Research Article

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Dephosphorization mechanism and phase change in the reduction of converter slag

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Abstract: In the steelmaking process, the remained converter slag with P-containing materials is harmful to the molten steel in the next furnace. By the slag-splashing process with air blowing, P in the molten slag can be reduced and separated from the slag in the form of gas. In this paper, the reduction experiments of converter slag were carried out by flowing N$_2$ at high temperatures, and the P-containing gas formed in this process was cooled and collected in water. It is found that the P gas was mainly composed of P$_2$, which matched well with the results predicted by the FactSage7.2 calculation. The reaction mechanism of gasification dephosphorization in molten slag was analyzed, which was mainly proceeded on the surface of the slag. SEM-EDS and XRD were used to detect and characterize the samples. The ore phase of the converter slag and the gasification dephosphorization slag was determined, and the phase change was analyzed and compared.

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1 Introduction

At present, more than 100 million tons of converter slag is generated every year in China. The utilization ratio of the steel slag is less than 30% due to the high P content and free CaO; thus, most of the slag cannot be recycled in the steel industry and in other fields [1–6]. After proper treatment, the converter slag can be applied in metallurgy, chemical industry, agriculture, construction, and other fields; however, so far, in these fields, it has not been applied on a large scale. The recycling of slag in the converter such as double slag steelmaking, duplex converter, and slag-remaining operation is the novel way of slag treatment, which can significantly reduce the production of new slag. The slag-remaining operation has no restrictions on the smelting process, and it is suitable for promotion in most converters with a slag-splashing process [7–12].

The reuse of untreated molten slag in the next furnace has an adverse effect on the quality of molten steel, in which S and P contents will increase in the next furnace. Some scholars have proved that S can be easily removed as gas in slag-splashing [13–15]. If P can be removed by reduction in this process, the slag after treatment can be recycled in the next heat. In the process of gasification dephosphorization, P$_2$O$_5$ in molten slag can be reduced by C pre-added, and the P-containing gas formed in the reduction, such as P$_2$, P$_4$, PO, and P, is separated from the slag. In this paper, the mechanism of gasification dephosphorization in molten slag was studied, and the gas product of dephosphorization was confirmed, while the slag phases were analyzed.

2 Experiment device and methods

2.1 Experiment device

The horizontal tube box furnace (SG-GL1700) was used in the experiment with a maximum working temperature
of 1,700°C, as shown in Figure 1. The equipment has the function of evacuating, and after evacuating, N\textsubscript{2} was injected into the system to prohibit the reoxidation of the P-containing gas by residual air.

### 2.2 Experimental procedure

Before the experiment, the slag and C were ground and mixed well and then put into a boat-like MgO crucible with a total weight of 900 g and a mass ratio of 15:1. The slag composition is listed in Table 1.

The MgO-crucible containing the sample was put into the SG-GL1700 furnace, then N\textsubscript{2} was introduced after the system was vacuumed to \(-0.08\) mPa. The furnace was heated to 1,550°C according to the preset temperature-rising program and holed there for 50 min. P and its isotopes are water-insoluble; the P gas formed in the experiments was introduced into the water with flowing N\textsubscript{2} and collected in the water.

A thermodynamic analysis of the reaction between C and molten slag was carried out, and the mechanism of slag gasification dephosphorization was the inference. X-ray fluorescence (XRF), X-ray diffraction (XRD), and S-3400N scanning electron microscope (SEM) were used to characterize the samples.

### 3 Experimental results and analysis

#### 3.1 Analysis of reduced products

A sample of the dephosphorization product with an appropriate amount was powdered and analyzed by SEM-DES in the state of wet, and the two typical SEM images are shown in Figure 2.

Figure 2(c) and (d) shows the EDS detection results of the white area in Figure 2(a) and (b) as marked by the red square. The detection results indicate that the areas with bright white were composed of P, Si, and O elements. The black areas were dark shadows. P\textsubscript{2}O\textsubscript{5} reacts with water to generate phosphoric acid; it can be determined that P in the sample existed in the form of a simple substance. The substance containing Si in the sample is most likely to be SiO\textsubscript{2}, which was brought into the sample with the flowing gas in the furnace.

The samples were further detected with XRD, and the results are shown in Figure 3.

According to the test results of XRD, the sample is mainly composed of P\textsubscript{4}, P\textsubscript{2}O\textsubscript{5}, KCl, and SiO\textsubscript{2}, so the substance containing P in the sample is P\textsubscript{4}. In the process of detection, it is inevitable that parts of P substance would be oxidized by air, so P\textsubscript{2}O\textsubscript{5} was formed and detected in the XRD detection. KCl was not found in the EDS detection due to the uneven distribution of the

**Table 1: Composition of the slag used in this experiment**

| Composition | FeO   | SiO\textsubscript{2} | CaO   | MgO   | S    | MnO   | P\textsubscript{2}O\textsubscript{5} | Al\textsubscript{2}O\textsubscript{3} |
|-------------|-------|----------------------|-------|-------|------|-------|-----------------------------|-----------------------------|
| Content/wt% | 22.34 | 15.49                | 44.91 | 13.68 | 0.12 | 3.15  | 2.65                        | 1.23                        |
sample. However, $P_4$ is unstable at the high temperature, when the system temperature is higher than 1,073 K, and most of $P_2$ is the production of $P_4$ decomposition as shown in Figure 4.

In Figure 4, the main production of $P_2O_5$ reduction at high temperatures is $P_2$, and it becomes $P_4$ during the cooling process. The transformation of P-containing gas at high temperatures is shown in equation (1) [16,17].

$$P_4 + 224.1(kJ) = 2P_2$$  

Besides, the thermodynamic analysis of the slag reduction process was conducted by FactSage7.2, and the results are shown in Figure 5.

As shown in Figure 5, when the reaction between the molten slag and C in a closed system is in the equilibrium state, the partial pressure of $P_2$ vapor is the highest, followed by $P$, $PO$, and $P_4$. Therefore, the reaction containing $P_2$ is preferred in the $P_2O_5$ reduction of the molten slag. It is found that the simulated results by FactSage7.2 are consistent with the experiment.
3.2 Thermodynamic calculation

3.2.1 Thermodynamic calculation of oxide reduction in the slag

At steelmaking temperature, FeO, MnO, and P2O5 in the slag can be reduced by C. The chemical reactions under standard conditions are listed in equations (2)–(4).

\[
P_{2}O_{5(l)} + 5C_{(s)} = P_{2(g)} + 5CO_{(g)} \quad \Delta G^{\theta} = 603609 - 648.94T \quad (2)
\]

\[
FeO_{(l)} + C_{(s)} = Fe_{(g)} + CO_{(g)} \quad \Delta G^{\theta} = 141660 - 139.45T \quad (3)
\]

\[
MnO_{(l)} + C_{(s)} = Mn_{(g)} + CO_{(g)} \quad \Delta G^{\theta} = 292954 - 174.14T \quad (4)
\]

Under standard conditions, the starting reaction temperatures of FeO, MnO, and P2O5 are 1015.85, 1682.29, and 930.15 K. Furthermore, the oxygen potentials above under standard conditions are shown in Figure 6.

The results shown in Figure 6 indicate that the priority of reductions in the slag can be in the order of P2O5, FeO, and MnO. The reduction of 3CaO-P2O5 in the slag is showed in equation (5), and the starting reaction temperature of it is 1619.58 K.

\[
3CaO\cdot P_{2}O_{5(s)} + 5C_{(s)} = P_{2(g)} + 5CO_{(g)} + 3CaO_{(s)} \quad \Delta G^{\theta} = 1662900 - 1026.75T \quad (5)
\]

The chemical reactions of pure P2O5 that contain other forms of P gas under standard conditions are listed in equations (6)–(8) [18–20].

\[
P_{2}O_{5(l)} + 5C_{(s)} = 2P_{4(g)} + 5CO_{(g)} \quad \Delta G^{\theta} = 1099262 - 767.09T \quad (6)
\]

\[
2P_{2}O_{5(l)} + 10C_{(s)} = P_{4(g)} + 10CO_{(g)} \quad \Delta G^{\theta} = 965073 - 1141.52T \quad (7)
\]

\[
1/2P_{2}O_{5(l)} + 3/2C_{(s)} = PO_{4(g)} + 3/2CO_{(g)} \quad \Delta G^{\theta} = 613650 - 461.50T \quad (8)
\]

The final temperature of steelmaking is more than 1,873 K; equations (2)–(8) can occur at the steelmaking temperature under standard conditions. In this experiment, all of the reactions were further enhanced for the...
gas productions of CO, and P₂ was taken away with the flowing N₂.

Taking equation (2) as an example, when the reaction is in the state of equilibrium, the equilibrium constant of the chemical reaction can be described with equation (9).

\[ K^\theta = \exp \left( -\frac{\Delta G^\theta}{RT} \right) = \frac{P_{P_2}P_{CO}}{a_{P_2}a_{CO}} = \frac{P_{P_2}P_{CO}}{Y_{P_2}x_{P_2}a_C^2} \]

where \( a_C \) is the activity of C, 1; \( Y_{P_2O_5} \) is the activity coefficient of \( P_2O_5 \); \( x_{P_2O_5} \) is the mole fraction of \( P_2O_5 \); and \( a_{P_2O_5} \) is the radioactivity of \( P_2O_5 \).

The value of \( K^\theta \) is constant when the experiment temperature does not change. The equilibrium partial pressures of \( P_2 \) and CO are close to zero when the gases of \( P_2 \) and CO are continuously diluted by the flowing \( N_2 \), so all of the \( P_2O_5 \) in the slag can be reduced from the thermodynamics. Kinetics has a greater effect on the reduction of slag, and \( P_2O_5 \) cannot be reduced 100%.

### 3.2.2 Mechanism of gasification dephosphorization in the molten slag

The reaction of slag and C is consistent with the interface chemical reaction model [21]. The reaction should occur on the three-phase interface of C-slag-gas when the gas nucleation of CO and \( P_2 \) is performed in a heterogeneous manner. The gas bubbles in molten slag are mainly composed of CO when C was used as a reductant, so the reaction of gasification dephosphorization is mainly proceeded on the surface of the slag and CO bubble.

The buoyancy force of CO in the slag can be expressed as

\[ df = \frac{4}{3} \pi dr^3 (\rho_g - \rho_s) g \]

where \( dr \) is the bubble radius; \( \rho_g, \rho_s \) is the density of the slag and bubbles; and \( g \) is the acceleration of gravity.

According to the Stokes formula, the floating speed \( dv \) can be expressed as follows:

\[ dv = \frac{2}{9} \left[ \frac{dr^2 (\rho_g - \rho_s)}{\eta} \right] g \]

where \( \eta \) is the slag viscosity, ranging from 0.15 to 0.5 Pa S.

Since the density of slag is much higher than that of gas, equation (11) can be further simplified as follows:

\[ dv = \frac{2g}{9} \frac{dr^2 \rho_s}{\eta} \]

![Figure 7: CO bubbles equilibrated with \( P_2 \) at the slag interface.](image)

According to equation (12), the slag floating speed is directly proportional to the slag density and inversely proportional to the slag viscosity. Extensive studies have proved that the diameter of the bubbles in the slag is 4–12, and 5 mm was taken in this section.

The stable existence of CO bubbles requires the pressure (\( P_{CO} \)) of it to meet the conditions as shown in equation (13).

\[ P_{CO} \geq P_g + P_s + \frac{2\sigma}{r} \]

where \( P_g \) is the atmospheric pressure, Pa; \( P_s \) is the bubble internal pressure, Pa; and \( \sigma \) is the additional pressure at the new interface between CO and molten slag with the \( \sigma \) value of 0.47 N/m.

As shown in Figure 7, when the bubble of CO reached the surface of the slag, the critical pressure of CO can be calculated with equation (14).

\[ P_{CO} = P_g + \frac{2\sigma}{r} \]

According to equation (14), the equilibrium partial pressure of CO at the slag interface is 1,013,67 Pa after calculation. According to equation (9), the equilibrium constant of \( P_2O_5 \) reduction is \( 4.00928 \times 10^{-16} \) at 1,550°C. Based on the experimental data, the equilibrium partial pressure of \( P_2O_5 \) in the CO is \( 0.435 \times 10^{-4} \) Pa after calculation.

The calculation results above indicate that the partial pressure of \( P_2 \) is largely less than that of CO and the content of \( P_2 \) is very small in the CO bubble. Therefore, CO in the molten slag has a smaller promotion effect on the reduction of \( P_2O_5 \) from the thermodynamics, even in the surface of C particles and the crucible wall. The reduction of \( P_2O_5 \) in the molten slag mainly occurs on the surface of the slag.
3.3 Detection and analysis of the slag phase

3.3.1 Phase of the converter slag

The sample of the converter slag was detected with SEM-DES, and the results are shown in Figure 8. The components of different color regions in the microzone of the converter slag were detected by DES, and the results are given in Table 2.

According to the phase morphology of the converter slag from the microzone, the slag is mainly composed of three phases.

The first type is the silicate minerals phase which is mainly composed of Si and Ca, marked as A and B in Figure 8. Phase A was detected with EDS, and the results are shown in Table 3. In Table 3, the average content of CaO and SiO₂ in phase A is 55% and 25%, respectively, so phase A is most likely 3CaO·SiO₂ and 2CaO·SiO₂. Furthermore, the

![Figure 8: The results of the converter slag detected by SEM. (a) SEM image 1, (b) SEM image 2, (c) SEM image 3, (d) SEM image 4.](image-url)
The basicity of phase A was calculated, as shown in Figure 9. According to Figure 9, the basicity of phase A is mainly distributed between 2.0 and 3.0. The Ca in free CaO was also calculated during the detection of EDS; the actual ratio of CaO to SiO2 in phase A is smaller than the detected value. The compound with a mass ratio of CaO to SiO2 around 2.0 is mainly 2CaO·SiO2; hence, it can be speculated that phase A is 2CaO·SiO2. The same method was used to calculate phase B, and it was found that the mass ratio of CaO to SiO2 is mostly distributed between 3 and 3.5, so phase B is 3CaO·SiO2.

Table 2: The components of different color regions in the slag sample detected by DES

| Spectrum | C   | O   | Mg  | Si  | P   | Ca   | Mn | Fe | Rm |
|----------|-----|-----|-----|-----|-----|------|----|----|----|
| A        | —   | 44.43 | 0.77 | 12.21 | 3.03 | 34.05 | 0.56 | 7.05 | 2.08 |
| B        | —   | 42.36 | 1.93 | 9.94  | 2.74 | 34.89 | 0.23 | 7.43 | 2.62 |
| C        | 0.44 | 35.42 | 1.42 | 3.2   | 1.12 | 16.59 | 1.5  | 40.31 | 3.87 |
| D        | 0.10 | 38.99 | 12.87 | 1.01  | 1.13 | 7.55  | 8.21 | 30.14 | 5.58 |
| E        | —   | 29.7 | 1.57 | 4.28  | 0.28 | 57.37 | 0.53 | 6.23 | 10.01 |
| F        | 0.12 | 33.96 | 47.19 | 2.35  | 0.21 | 6.91  | 1.32 | 7.94 | 2.20 |
| G        | 1.13 | 37.41 | 6.04 | 18.76 | 1.48 | 28.90 | 1.50 | 4.78 | 1.15 |
| H        | 28.49 | 9.49 | 43.74 | 5.45  | 0.39 | 4.66  | 2.12 | 5.66 | 0.64 |
| K        | 2.06 | 29.85 | 1.60 | 2.12  | 2.31 | 5.29  | 1.82 | 54.95 | 1.86 |

Table 3: Composition of phase A

| Amount | Type | Chemical components (wt/%) |
|--------|------|----------------------------|
|        |      | MgO | SiO2 | P2O5  | CaO | MnO | Fe2O3 |
| 20     | Range | 0–7 | 16–26 | 2–9 | 40–68 | 0–3 | 0–15 |
|        | Average | 2.2 | 25 | 6.5 | 55 | 0.5 | 8 |

Table 4: Composition of phase C

| Amount | Type | Chemical components (wt/%) |
|--------|------|----------------------------|
|        |      | MgO | SiO2 | P2O5  | CaO | MnO | Fe2O3 |
| 20     | Range | 0–4 | 0–10 | 0–2 | 20–45 | 0–4 | 50–70 |
|        | Average | 1 | 5 | 1.2 | 26 | 1 | 68 |

Figure 9: The basicity distribution in phase A.

Figure 10: Molar ratio of Fe2O3 to CaO in phase C.

The second type is the calcium–iron minerals phase, which is mainly composed of Ca and Fe, marked as C in Figure 8. Phase C is mainly composed of Fe2O3 (FeO at high temperature) and CaO; the detection results with EDS are shown in Table 4.

In the slag, the compounds mainly composed by Fe and Ca in the converter slag are most likely to be CaO·Fe2O3 or 2CaO·Fe2O3. Furthermore, the molar ratio of Fe2O3 to CaO of microarea in phase C was calculated, as shown in Figure 10.

According to Figure 10, the molar ratio of Fe2O3 to CaO in phase C is mainly distributed between 0.8 and
According to the phase morphology and the composition in Table 5, phase D is most likely to be the RO phase. In the metallurgical industry, the phase of RO is defined as an extensive solid solution formed mainly by FeO, MgO, and other divalent metal oxides such as MnO. Here, the phase of RO is described as MgO-xFeO. The molar ratio of Fe$_2$O$_3$ to MgO in phase D was calculated as shown in Figure 11.

According to Figure 11, the molar ratio of Fe$_2$O$_3$ to MgO in the RO phase is mainly distributed between 0.8 and 1.2. Hence, it can be determined that the RO phase is mainly MgO-FeO. There are also some CaO and MnO existing in the RO solid solution phase, while SiO$_2$ has few components in it.

In the converter slag, free MgO (marked as F), Fe (marked as K), MgC (marked as H), and the composite phase composed of Ca, Mg, Fe, and Si (marked as G) were also detected with low contents. Furthermore, XRD was used to analyze the slag samples from the same furnace, and the results are shown in Figure 12.

According to Figure 12, the phases in the slag sample are mainly composed of 2CaO-SiO$_2$, 3CaO-SiO$_2$, CaO-Fe$_2$O$_3$, Ca (Mg, Fe) SiO$_4$, RO phase, and free CaO phase, which is consistent with the results above.

### 3.3.2 Phase of the gasification dephosphorization slag

The slag formed after the reaction of converter slag and CaO-Fe$_2$O$_3$ is defined as the gasification dephosphorization slag. The sample of the gasification dephosphorization slag was detected with SEM-DES, and the results are shown in Figure 13.

![Figure 11: The molar ratio of Fe$_2$O$_3$ to MgO in phase D.](image)

![Figure 12: The results of XRD detection for converter slag samples. (a) XRD results 1, (b) XRD results 2.](image)
When compared with the converter slag, most of the gasification dephosphorization slag exists in the form of a small dispersive particle or a long strip. The slag is mainly composed of four phases. The first type is the composite phase of Si and Ca, where phase A is 2CaO·SiO₂ in the form of dots, while phase B is 3CaO·SiO₂ in the tetragonal state. The second type is a composite phase that was composed of two or more compounds including Ca, Mg, and Fe, marked as Cf in Figure 13. The CaO·Fe₂O₃ and the RO phases in the gasification dephosphorization slag are difficult to detect; it is speculated that the Cf phase was formed from the reduction of them. The third type is C phase from the surplus reductant, marked as M in Figure 13. The fourth type is a composite phase which mainly

![Figure 13: The results of the gasification dephosphorization slag detected by SEM. (a) SEM image 1, (b) SEM image 2, (c) SEM image 3, (d) SEM image 4.](image)

| Amount Type | Chemical components (wt/%) |
|-------------|----------------------------|
| MgO | SiO₂ | P₂O₅ | CaO | MnO | Fe₂O₃ |
| Range | 9–16 | 28–40 | 0–3 | 50–65 | 0–5 | 0–8 |
| Average | 12 | 29 | 0.78 | 58 | 2 | 3 |
composed of Ca, Mg, and Si, marked as G phase in Figure 13. G phase was detected with EDS, and the results are given in Table 6. According to Table 6, the average molar ratio of CaO, MgO, and SiO₂ in the G phase is 1:0.3:0.48. Hence, it can be speculated that phase G is most likely to be 3CaO·MgO·2SiO₂. Furthermore, XRD was used to characterize the samples, and the results are shown in Figure 14.

According to Figure 14, the phases in the gasification dephosphorization slag are mainly composed of 2CaO·SiO₂,

| Time (min) | CaO | SiO₂ | MgO | Al₂O₃ | P₂O₅ | MnO | FeO | S |
|-----------|-----|------|-----|-------|------|-----|-----|---|
| 50        | 57.55 | 21.52 | 16.74 | 1.21  | 0.56 | 0.46 | 2.25 | 0.051 |

**Table 7:** Composition of converter slag after reduction (wt%)

**Figure 14:** The results of XRD detection. (a) XRD results 1, (b) XRD results 2.

**Figure 15:** The typical phase of converter slag and gasification dephosphorization slag. (a) Converter slag, (b) gasification dephosphorization slag.
3CaO·SiO₂, 3CaO·MgO·2SiO₂, 2CaO·Fe₂O₃, 2CaO·MgO·2SiO₂, and phase C, which is basically consistent with the results above. It can be seen that the free CaO and MgO in the converter slag were further reacted with other phases and the amount of 3CaO·MgO·2SiO₂ and 3CaO·SiO₂ increased. Based on the XRD results, 2CaO·MgO·2SiO₂ phase exists in the G phase, and 2CaO·Fe₂O₃ phase exist in the one phase of the C₁ mixed composite phase.

### 3.3.3 Phase change of converter slag after C reduction

After the reduction process, the chemical composition of the slag changes a lot, and the contents of Fe and P oxide in the slag are significantly reduced. After the reaction, the slag composition is given in Table 7.

The typical phase of the converter slag and the gasification dephosphorization slag is shown in Figure 15. According to Figure 15, 2CaO·SiO₂ and 3CaO·SiO₂ phases in the shape of a large-diameter particle or a strip in the converter slag were mostly dispersed and distributed in the form of small particles or strip after carbon reduction, while most of the CaO·Fe₂O₃ and the RO phases in the converter slag was reduced and formed a kind of multiple composite phases where Ca, Mg, and Fe were coexisted. The phase of converter slag was separated and cracked by the gas phase, such as CO and P₂, which were produced in the reduction of slag, and the free phase of CaO and MgO in the converter slag further reacted with other phases and existed in composite phases finally.

### 4 Conclusion

(1) The reduction of molten converter slag and C was carried out in flowing N₂ at high temperatures. Both the thermodynamics analysis and experiment prove that P₂O₅ in the converter slag can be reduced by C as reductant, and the P-containing gas formed in the reduction process is mainly composed of P₂. The experimental data were simulated with FactSage7.2, and the simulation results are consistent with the results above. The mechanism of gasification dephosphorization in the molten slag was analyzed, and it was proved that the reaction of gasification dephosphorization mainly proceeds with the slag surface.

(2) SEM-EDS and XRD were used to characterize the samples, and it is concluded that the phases in the slag sample are mainly composed of 2CaO·SiO₂, 3CaO·SiO₂, CaO·Fe₂O₃, RO phase, and free CaO, MgO phases. After reduction, 2CaO·SiO₂ and 3CaO·SiO₂ phases in the converter slag were separated and cracked by the gas phase, and the CaO·Fe₂O₃ and the RO phases in the converter slag were reduced and formed a coexist multiple composite phases of Ca, Mg, and Fe. However, the free phase of CaO and MgO in the converter slag further reacted with other phases and disappeared finally.

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### Author contributions:
In this work, Yuekai Xue and Peng Tian are responsible for the experimental design and data analysis. Chenxiao Li, Chaogang Zhou and Dingguo Zhao are responsible for the detection of samples, and shuhuan Wang is responsible for providing the overall idea.

### Conflict of interest:
The authors state no conflict of interest.

### References

[1] Jiang, M. F., Y. Y. Cui, D. Y. Wang, Y. Min, and C. J. Liu. Effect of modification treatment for reduction of dephosphorization slag in hot metal bath. *Journal of Iron and Steel Research International*, Vol. 1, No. 20, 2013, pp. 17–19.

[2] Carlini, R., I. Alfieri, G. Zanicchi, F. Soggia, E. Gombia, and A. Lorenzi. Synthesis and characterization of iron-rich glass ceramic materials: a model for steel industry waste reuse. *Journal of Materials Science and Technology*, Vol. 32, No. 11, 2016, pp. 1105–1110.

[3] Pathak, S., R. Choudhary, A. Kumar, and D. T. Damena. Feasibility assessment of the use of basic oxygen furnace slag in open graded asphalt courses. *International Journal of Pavement Research and Technology*, Vol. 12, No. 6, 2019, pp. 664–673.

[4] Cikmit, A. A., T. Tsuchida, G. Kang, R. Hashimoto, and H. Honda. Particle-size effect of basic oxygen furnace steel slag in stabilization of dredged marine clay - ScienceDirect. *Soils and Foundations*, Vol. 59, No. 5, 2019, pp. 1385–1398.

[5] Martinsson, J., B. Glaser, and D. Sichen, The structure of foaming BOF-converter slag. *Ironmaking and Steelmaking*, Vol. 46, No. 8, 2017, pp. 1–5.

[6] Wang, X. H. *Steel Metallurgy*, Education Press, Beijing, 2007, pp. 13–20.

[7] Zhou, H. M., Y. P. Bao, and L. Lin. Distribution of P₂O₅ between phosphorus-enrichment phase and matrix phase in
phosphorus slag. *Steel Research International*, Vol. 84, No. 9, 2013, pp. 78–86.

[8] Wang, S. H., Y. Q. Wu, Z. R. Xu, X. F. Lv, and X. Zhang, Thermodynamic analysis on gasifying dephosphorization of converter slag by silicon reduction. *Steelmaking*, Vol. 1, No. 24, 2008, pp. 31–34.

[9] Kim, K. D., W. H. Wan, and J. M. Dong. Effect of FeO and CaO on the sulfide capacity of the ferronickel smelting slag. *Metallurgical and Materials Transactions B*, Vol. 45, No. 3, 2014, pp. 889–895.

[10] Wang, Y., S. Yang, J. Li, et al. Dephosphorization by double-slag process in converter steelmaking. *High Temperature Materials and Processes*, Vol. 37, No. 7, 2018, pp. 625–633.

[11] Wu, W., S.-f. Dai, and Y. Liu, Dephosphorization stability of hot metal by double slag operation in basic oxygen furnace. *Journal of Iron and Steel Research International*, Vol. 24, No. 9, 2017, pp. 908–915.

[12] Zhou, C.-G., J. Li, C.-B. Shi, et al. Dephosphorization at the first deslagging in bof steelmaking process. *High Temperature Materials and Processes*, Vol. 35, No. 4, 2016, pp. 433–440.

[13] Chen, Q., R. Zhu, and J. Wu. Experimental study on desulfurization of copper slag by gasification. *Industrial Heating*, Vol. 46, No. 6, 2017, pp. 15–20.

[14] Wang, N., Z. G. Liang, and Z. S. Zou. Phosphorous enrichment in molten adjusted converter slag: part II enrichment behavior of phosphorus in CaO–SiO₂–FeOₓ–P₂O₅ molten slag. *Journal of Iron and Steel Research International*, Vol. 18, No. 12, 2011, pp. 22–26.

[15] Shengwen, W. U., W. Shuhuan, and J. Shantong, Kinetics of gas desulfurization in BOF slag. *Journal of University of Science and Technology Beijing*, Vol. 3, 2000, pp. 212–215.

[16] Liu, J., J. P. Xia, Z. J. Chen, Z. Q. Luo, and R. X. Geng, Yellow phosphorus production in electric furnace using potassium feldspar to replace silica as flux. *Journal of Chemical Engineering of Chinese Universities*, Vol. 31, No. 6, 2017, pp. 1419–1425.

[17] Meng, H., and S. W. Lu, Safety risks analysis and precautions for yellow phosphorus production with electric furnace process. *Inorganic Chemicals Industry*, Vol. 46, No. 6, 2014, pp. 56–58.

[18] Li, C. X., H. Li, and B. Zhou, Estimation of energy conservation and emissions reduction by substitution limestone for lime as the steelmaking slagging material. *China Metallurgy*, Vol. 10, No. 25, 2015, pp. 66–69.

[19] Cui, H. X., Q. W. Chen, and Y. Y. Shen, Technology research on phosphorus enrichment and application of converter steel slag. *China Metallurgy*, Vol. 20, No. 3, 2010, pp. 35–38.

[20] Liang Y. J., and C. Y. Che, *Handbook for Inorganic Thermodynamic Calculation*, Northeast University Press, Shenyang, 2001, pp. 219–222.

[21] L. V. Xiaofang, *Experimental Study on Kinetics of Gasifying Dephosphorization from Converter Slag under Flow Nitrogen Conditions*, Master’s thesis, Hebei Polytechnic University, Tangshan, 2006.