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Phosphate Capacities of CaO–FeO–SiO₂–Al₂O₃/Na₂O/TiO₂ 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 \((C_{\text{PO}_4^{-1}})\) of \((\text{CaO}–\text{FeO}–\text{SiO}_2–\text{Al}_2\text{O}_3/\text{Na}_2\text{O}/\text{TiO}_2)\) slags at 1300–1400°C were examined by laboratory experiments using equilibrating slag and pure solid iron foil. The data suggested that \((C_{\text{PO}_4^{-1}})\) 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 \(\text{Na}_2\text{O}\) and \(\text{FeO}\). Moreover, with the increase in the content of \(\text{FeO}\) and \(\text{Al}_2\text{O}_3\) in the slag, \((C_{\text{PO}_4^{-1}})\) decreased. A low content of \(\text{Na}_2\text{O}\) led to the increase in the phosphate capacities of slag, particularly at low temperatures of 1300–1350°C. The content of \(\text{TiO}_2\) in the slag considerably exhibited a weaker effect on \((C_{\text{PO}_4^{-1}})\). Furthermore, by regression analysis, \((C_{\text{PO}_4^{-1}})\) was expressed as a function of the temperature and slag compositions as follows:

\[
\log C_{\text{PO}_4^{-1}} = 0.041(\%\text{CaO}) - 0.086\log(\%\text{FeO}) - 0.024(\%\text{SiO}_2)
- 0.02(\%\text{Al}_2\text{O}_3) + 0.067(\%\text{Na}_2\text{O}) + 0.039(\%\text{TiO}_2)
+ 56767/T - 14.58, \quad (R = 0.978)
\]

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–SiO₂-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, \(\text{CaF}_2\) 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 \(\text{FeO}\) 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 \(\text{Al}_2\text{O}_3\), \(\text{Na}_2\text{O}\), \(\text{MnO}\), and \(\text{MgO}\) on the properties of the CaO–FeO–SiO₂ slag, as well as its dephosphorization ability, have been examined [1–5]. Diao has measured the melting temperature of \(\text{CaF}_2\)-free \(\text{CaO}–\text{FeO}–\text{SiO}_2–\text{Al}_2\text{O}_3\) dephosphorization slag by the hemisphere method. The results revealed that \(\text{Na}_2\text{O}\) and \(\text{Al}_2\text{O}_3\) decrease the melting temperature to less than 1200°C [1]. Li has reported the dephosphorization of molten steel using MgO-saturated CaO–FeO–SiO₂–Na₂O slag at 1550°C and 1600°C and found that the phosphate capacity increases with the increase in the Na₂O content. In contrast, the addition of \(\text{Al}_2\text{O}_3\) to the slag thermodynamically decreases the phosphate capacity [2]. Pak and Fruehan have reported that the addition of small amounts of \(\text{Na}_2\text{O}\) to conventional steelmaking slags considerably improves the dephosphorization rate [3]. Jung et al. have reported that the phosphorus distribution ratio between
CaO–MgO–SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$–MnO–P$_2$O$_5$ 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 Al$_2$O$_3$, Na$_2$O, 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–CaF$_2$–SiO$_2$–MnO–BaO and CaO–CaF$_2$–SiO$_2$–MnO–Na$_2$O slags under hot-metal conditions and found that BaO and Na$_2$O increase the phosphate capacities of the slags [5]. Liu et al. have reported that the addition of Al$_2$O$_3$ decreases the phosphorus distribution ratio between BaO–BaF$_2$–MnO–Al$_2$O$_3$ slag and carbon-saturated ferromanganese at 1300°C [6]. The experimental results from the study of Li revealed that the dephosphorization ability of CaO–SiO$_2$–FeO–P$_2$O$_5$-based slags increased on adding Na$_2$O and K$_2$O [7]. Apart from the studies described above, studies on the effects of Al$_2$O$_3$, Na$_2$O, and other similar materials on the ability of CaO–FeO–SiO$_2$-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 Al$_2$O$_3$/Na$_2$O-containing materials as fluxes of CaO–FeO–SiO$_2$-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–SiO$_2$–Al$_2$O$_3$/Na$_2$O/TiO$_2$ 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].

\[
\frac{1}{2}P_2(g) + \frac{5}{4}O_2(g) + \frac{3}{2}(O^2-) = (PO_4^{3-})
\]  
(1)

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

Here, (%PO$_4^{3-}$) is the weight percent of PO$_4^{3-}$ dissolved in the slag; P$_{O_2}$ is the partial pressure of oxygen, and P$_{P_2}$ is the partial pressure of phosphorus. To get the value of P$_{P_2}$, the eq. (3) is introduced [8]. $G^0_\gamma$ is the standard Gibbs free energy of P$_{in\ y\ -\ Fe}$, which can be calculated using eq. (5) [10]. $G^0_\gamma$ is the standard Gibbs free energy of P$_{P_2}$, 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).

\[
\frac{1}{2}P_2(g) = [P]_{in\ y\ -\ Fe} \Delta G^0_\gamma = G^0_\gamma - G^0_\gamma (J/mol)
\]  
(3)

\[
K_\gamma = \frac{[%P]}{P_{P_2}^{1/2}}
\]  
(4)

\[
G^0_\gamma = -128520 + 32.677T + RT \ln [\%P] (J/mol)
\]  
(5)[10]

\[
\log C_{PO_4^{3-}} = \log L_P + \log(\frac{MM_{PO_4^{3-}}}{MM_P}) - \log P_{O_2}^{5/4} + \log K_\gamma
\]  
(6)

Here, $MM_{PO_4^{3-}}/MM_P$ is the ratio of the molar mass of phosphate in the slag and phosphorus in the metal, which is equal to 3.07. P$_{O_2}$ 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.
Fe(s) + 1/2O₂(g) = (FeO) , ΔG₂ = 10.73T − 54501(cal/mol),[12][7]

\[ K_2 = \frac{a_{(FeO)}}{a_{Fe}(P_O)_{i/2}} \]  

(8)

\[ L_p = \frac{(\%P)}{[\%P]} \]  

(9)

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

According to eq. (6), P₂O₅ and Lp are important factors for obtaining \( (C_{P01}) \). \( P_O \) is determined by the activity of FeO \( (C_{PO1}) \) using eqs. (7) and (8). \( L_p \) between the slag and solid iron foil can be obtained from slag–metal equilibrium experiments. Hence, \( (C_{PO1}) \) for slag needs to be first known for obtaining \( (C_{PO1}) \). In this study, \( (C_{PO1}) \) 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-Ni 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 \( (C_{PO1}) \) 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–FeO₄ and CaO–SiO₂–FeO₄ slags at 1400°C. The results obtained from the calculation model of the IMCT were in reasonable agreement with the measured values of \( (C_{PO1}) \) (Figure 1), indicating that the model for calculating \( (C_{PO1}) \) is credible.

**Experiments**

**Samples**

The materials and chemical reagents included iron foil, CaO, FeO, SiO₂, Al₂O₃, Na₃SiO₅, 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 Fe₂O₃ 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_{PO_4}^-) | (C_{PO_4}^2-) |
|-----|----------|---------------------------------------------|---------------|--------------|
|     |          | CaO  FeO  SiO_2  Al_2O_3  Na_2O  TiO_2  (P)  |               |              |
| 1   | 1300°C Al_2O_3 | 29.85  34.05  29.10  0.14  0  0  2.105  0.005 | 1.0 | 421  22.11 |
| 2   | 1300°C Na_2O | 29.29  33.51  28.71  3.35  0  0  2.103  0.0078 | 1.0 | 270  21.94 |
| 3   | 1300°C TiO_2 | 28.15  32.43  28.11  6.15  0  0  2.137  0.013 | 1.0 | 164  21.76 |
| 4   | 1300°C FeO | 26.75  31.14  26.96  10.05  0  0  2.091  0.019 | 1.0 | 110  21.61 |
| 5   | 1300°C Basicity, R | 25.43  30.11  25.64  13.42  0  0  2.020  0.023 | 1.0 | 88  21.54 |

The statistics of slag iron composition at the end of experiment.
Nos. 1–15, quaternary CaO–FeO–SiO$_2$–Al$_2$O$_3$/Na$_2$O/TiO$_2$ slag systems were used to verify the effects of Al$_2$O$_3$, Na$_2$O, and TiO$_2$ on the phosphate capacity of slag. For experiments Nos. 16–54, the six-component slag system CaO–FeO–SiO$_2$–Al$_2$O$_3$/Na$_2$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 ±1°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 ($C_{PO_4}^{−}$) was calculated using the thermodynamic model of IMCT. Finally, $C_{PO_4}^{−}$ was determined using eq. (6).

Results and discussion

Effect of temperature on ($C_{PO_4}^{−}$)

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, ($C_{PO_4}^{−}$) 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 CaO–FeO$_3$–Al$_2$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, ($C_{PO_4}^{−}$) clearly decreased with increasing temperature, suggesting that temperature exerts a more significant effect on ($C_{PO_4}^{−}$) 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 ≤ R < 0.8, R = (CaO%)/(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$_2$O$_5$ in the slag (as most of the CaO is assumed to combine with SiO$_2$).
Effect of the slag basicity

Figure 4 shows the effect of the binary basicity on $(C_{PO_4}^{-})$. 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 $\text{FeO-Al}_2\text{O}_3-Na_2\text{O-TiO}_2$ but different (%CaO)/(%SiO$_2$) values. With increasing the binary basicity at 1300°C and 1350°C, $(C_{PO_4}^{-})$ increased. Similar results have been reported by Im et al. [8] during their study on the phosphate capacity of CaO–FeO–SiO$_2$–P$_2$O$_5$ with basicities of 0.5–1.0 at 1300°C. However, a larger slope between $(C_{PO_4}^{-})$ and basicity was observed at low temperature (1300°C) and low basicities ($R = 0.2–1.0$, black rectangle solid points in Figure 4(a)). Moreover, $(C_{PO_4}^{-})$ 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, $(C_{PO_4}^{-})$). This result indicated that under conditions of a slag basicity greater than 0.9, temperature considerably affects $(C_{PO_4}^{-})$ compared to basicity.

This result was further verified by the data shown in Figure 4(b), indicating the dependence of the binary basicity on $(C_{PO_4}^{-})$ 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
were similar to those observed in Figure 5(a). The largest $\left[\text{CPO}_3\right]^{-4}$ was observed for $R = 1.0$ at 1300°C (pink triangle solid points), while the lowest values were observed at $R = 0.8-1.2$ at 1350°C (Nos. 50–54 in Table 1) despite the large variation in the basicity ($R = 0.2-2.4$). This result indicated that temperature exerts a stronger effect on $\left[\text{CPO}_3\right]^{-4}$ compared to basicity and tends to be the most important influencing factor under the conditions utilized herein.

**Effect of the content of Na$_2$O in slag**

Figure 5(a) shows the dependence of $\left[\text{CPO}_3\right]^{-4}$ on the Na$_2$O content for all of the Na$_2$O-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 ($\left[\text{CPO}_3\right]^{-4} = 21.98$, $\left[\text{CPO}_3\right]^{-4} = 21.35$) even with an almost constant content of Na$_2$O (Na$_2$O = 3.06%, Na$_2$O = 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: $\left[\text{CPO}_3\right]^{-4}$ increased with increasing Na$_2$O content, indicating that the Na$_2$O content also significantly affects dephosphorization. On the other hand, the lowest $\left[\text{CPO}_3\right]^{-4}$ was still observed for experiments conducted at a high temperature of 1400°C despite the large variation in the Na$_2$O content (Na$_2$O% = 0.08%–8.33%). Further, this result strongly suggested that temperature increases by 0.416. With the increase in the Na$_2$O content by 4.07% at 1600°C in the latter study, $\left[\text{CPO}_3\right]^{-4}$ increases by 0.31. In general, the comparison of the three studies showed that Na$_2$O significantly affects the phosphate capacity.

Figure 5(b) shows the dependence of the phosphate capacity on the Na$_2$O content for all of the Na$_2$O-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 ($\left[\text{CPO}_3\right]^{-4} = 21.98$, $\left[\text{CPO}_3\right]^{-4} = 21.35$) even with an almost constant content of Na$_2$O (Na$_2$O = 3.06%, Na$_2$O = 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: $\left[\text{CPO}_3\right]^{-4}$ increased with increasing Na$_2$O content, indicating that the Na$_2$O content also significantly affects dephosphorization. On the other hand, the lowest $\left[\text{CPO}_3\right]^{-4}$ was still observed for experiments conducted at a high temperature of 1400°C despite the large variation in the Na$_2$O content (Na$_2$O% = 0.08%–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 \( \text{FeO}_3^{-} \), where the concentrations of all of the other slag constituents were nearly unchanged at a constant temperature. With the increase in the FeO content, \( \text{FeO}_3^{-} \) decreased by 0.69 and 0.64, respectively. Nakamura [20] and Wrampelmeyer [19] have calculated the phosphate capacities for the CaO satd.–BaO–SiO\(_2\)–Fe\(_t\)O slag system at 1600°C and the CaO–FeO–Al\(_2\)O\(_3\) slag system at 1550°C, 1600°C, and 1700°C. The results of the two studies revealed that \( \text{FeO}_3^{-} \) 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 CaO satd.–BaO–SiO\(_2\)–Fe\(_t\)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, \( \text{FeO}_3^{-} \) 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\(_2\)O\(_5\) by the dissolved oxygen (eq. (10)), and then, P\(_2\)O\(_5\) was fixed in the slag phase via the combination of basic materials such as CaO to form 3CaO·P\(_2\)O\(_5\) and 4CaO·P\(_2\)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.

\[
2[P] + 5[O] = P_2O_5 \quad (10)
\]

\[
100083 \cdot P_2O_5(x = 3, 4) \quad (11)
\]

**Effects of the content of Al\(_2\)O\(_3\) and TiO\(_2\)**

Figure 7(a) and (b) show the effects of the Al\(_2\)O\(_3\) content on \( \text{FeO}_3^{-} \) 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\(_2\)O\(_3\) content, \( \text{FeO}_3^{-} \) decreased. This result is in agreement with that
reported by Diao and Li et al. (Figure 7(a)). [1, 2] According to the ionic theory of slags, \(\text{CPO}_3^4\) replaces \(\text{CPO}_4^3\) and then precipitates as \(\text{Ca}_3(\text{PO}_4)_2\) during dephosphorization. At the same time, \(\text{CPO}_4^3\) is replaced by \(\text{CPO}_3^4\). At an extremely high \(\text{Al}_2\text{O}_3\) content, the precipitation of \(\text{CPO}_4^3\) is suppressed, which adversely affects the fixing of \(\text{CPO}_3^4\) in slag. In this case, \(\text{Al}_2\text{O}_3\) exhibited the characteristics of an acidic oxide [21]. Figure 7(c) shows the dependency of phosphate on the content of \(\text{TiO}_2\) in the slag. The content of \(\text{TiO}_2\) in the slag exerted a considerably weaker effect on \(\text{CPO}_3^4\) compared to other factors of temperature, basicity, and other slag components, e.g., \(\text{FeO}, \text{Na}_2\text{O}, \text{and Al}_2\text{O}_3\) content.

**Regression analysis of \(\text{CPO}_3^4\)**

Based on the data from Nos. 16–54 in Table 1, \(\text{CPO}_3^4\) was fitted as a function of various factors of temperature and the slag composition, i.e., of \(\text{CaO}, \text{SiO}_2, \text{Al}_2\text{O}_3, \text{Na}_2\text{O}, \text{TiO}_2, \text{and FeO}\) content using the Statistical Product and Service Solutions (SPSS) software [22], expressed in eq. (12). Figure 8 shows the calculation data using eq. (12) and the experimental results, which showed good agreement.

![Figure 7: Effects of \(\text{Al}_2\text{O}_3\) and \(\text{TiO}_2\) on \(\text{CPO}_3^4\): (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.](image1)

![Figure 8: Comparison of the observed values of \(\text{CPO}_3^4\) and the fitted curve.](image2)
\[
\log C_{P_3O_8} = 0.041(\%\text{CaO}) - 0.086\log(\%\text{FeO}) - 0.024(\%\text{SiO}_2)
- 0.02(\%\text{Al}_2\text{O}_3) + 0.067(\%\text{Na}_2\text{O}) + 0.039(\%\text{TiO}_2)
+ 56767/T - 14.58, \quad (R = 0.978)
\]

(12)

**Conclusions**

The phosphate capacities of the CaO–FeO–SiO\(_2\)–Al\(_2\)O\(_3\)/Na\(_2\)O/TiO\(_2\) 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. \((C_{P_3O_8})^{-1}\) 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 Na\(_2\)O and FeO.
3. With the increase in the content of FeO and Al\(_2\)O\(_3\) in slag, \((C_{P_3O_8})^{-1}\) decreases. A low Na\(_2\)O content leads to increased phosphate capacities of slag, particularly at low temperatures of 1300–1350°C. The content of TiO\(_2\) in the slag exhibits a weaker effect on \((C_{P_3O_8})^{-1}\).
4. Based on the experimental data, using regression analysis, \((C_{P_3O_8})^{-1}\) is expressed as a function of the temperature and concentration of the slag components, expressed as follows:

\[
\log C_{P_3O_8} = 0.041(\%\text{CaO}) - 0.086\log(\%\text{FeO}) - 0.024(\%\text{SiO}_2)
- 0.02(\%\text{Al}_2\text{O}_3) + 0.067(\%\text{Na}_2\text{O}) + 0.039(\%\text{TiO}_2)
+ 56767/T - 14.58, \quad (R = 0.978)
\]

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