

Fundamental Research on a Rational Steelmaking Slag Recycling System by Phosphorus Separation and Collection

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Abstract: Recently, reduction of the steelmaking slag stock in Japan has been required, but utilization of steelmaking slag is restricted due to its chemical properties. On the other hand, the price of phosphorus ore is increasing rapidly due to very tight supply/demand balance worldwide. In this work, (Fe₇O) and (P₂O₅) reduction in steelmaking slag and recovery as a phosphorus source were investigated in feasibility studies and laboratory-scale experiments in order to develop a rational recycling process for steelmaking slag. The results are summarized as follows: (a) Steelmaking slag was reduced by carbon under high temperature conditions (1373-1873 K), and high-P hot metal was recovered. The phosphorus content of the reduced slag was <0.3 mass %. (b) Higher temperatures were required for slag reduction with carbon, corresponding to increasing slag basicity. (c) The oxygen partial pressure calculated from the FeO content ranged from 10⁻¹³ to 10⁻¹⁷ atm. More than 50 mass % of phosphorus in the slag can be removed under the condition that FeO activity is less than 0.01. (d) From the mass balance of phosphorus, 0-30 mass % of undefined phosphorus was observed, which was estimated by thermodynamic calculations and SEM-EPMA analysis to be caused by gaseous dephosphorization. (e) Phosphorus was enriched in slag to be higher than 30 mass % P₂O₅ by dephosphorization of high-P (1.05 mass %) hot metal.

Keywords: dephosphorization from slag, steelmaking slag, basicity, thermodynamics

1. Introduction

The ironmaking process generates approximately 300 kg/ton-steel of blast furnace slag, which is effectively utilized in construction materials and as a raw material for cement. Steelmaking slag is generated at a rate around one-third that of blast furnace slag (120 kg/ton-steel). Steelmaking slag is also utilized in construction materials, but is less valuable than blast furnace slag because remained CaO in the steelmaking slag causes hygroscopic expansion. A technique to recycle the steelmaking slag to the ironmaking process for the recovery of iron and CaO has been reported^{1, 2)}. For this purpose, however, phosphorus must be removed before recycling in order to avoid phosphorus contamination in the ironmaking process.

On the other hand, phosphorus is an important resource for chemicals and fertilizers. Recently, the price of phosphorus ore tends to be expensive due to very tight supply/demand balance worldwide. Steelmaking slag generated in Japan contains 93 kt-P/year, which is close to the total amount of Japan's imports of phosphorus ore (111 kt-P/year)³⁻⁴⁾. However, the phosphorus in steelmaking slag is not utilized in any way.

Hence, a new slag recycling process has been proposed in order to meet the demand for both a rational slag recycling

system and recovery of phosphorus as a valuable resource. Our proposed process is as follows and shown in **Figure 1**.

- (1) Reduction of (Fe_2O) and (P_2O_5) in the steelmaking slag and removal of iron and phosphorus as high-P hot metal.
- (2) Dephosphorization of the high-P hot metal and phosphorus enrichment as high-P slag.
- (3) Return of the dephosphorized hot metal to usual steelmaking process.
- (4) Utilization of high-P slag as a substitute for phosphorus ore.
- (5) Recycling low iron and phosphorus slag in ironmaking process.

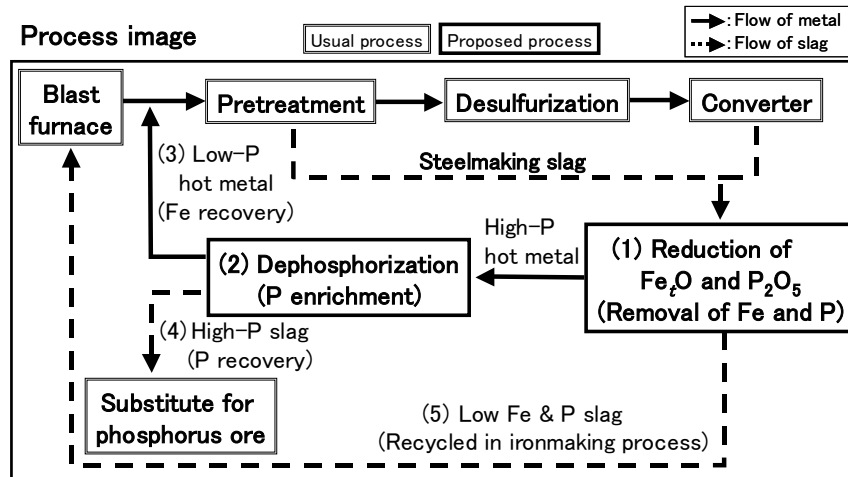


Fig. 1 Proposed process image.

Many studies have examined reduction of steelmaking slag. Shiomi *et al.*⁵⁾ reduced synthesized steelmaking slag (basicity 1.1-1.2) in a carbon crucible. They reported that FeO in the slag was reduced before P_2O_5 and 68-94 mass % of the phosphorus in the slag was removed at 1773-1873K. Takeuchi *et al.*⁶⁾ investigated the influence of the coexistence of Fe-Si alloys on the reduction of steelmaking slag (basicity 0.5-2.3) by carbon at 1873K, and reported that phosphorus in the steelmaking slag was removed through the gas phase and at least 60 mass % of the phosphorus was recovered as a simple substance. Moreover, Morita *et al.*⁷⁾ and Toishi *et al.*⁸⁾ investigated the influence of microwave irradiation heating on the reduction of steelmaking slag.

In order to save energy in steelmaking slag reduction, higher reduction rate at lower temperature is required. However, the reduction behavior of low-basicity slag at high temperatures over 1773 K under stirring condition has not yet been investigated.

In this work, (1) (Fe_2O) and (P_2O_5) reduction in steelmaking slag were investigated at 1323-1873K with mechanical stirring, and (2) dephosphorization experiments with high phosphorus hot metal were carried out in order to simulate phosphorus recovery.

2. Experimental method

2.1. Slag reduction

A schematic diagram of the experimental apparatus is shown in **Figure 2**. A slag sample and graphite powder were charged in a MgO crucible and heated to the set temperature (1373-1873K) at the average rate of 15 K/min by a high frequency induction furnace. The experiment was conducted with an argon gas flow (5 NL/min) over

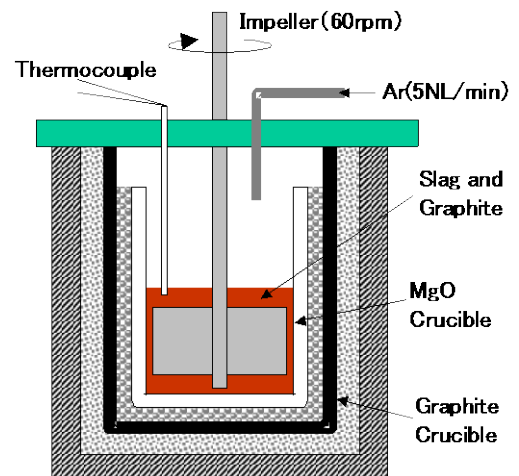


Fig. 2 Schematic diagram of experimental apparatus.

the slag sample and mechanical stirring (60 rpm) by means of an impeller. The temperature was measured by a thermocouple at the top of the slag sample. The compositions of the slag samples are shown in **Table 1**. The carbon content of the graphite powder was more than 99 mass %, and its weight was adjusted to be 2.5 times that of the stoichiometric weight necessary to reduce all the (Fe₂O) and (P₂O₅) in the initial slag sample. After holding for 40 min at the set temperature, mechanical stirring and heating were switched off and the sample was cooled in air. After magnetically separating the sample into slag and metal, their chemical compositions were analyzed.

Table 1 Chemical composition of slag used in the experimental work.

	Slag composition (mass%)										Basicity (-)
	CaO	SiO ₂	Al ₂ O ₃	MgO	MnO	P ₂ O ₅	T.Fe	M.Fe	FeO	Fe ₂ O ₃	
De-P slag	21.1	17.8	4.1	4.9	3.9	2.4	36.9	17.3	19.8	6.1	1.2
Converter slag I	40.0	13.5	5.4	5.8	2.8	2.2	20.6	2.2	12.0	12.9	3.0
Converter slag II	47.0	11.7	4.0	6.0	3.0	2.8	16.3	1.0	10.4	10.3	4.0

2.2. Phosphorus enrichment

200 kg of hot metal was prepared using a 350 kg scale high frequency induction furnace. The carbon and phosphorus contents of the hot metal were adjusted to 4.5 mass % and 1.05 mass % respectively by adding graphite and Fe-P alloy. The composition of this hot metal was selected by assuming the metal product generated in the experiment mentioned above. Oxygen gas (2.25 Nm³/min/t) was blown on the hot metal from a top-blowing lance with the lance toe separated from the hot metal surface. Argon gas (0.15 Nm³/min/t) was injected from bottom-blowing tuyeres. The temperature was controlled to 1623 K by adding electrolytic iron as a cooling agent, and 15 kg/t of the CaO powder was added as a dephosphorization agent for 15 min.

3. Results

3.1. Reduction of (Fe₂O) in slag

After the experiments, the samples were magnetically separated into iron droplet, magnetic slag, and non-magnetic slag. Many minute iron particles were dispersed in the slag samples. In some cases, they gathered in the bottom of the MgO crucible and became some iron droplets. Such iron droplets were obtained for hot metal dephosphorization slag (basicity 1.2) at 1473K and for the converter slag I (basicity 3.0) at 1873K. In the early stage of reduction, slag was observed as a liquid or a liquid-solid mixture. After reduction of iron oxides, the slag seemed to have higher solid ratio due to the increased melting point of the slag.

The recovery ratio of iron droplets is plotted against temperature in **Figure 3**. Here, the recovery ratio of iron droplets means the ratio of the weight of recovered iron droplets and the total iron weight contained in the initial slag sample. From **Fig. 3**, it is found that a higher temperature is needed to recover iron droplets from higher basicity slag. This result suggests that the fluidity of the slag is important for recovery of iron droplets.

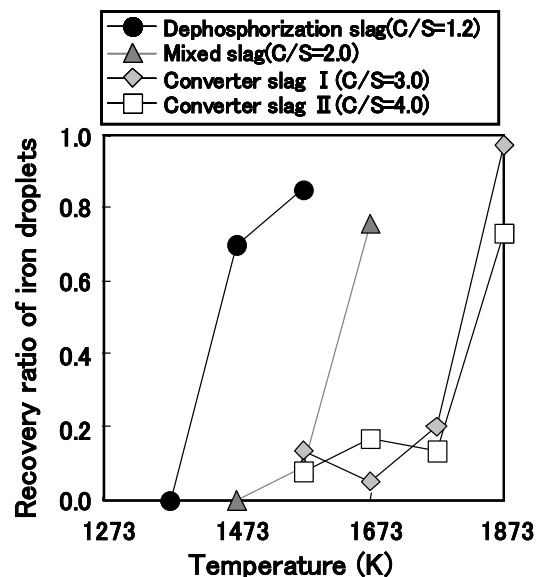


Fig. 3 Effects of experimental temperature and slag composition on recovery ratio of iron droplet.

3.2. Reduction of P₂O₅ in slag

Figure 4 shows the mass balance of phosphorus in each experiment. The vertical axis is the ratio of the phosphorus weight distributed in each phase and the total phosphorus weight contained in the initial slag sample. Here, phosphorus is distributed in slag as phosphorus oxide, iron particles in slag, iron droplets and an undefined phase. The final phosphorus content of the reduced slag was less than 0.3 mass % after the experiments at 1873K. Reduced slag with phosphorus content of less than 0.3 mass % can be recycled in the ironmaking process as a CaO substitute and iron source without causing phosphorus contamination.

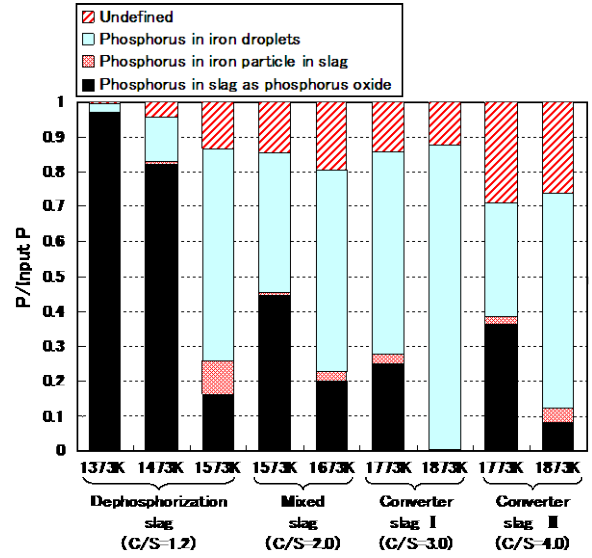


Fig. 4 Phosphorus mass balance in experimental work.

3.3. Phosphorus enrichment from high-P hot metal

The hot metal with high phosphorus content (1.05 mass %) was dephosphorized, and the phosphorus was enriched in the slag to be higher than 30 mass % P₂O₅. Because phosphorus ore used as an industrial raw material contains about 35 mass % P₂O₅³⁾, the phosphorus-enriched slag obtained in this experiment is suitable for use as a substitute for phosphorus ore.

4. Discussion

4.1. Relationship between reduction behaviors of Fe₇O and P₂O₅

As mentioned in the former chapter, greater reduction and recovery ratios of (Fe₇O) and (P₂O₅) in steelmaking slag were obtained at higher reduction temperature. Here, the influence of the oxygen partial pressure on slag reduction is evaluated. The assumptions for the calculation of oxygen partial pressure are as follows.

- (A) The oxygen partial pressure is determined by the equilibrium between Fe and FeO.
- (B) The equilibrium between Fe and FeO is expressed by Eqs. (1) and (2).
- (C) The activity of iron is unity.
- (D) The activity of FeO is calculated using the regular solution model proposed by Ban-ya⁹⁾ for CaO-SiO₂-FeO-Fe₂O₃-MgO-MnO systems.

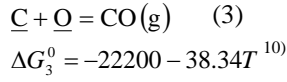
$$(\text{Fe}_7\text{O}) = t\text{Fe}(l) + \underline{\text{O}} \quad \log K_1 = -\frac{6150}{T} + 2.604 \quad (1)$$

$$\frac{1}{2} \text{O}_2(\text{g}) = \underline{\text{O}} \quad \Delta G_2^0 = -117110 - 3.39T \quad (2)$$

where $\underline{\quad}$ and (\quad) denote the component in metal and slag, respectively.

The calculated oxygen partial pressure is plotted against temperature in **Figure 5**. The broken lines in the figure show the equilibrium relationships between oxygen partial pressure and temperature when the FeO activities are 0.1, 0.03 and 0.01. The dash-dotted line shows that of the equilibrium between $\underline{\text{C}}$ and CO gas, calculated by the following assumptions.

- (E) The equilibrium between \underline{C} and CO gas is expressed by Eqs. (2) and (3).
- (F) The concentrations of carbon and phosphorus in metal are 4 mass % and 1 mass %, respectively; these values are based on experimental results.
- (G) The CO gas partial pressure is 1 atm.
- (H) The interaction parameters of carbon and phosphorus for carbon are as follows. $e_C^C = 0.243, e_C^P = 0.051^{10}$

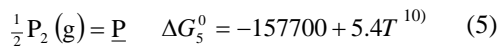
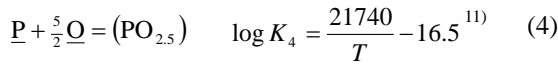


In **Fig. 5**, results in which the phosphorus removal ratio is above 50 mass % are expressed by solid symbols (●, ▲, ◆, ■), and those below 50 mass % are represented by open symbols (○, △, ◇, □). From **Fig. 5**, it can be stated that more than 50 mass % of phosphorus is removed under the condition that the activity of FeO is below 0.01. This fact indicates that reduction of (P_2O_5) begins after the concentration of FeO becomes sufficiently low.

4.2. Gaseous dephosphorization

From **Fig. 4**, 0-30 mass % of phosphorus removal as undefined species was observed during high temperature reduction, which was estimated to be caused by gaseous dephosphorization from the slag. Here, a possibility of gaseous dephosphorization is discussed based on thermodynamic calculations and SEM-EPMA observation. First, the partial pressure of P_2 during the experiments was calculated by the following assumptions.

- (I) The equilibrium between \underline{P} and ($\text{PO}_{2.5}$) is expressed by Eq. (4).
- (J) By using Eqs. (2), (4) and (5), the equilibrium between P_2 gas and ($\text{PO}_{2.5}$) is expressed by Eq. (6).
- (K) The activity of $\text{PO}_{2.5}$ is calculated using the regular solution model proposed by Ban-ya⁹⁾ for $\text{CaO-SiO}_2\text{-FeO-Fe}_2\text{O}_3\text{-MgO-MnO}$ systems.



Here, the oxygen partial pressure was determined in the same way as in 4.1. **Figure 6** shows the relationship between the calculated P_2 gas partial pressure and the undefined ratio of phosphorus shown in **Fig. 4**. **Fig. 6** shows that the ratio of undefined phosphorus tends to increase with increasing P_2 gas partial pressure. This result suggests that undefined phosphorus may correspond to phosphorus removed through the gas phase. However, **Fig. 6** also indicates that the

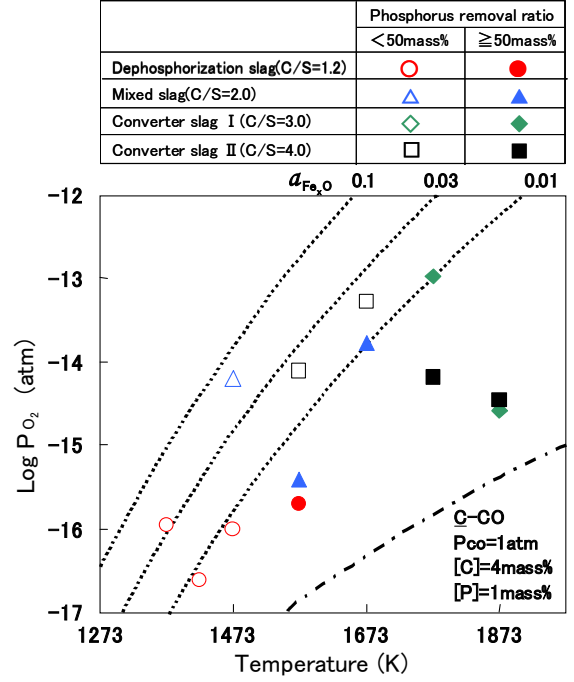


Fig. 5 Comparison of oxygen potential in experimental work.

undefined phosphorus ratio varies even at the same P_2 gas partial pressure condition. This implies that the undefined phosphorus ratio may also be affected by other factors.

The slag samples after experiments were observed by SEM and analyzed by EPMA. **Figure 7** shows the result of mapping image by EPMA. The important findings in **Fig. 7** are (a) presence of small iron particles in the slag and (b) phosphorus enrichment at the surface of the iron particles not contacted with slag. If it is assumed that phosphorus is removed from slag only by the reaction between metal and slag, phosphorus should be enriched only at the surface of the iron particles contacted with slag. This indicates that gaseous dephosphorization occurred during the experiments, and some of the P_2 gas was captured by the iron particles, while the other P_2 gas was removed through the gas phase. In discussing the mechanism of gaseous dephosphorization, it is necessary to consider the separation of iron particles from slag.

5. Conclusions

This study investigated (1) (Fe, O) and (P_2O_5) reduction in steelmaking slag at 1323-1873K with mechanical stirring and (2) simulation of phosphorus recovery from high phosphorus hot metal. The main results are summarized below.

(a) Steelmaking slag was reduced by carbon under high temperature conditions (1373-1873K), and high-P hot metal was recovered. The phosphorus content of the reduced slag was <0.3 mass %.

(b) Higher temperatures were required for slag reduction with carbon, corresponding to increasing slag basicity.

(c) The oxygen partial pressure calculated from the FeO content ranged from 10^{-13} to 10^{-17} atm. More than 50 mass % of phosphorus in the slag can be removed under the condition that the activity of FeO is less than 0.01.

(d) From the mass balance of phosphorus, 0-30 mass % of undefined phosphorus was observed, which was estimated by thermodynamic calculations and SEM-EPMA analysis to be caused by gaseous dephosphorization.

(e) Phosphorus was enriched in slag to be higher than 30 mass % P_2O_5 by dephosphorization of high phosphorus (1.05 mass %) hot metal.

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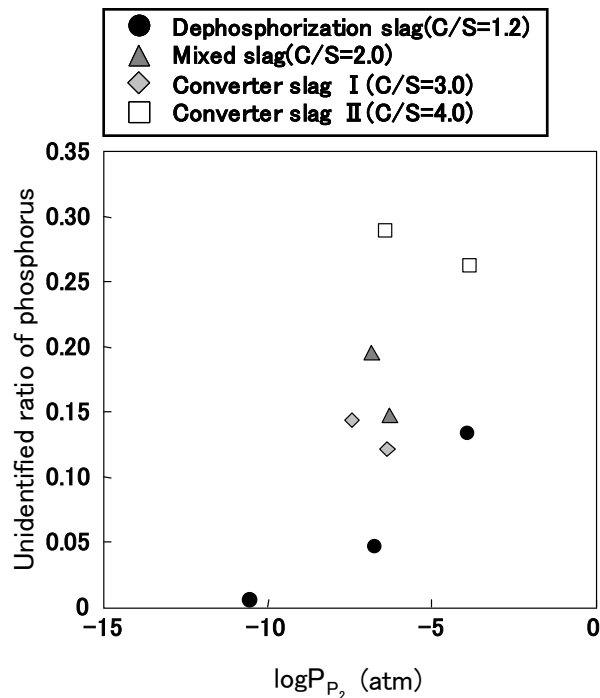


Fig. 6 Relationship between $\log P_2$ and ratio of unidentified phosphorus.

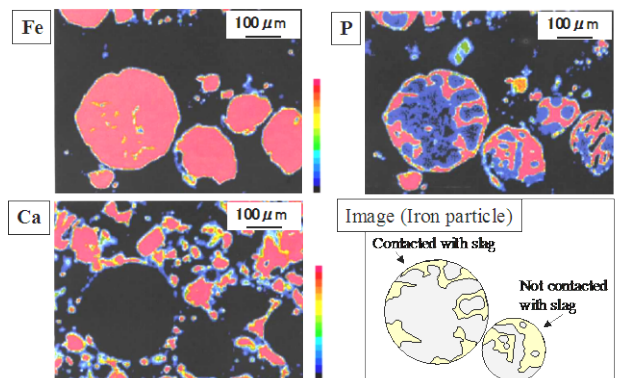


Fig. 7 EPMA mapping image of slag after reduction.

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