mass%. In the case of high Fe_2O_3 content, the dissolution ratio of P reached 80%, and about 70% of the Ca and 40% of the Si was also dissolved. Overall, increasing the Fe_2O_3 content in slag was beneficial for selective leaching of P from slag.

Figure 7 shows the changes in the concentrations of Ca, P, and Fe under different slag basicities. The concentration of Ca was far higher than those of other elements. With the increase in slag basicity, the concentrations of Ca and P both increased. When the basicity changed from 1.4 to 2.0, Ca concentration almost doubled, and P concentration increased from 56.7 to 70.9 mg/L. Fe was difficult to dissolve and its concentration was only several mg/L in each case.

As shown in **Fig. 8**, Ca, Si, P, and Na were more readily dissolved from slag, exhibiting higher dissolution ratios. The dissolution ratio of Fe was the lowest, less than 2% in each case. Compared with other slags, the presence of MnO and Al_2O_3 in slag had little influence on the dissolution behavior of P and Fe. The dissolution of Mn and Al was not significant, similar with that of Mg and Fe. With the increase in slag basicity, the dissolution ratios of Ca, Si, and P increased significantly. In the case of high basicity, although almost all of the P was dissolved from slag, the dissolution ratio of Ca increased to 82% and half of the Si

Fig. 6. Dissolution ratios of each element from slags with various Fe_2O_3 contents.

Fig. 8. Dissolution ratios of each element from slags with different basicities (R).

Fig. 7. Changes in the concentrations of Ca, P, and Fe under different slag basicities (R).

was also dissolved. When slag basicity decreased to 1.4, the dissolution ratio of P reached approximately 72% and only a small fraction of Si was dissolved. In addition, the consumption of citric acid during leaching was smaller compared with that under higher basicity. To achieve a better selective leaching of P, slag basicity should be not too high to avoid

Table 5. Compositions of the residue after leaching at pH 6 (mass%).

Residue	CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	MgO	Na ₂ O
Slag A (3.0%P ₂ O ₅)	16.06	20.66	52.32	0.79	5.33	4.83
Slag B (5.5%P ₂ O ₅)	21.37	19.61	49.21	1.28	5.06	3.47
Slag C (8.0%P ₂ O ₅)	26.17	19.20	44.85	2.09	4.59	3.10
Slag D (10.0%P ₂ O ₅)	26.12	20.38	44.01	1.95	4.59	2.95
Slag E (24.0%Fe ₂ O ₃)	16.72	27.57	44.58	1.35	5.27	4.47
Slag F (36.0%Fe ₂ O ₃)	14.78	18.32	57.07	0.66	4.63	4.48
Slag G (R=1.4)	24.88	22.34	38.72	1.99	5.52	2.72
Slag H (R=1.7)	19.80	18.77	46.69	1.93	6.29	2.52
Slag I (R=2.0)	13.32	17.10	53.82	1.58	7.05	2.08

a large dissolution of Ca and Si.

3.3. Residue Composition

The average compositions of residues obtained after leaching at pH 6 are listed in Table 5. Compared with the original slag (listed in Table 2), the P_2O_5 content in the residue decreased significantly corresponding to an increase in the Fe_2O_3 content. Because the dissolution ratio of P from slags with various P_2O_5 contents was almost the same, a higher P_2O_5 content in the original slag resulted in a higher P_2O_5 content in its residue. In the case of slag with high P_2O_5 content, the P_2O_5 content in the residue reached approximately 2.0 mass%. With the increase in the P_2O_5 content in slag, the CaO content in the residue increased and the Fe_2O_3 content decreased. For the slag with high Fe_2O_3 content, a residue with lower P_2O_5 content and higher Fe_2O_3 content was obtained as the result of the excellent selective leaching of P. With the increase in slag basicity, the P_2O_5 and CaO contents in the residue decreased and Fe_2O_3 content increased.

Figure 9 shows the XRD patterns of slags with various P_2O_5 contents and their residues. Two crystalline phases were observed in each slag. The crystal form of the solid solution was changed with the variation of P_2O_5 content in slag. Through selective leaching of P, the peaks asso-

Fig. 9. XRD patterns for slags with various P_2O_5 contents and their residues.

ciated with solid solution almost disappeared regardless of the P_2O_5 content in slag, and those associated with magnesioferrite intensified. These results indicated that the P-concentrated solid solution was easily dissolved in the aqueous solution and thereby separated from the slag, while other phases remained in the residue. Therefore, the P-removed slag has a potential to be recycled within the ironmaking and steelmaking process.

4. Discussion

Because of the formation of soluble complexes between $C_6H_5O_7^{3-}$ and Ca^{2+} ions in the citric acid solution,¹³⁾ $Ca_{10}(PO_4)_6(OH)_2$ is difficult to precipitate in this case.^{15,17)} Therefore, the precipitation of calcium phosphate was ignored in this study. The measured content in the aqueous solution is considered to be the dissolved P content without precipitates. To evaluate the dissolution behavior of each phase, the mass fractions of each phase in slag were compared with those of the dissolved mass and residue. First, the mass fractions of each phase in different slags were calculated using the above EPMA results (listed in Tables 3 and 4). The mass balance of each oxide and phase fraction can be expressed as:

Fig. 10. Fractions of the dissolved mass and residue, compared with phase fractions of slags with various P_2O_5 contents.

$$(\%MO)_{slag} = \alpha(\%MO)_{SS} + \beta(\%MO)_{Matrix} + \gamma(\%MO)_{MF} \quad (4)$$

$$\alpha + \beta + \gamma = 1 \quad (5)$$

where α , β , and γ are the mass fractions of solid solution, matrix phase, and magnesioferrite respectively, and the subscript MF denotes the magnesioferrite. By the combination of mass balance of CaO , SiO_2 , Fe_2O_3 , and P_2O_5 , the mass fraction of each phase can be evaluated. The calculated phase fraction of slags with various P_2O_5 contents is shown in Fig. 10. With the increase in the P_2O_5 content in slag, the mass fraction of solid solution decreased and that of matrix phase increased correspondingly; there was a little change in the mass fraction of magnesioferrite. On the basis of the dissolution ratios of each element, the fraction of the dissolved mass ($R_{dissolved}$) is calculated as:

$$R_{dissolved} = \sum (R_M \cdot (\%MO)_{slag}) / 100 \quad (6)$$

The mass fraction of the residue is obtained by weighting the mass of the dried slag after leaching. As shown in Fig. 10, the fraction of the dissolved mass also decreased with the increase in the P_2O_5 content, and its value was a little higher than that of solid solution. The lower dissolution ratio of Fe illustrates that the dissolution of the Fe-concentrated matrix phase and magnesioferrite was not large. Consequently, it was determined that, independent of the P_2O_5 content, most of the solid solution was dissolved from the slag.

Assuming that only solid solution was dissolved, the dissolution ratios of each element from the slag were calculated by Eq. (7).

$$R_M^{Cal.} = \frac{\alpha \cdot (\%MO)_{SS}}{(\%MO)_{slag}} \quad (7)$$

where $R_M^{Cal.}$ is the calculated dissolution ratio of M, which is actually equal to the mass fraction of MO distributed in the solid solution. As most of the P was concentrated in the solid solution, the dissolution ratio of solid solution (R_{SS}) can be evaluated using Eq. (8):

$$R_{SS} = \frac{R_P}{R_P^{Cal.}} \quad (8)$$

Fig. 11. Calculated dissolution ratios of each element and experimental results under various P_2O_5 contents.

Figure 11 shows the calculated dissolution ratios and experimental results. As the experimental values of P were close to the calculated values, this result indicated that most of the solid solution was dissolved irrespective to the P_2O_5 content. In general, the increase in the P_2O_5 content in the solid solution deteriorates its solubility in the aqueous solution.⁹⁾ However, the addition of Na_2O renders the solid solution more readily soluble.¹⁵⁾ The difference between the calculation and experimental results narrowed with the increase in the P_2O_5 content. As listed in Table 6, the dissolution ratio of solid solution increased from 81.8% to 86.9% when the P_2O_5 content changed from 3 to 10 mass%, resulting from the increase of the Na_2O content in the solid solution. With the increase in the P_2O_5 content in slag, the calculated dissolution ratios of Ca and Si decreased because more Ca and Si were distributed in the matrix phase. In each case, the experimental values and the calculated values for Ca and Si were much closer than that for P. As Ca and Si is distributed between the solid solution and matrix phase, a part of the dissolved Ca and Si might have been supplied from the matrix phase. Using these results and the dissolution ratio of solid solution, the dissolution ratio of matrix phase can be estimated as follows:

$$R_{Matrix} = \frac{(R_M - R_{SS} \cdot R_M^{Cal.})}{1 - R_M^{Cal.}} \quad \text{..... (9)}$$

Its value is defined as the average of the calculated results for Ca and Si. Table 6 shows that the dissolution ratio of matrix phase was not so large and decreased with the increase in the P_2O_5 content in slag. The slag with high P_2O_5 content performs a better selective leaching of solid solution.

On the basis of the concentrations of each element in the leachate, the composition of the dissolved part was evaluated as follows:

$$(\%MO)_{Cal.} = \frac{C_M \cdot V \cdot M_{MO} / M_M}{R_{dissolved} \cdot m_{slag}} \times 100\% \quad \text{..... (10)}$$

where $(\%MO)_{cal.}$ denotes the calculated MO content in the dissolved part, m_{slag} is the mass of slag during leaching (mg), and M is the molar mass. In Fig. 12, the compositions of the dissolved parts are compared with those of solid solution in slags with various P_2O_5 contents. The dissolved

Table 6. Dissolution ratios of solid solution and matrix phase from each slag.

Sample	Dissolution ratio of solid solution	Dissolution ratio of matrix phase
Slag A (3.0% P_2O_5)	0.818	0.273
Slag B (5.5% P_2O_5)	0.823	0.204
Slag C (8.0% P_2O_5)	0.846	0.128
Slag D (10.0% P_2O_5)	0.869	0.106
Slag E (24.0% Fe_2O_3)	0.780	0.431
Slag F (36.0% Fe_2O_3)	0.847	0.258
Slag G (R=1.4)	0.869	0.130
Slag H (R=1.7)	0.871	0.287
Slag I (R=2.0)	0.964	0.267

Fig. 12. Compositions of solid solution and the dissolved part.

part mainly consisted of CaO , SiO_2 , and P_2O_5 , which was consistent with the solid solution. In the case of slag with low P_2O_5 content, the CaO and SiO_2 contents in the dissolved part was high while the P_2O_5 content was lower, less than 8 mass%. The difference in composition between the solid solution and the dissolved part is attributed to the dissolution of matrix phase. With the increase in the P_2O_5 content in slag, the CaO and SiO_2 contents in the dissolved part decreased and the P_2O_5 content increased. For the slag with 10 mass% of P_2O_5 , the P_2O_5 content in the dissolved part reached 26 mass%. The composition of the dissolved part was similar with that of the solid solution indicating that the dissolution of matrix phase was slight, in agreement with the above calculations. Owing to the high P_2O_5 content, the leachate obtained from the slag with high P_2O_5 content is more suitable to be treated in the subsequent process of P recovery.

The phase fractions of slags with various Fe_2O_3 contents were calculated, and compared with the fractions of the dissolved mass and residue in Fig. 13. With the increase in the Fe_2O_3 content in slag, the mass fraction of solid solution decreased while that of magnesioferrite increased. Because the composition of slag with high Fe_2O_3 content was closer to the liquidus of the $2CaO-SiO_2$ saturated region in the $CaO-SiO_2-Fe_2O_3$ phase diagram and the mass fraction of magnesioferrite was higher, the amount of C_2S-C_3P solid

Fig. 13. Fractions of the dissolved mass and residue compared with phase fraction of slags with various Fe_2O_3 contents.

Fig. 15. Fractions of the dissolved mass and residue compared with phase fraction of slags with different basicities.

Fig. 14. Calculated dissolution ratios of each element and experimental results under various Fe_2O_3 contents.

Fig. 16. Calculated dissolution ratios of each element and experimental results under different basicities.

solution in this slag was less than that in the slag with low Fe_2O_3 content. Although the fraction of the dissolved mass was decreased by increasing the Fe_2O_3 content in slag, it was higher than that of solid solution in each case. These results indicate that the majority of the solid solution was dissolved from slag.

Figure 14 shows the experimental results and the calculated dissolution ratios of each element when the solid solution alone was dissolved. With the increase in the Fe_2O_3 content in slag, the dissolution ratio of P gradually approached the calculated value, indicating that the dissolution of solid solution was promoted. As listed in Table 6, the dissolution ratio of solid solution reached approximately 85% in the case of high Fe_2O_3 content. This is because a higher Na_2O content in the solid solution caused higher water solubility. The calculated dissolution ratios of Ca and Si decreased with the increase in the Fe_2O_3 content in slag, resulting from a decrease in the mass fraction of solid solution. These values were close to the experimental values. As mentioned above, the dissolution ratio of matrix phase was evaluated using these results. Table 6 shows that a part of the matrix phase was dissolved from the slag with low Fe_2O_3 content. This is the primary reason for a higher dissolution ratio of Mg from this slag, shown in Fig. 6. Increasing the Fe_2O_3 content in slag significantly suppressed the dissolution of matrix phase. In this case, the dissolution ratio of

matrix phase was lower, which was beneficial for selective leaching of P.

Figure 15 shows the fractions of the dissolved mass and residue, compared with phase fraction of slags with different basicities. Increasing slag basicity resulted in a higher mass fraction of solid solution. In the case of low basicity, approximately 25% of slag was dissolved; this value was similar to the mass fraction of solid solution. The dissolution of slag was significantly promoted by increasing slag basicity. However, the fraction of the dissolved mass did not greatly exceed that of solid solution, indicating that the solid solution was selectively dissolved.

Figure 16 shows the calculated dissolution ratios of Ca, Si, and P when the solid solution alone was dissolved under different basicities. These values all increased with slag basicity because of the enlargement of the solid solution. The dissolution ratio of P was close to the calculated value in each case. Calculation demonstrated that more than 87% of the solid solution was dissolved from slag. The slag with high basicity gave the highest dissolution ratio of solid solution. The dissolution ratios of Ca and Si were a little higher than the calculated values, showing that a part of matrix phase was also dissolved. As listed in Table 6, the dissolution ratio of matrix phase from the slag with low basicity was only 13.0%. When slag basicity increased, the dissolution ratio of matrix phase increased, but was not very

large. In summary, selective leaching of the P-concentrated solid solution from steelmaking slag was achieved at pH 6 in a wide range of slag compositions.

5. Conclusions

To clarify the applicability of this process to the steel-making slags with various compositions, the effects of P_2O_5 content, Fe_2O_3 content, and slag basicity on the dissolution behavior of slags modified with the addition of Na_2O were investigated in this study. The results obtained are summarized as follows:

(1) Increasing the P_2O_5 and Fe_2O_3 contents in slag resulted in a higher P_2O_5 content in the solid solution, while the mass fraction of solid solution decreased. With the increase in slag basicity, the P_2O_5 content in the solid solution decreased and the mass fraction of solid solution increased.

(2) The dissolution ratio of P reached approximately 76% regardless of the P_2O_5 content in slag, while the dissolution of Fe and Mg was slight. In the case of high P_2O_5 content, a leachate with higher P concentration and lower Ca and Si concentrations was obtained, exhibiting excellent selective leaching of P.

(3) Increasing the Fe_2O_3 content in slag not only promoted dissolution of P but also decreased the dissolution ratios of other elements. With the increase in slag basicity, the dissolution ratios of Ca, Si, and P all increased.

(4) Most of the solid solution was dissolved from each slag without a large dissolution of other phases at pH 6, indicating that selective leaching of solid solution was achieved in a wide range of slag compositions. After leaching, a residue with low P_2O_5 content and high Fe_2O_3 content was obtained.

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