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Phosphate Capacities of $\text{CaO-FeO-SiO}_2\text{-Al}_2\text{O}_3/\text{Na}_2\text{O/TiO}_2$ Slags

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Abstract: To effectively increase the dephosphorization efficiency of hot metals or the previous stage in the converter steelmaking process, phosphate capacities ($C_{\text{PO}_4^{3-}}$) of $\text{CaO-FeO-SiO}_2\text{-Al}_2\text{O}_3/\text{Na}_2\text{O/TiO}_2$ slags at 1300–1400°C were examined by laboratory experiments using equilibrating slag and pure solid iron foil. The data suggested that ($C_{\text{PO}_4^{3-}}$) increases with decreasing temperature and increasing slag basicity. Compared to basicity, temperature considerably affected the phosphate capacities and tended to be the most important factor. The phosphate capacities of slag considerably decreased at a high temperature of 1400°C even under high binary basicity as well as high contents of Na_2O and FeO . Moreover, with the increase in the content of FeO and Al_2O_3 in the slag, ($C_{\text{PO}_4^{3-}}$) decreased. A low content of Na_2O led to the increase in the phosphate capacities of slag, particularly at low temperatures of 1300–1350°C. The content of TiO_2 in the slag considerably exhibited a weaker effect on ($C_{\text{PO}_4^{3-}}$). Furthermore, by regression analysis, ($C_{\text{PO}_4^{3-}}$) was expressed as a function of the temperature and slag compositions as follows:

$$\log C_{\text{PO}_4^{3-}} = 0.041(\% \text{CaO}) - 0.086 \log(\% \text{FeO}) - 0.024(\% \text{SiO}_2) - 0.02(\% \text{Al}_2\text{O}_3) + 0.067(\% \text{Na}_2\text{O}) + 0.039(\% \text{TiO}_2) + 56767/T - 14.58, (R = 0.978)$$

Keywords: phosphate capacity, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ -containing slag, thermodynamics, equilibrium experiments

Introduction

There is an increasing demand for high-quality steel with few impurities such as phosphorus. In the current

converter steelmaking process, it is increasingly expected to achieve a high phosphorus removal ratio as early as possible because the over-oxidation caused by dephosphorization toward the end of the process significantly deteriorates the purity of the molten steel, leading to a high oxygen content; therefore, a large number of inclusions are formed. In reality, the removal of phosphorus is thermodynamically favorable before the occurrence of considerable decarburization (the previous stage in the steelmaking process) because of the relatively low temperature and high activity coefficient of phosphorus in the metal phase. However, in this stage, the typical steelmaking slag, i.e., the CaO-FeO-SiO_2 -based system, generally exhibits poor fluidity because of its high melting point and low temperatures (1300–1400°C), which considerably limit the increase in the dephosphorization efficiency.

Meanwhile, fluxes are typically added to slag to decrease its melting point, improve the solubility of lime, and enhance the kinetic efficiency of dephosphorization. Historically, CaF_2 has been widely used as an additive to decrease the melting point of the slag. However, currently, its use has been considerably restricted because of its toxic effects on human health. Alternatively, the increase in the FeO content is a typical solution for decreasing the melting point of the slag. However, this method leads to a considerable loss of iron. The development of a fluoride-free steelmaking slag has been attracting increasing attention. Previously, the effects of additives such as Al_2O_3 , Na_2O , MnO , and MgO on the properties of the CaO-FeO-SiO_2 slag, as well as its dephosphorization ability, have been examined [1–5]. Diao has measured the melting temperature of CaF_2 -free $\text{CaO-Fe}_2\text{O}_3\text{-Na}_2\text{O-Al}_2\text{O}_3$ dephosphorization slag by the hemisphere method. The results revealed that Na_2O and Al_2O_3 decrease the melting temperature to less than 1200°C [1]. Li has reported the dephosphorization of molten steel using MgO -saturated $\text{CaO-FeO-SiO}_2\text{-Na}_2\text{O}$ slag at 1550°C and 1600°C and found that the phosphate capacity increases with the increase in the Na_2O content. In contrast, the addition of Al_2O_3 to the slag thermodynamically decreases the phosphate capacity [2]. Pak and Fruehan have reported that the addition of small amounts of Na_2O to conventional steelmaking slags considerably improves the dephosphorization rate [3]. Jung et al. have reported that the phosphorus distribution ratio between

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CaO–MgO_{sat}–SiO₂–Al₂O₃–FeO–MnO–P₂O₅ ladle slag and liquid iron increases with the increase in the MnO content at 1600°C [4]. As can be observed, the above study mainly focused on the removal of phosphorus from molten steel at high temperatures of 1550–1600°C. Hence, under hot metal conditions, fluxes such as Al₂O₃, Na₂O, MnO, and MgO considerably contribute to the improvement of slag fluidity and increase of the dephosphorization efficiency at low temperatures of 1300–1400°C. Simeonov and Sano have examined the phosphate capacities of CaO–CaF₂–SiO₂–MnO–BaO and CaO–CaF₂–SiO₂–MnO–Na₂O slags under hot-metal conditions and found that BaO and Na₂O increase the phosphate capacities of the slags [5]. Liu et al. have reported that the addition of Al₂O₃ decreases the phosphorus distribution ratio between BaO–BaF₂–MnO–Al₂O₃ slag and carbon-saturated ferromanganese at 1300°C [6]. The experimental results from the study of Li revealed that the dephosphorization ability of CaO–SiO₂–FeO–P₂O₅-based slags increased on adding Na₂O and K₂O [7]. Apart from the studies described above, studies on the effects of Al₂O₃, Na₂O, and other similar materials on the ability of CaO–FeO–SiO₂-based slag to remove phosphorus under hot-metal conditions at low temperatures of 1300–1400°C are considerably limited to the best of our knowledge.

To examine the feasibility of using Al₂O₃/Na₂O-containing materials as fluxes of CaO–FeO–SiO₂-based slag and to effectively increase the dephosphorization efficiency in the previous stage of the converter steelmaking process or under hot-metal conditions, the phosphate capacities of CaO–FeO–SiO₂–Al₂O₃/Na₂O/TiO₂ slags at 1300–1400°C were estimated. As the FeO in the slag can react with the carbon dissolved in the liquid metal, a direct equilibrium state between the FeO-containing slag and carbon-saturated iron cannot be achieved. Accordingly, the method developed by IM et al [8]. has been employed in this study for measuring the phosphorus distribution ratios between slags and iron foil instead of those between slags and hot metal. Then, the phosphate capacity of the slag was obtained by utilizing the phosphorus distribution ratio data between the slag and iron foil.

Principles

Definition of phosphate capacity

Phosphate capacity is an important indicator of the dephosphorization ability of slag. According to Wagner,

dephosphorization can be expressed as shown in eq. (1). The phosphate capacity of the slag was defined by Wagner and expressed in eq. (2) [9].

$$C_{PO_4^{3-}} = \frac{(\%PO_4^{3-})}{P_{P_2}^{1/2} \cdot P_{O_2}^{5/4}} \quad (2)$$

Here, (%PO₄³⁻) is the weight percent of PO₄³⁻ dissolved in the slag; P_{O₂} is the partial pressure of oxygen, and P_{P₂} is the partial pressure of phosphorus. To get the value of P_{P₂}, the eq. (3) is introduced [8]. G_Y⁰ is the standard Gibbs free energy of P_{in γ-Fe}, which can be calculated using eq. (5) [10]. G_{P₂}⁰ is the standard Gibbs free energy of P_{P₂}, whose values at 1300, 1350, and 1400°C are –250,446, –263,147, and –276,217 J/mol, respectively (extracted from FactSage 7.0). Then, by substituting eq. (4) into eq. (2), the logarithmic form of the phosphate capacity can be obtained as shown in eq. (6).

$$\frac{1}{2}P_2(g) = [P]_{in \gamma-Fe} \Delta G_1^0 = G_Y^0 - G_{P_2}^0 \text{ (J/mol)} \quad (3)$$

$$K_1 = \frac{[\%P]}{P_{P_2}^{1/2}} \quad (4)$$

$$G_Y^0 = -128520 + 32.677T + RT \ln [\%P] \text{ (J/mol)} \quad (5)[10]$$

$$\log C_{PO_4^{3-}} = \log L_P + \log (MM_{PO_4^{3-}} / MM_P) - \log P_{O_2}^{5/4} + \log K_1 \quad (6)$$

Here, MM_{PO₄³⁻} / MM_P is the ratio of the molar mass of phosphate in the slag and phosphorus in the metal, which is equal to 3.07. P_{O₂} is determined by the activity of FeO from eqs. (7) and (8) [11, 12]. Where a_{Fe} = 1 for the pure solid iron. L_P, which is expressed in eq. (9), is the phosphorus distribution ratio between the slag and metal at equilibrium, and it is experimentally determined. (%P) and [%P] are the contents of phosphorus in the slag and the solid iron, respectively.

$$\text{Fe(s)} + 1/2 \text{O}_2(\text{g}) = (\text{FeO}), \Delta G_2^0 = 10.73T - 54501(\text{cal/mol}), \quad [12](7)$$

$$K_2 = \frac{a_{\text{FeO}}}{a_{\text{Fe}} (\text{P}_{\text{O}_2})^{1/2}} \quad (8)$$

$$L_P = \frac{(\%P)}{[\%P]} \quad (9)$$

Calculation of the activity of FeO in CaO–FeO– SiO₂– Al₂O₃– Na₂O–TiO₂– P₂O₅ slag system

According to eq. (6), P_{O_2} and L_P are important factors for obtaining $(\text{C}_{\text{PO}_4^{3-}})$. P_{O_2} is determined by the activity of FeO ($(\text{C}_{\text{PO}_4^{3-}})$) using eqs. (7) and (8). L_P between the slag and solid iron foil can be obtained from slag–metal equilibrium experiments. Hence, $(\text{C}_{\text{PO}_4^{3-}})$ for slag needs to be first known for obtaining $(\text{C}_{\text{PO}_4^{3-}})$. In this study, $(\text{C}_{\text{PO}_4^{3-}})$ was calculated using the thermodynamic model of the ion and molecule coexistence theory (IMCT).

IMCT was originally developed to reflect the reaction ability of components in the metallurgical slag according to the defined mass action concentrations, N_i , of the structural units or ion couples in terms of the mass action law. The defined N_i in the structural unit or ion couples in the slag has been verified to be consistent with the reported activities of the components relative to the pure solid or liquid in the standard state. The basic hypothesis of the IMCT- N_i thermodynamic model for calculating the N_i of the structural units or ion couples in the metallurgical slag has been reported in detail elsewhere [13, 14]. The chemical formulae of the possibly formed complex molecules, their standard molar Gibbs free energies, and standard reaction equilibrium constants K_i were obtained from the database of the thermodynamic computing software FactSage and previous studies [14–16]. For the process of model establishment and calculation, please refer to the classical references on the IMCT thermodynamic model reported in detail elsewhere [13–16].

To verify the accuracy of the calculation model based on the IMCT, values of $(\text{C}_{\text{PO}_4^{3-}})$ measured and those estimated from the model for different slag systems were compared (Figure 1). Espejo [17] and Ogura [18] have independently measured the activity of FeO in the CaO–Al₂O₃–FeO_t and CaO–SiO₂–FeO_t slags at 1400°C. The results obtained from the calculation model of the

Figure 1: Comparison of the calculated and observed values of $(\text{C}_{\text{PO}_4^{3-}})$.

IMCT were in reasonable agreement with the measured values of $(\text{C}_{\text{PO}_4^{3-}})$ (Figure 1), indicating that the model for calculating $(\text{C}_{\text{PO}_4^{3-}})$ is credible.

Experiments

Samples

The materials and chemical reagents included iron foil, CaO, Fe₃O₄, SiO₂, Al₂O₃, Na₂SiO₃, TiO₂, and P₂O₅. High-purity iron foil (0.1 mm thickness, mass Fe > 99.999%) was used, and the content of P in the iron foil was less than 0.0001 mass%. FeO was produced by the reduction of Fe₃O₄ under CO (flow rate: 3 L/min) for 5 h at 900°C and subsequent quenching under pure argon. After cooling, the solid material was ground to a particle size of 200 μm. The sample was analyzed by X-ray diffraction (XRD). The XRD pattern confirmed that high-purity FeO is obtained. Na₂O in the form of Na₂SiO₃ was added to prevent the evaporation during the high-temperature process [3]. The P₂O₅ content was maintained constant in all experiments conducted in a group but was changed between experimental groups. CaO was dried in a drying box at 120°C for 24 h before use.

The slag sample was formed by mixing CaO, FeO, SiO₂, P₂O₅, Al₂O₃, Na₂SiO₃, and TiO₂ in a porcelain mortar. After mixing well, the slagging agent was dried at 120°C for 24 h and then formed into cylindrical pellets using a presser.

Table 1 summarizes all the experimental results including the slag and metal compositions. For experiments

Table 1: The statistics of slag iron composition at the end of experiment.

No.	Variable	Slag specimen and iron foil composition (wt/%)								R	(C _{PO₄³⁻})	(C _{PO₄³⁻})		
		CaO	FeO	SiO ₂	Al ₂ O ₃	Na ₂ O	TiO ₂	(P)	[P] ^{Fe-γ}					
1	1300°C Al ₂ O ₃	29.85	34.05	29.10	0.14	0	0	2.105	0.005	1.0	421	22.11		
2		29.29	33.51	28.71	3.35	0	0	2.103	0.0078	1.0	270	21.94		
3		28.15	32.43	28.11	6.15	0	0	2.137	0.013	1.0	164	21.76		
4		26.75	31.14	26.96	10.05	0	0	2.091	0.019	1.0	110	21.61		
5		25.43	30.11	25.64	13.42	0	0	2.202	0.023	1.0	88	21.54		
6	1300°C Na ₂ O	28.85	31.95	28.28	0	0.08	0	4.507	0.027	1.0	167	21.90		
7		27.85	31.45	28.21	0	1.61	0	4.575	0.02	1.0	229	21.99		
8		27.31	30.71	27.67	0	3.35	0	4.623	0.01	1.0	462	22.24		
9		26.29	29.00	26.63	0	4.95	0	4.701	0.0085	1.0	553	22.28		
10		25.91	28.96	26.56	0	6.94	0	4.903	0.0067	1.0	732	22.35		
11	1300°C TiO ₂	29.85	34.05	29.10	0	0	0.01	2.105	0.005	1.0	421	22.11		
12		29.51	33.25	29.40	0	0	2.06	2.219	0.0057	1.0	389	22.18		
13		29.49	33.60	28.54	0	0	4.03	2.174	0.0062	1.0	351	22.15		
14		27.68	32.08	28.84	0	0	5.90	2.149	0.0065	1.0	331	22.26		
15		27.06	30.80	28.22	0	0	7.81	2.235	0.0073	1.0	306	22.31		
16	1300°C FeO	29.41	12.31	28.22	11.77	4.33	2.27	4.59	0.044	1.0	104	22.24		
17		25.24	20.40	26.50	11.11	3.93	1.97	4.615	0.042	1.0	110	21.89		
18		21.17	29.55	23.50	9.72	3.64	1.59	4.603	0.035	0.9	132	21.73		
19		18.15	37.52	19.67	7.34	3.49	1.32	4.463	0.019	0.9	235	21.77		
20		14.31	45.27	17.20	6.38	3.00	1.04	4.554	0.025	0.8	182	21.55		
21	1300°C Basicity, R	19.66	35.97	20.90	7.87	3.06	1.40	4.417	0.013	0.9	340	21.98		
22		17.40	36.75	22.70	7.67	3.13	1.38	4.413	0.032	0.8	138	21.63		
23		14.78	37.92	24.88	7.36	3.01	1.40	4.422	0.07	0.6	63	21.35		
24		11.41	38.56	28.26	7.15	2.75	1.40	4.438	0.18	0.4	25	21.07		
25		7.10	40.32	32.18	7.06	2.66	1.37	4.407	0.62	0.2	7	20.66		
26	T/°C	1300	15.70	27.55	16.86	14.22	5.03	6.07	4.514	0.027	0.9	167	21.95	
27			19.11	26.84	20.10	14.11	3.36	4.22	5.226	0.033	1.0	158	21.97	
28			24.71	22.53	27.33	10.27	2.33	2.20	4.517	0.064	0.9	71	21.71	
29			21.07	21.06	22.49	17.67	3.29	3.20	4.762	0.075	0.9	64	21.70	
30			18.08	29.39	19.26	13.73	3.52	4.19	5.047	0.03	0.9	168	21.92	
31		1350	14.26	33.84	15.81	11.45	5.80	5.97	5.067	0.014	0.9	362	22.17	
32			22.83	26.93	23.83	3.41	5.09	6.21	4.972	0.011	1.0	452	22.41	
33			21.51	24.98	21.95	10.32	4.17	5.18	5.086	0.028	1.0	182	22.05	
34			20.05	23.39	20.98	16.31	2.52	5.32	4.857	0.063	1.0	77	21.81	
35			19.70	29.37	20.54	13.67	1.69	2.20	5.058	0.055	1.0	92	21.66	
36			18.13	29.84	19.79	14.02	4.76	2.10	4.702	0.032	0.9	147	20.91	
37			17.85	25.16	19.12	14.03	8.79	2.02	4.463	0.012	0.9	372	21.34	
38			25.86	24.57	23.95	8.31	4.01	2.18	4.723	0.038	1.1	124	20.91	
39			27.83	25.29	23.37	6.25	3.08	3.23	4.678	0.025	1.2	187	21.08	
40			29.44	26.28	23.27	6.28	1.62	2.16	4.678	0.03	1.3	156	20.97	
41	1400		27.73	22.14	22.63	9.88	7.82	5.93	1.666	0.0035	1.2	499	21.49	
42			30.77	22.13	19.26	9.99	7.99	5.96	1.677	0.0021	1.6	832	21.64	
43			33.44	22.28	16.55	9.88	7.98	5.99	1.682	0.0015	2.0	1164	21.75	
44			35.29	22.32	14.71	9.93	7.89	5.97	1.671	0.0012	2.4	1455	21.84	
45			36.31	15.13	18.14	10.95	8.76	6.57	1.702	0.0022	2.0	794	21.83	
46			34.22	20.33	17.03	10.27	8.02	6.11	1.713	0.002	2.0	873	21.68	
47			28.63	31.01	14.76	8.92	7.34	5.35	1.685	0.0016	1.9	1092	21.53	
48			25.02	40.59	12.21	7.57	6.15	4.54	1.696	0.0014	2.0	1247	21.46	
49			20.32	50.64	10.16	6.22	4.97	3.73	1.716	0.002	2.0	873	21.19	
50			18.52	28.22	20.54	14.11	4.90	2.09	4.914	0.065	0.9	76	19.87	
51			16.10	27.25	20.42	14.91	8.33	2.20	4.394	0.034	0.8	129	20.10	
52			25.96	25.58	23.40	7.31	3.87	2.17	4.937	0.07	1.1	71	19.84	
53			27.87	24.26	23.95	6.52	2.99	3.21	4.678	0.058	1.2	81	19.95	
54			29.53	25.68	23.83	6.43	1.56	2.16	4.544	0.061	1.2	75	19.86	

Nos. 1–15, quaternary $\text{CaO-FeO-SiO}_2\text{-Al}_2\text{O}_3/\text{Na}_2\text{O/TiO}_2$ slag systems were used to verify the effects of Al_2O_3 , Na_2O , and TiO_2 on the phosphate capacity of slag. For experiments Nos. 16–54, the six-component slag system $\text{CaO-FeO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-TiO}_2$ was used, and the effects of the temperature, binary basicity, and FeO content were examined.

Apparatus and procedure

Figure 2 shows the schematic of the experimental apparatus used, which included a horizontal electric resistance furnace, a water-cooling system, and an associated purification plant for argon. The furnace equipped with MoSi_2 heating elements was controlled by a PID controller using a Pt–30%Rh/Pt–6%Rh thermocouple as the sensor, which was calibrated before use. The temperature of the furnace was controlled at 25–1700°C within $\pm 1^\circ\text{C}$. The equilibrium experiments were conducted under pure argon. The associated purification plant for argon consisted of allochroic silica gel for dehydration and magnesium and copper chips (heated to 500°C) for deoxidation.

First, 20 g of the slagging pellets were added into an Armco iron crucible (mass Fe > 99.8%, with an outer diameter of 27 mm, inner diameter of 25 mm, and a height of 31 mm). With the addition of the pellets in the crucible, 2 g of iron foil was cut into suitable pieces and placed in the gap between every two pellets. Each porcelain boat could hold five iron crucibles, which was placed in the heating zone and tied by a molybdenum wire. Then, argon (flow: 400 mL/min) was allowed to flow, and the furnace was switched on. In this study, the target temperatures were 1300°C, 1350°C, and 1400°C. The melt was equilibrated for 8–12 h. Previously, IM and MORIT [8] have determined that this equilibration time is sufficiently long to establish equilibrium. An equilibration time of 12 h was utilized herein. After equilibration, the porcelain boat was rapidly placed into the cooling zone under argon. The samples were quenched and removed from the furnace.

Analysis

After the iron pieces were cooled, the pieces were separated from the slag. Next, the slag was ground to a particle size of 200 μm and analyzed by X-ray fluorescence. As the presence of even a small amount of the

slag in the iron phase can lead to significant errors in the phosphorus content, the iron foil pieces were carefully polished using a stainless-steel brush. Finally, the pieces were ultrasonically cleaned in a citric acid/acetone mixture and subsequently in deionized water. The content of P in the cleaned iron foil pieces was analyzed by the molybdenum blue colorimetric method. Then, L_P was determined, and $(C_{\text{PO}_4^{3-}})$ was calculated using the thermodynamic model of IMCT. Finally, $C_{\text{PO}_4^{3-}}$ was determined using eq. (6).

Results and discussion

Effect of temperature on $(C_{\text{PO}_4^{3-}})$

Figure 3 shows the dependence of temperature on the phosphate capacity. Figure 3(a) shows the results obtained from experiment Nos. 36–40 and 50–54 in Table 1. For these experiments, the slag composition was similar. For similar slag compositions, $(C_{\text{PO}_4^{3-}})$ decreased with increasing temperature (Figure 3(a)). This result is in good agreement with the thermodynamic predictions for dephosphorization, which is exothermic and hence occurs at low temperatures. Wrampelmeyer [19] has measured and calculated the phosphate capacity of $\text{CaO-FeO-Al}_2\text{O}_3$ slag at 1550, 1600, and 1700°C. The results from his study indicate that the phosphate capacity decreases with increasing temperature, which is in agreement with that reported herein.

Figure 3(b) shows the dependence of the phosphate capacity on the temperature for the complete six-component slag system (Nos. 16–54 in Table 1). Although their composition significantly varied, $(C_{\text{PO}_4^{3-}})$ clearly decreased with increasing temperature, suggesting that temperature exerts a more significant effect on $(C_{\text{PO}_4^{3-}})$ compared to the other influencing factors. However, from Figure 3(b), the data encircled by a solid line (Nos. 23–25 in Table 1) revealed considerably lower phosphate capacities even at a low temperature of 1300°C because these samples exhibited low basicity ($0.2 \leq R < 0.8$, $R = (\text{CaO}\%)/(\text{SiO}_2\%)$). This result suggested that an extremely low basicity ($R < 0.8$) leads to an extremely weak phosphate fixing ability, related to the fact that extremely limited CaO is available for combination with P_2O_5 in the slag (as most of the CaO is assumed to combine with SiO_2).

Figure 2: Schematic of the experiment setup (1-heating zone; 2-iron crucible; 3-thermocouple; 4-porcelain boat composed of Al_2O_3 ; 5-water-cooling device; 6-magnesium pieces; 7-copper pieces; 8-molecular sieve; 9-allochroic silica gel).

Figure 3: Effect of temperature on $(C_{\text{PO}_4^{3-}})$: (a) Samples for Nos. 36–40 and 50–54 in Table 1 and (b) Samples for Nos. 16–54 in Table 1.

Effect of the slag basicity

Figure 4 shows the effect of the binary basicity on $(C_{\text{PO}_4^{3-}})$. Figure 4(a) summarizes the results from the two experimental groups, Nos. 21–25 and 41–44, in Table 1: Both groups showed similar compositions of $\text{FeO-Al}_2\text{O}_3\text{-Na}_2\text{O-TiO}_2$ but different $(\% \text{CaO})/(\% \text{SiO}_2)$ values. With increasing the binary basicity at 1300°C and 1350°C, $(C_{\text{PO}_4^{3-}})$ increased. Similar results have been reported by Im et al. [8] during their study on the phosphate capacity of $\text{CaO-FeO-SiO}_2\text{-P}_2\text{O}_5$ with basicities of 0.5–1.0 at 1300°C. However, a larger slope between $(C_{\text{PO}_4^{3-}})$ and basicity was observed at low temperature (1300°C) and low basicities

($R=0.2\text{--}1.0$, black rectangle solid points in Figure 4(a)). Moreover, $(C_{\text{PO}_4^{3-}})$ was 22.0 at a low basicity of 0.9 but at a low temperature (1300°C). This value is greater than that in all cases in which the basicity of slag ranges from 1.2 to 2.4 but at a high temperature (1350°C, $(C_{\text{PO}_4^{3-}})$). This result indicated that under conditions of a slag basicity greater than 0.9, temperature considerably affects $(C_{\text{PO}_4^{3-}})$ compared to basicity.

This result was further verified by the data shown in Figure 4(b), indicating the dependence of the binary basicity on $(C_{\text{PO}_4^{3-}})$ for all of the six-component slag samples under different compositions and temperatures (Nos. 16–54 in Table 1). Even the dependencies of the basicity

Figure 4: Dependence of $(C_{PO_4^{3-}})$ on the slag binary basicity: (a) Samples for Nos. 21–25 and 41–44 in Table 1 and (b) Samples for Nos. 16–54 in Table 1.

Figure 5: Effect of Na_2O on $(C_{PO_4^{3-}})$: (a) Samples for Nos. 6–10 in Table 1 and (b) Samples for Nos. 6–10 and 16–54 in Table 1.

were similar to those observed in Figure 5(a). The largest $(C_{PO_4^{3-}})$ was observed for $R=1.0$ at 1300°C (pink triangle solid points), while the lowest values were observed at $R=0.8\text{--}1.2$ at 1350°C (Nos. 50–54 in Table 1) despite the large variation in the basicity ($R=0.2\text{--}2.4$). This result indicated that temperature exerts a stronger effect on $(C_{PO_4^{3-}})$ compared to basicity and tends to be the most important influencing factor under the conditions utilized herein.

Effect of the content of Na_2O in slag

Figure 5(a) show the dependence of $(C_{PO_4^{3-}})$ on the content of Na_2O in the slag while simultaneously maintaining the temperature and other slag constituents constant (Nos. 6–10 in Table 1, quaternary slags). With increasing Na_2O content, $(C_{PO_4^{3-}})$ increased linearly. With the increase in the Na_2O content from 0.08% to 6.94%, $(C_{PO_4^{3-}})$ increased by approximately 0.44. The same trend has been reported by Diao and Li et al. [1, 2]. With the increase in the Na_2O content by 2.3% at 1350°C in the former study, $(C_{PO_4^{3-}})$

increases by 0.416. With the increase in the Na_2O content by 4.07% at 1600°C in the latter study, $(C_{PO_4^{3-}})$ increases by 0.31. In general, the comparison of the three studies showed that Na_2O significantly affects the phosphate capacity.

Figure 5(b) shows the dependence of the phosphate capacity on the Na_2O content for all of the Na_2O -containing six-component slag system samples (Nos. 6–10 and 16–54 in Table 1). As can be observed from the figure, the phosphate capacity was considerably affected ($(C_{PO_4^{3-}})=21.98$, $(C_{PO_4^{3-}})=21.35$) even with an almost constant content of Na_2O ($Na_2O=3.06\%$, $Na_2O=3.01\%$) because of the variations in the other factors such as the basicity and temperature. However, a clear trend was still observed with the exception of cases at temperatures less than 1400°C : $(C_{PO_4^{3-}})$ increased with increasing Na_2O content, indicating that the Na_2O content also significantly affects dephosphorization. On the other hand, the lowest $(C_{PO_4^{3-}})$ was still observed for experiments conducted at a high temperature of 1400°C despite the large variation in the Na_2O content ($Na_2O\%=0.08\%\text{--}8.33\%$). Further, this result strongly suggested that temperature

exerts the most significant effect. A high temperature of 1400°C considerably decreases the phosphate capacity of slag.

Effect of FeO content

Figure 6(a) (data from No. 16–20 and 45–49 in Table 1) shows the effect of the FeO content on $(C_{\text{PO}_4^{3-}})$, where the concentrations of all of the other slag constituents were nearly unchanged at a constant temperature. With the increase in the FeO content, $(C_{\text{PO}_4^{3-}})$ decreased. With the increase in the FeO content from 12.3% to 45.3% at $R=1$ (1300°C) and from 15.1% to 50.64% at $R=2$ (1350°C), $(C_{\text{PO}_4^{3-}})$ decreased by 0.69 and 0.64, respectively. Nakamura [20] and Wrampelmeyer [19] have calculated the phosphate capacities for the $\text{CaO}_{\text{satd.}}-\text{BaO}-\text{SiO}_2-\text{Fe}_t\text{O}$ slag system at 1600°C and the $\text{CaO}-\text{FeO}_t-\text{Al}_2\text{O}_3$ slag system at 1550°C, 1600°C, and 1700°C. The results of the two studies revealed that $(C_{\text{PO}_4^{3-}})$ linearly decreases with the increase in the FeO content. This result is consistent with those obtained from this study. The phosphate capacity reported by Nakamura is considerably higher than that reported by Wrampelmeyer because of the addition of strong alkaline substances such as BaO in the $\text{CaO}_{\text{satd.}}-\text{BaO}-\text{SiO}_2-\text{Fe}_t\text{O}$ slag system.

Figure 6(b) shows the dependence of the phosphate capacity on the FeO content with various slag components and temperatures (Nos. 16–54 in Table 1). With the exception of cases at a temperature of 1400°C, $(C_{\text{PO}_4^{3-}})$ decreased with the increase in the FeO content, even with a large fluctuation, because of the different parameters, e. g., variation in basicity and temperature. This result revealed that the FeO content in slag acts as another important factor and the high FeO content does not lead to the improvement in the phosphate capacity. Generally, the

high FeO content leads to the increase in the dephosphorization efficiency. Actually, the dephosphorization of hot metal or liquid steel is divided into two steps: first, P in the metal phase was oxidized to P_2O_5 by the dissolved oxygen (eq. (10)), and then, P_2O_5 was fixed in the slag phase via the combination of basic materials such as CaO to form $3\text{CaO} \cdot \text{P}_2\text{O}_5$ and $4\text{CaO} \cdot \text{P}_2\text{O}_5$ (eq. (11)). A high content of FeO in slag promoted the performance of the first step via the increase in the oxygen activity of the metal phase to push the equilibrium of eq. (10) to the right side. However, the phosphate capacity theoretically reflects the phosphorus fixing ability of slag, and basic materials such as CaO play an important role for the fixation of phosphorus. The phosphate capacity increased with basicity. The high FeO content decreased the amount of the available CaO, thereby retarding the reaction in eq. (11). Hence, the phosphate capacity decreases with the increase in the FeO content.

Effects of the content of Al_2O_3 and TiO_2

Figure 7(a) and (b) show the effects of the Al_2O_3 content on $(C_{\text{PO}_4^{3-}})$ while simultaneously maintaining the remaining components of the slag and temperature constant (Nos. 1–5 in Table 1, quaternary slags) and under varying similar conditions (Nos. 1–5 and 16–54 in Table 1), respectively. With the increase in the Al_2O_3 content, $(C_{\text{PO}_4^{3-}})$ decreased. This result is in agreement with that

Figure 6: Effect of FeO on $(C_{\text{PO}_4^{3-}})$: (a) Samples for Nos. 16–20 and 45–49 in Table 1 and (b) samples for Nos. 6–10 and 16–54 in Table 1.

Figure 7: Effects of Al_2O_3 and TiO_2 on $(C_{PO_4^{3-}})$: (a) Samples for Nos. 1–5 in Table 1 and (b) samples for Nos. 1–5 and 16–54 in Table 1, and (c) samples for Nos. 11–54 in Table 1.

reported by Diao and Li et al. (Figure 7(a)). [1, 2] According to the ionic theory of slags, $(C_{PO_4^{3-}})$ replaces $(C_{PO_4^{3-}})$ and then precipitates as $Ca_3(PO_4)_2$ during dephosphorization. At the same time, $(C_{PO_4^{3-}})$ is replaced by $(C_{PO_4^{3-}})$. At an extremely high Al_2O_3 content, the precipitation of $(C_{PO_4^{3-}})$ is suppressed, which adversely affects the fixing of $(C_{PO_4^{3-}})$ in slag. In this case, Al_2O_3 exhibited the characteristics of an acidic oxide [21]. Figure 7(c) shows the dependency of phosphate on the content of TiO_2 in the slag. The content of TiO_2 in the slag exerted a considerably weaker effect on $(C_{PO_4^{3-}})$ compared to other factors of temperature, basicity, and other slag components, e. g., FeO, Na_2O , and Al_2O_3 content.

Regression analysis of $(C_{PO_4^{3-}})$

Based on the data from Nos. 16–54 in Table 1, $(C_{PO_4^{3-}})$ was fitted as a function of various factors of temperature and the slag composition, i.e., of CaO, SiO₂, Al_2O_3 , Na_2O , TiO_2 , and FeO content using the Statistical Product and Service Solutions (SPSS) software [22], expressed in

Figure 8: Comparison of the observed values of $(C_{PO_4^{3-}})$ and the fitted curve.

eq. (12). Figure 8 shows the calculation data using eq. (12) and the experimental results, which showed good agreement.

$$\log C_{\text{PO}_4^{3-}} = 0.041(\% \text{CaO}) - 0.086 \log(\% \text{FeO}) - 0.024(\% \text{SiO}_2) - 0.02(\% \text{Al}_2\text{O}_3) + 0.067(\% \text{Na}_2\text{O}) + 0.039(\% \text{TiO}_2) + 56767/T - 14.58, (R = 0.978)$$

(12)

Conclusions

The phosphate capacities of the CaO–FeO–SiO₂–Al₂O₃/Na₂O/TiO₂ slag at temperatures of 1300°C–1400°C were examined by conducting equilibrating experiments with a pure solid iron foil. Based on the experimental data obtained, the following conclusions were drawn.

- (1) According to the slag coexistence theory, the calculation model for the FeO activity is established. The comparison of the calculated and observed values for the FeO activity in different slag systems verifies the accuracy of the model.
- (2) ($C_{\text{PO}_4^{3-}}$) increases with the decrease in temperature and increase in the slag basicity. Temperature exhibits a considerably higher effect compared to basicity and tended to be the most important factor. A high temperature of 1400°C considerably decreases the phosphate capacities of slag even under high binary basicity as well as high contents of Na₂O and FeO.
- (3) With the increase in the content of FeO and Al₂O₃ in slag, ($C_{\text{PO}_4^{3-}}$) decreases. A low Na₂O content leads to increased phosphate capacities of slag, particularly at low temperatures of 1300–1350°C. The content of TiO₂ in the slag exhibits a weaker effect on ($C_{\text{PO}_4^{3-}}$).
- (4) Based on the experimental data, using regression analysis, ($C_{\text{PO}_4^{3-}}$) is expressed as a function of the temperature and concentration of the slag components, expressed as follows:

$$\log C_{\text{PO}_4^{3-}} = 0.041(\% \text{CaO}) - 0.086 \log(\% \text{FeO}) - 0.024(\% \text{SiO}_2) - 0.02(\% \text{Al}_2\text{O}_3) + 0.067(\% \text{Na}_2\text{O}) + 0.039(\% \text{TiO}_2) + 56767/T - 14.58, (R = 0.978)$$

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