Article

Leaching of Phosphorus from Quenched Steelmaking Slags with Different Composition

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Abstract: Separating P_2O_5 from steelmaking slag is the key to achieving optimum resource utilization of slag. If the P-concentrating $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$ solid solution was effectively separated, it can be a potential phosphate resource and the remaining slag rich in Fe_2O_3 and CaO can be reutilized as a flux in steelmaking process. In this study, a low-cost method of selective leaching was adopted, and hydrochloric acid was selected as leaching agent. The dissolution behavior of quenched steelmaking slags with different composition in the acidic solution was investigated and the dissolution mechanism was clarified. It was found that the P dissolution ratio from each slag was higher than those of other elements, achieving an effective separation of P and Fe. The dissolution ratios of P, Ca, and Si decreased as the P_2O_5 content in slag increased. A higher Fe_2O_3 content in slag led to a lower P dissolution ratio. Increasing slag basicity facilitated the dissolution of P from slag. The residue mainly composed of matrix phase and the P_2O_5 content decreased significantly through selective leaching. The P dissolution ratio from slag was primarily determined by the P distribution ratio in the $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$ solid solution and the precipitation of ferric phosphate in the leachate. The P-concentrating solid solution was effectively separated from quenched steelmaking slag, even though hydrochloric acid was used as leaching agent.

Keywords: steelmaking slag; phosphorus; leaching; $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$

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1. Introduction

Phosphorus is a significant nutrient element for animal and plant growth; however, it is one of the most detrimental impurities in the iron and steel industry, and most of the phosphorus is eliminated into slag in the steelmaking process [1]. To improve dephosphorization efficiency and reduce slag generation, hot metal dephosphorization was developed in Japan and widely adopted in steel plants [2]. In this process, dephosphorization and decarburization was conducted in converter, respectively, and dephosphorization slag and converter slag were generated [3]. Due to lower P_2O_5 content, converter slag can be recycled as a flux in dephosphorization process, and then only dephosphorization slag with relatively low basicity is emitted. The hot metal dephosphorization slag normally consists of $CaO-SiO_2-FeO-P_2O_5$ system, and the industrial operation is mainly carried out in the dicalcium silicate ($2CaO \cdot SiO_2$)-saturated composition range [4,5]. The amount of steelmaking slag is approximately 100~150 kg of per ton of steel [6], while the utilization ratio of steelmaking slag is not high. Large amounts of steelmaking slag are piled up or landfilled directly, causing tremendous waste of valuable components.

As the utilization of iron ores with higher P content, the P_2O_5 content in steelmaking slag is continuously increasing, and then steelmaking slag is regarded an important material to substitute for phosphate rocks [7]. It is well known that $2CaO \cdot SiO_2$ forms a solid solution with tricalcium phosphate ($3CaO \cdot P_2O_5$) at the treatment temperature over a wide

composition range [8,9]. This implies that the product of dephosphorization reaction can be concentrated in the $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ ($\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$) solid solution, which provides the foundation for P recovery. The P-concentrating $\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solution separated from slag can be used as phosphate resource and the remaining slag rich in Fe_tO and CaO can be reutilized as a flux in the ironmaking and steelmaking process, achieving the comprehensive utilization of steelmaking slag.

Various studies have been conducted on the removal of phosphorus from steelmaking slag. Li et al. [10] used centrifugal separation to remove $\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solution from the molten slag at high temperature according to the density differences for different mineral phases. Kubo et al. [11] and Lin et al. [12] studied the removal of $\text{nC}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solution from steelmaking slag according to the differences in the magnetic properties of mineral phases. Recently, some researchers focused on the P recovery from steelmaking slag using acid leaching. Numata et al. [13] reported that in the case of Fe_2O_3 -containing slag, the dissolution ratio of each element in the matrix phase was lower than that in the solid solution at various pH conditions. Qiao et al. [14] investigated the dissolution behavior of slag in the buffer solution of $\text{C}_6\text{H}_8\text{O}_7\text{--NaOH--HCl}$ system and found that most of the P was dissolved while the Fe dissolution ratio was also high. Du et al. [15,16] clarified that Na_2O modification and oxidization of molten slag was beneficial for the dissolution of $\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solution from steelmaking slag with high P_2O_5 content in the citric acid solution. Under the optimum conditions, the P dissolution ratio exceeded 85% and the dissolution of Fe was negligible, achieving selective leaching of P. After leaching, most of the P dissolved in leachate can be recovered as calcium phosphates by chemical precipitation, illustrating that acid leaching is an effective and low-cost method to recover P from steelmaking slag [17].

Concerning steelmaking slag with high P_2O_5 content, previous studies primarily studied the selective leaching of P from the furnace-cooled slag in the citric acid solution. Because of slow cooling and the use of organic acid, it resulted in a high treatment cost. In this study, to reduce treatment cost, hydrochloric acid (HCl) was selected as a leaching agent and the quenched slag from dephosphorization process was used. The dissolution behavior of P from quenched steelmaking slags with different composition were investigated. The aim of this study is to achieve an efficient separation of P from steelmaking slag with a simple and low-cost method. It is expected that this will provide theoretical and technical basis for the high value-added utilization of steelmaking slag.

2. Experimental

As reported in previous studies [17,18], the existence of Fe_2O_3 and Na_2O modification was beneficial for the selective leaching of P from slag. In this study, slag composition was simplified, and dephosphorization slags consisting of $\text{CaO}\text{--}\text{SiO}_2\text{--}\text{Fe}_2\text{O}_3\text{--}\text{P}_2\text{O}_5\text{--}\text{Na}_2\text{O}$ system were used. Compared with converter slag, these slags had relatively low slag basicity. Eight kinds of slags with different P_2O_5 , Fe_2O_3 , and basicity (CaO/SiO_2) were synthesized using reagent-grade CaCO_3 , SiO_2 , Fe_2O_3 , $\text{Ca}_3(\text{PO}_4)_2$, and Na_2SiO_3 . The mixed chemical reagents were firstly heated to 1823 K to form a homogeneous liquid slag in a Pt crucible under air. Then, it was cooled to 1673 K at a cooling rate of 3 K/min and held 20 min to precipitate the $\text{C}_2\text{S}\text{--}\text{C}_3\text{P}$ solid solution. Finally, slag was quickly taken out of the furnace and quenched in water. The synthesized slag was ground and sieved into particles of less than 53 μm . After performing aqua-regia digestion, the element concentration in each slag was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (SPECTRO, Kleve, Germany). Table 1 lists the actual composition of synthesized steelmaking slags. The mineralogical composition and morphology of mineral phases in slag was determined using X-ray diffraction (XRD) (Rigaku Corporation, Tokyo, Japan) analysis and electron probe microanalysis (EPMA) (JEOL, Tokyo, Japan).

Table 1. Actual composition of synthesized slags (mass%).

No.	CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	Na ₂ O	Basicity (C/S)
Slag 1	42.1	24.6	20.4	7.6	5.3	1.71
Slag 2	40.7	23.9	19.6	10.5	5.3	1.70
Slag 3	39.3	23.1	19.1	13.3	5.2	1.70
Slag 4	38.0	22.1	18.2	16.3	5.4	1.72
Slag 5	43.8	25.6	14.9	10.4	5.3	1.71
Slag 6	37.2	21.6	25.4	10.3	5.5	1.72
Slag 7	38.5	26.3	19.8	10.1	5.3	1.46
Slag 8	42.4	22.1	19.9	10.4	5.2	1.92

A Teflon vessel containing 300 mL of distilled water was placed in an isothermal water bath. 1.5 g of slag was added to keep the mass ratio (slag to solution) as 1:200 to cause the slag to fully dissolve, as described in previous study [19]. The slurry was agitated using a rotating stirrer at 200 rpm at room temperature (298 K). The diluted hydrochloric acid (0.4 mol/L) was used as a leaching agent and it was added to the slurry by a pH control and solution addition system. In previous study [18], most of the P could be dissolved from the furnace-cooled slag at pH 4. Hence, the pH of slurry was maintained at 4 to achieve the selective leaching of P. At appropriate intervals, approximately 4 mL of slurry was sampled, and filtered using a syringe filter (<0.45 µm). The concentration of each element in the leachate was analyzed using ICP-AES. After 120 min, the slurry was separated by vacuum filtration and the obtained residue was dried at 373 K. The residue was weighed and analyzed by XRD and EPMA. The chemical composition of residue was determined using the same method for slag analysis.

The dissolution ratio of element X (R_X) from steelmaking slag was calculated using the element concentration in the leachate, as expressed in Equation (1):

$$R_X = \frac{C_X \cdot V \cdot M_{XO}}{m \cdot w_{XO} \cdot M_X} \quad (1)$$

where C_X is the element X concentration in the leachate (mg/L); V is the final leachate volume (L); m is the slag mass (mg); w_{XO} is the oxide XO content in slag; M is molar mass.

3. Results

3.1. Mineralogical Composition

The morphology of mineral phases in synthesized slags with various composition is shown in Figure 1. Each slag principally composed of two mineral phases, and the mass fractions of mineral phases in different slag were obviously different. Table 2 lists the average composition of each mineral phase in slag. The black mineral phase consisting of CaO–SiO₂–P₂O₅ slag system is considered the C₂S–C₃P solid solution; the grey mineral phase consisting of CaO–SiO₂–Fe₂O₃ slag system is regarded the amorphous matrix phase. The high distribution ratio of P₂O₅ between the solid solution and the matrix phase indicated that the majority of P₂O₅ was concentrated in the C₂S–C₃P solid solution. The enrichment of P₂O₅ and Fe₂O₃ in different mineral phases was the basis of P separation by selective leaching. A part of Na₂O was also distributed in the C₂S–C₃P solid solution, which could promote the dissolution of solid solution. As the P₂O₅ content in slag increased, the P₂O₅ contents in the solid solution and in the matrix phase both increased. In the case of Slag 4, containing 16.3% P₂O₅, the solid solution almost consisted of 3CaO·P₂O₅. As the Fe₂O₃ content in slag increased, the P₂O₅ content in the solid solution increased, whereas that in the matrix phase had little change. The P₂O₅ contents in the solid solution and in the matrix phase both decreased with the increase in slag basicity, but the distribution ratio of P₂O₅ was still high. If P₂O₅ was sufficiently concentrated in the C₂S–C₃P solid solution which could be fully dissolved, separation of P from steelmaking slag could be achieved.

Figure 1. Morphology of mineral phases in the quenched steelmaking slags (EPMA analysis).

Table 2. Average composition of each phase in steelmaking slag (mass%).

		CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	Na ₂ O
Solid Solution	Slag 1	54.8	22.4	1.2	16.2	5.4
	Slag 2	52.3	14.7	1.1	25.1	6.7
	Slag 3	49.9	10.2	1.0	32.1	6.8
	Slag 4	48.0	5.7	0.9	38.5	6.8
	Slag 5	52.6	19.2	1.1	21.2	6.0
	Slag 6	48.1	12.6	1.0	30.2	8.0
	Slag 7	50.7	12.1	1.1	29.4	6.8
	Slag 8	53.7	18.7	1.1	20.8	5.8
Matrix Phase	Slag 1	32.7	28.2	32.5	1.7	4.9
	Slag 2	35.3	28.6	27.8	4.0	4.3
	Slag 3	34.1	29.1	27.0	5.5	4.2
	Slag 4	32.2	30.7	26.2	6.4	4.4
	Slag 5	34.9	31.7	24.9	3.9	4.5
	Slag 6	31.0	26.1	34.5	4.0	4.4
	Slag 7	35.8	30.7	22.5	6.7	4.4
	Slag 8	33.4	26.5	33.1	2.9	4.1

3.2. Leaching Results

The effect of P₂O₅ content on the change in Ca and P concentrations with leaching time is shown in Figure 2a. The dissolution of each slag primarily occurred in the initial period, resulting in significant increase in Ca and P concentrations. Their concentrations had a little increase after 60 min. With the increase in P₂O₅ content in slag, the P concentration increased significantly in the leachate, while the Ca concentration decreased. For Slag 4, containing 16.3% P₂O₅, the Ca and P concentrations reached 507.4 mg/L and 211.8 mg/L, respectively, after 120 min. The calculated dissolution ratios of main elements from slag are shown in Figure 2b. It is worth noting that these elements presented different dissolution

behavior. The P dissolution ratio was the highest, and it was approximately 70% in the case of Slag 1. Fe was hard to dissolve, and its dissolution ratio was almost zero. As the P_2O_5 content in slag increased, the dissolution ratios of P, Ca, and Si all decreased, indicating that slag dissolution became difficult. Compared with the leaching results of furnace-cooled slag in the citric acid solution [17], the P dissolution ratio was a little lower, but the dissolution of Fe was negligible, achieving an effective separation of P and Fe as well. The majority of P was dissolved from each slag without a large dissolution of other elements.

Figure 2. (a) Change in the Ca and P concentrations with leaching time; (b) Dissolution ratios of main elements from slags with different P_2O_5 contents.

Figure 3a shows the change in Ca and P concentrations with time when slags with different Fe_2O_3 contents were leached. With the increase in Fe_2O_3 content, the Ca concentration in the leachate decreased, whereas the P concentration showed little change, approximately 140 mg/L after 120 min. The dissolution ratios of the main elements from slags with different Fe_2O_3 contents are presented in Figure 3b. The dissolution of Fe was very difficult regardless of Fe_2O_3 content. When the Fe_2O_3 content increased from 14.9% to 19.6%, the Ca and Si dissolution ratios decreased dramatically, while the P dissolution ratio decreased by only 3%. If the Fe_2O_3 content continued to increase, it had a little influence on the dissolution ratio. Although increasing Fe_2O_3 content slightly decreased P dissolution, it significantly suppressed the dissolution of other elements, which was beneficial for selective leaching.

Figure 3. (a) Change in the Ca and P concentrations with leaching time; (b) Dissolution ratios of main elements from slag with different Fe_2O_3 contents.

The effect of slag basicity on the dissolution behavior of slag is shown in Figure 4. The Ca and P concentrations both increased significantly with slag basicity. The increasing tendency toward dissolution ratios of P, Ca, and Si was almost the same. In the case of low basicity, the dissolution of slag was difficult, resulting in a lower P dissolution ratio. When slag basicity increased to 1.92, the P dissolution ratio reached 77.4% and Fe did not dissolve, illustrating that selective leaching was achieved. The Ca and Si dissolution ratios were 61.7% and 42.2%, respectively. These results suggest that increasing slag basicity facilitates the dissolution of P from slag. Combining with mineralogical composition, it was found that a higher P_2O_5 content in the C_2S - C_3P solid solution caused lower dissolution ratio of each element from slag. To promote P dissolution, the P_2O_5 content in the solid solution should be lowered.

Figure 4. (a) Change in the Ca and P concentrations with leaching time; (b) Dissolution ratios of main elements from slags with different basicity.

3.3. Characterization of Residue

The XRD patterns of Slag 2 and its residue after leaching is shown in Figure 5. For Slag 2, the characteristic peaks associated with C_2S – C_3P solid solution and the broad peaks of non-crystalline phase were observed, confirming the existence of two mineral phases. Following leaching, the characteristic peaks of C_2S – C_3P solid solution all disappeared, and the broad peaks of non-crystalline phase intensified, illustrating that the P-concentrating phase was fully dissolved. Figure 6 shows the morphology of residue after the leaching of Slag 2. This residue consisted of some irregular particles with single mineral phase. As listed in Table 3, this mineral phase mainly containing CaO , SiO_2 , and Fe_2O_3 was similar to the matrix phase. It indicates that only the matrix phase remains in the residue, which is consistent with the XRD results. The average composition of residue is shown in Table 4. Compared with the composition in Table 1, the P_2O_5 content decreased from 10.5% to 4.3%, proving that the C_2S – C_3P solid solution was effectively separated, while the Fe_2O_3 content increased from 19.6% to 31.0%.

Figure 5. XRD patterns of Slag 2 and its residue after leaching.

Figure 6. (a,b) Morphology of residue surface of Slag 2 (EPMA analysis).

Table 3. Average composition of mineral phases on the residue surface (mass%).

Matrix Phase	Ca	Si	Fe	P	Na	O
1	24.2	12.8	21.1	1.8	3.0	37.1
2	24.2	10.1	17.6	2.1	3.4	42.6

Table 4. Chemical composition of the residue of Slag 2 (mass%).

	CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	Na ₂ O
Residue (Slag 2)	32.9	28.2	31.0	4.3	3.6

Overall, in this process, the P-containing leachate can be used to extract calcium phosphates by chemical precipitation, and the residue consisting of CaO–SiO₂–Fe₂O₃ system has lower P₂O₅ content, which can be used as a flux in the steelmaking process. These results will promote the comprehensive utilization of steelmaking slag and ease environmental burden.

4. Discussion

To achieve the selective leaching of P, the dissolution behavior and mechanism of P from quenched steelmaking slag should be understood. Several kinds of cations and anions exist in the leachate. Since phosphate ions can precipitate with metallic ions, it is necessary to consider the possibility of phosphate formation. In the aqueous solution, hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) and strengite (FePO₄·2H₂O) readily precipitate when Ca²⁺ and Fe³⁺ ions coexist with phosphate ions [20]. The precipitation of these phosphates plays a significant role in determining the P concentration in the leachate. Therefore, we investigated the concentration relationship between phosphate ions and metallic ions in the aqueous solution. There are several types of phosphate ions in the aqueous solution depending on pH, including PO₄^{3−}, HPO₄^{2−}, and H₂PO₄[−] [21]. In thermodynamic calculation, these phosphates ions were considered, and the activity coefficients of ions were assumed to be 1 because their concentrations were relatively low. The solubility lines of FePO₄·2H₂O and Ca₁₀(PO₄)₆(OH)₂ were calculated using the reaction equilibrium constants of Equations (2)–(5) at pH 4, respectively [22,23].

Figure 7 shows the relationship between P and Fe concentrations in the aqueous solution and experimental results. It was found that the solubility of FePO₄·2H₂O was very low at pH 4 and large amounts of phosphate and Fe³⁺ ions could not coexist in the aqueous solution. The saturation concentration of P decreased with the increase in Fe concentration. The P concentration in the leachate was high while the Fe concentration was very low, near zero. The points of experimental result all located above the solubility line of FePO₄·2H₂O, indicating that the P and Fe concentrations were supersaturated and FePO₄·2H₂O could precipitate. During leaching, the C₂S–C₃P solid solution dissolved well, and the dissolution of the Fe-containing matrix phase was low, resulting in high concentrations of Ca, Si, and P. As approximately 1.0% Fe₂O₃ existed in the solid solution, some Fe was also dissolved. However, it was difficult for these Fe³⁺ ions to coexist with phosphate ions, and then Fe³⁺ ions precipitated in the form of FePO₄·2H₂O. Owing to a small quantity of Fe dissolved from slag, the formation of FePO₄·2H₂O had little influence on the decrease in P concentration in the leachate. To make phosphate ions exist stably in the leachate, the dissolution of Fe from slag should be suppressed as much as possible.

Figure 7. Relationship between P and Fe concentrations in the aqueous solution and experimental results.

Because the Ca concentration was higher than other elements in the leachate, the possibility of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ formation was evaluated. As shown in Figure 8, it was difficult for the precipitation of calcium phosphates to occur in the aqueous solution at pH 4 unless concentrations on Ca and P were high. In this study, the maximum P concentration was 211.8 mg/L and it was far lower than the saturation concentration. The points of P and Ca concentrations were located far below the solubility line of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, illustrating that Ca concentration has no effect on phosphate precipitation. The P concentration in the leachate primarily depended on the Fe concentration. Under this condition, most of the P dissolved from slag existed stably in the leachate, proving that selective leaching of P from quenched steelmaking slag with high P_2O_5 content was possible, even in the hydrochloric acid solution.

To evaluate P-selective leaching from each slag, we compared the P distribution ratio in the C_2S – C_3P solid solution with the P dissolution ratio from slag. The mass fractions of solid solution and matrix phase were first calculated using Equations (6) and (7), where α and β are the mass fraction of solid solution and matrix phase, respectively, w_{XO}^α and w_{XO}^β are the XO content in the solid solution and matrix phase, respectively. The mass fraction was defined as the average results of each oxide. Then, the P distribution ratio in the solid solution (D) was calculated using Equation (8).

$$w_{\text{XO}} = \alpha w_{\text{XO}}^\alpha + \beta w_{\text{XO}}^\beta \quad (6)$$

$$\alpha + \beta = 1 \quad (7)$$

$$D = \frac{\alpha w_{\text{P}_2\text{O}_5}^\alpha}{w_{\text{P}_2\text{O}_5}} \quad (8)$$

Figure 8. Relationship between P and Ca concentrations in the aqueous solution and experimental results.

As shown in Figure 9, most of the P in slag was distributed in the C_2S – C_3P solid solution. With the P_2O_5 content increased, the P distribution ratio in the solid solution decreased, suggesting that the slag with lower P_2O_5 content facilitated P enrichment. 70.8% of P in Slag 4 containing 16.3% P_2O_5 was concentrated in the solid solution. Increasing Fe_2O_3 content was not beneficial for P enrichment. A higher slag basicity resulted in a higher P distribution ratio in the solid solution. For Slag 7 with low basicity, only half of the P in slag was distributed in the solid solution, which made it difficult to achieve P-selective leaching. In each case, the P dissolution ratio from slag was a little lower than the P distribution ratio in the solid solution. Its variation tendency was the same as that of P distribution ratio. One reason for this was considered to be that a small part of P-concentrating solid solution was not dissolved. The other reason was that a small amount of P dissolved from slag precipitated with Fe^{3+} ions, resulting in a little decrease in P dissolution ratio. Although the P dissolution ratio was not very high, the effective dissolution of P-concentrating solid solution from quenched steelmaking slag was achieved under this condition, similar with the furnace-cooled slags as reported in previous studies [16–18].

To better understand selective leaching, we weighted the mass of remained residue and compared that with the mass fraction of matrix phase. As shown in Figure 10, a large amount of slag was not dissolved under this condition, and the mass fraction of residue was almost equal to that of matrix phase in each slag. This proved that the vast majority of P-concentrating solid solution was dissolved, and the dissolution of matrix phase was difficult, which was consistent with the residue analysis. For Slag 8 with high basicity, the mass fraction of solid solution was high, and then a large amount of slag was dissolved. In summary, the P dissolution ratio from slag was mainly determined by the P enrichment in the C_2S – C_3P solid solution and phosphate precipitation in the leachate. The P-concentrating solid solution was effectively dissolved and separated from quenched steelmaking slag when hydrochloric acid was used as leaching agent.

Figure 9. P distribution ratio in the solid solution compared with P dissolution ratio from slag.

Figure 10. Mass fraction of matrix phase in each slag compared with that of residue.

5. Conclusions

To separate P from steelmaking slag using a simple and low-cost method, selective leaching of C_2S – C_3P solid solution was adopted, and hydrochloric acid was selected as leaching agent. In this study, the dissolution behavior of quenched steelmaking slags with different composition in the acidic solution was investigated. The results obtained are summarized below:

- (1) The P dissolution ratio from slag was higher than those of other elements in each case, achieving an effective separation of P and Fe. The C_2S – C_3P solid solution was fully dissolved from slag, and then the residue primarily composed of the matrix phase, causing a significant decrease in P_2O_5 content.
- (2) The dissolution ratios of P, Ca, and Si decreased as the P_2O_5 content in slag increased. A higher Fe_2O_3 content in slag resulted in a lower P dissolution ratio. Increasing slag basicity facilitated the dissolution of P from slag.
- (3) The P dissolution ratio from slag was mainly determined by the P distribution ratio in the solid solution and the precipitation of ferric phosphate in the leachate. The P-concentrating solid solution was effectively separated from quenched steelmaking slag, even though hydrochloric acid was used as leaching agent, which provided a simple and low-cost method to recover valuable components from steelmaking slag.

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References

1. Matsubae-Yokoyama, K.; Kubo, H.; Nakajima, K.; Nagasaka, T. A material flow analysis of phosphorus in Japan. *J. Ind. Ecol.* **2009**, *13*, 687–705. [\[CrossRef\]](#)
2. Ogawa, Y.; Maruoka, N. Progress of hot metal treatment technology and future outlook. *Tetsu Hagane* **2014**, *100*, 434–444. [\[CrossRef\]](#)
3. Kitamura, S.; Naito, K.; Okuyama, G. History and latest trends in converter practice for steelmaking in Japan. *Min. Proc. Ext. Met.* **2019**, *128*, 34–45. [\[CrossRef\]](#)
4. Ito, K.; Yanagisawa, M.; Sano, N. Phosphorus distribution between solid $2CaO \cdot SiO_2$ and molten $CaO-SiO_2-FeO-Fe_2O_3$ slags. *Tetsu Hagane* **1982**, *68*, 342–344. [\[CrossRef\]](#)
5. Kitamura, S.; Yonezawa, K.; Ogawa, Y.; Sasaki, N. Improvement of reaction efficiency in hot metal dephosphorization. *Ironmak. Steelmak.* **2002**, *29*, 121–124. [\[CrossRef\]](#)
6. Gao, X.; Okubo, M.; Maruoka, N.; Shibata, H.; Ito, T.; Kitamura, S.Y. Production and utilization of iron and steelmaking slag in Japan and the application of steelmaking slag for the recovery of paddy fields damaged by Tsunami. *Min. Proc. Ext. Met.* **2015**, *124*, 116–124.
7. Matsubae, K.; Yamasue, E.; Inazumi, T.; Webeck, E.; Miki, T.; Nagasaka, T. Innovations in steelmaking technology and hidden phosphorus flows. *Sci. Total. Environ.* **2016**, *542*, 1162–1168. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Fix, W.; Heymann, H.; Heinke, R. Subsolidus relations in the system $2CaO \cdot SiO_2-3CaO \cdot P_2O_5$. *J. Am. Ceram. Soc.* **1969**, *52*, 346–347. [\[CrossRef\]](#)
9. Zhu, B.; Zhu, M.M.; Luo, J.; Dou, X.F.; Wang, Y.; Jiang, H.J.; Xie, B. Distribution behavior of phosphorus in $2CaO \cdot SiO_2-3CaO \cdot P_2O_5$ solid solution phase and liquid slag phase. *Metals* **2020**, *10*, 1103. [\[CrossRef\]](#)
10. Li, C.; Gao, J.; Guo, Z. Separation of phosphorus- and iron-enriched phase from $CaO-SiO_2-FeO-MgO-P_2O_5$ melt with super gravity. *Metall. Mater. Trans. B* **2016**, *47*, 1516–1519. [\[CrossRef\]](#)
11. Kubo, H.; Matsubae-Yokoyama, K.; Nagasaka, T. Magnetic separation of phosphorus enriched phase from multiphase dephosphorization slag. *ISIJ Int.* **2010**, *50*, 59–64. [\[CrossRef\]](#)
12. Lin, L.; Bao, Y.P.; Wang, M.; Jiang, W.; Zhou, H.M. Separation and recovery of phosphorus from P-bearing steelmaking slag. *J. Iron Steel Res. Int.* **2014**, *21*, 496–502. [\[CrossRef\]](#)
13. Numata, M.; Maruoka, N.; Kim, S.; Kitamura, S. Fundamental experiment to extract phosphorous selectively from steelmaking slag by leaching. *ISIJ Int.* **2014**, *54*, 1983–1990. [\[CrossRef\]](#)
14. Qiao, Y.; Diao, J.; Liu, X.; Li, X.S.; Zhang, T.; Xie, B. Dephosphorization of steelmaking slag by leaching with acidic aqueous solution. *JOM* **2016**, *68*, 2511–2519. [\[CrossRef\]](#)

15. Du, C.M.; Gao, X.; Ueda, S.; Kitamura, S. Effect of Na₂O addition on phosphorus dissolution from steelmaking slag with high P₂O₅ content. *J. Sustain. Metall.* **2017**, *3*, 671–682. [[CrossRef](#)]
16. Du, C.M.; Gao, X.; Ueda, S.; Kitamura, S. Recovery of phosphorus from modified steelmaking slag with high P₂O₅ content via leaching and precipitation. *ISIJ Int.* **2018**, *58*, 833–841. [[CrossRef](#)]
17. Du, C.M.; Gao, X.; Ueda, S.; Kitamura, S. Optimum conditions for phosphorus recovery from steelmaking slag with high P₂O₅ content by selective leaching. *ISIJ Int.* **2018**, *58*, 860–868. [[CrossRef](#)]
18. Du, C.M.; Gao, X.; Ueda, S.; Kitamura, S. Effect of Fe²⁺/T.Fe ratio on the dissolution behavior of P from steelmaking slag with high P₂O₅ content. *J. Sustain. Metall.* **2018**, *4*, 443–454. [[CrossRef](#)]
19. Teratoko, T.; Maruoka, N.; Shibata, H.; Kitamura, S. Dissolution behavior of dicalcium silicate and tricalcium phosphate solid solution and other phases of steelmaking slag in an aqueous solution. *High. Temp. Mater. Processes.* **2012**, *31*, 329–338. [[CrossRef](#)]
20. Lindsay, W.L.; Moreno, E.C. Phosphate phase equilibria in soils. *Soil. Sci. Soc. Am. J.* **1960**, *24*, 177–182. [[CrossRef](#)]
21. Shen, H.Y.; Wang, Z.J.; Zhou, A.M.; Chen, J.L.; Hu, M.Q.; Dong, X.Y.; Xia, Q.H. Adsorption of phosphate onto amine functionalized nano-sized magnetic polymer adsorbents: Mechanism and magnetic effects. *RSC Adv.* **2015**, *5*, 22080–22090. [[CrossRef](#)]
22. Markich, S.J.; Brown, P.L. *Thermochemical Data for Environmentally-Relevant Elements*; ANSTO Environment Division: Sydney, NSW, Australia, 1999.
23. Futatsuka, T.; Shitogiden, K.; Miki, T.; Nagasaka, T.; Hino, M. Dissolution behavior of nutrition elements from steelmaking slag into seawater. *ISIJ Int.* **2004**, *44*, 753–761. [[CrossRef](#)]