Analysis of Dephosphorization Thermodynamics Based on the Melt Structure of CaO–SiO₂–FeO–MgO System

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To reduce the phosphorus content in steel, the CaO–SiO₂–FeO–MgO-based dephosphorization slag was designed to clarify the microscopic reaction behavior of phosphorus. In the present study, Raman spectra of final slag were measured and deconvoluted. The spectral analysis showed that P⁵⁺ ions removed from liquid iron existed in the form of Q⁰(P) and Q¹(P) groups. According to the result, phosphate capacity and phosphorus distribution ratio (Lₚ*) were redefined. The results showed that lgLₚ* was proportional to molar ratio of Q⁰(P)/Q¹(P), indicating that Q⁰(P) exerted a significant influence on Lₚ* compared with Q¹(P). As the increases of CaO/SiO₂ from 0.15 to 1.25 and FeO from 7.2 to 21.9 mass% in the final slag, lgLₚ* gradually increased, whereas lgLₚ* showed a downward trend when FeO increased to 29.2 mass%. This was because the increase of O²⁻ ions generated by the dissociations of CaO, MgO and FeO continuously destroyed the network structure and formed more Q²(P) units, which were compensated by the increasing Ca²⁺, Mg²⁺, and Fe²⁺ cations to form stable groups. Meanwhile, the Q⁰(Si) units formed by slag depolymerization further played a role in fixing Q⁰(P). However, due to the stronger polarization of Fe²⁺ than Ca²⁺ and Mg²⁺, Q⁰(P) and Q¹(P) units were easily deformed and decomposed by Fe²⁺. The excessive Fe²⁺ diluted the proportion of Ca²⁺ and Mg²⁺, and made Q⁰(P) and Q¹(P) lose stability. The P⁵⁺ ions in the Q⁰(P) and Q¹(P) units were reduced to liquid iron, and the rephosphorization phenomenon occurred, resulting in a decrease of lgLₚ*.

KEY WORDS: dephosphorization thermodynamic; melt structure; Raman spectroscopy; phosphorus distribution ratio.

The modern refining process of liquid steel has almost no dephosphorization function, so basic oxygen smelting has become the key link to control the phosphorus content. Many scholars have carried out a lot of research on enhancing the dephosphorization efficiency of converter. Studies have reported that low temperature, high oxygen partial pressure, and high CaO/SiO₂ ratio are advantageous for dephosphorization from liquid steel. For example, Li et al. studied the phosphorus distribution ratio (Lₚ) of CaO–FeO–SiO₂–Al₂O₃/Na₂O/TiO₂ slag and carbon-saturated iron under different temperatures and compositions. The results showed that Lₚ decreased with the increase of temperature and increased with the increase of basicity and FeO content. Meanwhile, it was found that the effect of temperature on Lₚ was weaker than that of basicity, but stronger than that of FeO content. Im et al. also proposed that Lₚ depended more on the CaO content than on the FeO content of slag. Furthermore, Basu et al. experimentally determined the influences of FeO concentration and basicity on the equi-

1. Introduction

With the increasingly fierce competition in the steel market and the increasing demand for high-quality steel, the phosphorus content has become one of the important factors to measure the steel product quality. Phosphorus is an element of representative impurities that tends to segregate at grain boundaries, leading to the reduction of brittle characteristic at low temperature, crack resistance, weldability and mechanical properties of steel. Low phosphorus content is essential for steel applications where high ductility is required, such as thin sheets, deep drawn structures, pipelines, and automobile exteriors. The ability of phosphorus to strengthen and embrittle ferrite imposes restrictions on the maximum phosphorus content for the aforementioned applications. Therefore, phosphorus content should be kept as low as possible in conventional steel grades.

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librium phosphorus partition ratios of CaO–SiO2–FeO–P2O5–MgO slags at temperatures of 1 600 and 1 650°C. The results showed that the \( L_f \) initially increased with basicity but attained a constant value basically of 2.5. An increase in FeO concentration up to approximately 13 to 14 mass% was beneficial for phosphorus partition.

In addition, the mineral structure and the composition of phosphorus-rich phase in dephosphorization slag have been studied.\(^{15-17}\) It was reported that the phosphorus was mainly enriched with the form of \( n \)CaO\( \cdot \)SiO2\( \cdot \)Ca\( (PO_4)_2 \) (hereafter denoted as \( n \)Ca\( S\cdotC\cdotP \)) in the phosphorus-rich phase whether the dephosphorization slag was cooled in the atmosphere of air or argon.\(^{18-21}\) Besides, the measurements of the equilibrium distribution ratio of \( P_2O_5 \) between the solid \( C_2S\cdotC_3P \) and the liquid phase indicated that \( P_2O_5 \) was concentrated in the solid \( C_2S\cdotC_3P \) with a high distribution ratio.\(^{22}\) Hence, phosphorus in the liquid steel is usually considered to be oxidized to \( P_2O_5 \) and enter into the slag, and then is fixed by CaO to form \( C_3P \), which forms a solid solution with \( C_2S \) in the slag. However, the above-mentioned solid solution does not really exist in the molten slag. For phosphorus-containing slag, phosphorus exists in the form of a tetrahedron containing one \( P=O \) double bond and three \( P–O \) or \( P–O–P \) bonds, and is divided into four structural units, \( Q^0(P) \), \( Q^1(P) \), \( Q^2(P) \), and \( Q^3(P) \), according to the bridging oxygen number from low to high.\(^{23,24}\) Similarly, silicon also acts as a network former to form five silicon-oxygen tetrahedrons, \( Q^0(Si) \), \( Q^1(Si) \), \( Q^2(Si) \), \( Q^3(Si) \), and \( Q^4(Si) \),\(^{25,26}\) In order to truly evaluate the dephosphorization ability of molten slag, it is necessary to analyze the dephosphorization mechanism based on the real structure of molten slag.

In the present work, a typical dephosphorization slag of \( CaO/FeO/MgO \) was selected to determine the composition of the initial slag of dephosphorization, as shown in Fig. 1 and Table 1. The initial slags 1–4 and 5–8 were designed to investigate the effect of FeO and CaO/SiO2 on the dephosphorization efficiency, respectively. The initial slags were prepared with AR-grade \( CaO \), \( SiO_2 \), \( FeC_2O_4\cdot2H_2O \), and \( MgO \). FeO was added in the form of \( FeC_2O_4\cdot2H_2O \). To remove moisture and impurities, each reagent except \( FeC_2O_4\cdot2H_2O \) was pretreated with high-temperature calcination in a muffle furnace.

The iron block containing phosphorus was prepared by melting a pure iron of 280 g and a ferrophosphorus alloy of 5 g in a MoSi2 furnace under an argon atmosphere. The final phosphorus content of iron block was confirmed by using ICP-OES with a resolution of 0.006 nm to be 0.47 mass%P.

### 2.2. Dephosphorization Experiment

Eight sets of laboratory-scale dephosphorization experiments were carried out in a high-temperature quenching furnace. The mass ratio of molten slag and liquid iron used in the dephosphorization experiment was 1:4. A Fe-0.47 mass%P of 20±0.5 g and a mixed initial slag of 5 g were

### Table 1. Compositions of initial slags and the matrix phase in final slags (mass%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>CaO/SiO2</th>
<th>Initial composition/Composition of matrix phase in final slags</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>1</td>
<td>1.0/0.83</td>
<td>40/34.025</td>
</tr>
<tr>
<td>2</td>
<td>1.0/0.83</td>
<td>35/28.963</td>
</tr>
<tr>
<td>3</td>
<td>1.0/0.80</td>
<td>30/26.560</td>
</tr>
<tr>
<td>4</td>
<td>1.0/0.85</td>
<td>25/24.875</td>
</tr>
<tr>
<td>5</td>
<td>0.2/0.15</td>
<td>10/6.356</td>
</tr>
<tr>
<td>6</td>
<td>0.5/0.43</td>
<td>20/16.542</td>
</tr>
<tr>
<td>7</td>
<td>0.7/0.67</td>
<td>25/22.572</td>
</tr>
<tr>
<td>8</td>
<td>1.4/1.25</td>
<td>35/37.295</td>
</tr>
</tbody>
</table>

Fig. 1. Isothermal liquidus of the CaO–SiO2–FeO-10%MgO slag system. (Online version in color.)
placed in the MgO crucible (31 mm ID) hung with Mo wire in the hot zone of furnace. High-purity argon gas (99.999%) was introduced at a fixed flow rate of 1 L·min⁻¹ to maintain the oxygen partial pressure at about 10⁻⁴ atm. Then, the temperature was raised to 1600°C and kept for 3 h. The preliminary experiment confirmed that the phosphorus content in molten slag and liquid iron remained constant after 15 minutes, which can be regarded as a quasi-equilibrium state. Therefore, a constant temperature of 3 hours was considered to be sufficient to reach the equilibrium of the dephosphorization reaction. Finally, Mo wire was loosened, and molten slag and liquid iron fell into the bucket directly below with MgO crucible to complete the quenching.

2.3. Analysis Method

The chemical analysis of the iron samples after the dephosphorization experiment was determined by ICP-OES, as listed in Table 2. The morphology and chemical composition of final slags were analyzed by SEM-EDS and XRD, as shown in Figs. 2 and 3. A small amount of precipitated phase was found in the final slag. Combining with XRD analysis, the precipitated phase was (Fe, Mg)O, which is generally considered to be caused by the fact that the quenching rate is insufficient.

The composition analysis of the matrix phase and precipitated phase of final slag was performed by using SEM-EDS to obtain the mass fractions of CaO, SiO₂, MgO, P₂O₅, and total iron (TFe₁) in the matrix phase. The mass fractions of total iron (TFe₂) and FeO of final slags were determined by XRF. Then Fe₂O₃ in the matrix phase could be obtained by subtracting FeO content from TFe₂ content. Since Fe₂O₃ was not contained in the precipitated phase, Fe₂O₃ was considered to originate entirely from the matrix phase. The mass fraction of FeO in the matrix phase was calculated by the content of TFe₁ and Fe₂O₃. The composition of matrix phase is shown in Table 1.

The melt structures of final slags were measured by LabRAM HR800 Raman spectrometer equipped with a CCD detector. The specific measurement conditions are as follows: An Ar⁺ laser with an excitation wavelength of 633 nm was used as the light source to record the Raman spectrum. Before the test, a single crystal silicon standard sample with a known characteristic peak (520 cm⁻¹) was used to calibrate the wavenumber. The scanning range of the band was 200–2,000 cm⁻¹, and the spectral resolution was 0.65 cm⁻¹. Although a small amount of FeO was precipitated in the final slag, the reason why we still used Raman spectroscopy to measure its melt structure was that the precipitation FeO as a network modification did not affect the formation of the main vibrational peaks in the Raman spectra. The subsequent result is discussed in terms of the composition of matrix phase.

3. Results and Discussion

3.1. Dephosphorization Rate and Equilibrium Distribution Ratio of Phosphorus

Figure 4 shows the P content in the iron samples and P₂O₅ content in the final slags under the condition of different initial slags. As the FeO concentration in final slag increases from 7.2 to 29.2 mass%, the P content in the iron samples first decreases from 0.18 to 0.05 mass% and then increases to 0.072 mass%, whereas the P₂O₅ content in final slags increases from 0.746 to 3.634 mass% and then decreases to 3.501 mass%. FeO exhibits the dual roles of promoting and hindering dephosphorization. As CaO/SiO₂
ratio increases from 0.15 to 1.25, the P content in the iron samples gradually decreases from 0.37 to 0.032 mass%, and P$_2$O$_5$ content gradually increases from 0.077 to 4.165 mass%, indicating that high CaO/SiO$_2$ ratio is beneficial to dephosphorization. However, the P content in the iron samples and the P$_2$O$_5$ content in final slag cannot truly represent the reaction of molten slag and liquid iron due to the continuous changes in the total amount of iron and slag. Therefore, according to Eqs. (1) and (2), the dephosphorization rate ($\eta_P$) and the equilibrium distribution ratio of phosphorus ($L_P$) are calculated to evaluate the dephosphorization capacity of molten slag.

$$\eta_P = \frac{(m_P)_{\text{final slag}} - (m_P)_{\text{initial slag}}}{(m_P)_{\text{initial iron}}} \times 100\% \quad \ldots (1)$$

$$L_P = \frac{w(P_2O_5)_{\text{final slag}}}{w(P)_{\text{final iron}}} \quad \ldots (2)$$

where $(m_P)_{\text{final slag}}$ represents the mass of (P) in final slag; $(m_P)_{\text{initial slag}}$ represents the mass of (P) in initial slag; $(m_P)_{\text{initial iron}}$ represents the mass of [P] in the initial iron samples; $w(P_2O_5)$ is the mass fraction of P$_2$O$_5$ in final slag; $w(P)$ is the mass fraction of P in the iron sample after dephosphorization.

According to the result of dephosphorization experiment, the calculated values of $\eta_P$ and $L_P$ are shown in Fig. 5. Through comparison, it is found that when FeO content is less than 21.9 mass% and CaO/SiO$_2$ ratio is less than 1.25, the values of $\eta_P$ and $L_P$ increase with increasing FeO and CaO/SiO$_2$. This phenomenon shows the same trend as the changes of P content in the iron samples and P$_2$O$_5$ content in final slag, and accords with the thermodynamic conditions of enhancing dephosphorization. Meanwhile, it can be seen from the increasing magnitude in the values of $\eta_P$ and $L_P$ that the increase of CaO/SiO$_2$ ratio has a more significant influence on $\eta_P$ and $L_P$ than the increase of FeO, which is consistent with the result reported by Basu et al. As FeO content exceeds 21.9 mass%, $\eta_P$ and $L_P$ tend to decrease with the increase of FeO, where FeO play a role in hindering dephosphorization.

3.2. Structural Analysis of Final Slag

Figure 6 shows the Raman spectra of final slags. Referring to the existing literature, the vibration peaks in the wavenumber range of 400–1200 cm$^{-1}$ are deconvoluted. In the process of deconvolution, each characteristic peak is continuously fitted until the minimum correlation coefficient between the original curve and the fitted curve is greater than 0.99. The deconvolution result is shown in Fig. 7.

According to the information of the structural units in Fig. 7, the relative area fraction of each characteristic peak is counted. Actually, the area fraction fails to accurately reflect the change in the proportion of structural units caused by the variation of slag composition. Hence, its molar fraction can be calculated with the aid of Raman scattering coefficients according to Eq. (3), and the calculation results are shown in Fig. 8.

$$X_n = \frac{A_n}{S_n}, \quad n = 0, 1, 2, 3, 4 \quad \ldots (3)$$

Where $X_n$ represents the molar fractions of Q$^n$(Si) and Q$^n$(P); $A_n$ represents the relative area fractions of Raman characteristic peaks; $S_n$ represents the Raman scattering coefficients of Q$^n$(Si) and Q$^n$(P); $S_0$, $S_1$, $S_2$, $S_3$, and $S_4$ for Q$^0$(Si) is 1.000, 28, 30, 31, 32, 33, and 34.
0.514, 0.242, 0.090, 34) and 0.015; S0 and S1 for Qn(P) is 1.000 and 0.576. 23) To verify the accuracy of the deconvolution results, the experimental and theoretical values of the non-bridging oxygen number (NBO/Texp and NBO/Ttheor) were calculated using Eqs. (4) and (5), as shown in Fig. 9. NBO/Texp in Fig. 9 is close to NBO/Ttheor, which indicates that the molar fractions of structural units obtained by the present experiment have higher accuracy.

\[
\frac{\text{NBO}}{T_{\text{exp}}} = \frac{x_{\text{Si}}}{x_{\text{Si}} + x_P} \sum_{Q_{\text{Si}}} X_n \cdot (4-n) + \frac{x_P}{x_{\text{Si}} + x_P} \sum_{Q_{\text{P}}} X_n \cdot (3-n) \tag{4}
\]

\[
\frac{\text{NBO}}{T_{\text{theor}}} = 2x_{\text{O}} - 4x_{\text{Si}} - 5x_P \frac{x_{\text{Si}} + x_P}{x_{\text{Si}} + x_P} \tag{5}
\]

Where \(x\) represents the molar fraction of elements in final slag.

As can be seen from Fig. 8, three silicon-oxygen tetrahedrons (Q0(Si), Q1(Si), and Q2(Si)) and two phosphorus-oxygen tetrahedrons (Q0(P) and Q1(P)) exist in final slag after dephosphorization. Due to less Fe2O3 content, the Fe3+-related structural units were not detected in the slag.

With the increase in the CaO/SiO2 ratio and FeO concentration, the molar fractions of simple silicon-oxygen tetrahedron and phosphorus-oxygen tetrahedron such as Q0(Si) and Q0(P) gradually increase, indicating gradual depolymerization of molten slag.

3.3. Redefinition of Phosphorus Distribution Ratio and Phosphate Capacity

The transfer process of phosphorus between molten slag and liquid iron can be described as follows: The P dissolved in liquid iron loses electrons at the interface and is oxidized to P5+ and diffuses into the molten slag; the O dissolved in liquid iron gains electrons at the interface and is reduced to O2-. Due to the strong electrostatic force between P5+ and O2- ions, P5+ exists in the molten slag in the form of PO43− unit. This process can be represented by Eq. (6). Based on the ion theory of dephosphorization, the phosphate capacity of molten slag (CP) was defined.\(^{27}\) The formula is shown in Eq. (7).

\[
2[P] + 5[O] + 3[O^{2-}] = 2[PO_4^{3-}] \tag{6}
\]

\[
C_P = K_P \frac{a_{P}^3}{f_{(PO_4^{3-})}} = L_P^2 \frac{1}{f_P \cdot a_{[O]}} \tag{7}
\]
Where $a_{O^{2-}}$ and $a_{(SiO)}$ represent the activities of $O^{2-}$ in molten slag and the dissolved O in liquid iron, respectively; $f_P$ and $f_{(PO)}$ represent the activity coefficients of P dissolved in liquid iron and PO$_4^{3-}$ in molten slag, respectively; $K_P$ represents the equilibrium constant of dephosphorization reaction (Eq. (6)).

However, PO$_4^{3-}$ unit is, in fact, not the only form of P$^{2+}$. According to previous structure analysis and the abovementioned Raman deconvolution results, P$^{2+}$ in the CaO–SiO$_2$–FeO–MgO–P$_2$O$_5$ slag mainly exists as PO$_4^{3-}$ (Q$^0$(P)) and P$_2$O$_4^{2-}$ (Q$^1$(P)) units. Hence, the ion equation and equilibrium constant ($K_P^*$) of the dephosphorization reaction at the interface of molten slag and liquid iron can be expressed as follows:

$$4[P]+10[O]+5(O^{2-}) = 2(PO_4^{3-})+(P_2O_5^{2-}) \quad \cdots \cdots \cdots (8)$$

$$K_P^* = \frac{\gamma_{(PO_4)}^2 \cdot w(PO_4^{3-}) \cdot \gamma_{(PO_2)} \cdot w(P_2O_5^{2-})}{f_P^4 \cdot w[P]^4 \cdot a_{(O)}^{10} \cdot a_{(O)}^5} \quad \cdots \cdots (9)$$

Where $\gamma_{(PO_4)}^*$ and $\gamma_{(PO_2)}^*$ represent the activity coefficients of PO$_4^{3-}$ and P$_2$O$_5^{2-}$ dissolved in molten slag, respectively.

According to Eqs. (8) and (9), the equilibrium distribution ratio of phosphorus ($L_P^*$) and phosphate capacity ($C_P^*$) are redefined as Eqs. (10) and (11), respectively. In Eqs. (10) and (11), the mass fractions of phosphorus-oxygen groups and free oxygen ions (FO) can be obtained from the analysis results of melt structure and the calculation formulae are shown in Eqs. (4), (12), and (13). The calculation results of $L_P^*$ and $C_P^*$ are shown in Fig. 10. The newly defined $L_P^*$ shows the same change trend as the result of previous $L_P$ mentioned in Section 3.1 with the increases of FeO content and CaO/SiO$_2$. The difference is that the newly defined $L_P^*$ and $C_P^*$ amplify the trend of change due to the high exponential form in the new formulæ and show the sensitivity to the changes in structure and composition. The newly defined phosphorus distribution ratio realizes the analysis of the dephosphorization efficiency from the ionic point of view, which can lay a good foundation for the thermodynamic calculation of the ionic reaction of dephosphorization.

$$L_P^* = \frac{w(PO_4^{3-}) \cdot w(P_2O_5^{2-})}{w[P]^4} \quad \cdots \cdots (10)$$

$$C_P^* = K_P^* \cdot \frac{a_{(O)}^5}{\gamma_{(PO_4)}^* \cdot \gamma_{(PO_2)}^*} = L_P^* \cdot \frac{1}{f_P^4 \cdot a_{(O)}^{10} \cdot a_{(O)}^5} \quad \cdots \cdots (11)$$

$$x_{O^{2-}} = x_{O^2} = x_{O} - x_{BO} - x_{NBO} \quad \cdots \cdots (12)$$

$$x_{BO} = \frac{1}{2} \left( x_{Si} \cdot \frac{x_{Si} + x_{P}}{x_{Si} + x_{P}} \sum_{for\ Q^0(Si)} X_n \cdot n + \frac{1}{2} x_{Si} \cdot x_{P} \sum_{for\ Q^1(P)} X_n \cdot n \right) \quad \cdots \cdots (13)$$

Where BO represents the bridging oxygen in the [SiO$_4$] and [PO$_4$]-tetrahedrons.

**Figure 10.** Phosphate capacity and the equilibrium distribution ratio of phosphorus under the condition of initial slags: (a) different FeO content; (b) different CaO/SiO$_2$ ratios. (Online version in color.)

**Figure 11.** Comparison of phosphorus distribution ratio. (Online version in color.)

### 3.4 Relationship of the Equilibrium Distribution Ratio of Phosphorus and Melt Structure

Figure 12 shows the relationships of the equilibrium distribution ratio of phosphorus, the molar ratios of structural units, NBO/T and the moles fraction of FO under the condition of different FeO content and CaO/SiO$_2$. In figure, $L_P^*$ is positively correlated with the molar ratio of Q$^0$(P)/Q$^1$(P), indicating that the high concentration of Q$^1$(P) is beneficial to dephosphorization. In other words, phosphorus is more stable in the form of Q$^1$(P) in the molten slag after
being removed from the liquid iron. To prove this point, we try to explain in conjunction with the molecular theory of dephosphorization. The dephosphorization reaction occurs at the interface of molten slag and liquid steel and is generally considered to produce C₃P. The ionic formula of Q₀(P) is PO₄³⁻, and three P–O non-bridging oxygen bonds in the ionic groups are connected to 3/2 Ca²⁺ to form 3/2Ca∙PO₄, as shown in Fig. 13. When this ionic group is enlarged by 2 times, it is actually C₃P. The conclusion further illustrates that the stable phosphate ion existing in the molten slag is Q₀(P). In fact, Q₁(P) is also a group formed after fixing P⁵⁺ ion. In Eq. (10), \( L_P^* \) is proportional to the square of the concentration of Q₀(P) and the first power of the concentration of Q₁(P). Through the comparison the powers of the concentration of structural units, it can be found that the effect of Q₀(P) content on \( L_P^* \) is more significant than that of Q₁(P), which also confirms the above results.

It is noted that \( \lg L_P^* \) is also in proportion to Q₀(Si)/(Q₁(Si)+Q₂(Si)), NBO/T, and FO with increasing FeO content and CaO/SiO₂ when FeO content is less than 21.9 mass%. According to the above discussion, it is not difficult to understand the reason why \( \lg L_P^* \) increases with the increase of NBO/T and FO. An increase in NBO/T and FO means that the polymerization degree of slag is lower and more O²⁻ ions exist in the network structure, which is conducive to the formation of Q₀(P), so \( \lg L_P^* \) increases. Meanwhile, it can be seen from Eq. (6) that when the concentration of FO in the molten slag increases, the activity of O²⁻ increases, which promotes the dephosphorization reaction and is beneficial to the improvement of the phosphorus distribution ratio.

The increase of NBO/T also indicates the increase of simple Q₀(Si) units. The observations on the mineralogical phase of the dephosphorization slag suggested that C₂S precipitation accompanied with phosphorus enrichment in the slag was key to the increase of \( L_P^* \). In the melt structure, C₂S is actually the combination of Q₀(Si) (SiO₄²⁻) and two charge compensators (Ca²⁺), as shown in Fig. 14. Hence, the increase of Q₀(Si) also plays a role in fixing \( L_P^* \) unit. However, the inverse proportion of NBO/T, Q₀(Si)/(Q₁(Si)+Q₂(Si)), FO and \( \lg L_P^* \) when FeO content exceeds 21.9% is speculated to be related to the cations in the molten slag, which will be explained in the following discussion.

In Fig. 12, \( \lg L_P^* \) gradually increases with increasing CaO/SiO₂ from 0.15 to 1.25. The increase of CaO introduces more free O²⁻ ions that can fix P⁵⁺, resulting in the formation of more Q₀(P) groups in the slag. Meanwhile, the introduced Ca²⁺ compensates the charge of anionic group, so that Q₀(P) can stably exist in the network structure, which is the dephosphorization product C₃P considered by molecular theory. The process of P⁵⁺ being fixed by CaO can be represented in Fig. 15(a).

A special phenomenon, different from the increasing CaO/SiO₂, is found that \( \lg L_P^* \) increases initially, followed by a decrease with the gradual increase of FeO content. By comparing the relationship between \( \lg L_P^* \) and the molar ratio of cations (as shown in Fig. 16), it was found that this
phenomenon is considered to be closely related to the molar ratio of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ to $\text{Fe}^{2+}$. In Fig. 16, the molar ratio of $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{Fe}^{2+}$ has a decreasing trend with the increase of FeO content and CaO/SiO$_2$. When $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{Fe}^{2+}$ is lower than 2.905, $\lg L_P^*$ shows a sudden drop. It is known that both $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Fe}^{2+}$ act as network modifiers to compensate for the charge of anionic groups. However, due to the stronger polarization of $\text{Fe}^{2+}$ than $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$, $\text{Fe}^{2+}$ can cause an obvious deformation of anionic group, resulting in the instability of $Q_0(P)$ and $Q_1(P)$ groups. The excessive increase of $\text{Fe}^{2+}$ dilutes the molar concentrations of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$, which decompose $Q_0(P)$ and $Q_1(P)$. The $\text{P}^{5+}$ ions in the decomposed $Q_0(P)$ and $Q_1(P)$ groups diffuse to the slag-metal interface and are reduced to the dissolved phosphorus in the liquid iron. For the increase of FeO content, on the one hand, the introduced $\text{O}^{2-}$ can combine with $\text{P}^{5+}$ to form $Q_0(P)$, and on the other hand, the introduced $\text{Fe}^{2+}$ cannot stabilize the $Q_0(P)$ and $Q_1(P)$ units. In the present study, hence, when FeO content is less than 21.9 mass%, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ plays a major role in fixing $\text{P}^{5+}$ and causes an increase in $\lg L_P^*$; when FeO content is greater than 21.9 mass%, the increasing $\text{Fe}^{2+}$ weakens the effect of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$, resulting in a decrease in $\lg L_P^*$. The Steps 2 and 3-1 in Fig. 15(b) demonstrate the fixation process of $\text{P}^{5+}$ and the Step 3-2 shows the decomposition process of $Q_0(P)$ and $Q_1(P)$ by FeO.

3.5. Analysis of the Thermodynamic Conditions of Dephosphorization

It can be known from the thermodynamic equilibrium condition that the oxidative atmosphere and high basicity (CaO/SiO$_2$) are favorable for dephosphorization. It can be understood from the point of view of ion theory that in the case of high oxygen potential, the more oxygen can be dissolved into the liquid iron, and continuously diffuse to the slag-metal interface. The process can be depicted in the Step 1 of Fig. 15(b). At the interface, the reduction reaction of oxygen leads to the corresponding increase of $\text{O}^{2-}$ in the slag, so $Q_0(P)$ increases accordingly, $L_P$ gradually increases, and the dephosphorization rate is improved significantly. However, at a higher oxygen potential, the excessive iron is oxidized into the molten slag, resulting in a sharp increase in
Fe	extsuperscript{2+} in the slag. Fe	extsuperscript{2+} has a strong polarization force, which tends to be around Q	extsuperscript{0}(P) and Q	extsuperscript{1}(P), and thereby Q	extsuperscript{0}(P) and Q	extsuperscript{1}(P) are polarized and deformed. The polarized Q	extsuperscript{0}(P) and Q	extsuperscript{1}(P) units are difficult to exist stably, dissociate into P	extsuperscript{5+} and enter the liquid iron after being reduced.

When the basicity of molten slag is higher, both O	extsuperscript{2−} and Ca	extsuperscript{2+} generated by the decomposition of CaO increase, which play the major role in binding P	extsuperscript{5+} ion and stabilizing Q	extsuperscript{0}(P) and Q	extsuperscript{1}(P) units, respectively, resulting in an increase in IgL	extsuperscript{P} and a higher dephosphorization rate. However, excessive CaO content can make the slag viscous, which is not conducive to dephosphorization from a kinetic point of view. Meanwhile, considering the dual roles of FeO on dephosphorization, the effect of Fe	extsuperscript{2+} on the deformation of phosphorus-oxygen group can be eliminated by replacing part of Fe	extsuperscript{2+} with Ca	extsuperscript{2+}. Therefore, the CaO/FeO ratio in the slag should be at an appropriate value to obtain a higher phosphorus distribution ratio. According to the above results, metallurgists can appropriately control the basicity and FeO content of steelmaking slag to improve the dephosphorization efficiency, reduce the phosphorus content in the steel, and further improve the quality of the steel.

4. Conclusions

In the present study, the effect of FeO and CaO/SiO	extsubscript{2} on the equilibrium distribution ratio of phosphorus was studied through the dephosphorization equilibrium experiment of molten slag and liquid iron at 1600°C. Then, the melt structure of final slag was determined by Raman spectroscopy. According to the analysis results of Raman spectra, it was found that there were only two forms of phosphorus ions in the slag, Q	extsuperscript{0}(P) and Q	extsuperscript{1}(P). Hence, the ionic equation of dephosphorization reaction was established, the formulas for phosphate capacity and the equilibrium distribution ratio of phosphorus were redefined and the thermodynamic conditions for enhanced dephosphorization were analyzed in detail. The results showed that the presence of P	extsuperscript{5+} in the slag in the form of Q	extsuperscript{0}(P) could significantly improve L	extsuperscript{P}, indicating that Q	extsuperscript{0}(P) was more stable than Q	extsuperscript{1}(P). With increasing CaO/SiO	extsubscript{2} from 0.15 to 1.25, the increasing free O	extsuperscript{2−} ions could combine with P	extsuperscript{5+} to form a stable Q	extsuperscript{0}(P) unit, which was fixed by Ca	extsuperscript{2+} and Mg	extsuperscript{2+}; hence, the dephosphorization rate, equilibrium distribution ratio of phosphorus and phosphate capacity both showed an increasing trend. As the molar concentration of FeO gradually increased, the O	extsuperscript{2−} ion dissociated by FeO also played the role in forming Q	extsuperscript{0}(P). However, when the FeO content increases to 29.2 mass%, the excessive Fe	extsuperscript{2+} ion decreased the proportion of Ca	extsuperscript{2+} and Mg	extsuperscript{2+} ion, thereby reducing the stability of Q	extsuperscript{0}(P) and Q	extsuperscript{1}(P), so that P	extsuperscript{5+} at the interface was reduced to the dissolved phosphorus in the liquid iron.

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