Enrichment of Phosphorus Oxide in Steelmaking Slag by Utilizing Capillary Action

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Abstract The recoverability of phosphorus oxide from steelmaking slag was investigated using a mechanical approach involving capillary action. It was found that P_2O_5 was concentrated in the $2CaO \cdot SiO_2$ phase. To separate the P_2O_5 -enriched solid $2CaO \cdot SiO_2$ phase and FeO-rich liquid phase in steelmaking slag, capillary action was used to facilitate penetration into absorbers such as sintered CaO , Fe_2O_3 , and $CaCO_3$ tablet. Once the liquid phase had penetrated the absorber, it was found that the solid $2CaO \cdot SiO_2$ phase and FeO-rich phase could be effectively separated. When $CaCO_3$ was used as an absorber, 91 % of phosphorus oxide in the steelmaking slag was recovered in solid $2CaO \cdot SiO_2$ phase. The recovered absorber, which includes a FeO-rich liquid phase, may be used as Fe source, and the $2CaO \cdot SiO_2$ phase, which includes P_2O_5 , may be used as P source.

Keywords Phosphorus · Iron · Separation · Recovery

Introduction

Global production of crude steel production increased from 850 million tons a year in 2000 to 1649 million metric tons in 2013 [1]. Steelmaking slag is an inevitable by-product of steel, with 14.4 million tons produced in Japan

alone in FY2013 [2]. Steelmaking slag contains 20–30 mass%FeO and often more than 1 mass% of P_2O_5 , but despite the value of these two components, it tends to be utilized as a road construction material, and in cement [3]. If FeO in steelmaking slag can be recovered and reused as FeO source in ironmaking process, it will have large benefit for steel producers. Also, the annual amount of P_2O_5 included in steelmaking slag has been estimated to be roughly equivalent to the total annual imports of P_2O_5 into Japan [4]. Hence, if it is possible to separate P_2O_5 from slag, steelmaking slag will be an alternative resource of P_2O_5 .

The composition of steelmaking slag varies considerably according to the type of process, and the conditions in the workshops, for instance. Even so, it can be safely assumed that the primary phase that precipitates during cooling is $2CaO \cdot SiO_2$, and that this phase will separate with the FeO-rich liquid phase. It is known that the distribution of phosphorus in the $2CaO \cdot SiO_2$ phase is higher than in the liquid slag phase [5–14]. If it is possible to separate the solid $2CaO \cdot SiO_2$ phase that includes P_2O_5 with the FeO-rich liquid phase, it will be possible to use these phases as sources of phosphorus and iron. Tanaka et al. [15] reported that FeO slag containing P_2O_5 penetrates the CaO sinter and that P_2O_5 is fixed as $4CaO \cdot P_2O_5$. The liquid FeO-rich phase is absorbed into the CaO sinter. By applying this mechanism, one of the present authors [16] has successfully separated solid $2CaO \cdot SiO_2$ phase that includes P_2O_5 with the FeO-rich liquid phase by use of CaO sinter. Various kinds of materials can be a candidate to absorb FeO-rich liquid from solid/liquid phase coexisting steelmaking slag. In this work, capillary action into sintered CaO , Fe_2O_3 , and $CaCO_3$ tablets was investigated to confirm the separation of the solid $2CaO \cdot SiO_2$ phase and liquid phase.

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Experimental

Reagent grade CaCO_3 was heated to 1223 K to obtain CaO . The FeO was made by mixing an equivalent molar electrolytic Fe powder with reagent grade Fe_2O_3 powder and heating the mixture in a Fe crucible at 1473 K under a purified Ar atmosphere for 6 h. Magnetic separation was used to remove metallic Fe and Fe_3O_4 from FeO after crushing.

Prepared CaO and FeO were mixed with reagent grade SiO_2 and $3\text{CaO}\cdot\text{P}_2\text{O}_5$. Mixed oxides were placed in an MgO crucible (I.D. 14 mm, O.D. 18 mm, H 60 mm) and were heated under a purified Ar flowing atmosphere in a vertical electric resistance furnace with MoSi_2 heating elements. The reaction tube was Al_2O_3 , 60 mm in ID, and 1000 mm length. Samples were heated at 200 K/h to 1823 K and held for 1 h to melt the sample oxide. Then, the slag samples were cooled at 200 K/h to 1673 K and held for 1 h followed by quenching. Composition of the slag samples prepared by the above-mentioned procedure was 42.7 mass% CaO –40.0 mass% FeO –10.2 mass% SiO_2 –3.1 mass% P_2O_5 –4.0 mass% MgO .

Sintered CaO , Fe_2O_3 , and CaCO_3 tablets were used as an absorber of liquid phase in solid/liquid slag mixture. The sintered CaO was prepared as follows. Prepared CaO powder was pressed into 15 mm ϕ tablets and sintered in a Pt crucible under air at 1373 or 1673 K for 3 h, and the porosity was 53 and 35 %, respectively. Sintered Fe_2O_3 was prepared by pressing Fe_2O_3 powders into 15 mm ϕ tablets and sintered in Al_2O_3 crucible under air at 1373 K for 3 h, and the porosity was 28 %. Also, CaCO_3 tablet was prepared by pressing CaCO_3 powders into 15 mm ϕ tablets, and the estimated porosity was 31 %. Physical strength of CaCO_3 tablet was enough for experiment, and sintering was not conducted. The prepared tablets were ground by hand into a crucible shape and the weight was approximately 2.8 g.

Approximately, 0.2 g of premelted slag was put in a crucible made from sintered CaO , Fe_2O_3 , and CaCO_3 tablets. This crucible was set in an outer MgO crucible and was heated in a purified Ar flowing atmosphere. The sample was heated at 200 K/h to 1673 K and held for 1 h. Then, the sample was cooled at 200 K/h to room temperature.

Samples were analyzed by SEM–EDS (JEOL JSM-6510/Oxford INCA Energy250). Analysis was conducted after calibration with standard samples, and ZAF correction method was used in this study. At least six points were analyzed for determination of phase composition for all samples. Analytical fluctuation within the same phase was less than ± 5 %.

Results and Discussion

Image of the sample after the experiment using CaO absorber sintered at 1673 K is shown in Fig. 1. Liquid phase in the slag was successfully absorbed into sintered

Fig. 1 Image of sample after experiment using CaO absorber sintered at 1673 K

CaO . Residue slag was able to be separated easily from sintered CaO . Liquid phase in the slag was also absorbed when using other kinds of absorbers, and slag residue could be easily separated after experiment. The average compositions of slag residue, absorbers, and observed phases are shown in Table 1. Also, SEM images of residue slag and absorber are shown in Figs. 2, 3, 4, and 5. Recovery ratio of P_2O_5 and FeO is defined in Eqs. (1) and (2), respectively. Experiments results are summarized in Table 2.

Recovery ratio of P_2O_5 (%)

$$= \frac{(\text{mass}\%\text{P}_2\text{O}_5) \text{ in slag residue} \times \text{weight of slag residue}}{(\text{mass}\%\text{P}_2\text{O}_5) \text{ in initial slag} \times \text{weight of initial slag}} \times 100 \quad (1)$$

Recovery ratio of FeO (%)

$$= \frac{(\text{mass}\%\text{FeO}) \text{ in slag residue} \times \text{weight of slag residue}}{(\text{mass}\%\text{FeO}) \text{ in initial slag} \times \text{weight of initial slag}} \times 100 \quad (2)$$

Phases found in residue slag were $2\text{CaO}\cdot\text{SiO}_2$, (Mg , Fe) O and liquid. Concentration of FeO in liquid was approximately 52 mass%, and P_2O_5 content was lower than 0.8 mass%. On the other hand, FeO content in solid $2\text{CaO}\cdot\text{SiO}_2$ phase was approximately 3 mass%, and P_2O_5 content was approximately 9 mass%. It can be clearly seen that P_2O_5 was concentrated in $2\text{CaO}\cdot\text{SiO}_2$ phase and FeO remained in the liquid phase. Liquid phase was successfully absorbed into the voids of the absorber, leaving the solid $2\text{CaO}\cdot\text{SiO}_2$ phase in the slag phase.

Recovery ratios of FeO for all experiments were approximately 90 %, and the efficiency was high. However, recovery rate of P_2O_5 for sintered CaO and Fe_2O_3 was around 40 % and it was not good as expected. The recovery rate of P_2O_5 using CaCO_3 tablet was 91 % and was much better than the other absorbers. The P_2O_5 content in slag after experiment was 5–7 mass%, and no large difference

Table 1 The average compositions of slag residue, absorbers, and observed phases

Sample	Phase	Mass%CaO	Mass%MgO	Mass%FeO	Mass%SiO ₂	Mass%P ₂ O ₅
Slag	Average	48.2	13.6	13.1	19.6	5.6
	2CaO·SiO ₂	60.4	0.2	3.0	26.6	9.8
	Liquid	44.5	0.6	52.2	1.9	0.8
	(Mg, Fe)O	0.9	81.2	17.4	0.4	0.2
CaO sintered at 1373 K	Average	94.0	0.9	3.2	1.7	0.2
	Liquid	48.4	0.4	48.3	2.4	0.5
	CaO	96.8	0.6	2.1	0.3	0.1
Slag	Average	49.7	12.1	11.9	20.0	6.3
	2CaO·SiO ₂	61.2	0.3	3.2	26.1	9.2
	Liquid	45.1	0.6	51.6	2.1	0.7
	(Mg, Fe)O	0.9	86.1	12.4	0.5	0.2
CaO sintered at 1673 K	Average	94.4	0.7	3.9	0.7	0.2
	Liquid	47.7	0.5	49.8	1.6	0.4
	CaO	96.7	0.7	2.1	0.3	0.2
Slag	Average	49.7	3.6	20.3	20.0	6.4
	2CaO·SiO ₂	59.4	0.7	1.9	28.5	9.5
	Liquid	43.8	1.0	52.4	2.6	0.3
	(Mg, Fe)O	0.9	85.8	12.4	0.8	0.12
Fe ₂ O ₃ sintered at 1373 K	Average	3.8	1.9	89.7	4.4	0.6
	2CaO·SiO ₂	57.0	0.1	5.6	27.6	9.8
	FeO	1.9	2.0	95.4	0.5	0.2
Slag	Average	45.8	6.4	9.1	31.9	6.9
	2CaO·SiO ₂	60.0	0.7	2.5	28.0	8.8
	Liquid	44.3	0.8	52.3	2.2	0.5
	(Mg, Fe)O	0.8	86.2	12.1	0.6	0.3
CaCO ₃ tablet	Average	91.0	1.0	4.2	3.8	0.1
	Liquid	46.4	0.6	51.2	1.6	0.1
	CaO	97.6	0.7	1.3	0.3	0.0

Fig. 2 SEM image of residue slag (*left*) and absorber (*right*) after experiment using CaO absorber sintered at 1373 K

between the type of absorbers was observed. However, amount of slag collected after experiment was clearly different. The weight of the remaining slag using CaCO₃ absorber was approximately two times compared with the other experiments.

The relation between estimated absorption ratio of liquid phase into absorber and the recovery ratio of FeO, P₂O₅ is shown in Fig. 6. Recovery ratio of P₂O₅ was estimated from

P distribution ratio between 2CaO·SiO₂ phase and liquid phase [5] and solid/liquid ratio at 1673 K estimated from CaO–FeO–SiO₂ phase diagram [17]. Recovery ratio of FeO is linear to the ratio of liquid phase absorption ratio into absorber and it was assumed that FeO solubility in solid phases can be neglected. Recovery ratio of P₂O₅ will decrease with increase of liquid phase absorption ratio into absorber, because liquid phase will contain P₂O₅ and it will

Fig. 3 SEM image of residue slag (*left*) and absorber (*right*) after experiment using CaO absorber sintered at 1673 K

Fig. 4 SEM image of residue slag (*left*) and absorber (*right*) after experiment using Fe_2O_3 absorber sintered at 1373 K

Fig. 5 SEM image of residue slag (*left*) and absorber (*right*) after experiment using CaCO_3 absorber

Table 2 Recovery ratio of P_2O_5 and FeO

Absorber	Initial slag weight (g)	Final slag weight (g)	Recovery ratio (%)	
			FeO	P_2O_5
CaO sintered at 1373 K	0.2014	0.0473	92	42
CaO sintered at 1673 K	0.2014	0.0393	94	40
Fe_2O_3 sintered at 1373 K	0.1977	0.0348	91	39
CaCO_3 tablet	0.1947	0.0791	89	91

be lost in the absorber. When the liquid phase is completely absorbed into absorber, the FeO recovery will be 100 % and P_2O_5 recovery will be estimated as 82 %. The FeO recovery ratio obtained in the present work was approximately 90 %, and the estimated P_2O_5 recovery will be approximately 85 %. However, recovery rate of P_2O_5 for sintered CaO and Fe_2O_3 was around 40 %. This discrepancy can be explained as follows. FeO-rich liquid phase was efficiently absorbed into the voids of the absorber, and at the same time, small $2\text{CaO}\cdot\text{SiO}_2$ particles were suggested to be also absorbed into the absorber. When CaCO_3 was used as an absorber, CO_2

gas was formed by CaCO_3 decomposition and avoided the liquid phase absorption at the early stage and the experiment. The average P_2O_5 content in absorber after experiment was 0.1 mass% when CaCO_3 absorber was used. This concentration is clearly lower than 0.2, 0.2, 0.6 mass% P_2O_5 using other type of absorbers, and this shows that more P_2O_5 was absorbed when compared with CaCO_3 tablet. It is suggested that during the period of CO_2 gas formation, the size of $2\text{CaO}\cdot\text{SiO}_2$ particles increased and separation efficiency of liquid phase and solid $2\text{CaO}\cdot\text{SiO}_2$ particles is improved as shown in Fig. 7.

It was shown from the present work that it is possible to separate FeO and P_2O_5 in steelmaking slag by physical separation of solid and liquid phases using capillary action. It is most efficient if FeO and P_2O_5 in steelmaking slag was

Fig. 6 Relation between estimated absorption ratio of liquid phase into absorber and the recovery ratio of FeO, P_2O_5

Fig. 7 Suggested difference between $CaCO_3$ and CaO absorber utilization

Fig. 8 Process image of onsite separation of steelmaking slag

separated onsite. Figure 8 shows a process image of onsite separation of steelmaking slag, and separated FeO and P_2O_5 can be reused as Fe and P resource. It should be emphasized that continuous research to reuse the FeO mixed with CaO as iron source and how to utilize P_2O_5 -rich phase as fertilizer and/or P ore substitute are required. Also, separation of FeO and P_2O_5 in steelmaking slag must be tested in large scale for industrial application.

Conclusion

The solid $2CaO \cdot SiO_2$ phase and FeO-rich liquid phase in steelmaking were separated by capillary action into sintered CaO, Fe_2O_3 , and $CaCO_3$ tablets. The liquid phase penetrated the absorber making separation of the solid $2CaO \cdot SiO_2$ phase and FeO-rich phase possible. It was

possible to recover 91 % of the P_2O_5 included in the initial slag as the $2CaO \cdot SiO_2$ phase by using $CaCO_3$ tablet. Also, 89 % of the FeO in steelmaking slag was able to be recovered in the $CaCO_3$ tablet. However, recovery of P_2O_5 using CaO and Fe_2O_3 sinter was approximately 40 % due to suggested P_2O_5 loss into absorber included in small $2CaO \cdot SiO_2$ particles. It was shown from the present work that it is possible to separate FeO and P_2O_5 in steelmaking slag by physical separation of solid and liquid phases using capillary action to be reused as Fe and P resource, respectively.

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