Study on Slag Forming Route of Dephosphorization in Combined Blown Converter

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Abstract: In order to achieve the purpose of high-efficiency dephosphorization by single-slag method during the combined blown converter steelmaking process, the CaO-SiO2-FeO-MgO-MnO-P2O5 slag system was taken as the research object, and the slag-forming route of dephosphorization was studied. The effects of slag compositions on the liquidus and the contour map of phosphorus distribution ratios (recorded as \(L_p\)) were calculated by thermodynamics software FactSage, and then the theoretic slag-forming route of dephosphorization was obtained. The effects of slag compositions on dephosphorization rate and \(L_p\) were studied by a high-temperature experiment. Based on the results of the theoretic calculation and high-temperature experiment, the actual slag-forming route of dephosphorization by the single-slag process in the combined blown converter was obtained: The initial slag composition should be around 15.0%CaO-44.0%SiO2-41.0%Fe2O. The composition of high-efficiency dephosphorization slag should be around 50.8%CaO-24.2%SiO2-25%Fe2O. The final slag composition should be around 65.6%CaO-28.3%SiO2-6.1%Fe2O. After using the actual slag-forming route in the production, the dephosphorization rate was increased by 3.6%, and the consumption of slagging materials was reduced by 3.78 kg/t.

Keywords: dephosphorization; slag-forming route; CaO-SiO2-FeO-MgO-MnO-P2O5 slag system; thermodynamic calculation; single-slag process

1. Introduction

With the continuous improvement of customers’ requirements for steel purity, the removal of harmful element phosphorus in steel has gradually become an important problem faced by steelmakers. In the converter blowing process, due to the continuous change of temperature and metal composition, coupled with the addition of lime and other slagging materials, the compositions of slag and its physical and chemical properties are constantly changing. In order to obtain the slag with refining function, the selection of a slag-forming route is very important. This is particularly important for the dephosphorization process because the dephosphorization reaction does not reach thermodynamic equilibrium during the converter blowing process, and the composition of slag plays a key role in the phosphorus content at the end-point of molten steel. The blowing method of the converter also has a great influence on the dephosphorization reaction. To the top blown converter, because of the poor stirring, the reaction is far from equilibrium. To the bottom blown converter, because the fluidity of the slag is poor in the early stage, the dephosphorization effect is not good. To the top and bottom blown converter, because the stirring ability is better than that of the top blown converter and the fluidity of the slag is better than that of the bottom blown converter, the dephosphorization reaction is near equilibrium, and
the dephosphorization effect is good. Therefore, most large and medium-sized converters adopt combined blown converters for steelmaking. In addition, the different slag-forming routes directly affect the stability of the converter operation, the hit ratio of the end-point, and the service life of the converter lining, etc., which has an important effect on the quality of steel products, the production cost and production efficiency of the enterprises.

Many scholars have studied the effect of slag composition and temperature on the dephosphorization efficiency under different conditions used by the methods such as theoretic calculation, high-temperature experiment and industrial test [1–16]. Some scholars have carried out research work on the slag-forming system and route of the converter process. Wang Yang et al. [17] discussed the dephosphorization by the double-slag process in converter steelmaking. A low-basicity slag (similar to 1.5–2.0) in the dephosphorization stage is required in the double-slag process. The dephosphorization ratio reached a maximum of 71% when the slag basicity was 1.7. Wang Xuebin et al. and Wu Wei et al. [18–20] discussed the slag-forming route for blowing the hot metal with medium or high phosphorus content in combined blown converter from the two aspects of slag basicity and oxidizability. The results showed that the slag-forming route with higher FeO content in the early and middle stages should be selected in the dephosphorization period. The FeO content and basicity of the slag for blowing the hot metal with the higher phosphorus content were much higher than those for blowing the hot metal with the lower phosphorus content. S. Basu et al. [21] studied the slag-forming route of the hot metal with the phosphorus content of 0.18–0.24% by the single-slag method at Tata Iron and Steel Plant. The phosphorus distribution ratio ($L_p$) was only 35–60% of the equilibrium value when the slag basicity was 1.7. The fluidity of the slag was the main reason that affected the dephosphorization during the final stage of blowing. A test study was carried out on a 150 t combined blown converter, and it was found that the FeO content in the slag should be maintained more than 20% during the whole blowing process to ensure that the slag had good fluidity and certain basicity. Wang Yang et al. [17] studied the effect of slag composition on the dephosphorization rate by the double-slag process in an industrial 150 t converter. The research results showed that when the basicity of slag was 1.7, the dephosphorization rate could reach 71%. When the FeO content was at about 16–20%, the dephosphorization slag could be discharged rapidly. The research work provided an important theoretic reference for the formulation and optimization of the slag-forming route.

In this paper, the CaO-SiO$_2$-Fe$_\text{O}$-MgO-MnO-P$_\text{2O}_5$ slag system was taken as the research object. The effects of slag compositions on liquidus and the contour map of the $L_p$ were calculated by thermodynamics software FactSage, and the theoretic slag-forming route of dephosphorization by the single-slag process was obtained. The effects of slag compositions on the $L_p$ were studied by a high-temperature experiment, and the actual slag-forming route of dephosphorization was obtained based on thermodynamic calculations and a high-temperature experiment. Then, the actual slag-forming route was applied to a 210 t combined blowing converter.

2. Calculation and Experiment

For the CaO-SiO$_2$-Fe$_\text{O}$-MgO-MnO-P$_\text{2O}_5$ six-element slag system, the calculated scheme was designed, and slag basicity (R, binary basicity, CaO/SiO$_2$) was in the range of 1.5–3.5%, FeO content was in the range of 10–35%, MgO content was in the range of 3–13%, MnO content was in the range of 3–13%, P$_\text{2O}_5$ content was in the range of 2–12%, and the temperature was in the range of 1573–1698K. The effect of different compositions and temperatures on $L_p$ were calculated by the calculated results.

The CaO-SiO$_2$-Fe$_\text{O}$-MgO-MnO-P$_\text{2O}_5$ six-element slag system with blowing the hot metal of about 0.15% phosphorus content by the single-slag process in combined blown converter was taken as the research object. The effects of binary basicity (%CaO/%SiO$_2$, recorded as R), FeO, MgO, MnO and P$_\text{2O}_5$ content of the slag composition on the $L_p$ were
calculated by using the regular ionic solution model [22]. The dephosphorization reaction is shown in Equation (1):

$$2[P] + 5(\text{FeO}) = (\text{P}_2\text{O}_5) + 5[\text{Fe}]$$

(1)

the standard equilibrium constant of the reaction can be expressed by Equation (2),

$$K^\Theta = \frac{\gamma_{\text{P}^{5+}} x(\text{P}^{5+})^2}{(w[P])^2 \cdot \gamma_{\text{Fe}^{2+}}^5 x(\text{Fe}^{2+})^5}$$

(2)

Among them, $K^\Theta$ is the Standard equilibrium constant, $K^\Theta = 2.34 \times 10^{-2}$. According to the experiment, it had little relationship with temperature [22]. Here, the simplified calculation method was used, and the effect of temperature on the reaction was ignored. $\gamma$ is the activity coefficient; $x$ is the molar percentage content, %; $w$ is the weight percentage content, %.

The $L_p$ was calculated by Equation (3). In Equation (3), $L_p$ is the ratio of P content in slag by molar percent to P content in metal by mass percent. In the paper, the calculation method was simplified. The solubility of P in molten iron is considered to be small, and the activity coefficient of P is taken as 1.

$$L_p = \frac{x(\text{P}^{5+})}{w[P]} = (K^\Theta)^{1/2} \cdot \frac{x(\text{Fe}^{2+})^{2.5} \cdot \gamma_{\text{Fe}^{2+}}^{2.5}}{\gamma_{\text{P}^{5+}}}$$

(3)

The liquidus of the CaO-SiO$_2$-FeO ternary slag system was calculated by the Equilib Module of the thermodynamic software FactSage. On this basis, the liquidus diagrams of different slag systems were calculated after adding MgO, MnO and P$_2$O$_5$ compositions. The iso-phosphorus partition ratio diagram was calculated by using the regular ionic solution model, and the calculated liquidus diagram and the iso-phosphorus partition ratio diagram were superimposed together to obtain Figure 1. In Figure 1., the calculation temperature of the iso-phosphorus partition ratio diagram of the slag system was 1350 °C. The calculation temperature on the dephosphorization reaction (phosphorus partition ratio) was ignored.

Figure 1. The superimposed liquidus diagram and the iso-phosphorus partition ratio diagram of the CaO-SiO$_2$-FeO-MgO-MnO-P$_2$O$_5$ six-element slag system.
**Experiment**

The effect of the compositions on dephosphorization was studied by the classical thermodynamic quasi-equilibrium method between slag and molten metal. The metal materials used in the experiment were industrial pure iron, ferrophosphorus and ferromanganese, which were prepared to obtain the hot metal for the experiment. The slagging materials were made up of chemical reagents CaO, SiO₂, MgO, Fe₂O₃, MnCO₃, and all chemical reagents were analytically pure. The experiment slag system was the CaO-SiO₂-Fe₂O₃-MgO-MnO-P₂O₅ six-element slag system. The content of Fe₂O₃ in the slag system is in the range of 10–35%, the content of P₂O₅ is in the range of 2–12%, the content of MgO and MnO are in the range of 3–13%, and the binary basicity (CaO/SiO₂) is in the range of 1.5–3.5. Because the dephosphorization reaction mainly occurred in the initial and middle stages of blowing, the dephosphorization slag system in the initial and middle stages of blowing was taken as the reference slag system, and the ranges of the composition were: slag basicity was in the range of 1.5–2.1, Fe₂O₃ content was in the range of 10–30%, MnO content was in the range of 1–9%, P₂O₅ content in the slag was calculated by material balance, SiO₂ and CaO contents in the slag were directly mixed into the initial slag, MgO content was added into the initial slag according to the final slag of 7%.

The main device used in the experiment was a high-temperature silicon molybdenum furnace (YiDing Technology Co., Ltd., Chongqing, China). The heating element consists of four silicon molybdenum (MoSi₂) rods, and the temperature control precision was ±2 °C, furnace size of Φ 90 mm, and the height of the constant temperature zone was 160 mm. The experiment device was shown in Figure 2.

![Figure 2](image.png)

**Figure 2.** A diagram of the experiment device. 1: Furnace shell, 2: Melt and slag, 3: Temperature control instrument, 4: Furnace cover, 5: Heating element, 6: Furnace chamber, 7: Corundum crucible, 8: Graphite crucible, 9: Corundum support tube, 10: Thermocouple, 11: Foam alumina support plug and 12: Furnace pallet.

In order to determine the quasi-equilibrium time of the thermodynamic distribution between slag and hot metal, the preliminary experiment was carried out. The 150 g iron sample containing phosphorus and 39 g slag were put into the corundum crucible. The corundum crucible was put into a 1370 °C high-temperature furnace, and N₂ was introduced into the furnace for protection. After the molten iron was melted, the slag was added into the crucible every 30 s three times. The initial iron sample and slag composition were the same in each experiment. After holding for different times, the crucible was quickly taken out of the furnace and cooled in water. The compositions of the iron sample and primary slag sample were analyzed after treatment. The steel samples during the experiment were drilled to analyze the composition of C and P content. The change of C
and P content with time was shown in Figure 3. According to Figure 3, dephosphorization was mainly concentrated in the first 5 min. After 50 min of the reaction, the P content in molten iron decreased to the lowest, and phosphorus returned at 65 min. However, after 35 min, the C content in molten iron decreased, which cannot meet the requirements of subsequent steelmaking. Therefore, the dephosphorization time was determined to be 35 min.

![Figure 3. Phosphorus and carbon content with time.](image)

In the experiment, first, the corundum crucible with iron and slag was put into the graphite crucible. Then, the graphite crucible was put into the high-temperature silicon molybdenum furnace. After the temperature rose to 1370 °C, the temperature was kept constant, and N₂ was introduced as a protective gas. After 35 min, we took out the crucible immediately and put it into water for cooling quickly. After the sample was processed, the contents of C, Mn, P and other elements in the steel were analyzed.

At the end of dephosphorization, the amount of slag was very small and could hardly be taken out. Therefore, the composition of the final slag was obtained by material balance calculation. The calculation method of the final slag composition was as follows:

During the steelmaking process, the main reaction of oxidation of element C is shown in Equation (4):

\[
C + Fe₂O₃ = Fe + 3CO \tag{4}
\]

The reaction of oxidation of element P is shown in Equation (5):

\[
2P + \frac{5}{3}Fe₂O₃ = \frac{10}{3}Fe + P₂O₅ \tag{5}
\]

The reaction of oxidation of element Mn is shown in Equation (6):

\[
3Mn + Fe₂O₃ = 3MnO + 2Fe \tag{6}
\]

Suppose that the weight of hot metal at the end of dephosphorization is \(A\); the initial weight of molten iron is \(a\); the initial carbon content is \(B\); the end-point carbon content is \(b\); the initial phosphorus content is \(P\); the end-point phosphorus content is \(p\); the initial manganese content is \(M\); the end-point manganese content is \(m\). Then, the relationship of \(A, a, b, P, p, M, \) and \(m\) can be expressed by Equation (7):

\[
A = a + \frac{560}{186} \times \left( \frac{aP}{100} - p \cdot A \right) + \frac{112}{36} \times \left( \frac{aB}{100} - b \cdot A \right) + \frac{112}{165} \times \left( \frac{aM}{100} - m \cdot A \right)
- \left( \frac{aP}{100} - p \cdot A \right) - \left( \frac{aB}{100} - b \cdot A \right) - \left( \frac{aM}{100} - m \cdot A \right) \tag{7}
\]

Equation (7) can be simplified by Equation (8)

\[
A = a + \frac{374}{186} \times \left( \frac{aP}{100} - p \cdot A \right) + \frac{76}{36} \times \left( \frac{aB}{100} - b \cdot A \right) - \frac{53}{165} \times \left( \frac{aM}{100} - m \cdot A \right) \tag{8}
\]
While \( a \) can be obtained by weighing, \( B, b, P, p, M, \) and \( m \) can be obtained by chemical analysis. Therefore, the final weight of molten iron can be obtained, and the oxidation degree can be obtained by inverse deduction, and then the final slag composition can be obtained.

### 3. Results and Discussion

#### 3.1. Thermodynamic Calculation Results

The effects of the slag composition and temperature on dephosphorization were calculated using the regular ionic solution model. The effects of \( \text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, \text{MgO}, \text{MnO} \) content and temperature on the \( L_p \) under different basicity conditions were shown in Figure 4a–e.

**Figure 4.** (a) The effect of \( \text{Fe}_2\text{O}_3 \) content on the equilibrium \( L_p \) (In the condition that \( \text{MgO} \) content was 7\%, \( \text{MnO} \) content was 5\%, \( \text{P}_2\text{O}_5 \) content was 5\%, and the temperature was 1623 K). (b) The effect of \( \text{P}_2\text{O}_5 \) content on the equilibrium \( L_p \) (In the condition that \( \text{MgO} \) content was 7\%, \( \text{MnO} \) content was 5\%, \( \text{Fe}_2\text{O}_3 \) content was 20\%, and the temperature was 1623 K). (c) The effect of \( \text{MgO} \) content on the equilibrium \( L_p \) (In the condition that \( \text{MnO} \) content was 5\%, \( \text{Fe}_2\text{O}_3 \) content was 20\%, \( \text{P}_2\text{O}_5 \) content was 5\%, and the temperature was 1623 K). (d) The effect of \( \text{MnO} \) content on the equilibrium \( L_p \) (In the condition that \( \text{MgO} \) content was 7\%, \( \text{Fe}_2\text{O}_3 \) content was 20\%, \( \text{P}_2\text{O}_5 \) content was 5\%, and the temperature was 1623 K). (e) The effect of temperature on the equilibrium \( L_p \) (In the condition that \( \text{MgO} \) content was 7\%, \( \text{MnO} \) content was 5\%, \( \text{Fe}_2\text{O}_3 \) content was 20\%, and \( \text{P}_2\text{O}_5 \) content was 5\%).
It can be seen from Figure 4a–e that $L_p$ increased with the increase of slag basicity because the increase of basicity improved the ability to retain phosphorus in slag. From Figure 4a, when the Fe$_2$O content was about 20%, and the $L_p$ was the largest. It should be noted that when the slag basicity was larger than 2.5, the phosphorus distribution ratio corresponding to 15% and 20% Fe$_2$O content have little difference. However, when the slag basicity was smaller than 2.0, the dephosphorization effect of 20% Fe$_2$O content was obviously better than that of 15% Fe$_2$O content. The reason is that, on the one hand, Fe$_2$O acts as oxidation and promotes dephosphorization. On the other hand, a large amount of Fe$_2$O dilutes the concentration of CaO, which is not conducive to dephosphorization. Therefore, the ratio of (% CaO)/(% Fe$_2$O) in the slag should be suitable to obtain a higher $L_p$. From Figure 4b, the $L_p$ gradually decreased with the increase of P$_2$O$_5$ content. For the dephosphorization reaction, P$_2$O$_5$ is the product of the chemical reaction. It is not conducive to the dephosphorization reaction when the product of the chemical reaction increased. Therefore, the $L_p$ gradually decreased. The reason is that the increase of P$_2$O$_5$ content increased the product of the dephosphorization reaction. From Figure 4c,d, the $L_p$ gradually decreased with the increase of MgO and MnO contents. The reason was that the effect of MgO and MnO in the dephosphorization process was much less than CaO and FeO, which directly participated in the reaction. The increase of MgO and MnO content diluted CaO and FeO content. In the actual production process, both MgO and MnO are oxides that cannot be avoided, and their role is not necessarily negative. An appropriate content range of these oxides can reduce the melting point of the slag, improve the fluidity of the slag, improve the melting of lime and play a beneficial role in dephosphorization. Therefore, the MgO and MnO contents need to be in an appropriate range to promote dephosphorization. From Figure 4e, the $L_p$ decreased with the increase of temperature because dephosphorization is an exothermic reaction. From the thermodynamic view, low temperature is beneficial to dephosphorization. In the actual production process, slag formation is difficult when the temperature is low. It is necessary to coordinate the relationship between low-temperature dephosphorization and forming slag.

The slag-forming route of dephosphorization was obtained by the above theoretic calculation, as shown in Figure 5. From Figure 5, it was suggested to select a slag-forming route with the $L_p$ rising rapidly and the slag melting point rising slowly, which is good for slugging rapidly and formation slag beneficial for dephosphorization. In the early stage of the converter steelmaking process, the temperature in the furnace is low. Especially when the basicity (R is about 0.5) is low in the initial stage of dephosphorization, the Fe$_2$O content of slag should be increased in order to form the slag with good fluidity quickly. From Figure 4a, when the basicity of the slag was about 2.0, and the Fe$_2$O content was about 20%, the theoretic $L_p$ was relatively high. Therefore, the composition of the high-efficiency dephosphorization slag is near the range in the middle stage of dephosphorization. At the final stage of dephosphorization, on the one hand, Fe$_2$O content in the slag should be reduced to decrease the iron loss; on the other hand, slag with the ability to retain phosphorus should be formed to prevent phosphorus returning to molten steel. Based on the analysis, the slag-forming route with higher Fe$_2$O content in the early and middle stages should be adopted for dephosphorization in the converter blowing process, as shown in the ABC route in Figure 5. In the initial stage of dephosphorization, we selected the area near point A where the slag melting point was low. The slag composition at point A was 15.0%CaO-41.0%Fe$_2$O-44.0%SiO$_2$. The melting temperature of slag at point A was only 1260 °C measuring by a hemispherical point device, which was beneficial for the rapid formation of initial dephosphorization slag. In the middle stage of dephosphorization, the high-efficiency dephosphorization slag should be formed. At this time, the slag composition should be near point B. The slag composition of B was 53.0%CaO-21.5%Fe$_2$O-25.5%SiO$_2$, the basicity of the slag was about 2.1, and the theoretic $L_p$ was relatively high. At the final stage of dephosphorization, the slag formed near point C had a slag composition of 65.6%CaO-6.1%Fe$_2$O-28.3%SiO$_2$. 

\[ \text{CaO} - 4 \text{Fe}_2\text{O}_3 - 2 \text{SiO}2 \]
of the converter steelmaking process, the temperature in the furnace is low. Especially when the basicity (R is about 0.5) is low in the initial stage of dephosphorization, the Fe content of slag should be increased in order to form the slag with good fluidity quickly.

3.2. Experiment Results

The effect of slag basicity and FeO content on dephosphorization was studied by the high-temperature experiment. The \( L_p \) in the high-temperature experiment was calculated by Equation (9).

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

(9)

In Equation (9), \( L_p \) is the ratio of P contents in slag and metal by mass percent.

The effect of slag basicity on the dephosphorization rate and the \( L_p \) is shown in Table 1 and Figure 6. From Table 1 and Figure 6, in the condition that the experiment temperature was 1370 °C, the P content in hot metal was 0.1%, and the FeO content in the slag was 20% when the slag basicity increased from 1.5 to 2.1, the dephosphorization rate increased from 52% to 72%, increasing by 1.4 times; the \( L_p \) increased from 10.7 to 26.6, increasing by 2.5 times. From the thermodynamic view, because P in hot metal is oxidized to P2O5 by FeO in the slag, and P2O5 and CaO can form a stable compound Ca3(PO4)2. With the increase of slag basicity, the higher the concentration of free CaO in the slag, the stronger the ability to retain phosphorus in slag and the higher the phosphorus distribution ratio.

Table 1. The effect of slag basicity on the dephosphorization rate.

| Case No. | R  | C Content in Hot Steel/wt.% | Mn Content in Hot Steel/wt.% | C Content in Semi-Steel/wt.% | P Content in Semi-Steel/wt.% | Dephosphorization Rate/% |
|----------|----|---------------------------|-----------------------------|-----------------------------|-----------------------------|--------------------------|
| 1        | 1.5| 4.15                      | 0.33                        | 3.60                        | 0.048                       | 52%                      |
| 2        | 1.7| 4.15                      | 0.33                        | 3.57                        | 0.038                       | 62%                      |
| 3        | 1.9| 4.15                      | 0.33                        | 3.55                        | 0.032                       | 68%                      |
| 4        | 2.1| 4.15                      | 0.33                        | 3.56                        | 0.028                       | 72%                      |
increased from 9.6 to 51.0, increasing by 5.3 times. From the observed experimental results, the experiment temperature was 1370 °C, the P content in hot metal was 0.1%, and the slag basicity was 2.1 when the Fe\textsuperscript{t} content in the slag increased from 6.7% to 30.0%, the dephosphorization rate increased from 42% to 84%, increasing by 2.0 times; the \( L_p \) increased from 9.6 to 51.0, increasing by 5.3 times. From the observed experimental results in Figure 6, when the Fe\textsuperscript{t} content increased from 15.0% to 25.0%, the \( L_p \) increased rapidly. When the Fe\textsuperscript{t} content was less than 15.0% or more than 25.0%, the \( L_p \) increased slowly. The dephosphorization rate and the \( L_p \) increased with the increase of Fe\textsuperscript{t}O content. The reason is that Fe\textsuperscript{t}O acts as an oxidant to oxidize P to P\textsubscript{2}O\textsubscript{5}, which increases the oxygen concentration at the interface between slag and metal, and promotes the dephosphorization reaction. When the Fe\textsuperscript{t}O content is less than 15.0%, the oxidizability of slag is relatively weak, and the fluidity of the slag is relatively not good, which is not beneficial for the dephosphorization reaction. When the Fe\textsuperscript{t}O content is more than 25.0%, the CaO content in the slag would be diluted, the basicity of the slag would be reduced, and the ability to retain phosphorus in slag is relatively worse, which will affect the dephosphorization efficiency.

![Figure 6. The effect of slag basicity on the \( L_p \).](image)

Table 2.

| Case | No. | Initial O Content in Slag | Final O Content in Slag | Fe\textsuperscript{t}O Content in Slag | \( L_p \) Obtained by Experimental Results | \( L_p \) Obtained by Theoretical Calculation |
|------|-----|----------------------------|-------------------------|----------------------------------------|------------------------------------------|------------------------------------------|
| 1    | 1   | 10.7                       | 21.7                    | 16.5                                   | 26.0                                     | 26.6                                     |
| 2    | 2   | 15.0                       | 30.0                    | 21.7                                   | 51.0                                     | 52.0                                     |
| 3    | 3   | 20.0                       | 40.0                    | 25.0                                   | 53.0                                     | 56.0                                     |
| 4    | 4   | 25.0                       | 50.0                    | 28.3                                   | 52.0                                     | 55.0                                     |
| 5    | 5   | 30.0                       | 60.0                    | 29.6                                   | 53.0                                     | 56.0                                     |
| 6    | 6   | 35.0                       | 70.0                    | 31.2                                   | 55.0                                     | 58.0                                     |
| 7    | 7   | 40.0                       | 80.0                    | 32.0                                   | 56.0                                     | 59.0                                     |
| 8    | 8   | 45.0                       | 90.0                    | 33.0                                   | 57.0                                     | 60.0                                     |
| 9    | 9   | 50.0                       | 100.0                   | 34.0                                   | 58.0                                     | 61.0                                     |

The effect of slag basicity on the dephosphorization rate and the \( L_p \) is shown in Table 2 and Figure 7, in the condition that the experiment temperature was 1370 °C, the P content in hot metal was 0.1%, and the slag basicity was 2.1 when the Fe\textsuperscript{t}O content in the slag increased from 6.7% to 30.0%, the dephosphorization rate increased from 42% to 84%, increasing by 2.0 times; the \( L_p \) increased from 9.6 to 51.0, increasing by 5.3 times. From the observed experimental results in Figure 6, when the Fe\textsuperscript{t}O content increased from 15.0% to 25.0%, the \( L_p \) increased rapidly. When the Fe\textsuperscript{t}O content was less than 15.0% or more than 25.0%, the \( L_p \) increased slowly. The dephosphorization rate and the \( L_p \) increased with the increase of Fe\textsuperscript{t}O content. The reason is that Fe\textsuperscript{t}O acts as an oxidant to oxidize P to P\textsubscript{2}O\textsubscript{5}, which increases the oxygen concentration at the interface between slag and metal, and promotes the dephosphorization reaction. When the Fe\textsuperscript{t}O content is less than 15.0%, the oxidizability of slag is relatively weak, and the fluidity of the slag is relatively not good, which is not beneficial for the dephosphorization reaction. When the Fe\textsuperscript{t}O content is more than 25.0%, the CaO content in the slag would be diluted, the basicity of the slag would be reduced, and the ability to retain phosphorus in slag is relatively worse, which will affect the dephosphorization efficiency.

![Figure 7. The effect of the Fe\textsuperscript{t}O content on the \( L_p \).](image)
Table 2. The effect of the Fe₂O content on the dephosphorization rate.

| Case No. | Fe₂O Content in Slag/wt.% | C Content in Hot Metal/wt.% | Mn Content in Hot Metal/wt.% | C Content in Semi-Steel/wt.% | P Content in Semi-Steel/wt.% | Dephosphorization Rate/% |
|----------|---------------------------|-----------------------------|----------------------------|----------------------------|-----------------------------|--------------------------|
| 5        | 6.7                       | 4.15                        | 0.33                       | 3.35                       | 0.058                       | 42%                      |
| 6        | 15.0                      | 4.15                        | 0.33                       | 3.01                       | 0.048                       | 52%                      |
| 7        | 18.0                      | 4.15                        | 0.33                       | 3.26                       | 0.047                       | 53%                      |
| 8        | 25.0                      | 4.15                        | 0.33                       | 3.50                       | 0.020                       | 80%                      |
| 9        | 30.0                      | 4.15                        | 0.33                       | 3.38                       | 0.016                       | 84%                      |

For Cases No. 5–9, the $L_p$ obtained by the experiment and by the theoretic calculation is shown in Figure 7. From Figure 7, when the Fe₂O content in the slag was about 25%, the $L_p$ obtained by the theoretic calculation reached the maximum value. However, when the Fe₂O content was about 30%, the $L_p$ obtained by the high-temperature experiment reached the maximum. There was a certain difference between the theoretic calculation and the experiment. Because the theoretic calculation is based on the equilibrium state, the experiment conditions do not reach the equilibrium state. Under the experiment conditions, the energy for the strong stirring of molten metal bath is insufficient, the contacting area between slag and metal is smaller, and the diffusion of reactants is slow. All these factors make it difficult for the reaction to reach the equilibrium condition. Although the increase of Fe₂O content in the slag is good for dephosphorization, the iron loss increases and the production cost increases too. Therefore, based on theoretic calculations and experiment results, it was appropriate that the Fe₂O content in the slag was about 25%.

The results of the high-temperature experiment showed that the $L_p$ increased with the increase of basicity. Considered the melting of slag, the basicity of the high-efficiency dephosphorization slag should be about 2.1, and the $L_p$ could reach 26.6. The Fe₂O content of the high-efficiency dephosphorization slag should be about 25.0%, and the $L_p$ could reach 42.8. Therefore, it was appropriate that the composition of high-efficiency dephosphorization slag was 50.8%CaO-24.2%SiO₂-25.0% Fe₂O.

3.3. Actual Slag Forming Route of Dephosphorization

The actual slag-forming route of dephosphorization is shown in Figure 8. The position of point B at the actual slag-forming route is different from the theoretic one. According to the experiment results, when the slag reached near point B (50.8%CaO-24.2%SiO₂-25.0%Fe₂O), the Fe₂O content was about 25%, and the basicity was about 2.1. the $L_p$ was relatively high at the time, which could form an efficient dephosphorization slag.

Figure 8. The actual slag-forming route of dephosphorization.
In summary, combined the thermodynamic calculations with the high-temperature experiment, the slag-forming route with high-efficiency dephosphorization was obtained: the composition of the initial slag was around 15.0%CaO-41.0%Fe\textsubscript{2}O-44.0%SiO\textsubscript{2}, the composition of the high-efficiency dephosphorization slag was around 50.8%CaO-25.0%Fe\textsubscript{2}O\textsubscript{2}-24.2%SiO\textsubscript{2}, and the composition of the final stage slag was around 65.6%CaO-6.1%Fe\textsubscript{2}O-28.3%SiO\textsubscript{2}. The actual slag-forming route can provide theoretical guidance for field tests.

3.4. Industrial Test

In the industrial test, the actual slag-forming route was applied to a 210 t combined blowing converter by the single-slag process. The process parameters, such as the feeding system, lance position and bottom blowing flow rate, were adjusted, and the optimized slag-forming route was carried out. Before and after the optimization of the slag-forming route, the slag samples of five heats were taken out from the early, middle and final stages. The compositions of slag samples were analyzed after treatment. The average values of slag compositions were shown in Table 3. The content of Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, Cr\textsubscript{2}O\textsubscript{3} and V\textsubscript{2}O\textsubscript{5} was little in the slag and is not listed in the table.

Table 3. A comparison of slag compositions of each stage before and after the optimization of the slag-forming route.

| Stage          | CaO Content/wt.% | SiO\textsubscript{2} Content/wt.% | FeO Content/wt.% | MgO Content/wt.% | P\textsubscript{2}O\textsubscript{5} Content/wt.% | MnO Content/wt.% | R   |
|----------------|------------------|-----------------------------------|------------------|------------------|----------------------------------|------------------|-----|
| Before optimization |                  |                                   |                  |                  |                                  |                  |     |
| Early          | 30.35            | 22.35                             | 13.36            | 8.18             | 3.50                            | 5.07             | 1.46 |
| Middle         | 40.35            | 18.43                             | 20.04            | 8.47             | 4.01                            | 3.10             | 2.19 |
| Final          | 38.23            | 11.17                             | 30.32            | 9.34             | 2.21                            | 2.26             | 3.42 |
| After optimization |                |                                   |                  |                  |                                  |                  |     |
| Early          | 19.45            | 27.97                             | 17.71            | 7.35             | 3.05                            | 6.98             | 0.70 |
| Middle         | 35.02            | 18.13                             | 18.72            | 8.21             | 5.95                            | 4.29             | 1.93 |
| Final          | 44.05            | 17.69                             | 13.27            | 9.53             | 2.96                            | 2.68             | 2.49 |

In order to compare the dephosphorization effect, the production data of 100 heats before and after optimization respectively were collected and calculated on the premise of ensuring that the Si content of hot metal before and after optimization was equivalent. The results of metallurgical effect before and after the optimization of slag-forming route were shown in Table 4. From Table 4, after optimizing the slag-forming route, the P\textsubscript{2}O\textsubscript{5} content in the slag increased from 2.23% to 2.86%, increased by 0.63%. The dephosphorization rate increased from 82.4% to 86.0%, increased by 3.6%. As a result of the industrial test, the dephosphorization rate was increased by 3.6%, and the consumption of slagging materials was reduced by 3.78 kg/t, in the condition that the phosphorus content of hot metal was increased. The purpose of improving the quality of steel products and saving costs were achieved.

Table 4. Comparison of metallurgical effect before and after the optimization of slag-forming route.

| Before Optimization | After Optimization |
|---------------------|--------------------|
| Hot metal data      |                    |
| Si content/wt.%     | 0.45               | 0.46               |
| P content/wt.%      | 0.128              | 0.149              |
| Data of end-point of blowing |            |                    |
| P content/wt.%      | 0.025              | 0.021              |
| Temperature/°C      | 1672               | 1670               |
| Consumption of lime/kgt\textsuperscript{-1} | 47.13 | 43.35 |
| P\textsubscript{2}O\textsubscript{5} content/wt.% | 2.23 | 2.86 |
| Dephosphorization rate/% | 82.4 | 86.0 |

4. Conclusions

In the paper, the CaO-SiO\textsubscript{2}-Fe\textsubscript{2}O-MgO-MnO-P\textsubscript{2}O\textsubscript{5} slag system was taken as the research object. The slag-forming route of dephosphorization by the single-slag process
in a combined blown converter was studied by thermodynamic calculation and a high-
temperature experiment, and the industrial test was carried out. The main results are
as follows:

1. The effects of slag compositions on the $L_p$ were studied by thermodynamic calculation.
The slag compositions at each stage were obtained: the compositions of the initial,
middle and final slag were around 15.0%CaO-41.0%FeO-44.0%SiO$_2$, 55.0%CaO-
24.5%FeO-25.5%SiO$_2$ and 65.6%CaO-6.1%FeO-28.3%SiO$_2$, respectively.
2. The results of the high-temperature experiment showed that, when the basicity was
about 2.1, and the FeO content was about 25.0% in the middle stage, the $L_p$ reached
the maximum. It was appropriate that the composition of high-efficiency dephosphor-
ization slag in the middle stage was around 50.8%CaO-25.0%FeO-24.2%SiO$_2$.
3. Based on the results of thermodynamic calculations and the high-temperature exper-
iment, the actual slag-forming route was obtained: the compositions of the initial,
middle and final slag were around 15.0%CaO-41.0%FeO-44.0%SiO$_2$, 50.8%CaO-
25.0%FeO-24.2%SiO$_2$ and 65.6%CaO-6.1%FeO-28.3%SiO$_2$, respectively.
4. The industrial test showed that, after using the actual slag-forming route, the dephos-
phorization rate was increased by 3.6%, and the consumption of slagging materials
was reduced by 3.78 kg/t. The purpose of improving the quality of steel products and
saving costs was achieved.

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