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EFFECT OF IRON OXIDE CONTENT ON DEPHOSPHORIZATION BEHAVIOR OF SLAG GASIFICATION

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The coke reduction gasification dephosphorization experiments were conducted on converter slag with FeO contents of 15 %, 20 %, 30 % and 35 %, respectively. Thermodynamic calculations , Scanning Electron Eicroscope(SEM) and Energy Dispersive Spectrometer (EDS) showed that the actual reduction Gibbs free energy of P_2O_5 was less than that of FeO for the coke reduction converter slag product of P_2, and the reactive driving force of P_2O_5 was greater under high FeO conditions. With the increase of FeO content, the gasification dephosphorization rate showed a trend of increasing first and then decreasing. After gasification dephosphorization, the presence of the Fe phase will adsorb more P elements, so the high FeO content is beneficial to increase the P_2O_5 activity, which is conducive to the gasification dephosphorization reaction.

Keywords: iron oxide, gasification dephosphorization, Gibbs free energy, converter slag, X-ray research

INTRODUCTION

Steel slag, as a by-product of the steelmaking process, is mainly composed of CaO, FeO, SiO_2, etc. It has a high recycling value, while the high phosphorus content in the slag limits its utilization in the next steelmaking furnace. In recent years, converter slag gasification dephosphorization operations have received increasing attention from researchhers[1-2], and gasification dephosphorization is a new method hat enables easier removal of phosphorus from the slag. M. Jiang[3] added SiO_2 or Al_2O_3 to the steel slag to remove the phosphorus from the slag by gasification and return it to the steelmaking process for smelting. Y. Miyashita[4] added carbon material and fluorite to the slag to destroy the $3CaO·P_2O_5$ - $2CaO·P_2O_5$ structure of the slag and found that 40 % of the phosphorus was removed by gasification. Y. Wang[5,6] conducted an experimental study on gasification dephosphorization of coke powder reduction converter slag, which confirmed the possibility of gasification dephosphorization reaction and provided a theoretical basis for realizing the recycling of converter slag. S. Wang[7] reduced converter slag with silicon, and the gasification dephosphorization rate was as high as 81,23 %,which is a good dephosphorization effect. In this paper, we mainly conducted gasification dephosphorization experiments on converter slag with different FeO contents and analyzed the effect of FeO contents on gasification dephosphorization by thermodynamic calculation and SEM - EDS detection based on experimental data.

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EXPERIMENTAL MATERIALS AND METHODS

Experimental materials

Take the final slag and coke of a steel plant's converter, and the composition is shown in Table 1 and Table 2. The slag and coke were crushed before the experiment, and the converter slag was reduced by 1,5 - 2 times the carbon equivalent in all heat experiments.

Table 1 **The composition of converter slage /wt.%**

FeO	CaO	SiO_2	MgO	MnO
20,24	48,57	17,45	7,36	2,25
P_2O_5				
3,09				

Table 2 **The composition of coke powder /wt.%**

C	CaO	SiO_2	MgO	S
86,7	1,37	6,77	0,24	0,71
other				
4,21				

Experimental methods

The main heating equipment for the thermal state experiment is a high temperature tube furnace. A corundum crucible was used for the experiments, and the corundum crucible was covered with graphite outside to protect the crucible. All furnace experiments were performed under the protection of nitrogen. The nitrogen flow rate was 0,4 m^3/h. Some heating experiments were adjusted by adding analytically pure FeO reagent, other experimental conditions were not changed.The slag composition was analyzed at the end of the experiment, and the gasification dephosphorization rate was calculated by equation (1).

$$\eta_P = \frac{w_1(P_2O_5)\text{-}w_2(P_2O_5)}{w_1(P_2O_5)} \times 100\ \% \qquad (1)$$

In the above equation, $w_1(P_2O_5)$ indicates the P_2O_5 content in the final slag of the converter, $w_2(P_2O_5)$ indicates the P_2O_5 content in the gasification dephosphorization slag after coke reduction.

ANALYSIS OF EXPERIMENT RESULTS

Analysis of products of gasification dephosphorization

Previous analysis of coke powder reduction converter slag gasification dephosphorization products [8] showed that in the standard state, the gaseous products of carbon reduction of P_2O_5 are P, P_2, P_4, and PO. Using FactSage simulation and XRD detection results are consistent, the gaseous product of carbon reduction of P_2O_5 is P_2.

As P and isotopic elements are easily spontaneous combustion and oxidation in air, the products exist in the form of small particles, and their products are collected and weighed against the products. Assuming that the idealized product is all P_2 gas, Figure 1 shows the amount of P_2 produced by gasification dephosphorization with different FeO content. When the temperature is higher than 1 600 K, the gas production increases continuously when the FeO content increases from 15 % to 30 %, and the gas production starts to decrease when the FeO content is further increased to 35 %. Therefore, it shows that the proper FeO content at a certain temperature is beneficial for gasification dephosphorization to proceed.

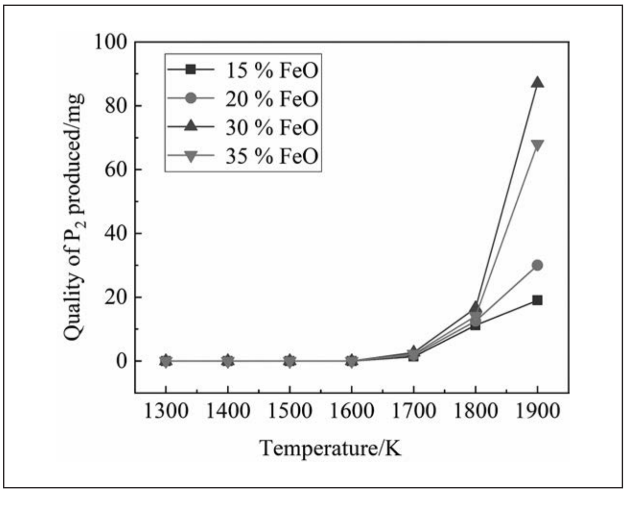


Figure 1 P_2 production under different FeO content

Effect of FeO content on gasification dephosphorization

The experimental data of the three groups of furnace times under FeO content were counted to obtain the gasification dephosphorization rate of coke reduction of P_2O_5 under different FeO content conditions, as shown in Figure 2. When the reaction was carried out for 40 min, the gasification dephosphorization reaction stopped in all furnace times, and the gasification dephosphorization rate remained the same. When the reaction is carried out 15 – 40 min, with the increase of FeO content gasification phosphorus removal is the first to increase and then decrease, When the FeO content increases from 15 % to 35 %, the highest gasification phosphorus removal rate increased from 39,8 % to 76,9 %, and then decreased to 74,6 %. The reason for the existence of this trend is that as the content increases, the fluidity of the slag becomes better, and high FeO causes a relative decrease in the CaO concentration in the slag, generating more unstable ($3FeO·P_2O_5$), which effectively increases the activity of P_2O_5 in the slag and facilitates the reduction of P_2O_5 by coke. But the presence of excessive FeO not only causes the reaction of C with a large amount of FeO leading to a decrease in temperature in some areas, but also causes a decrease in the temperature of the slag. Gasification dephosphorization is a heat absorption reaction, thus reducing the gasification dephosphorization rate. Therefore, to strengthen the effect of gasification dephosphorization, the gasification dephosphorization of converter slag should keep the final slag FeO content in the range of 20 % - 30 %.

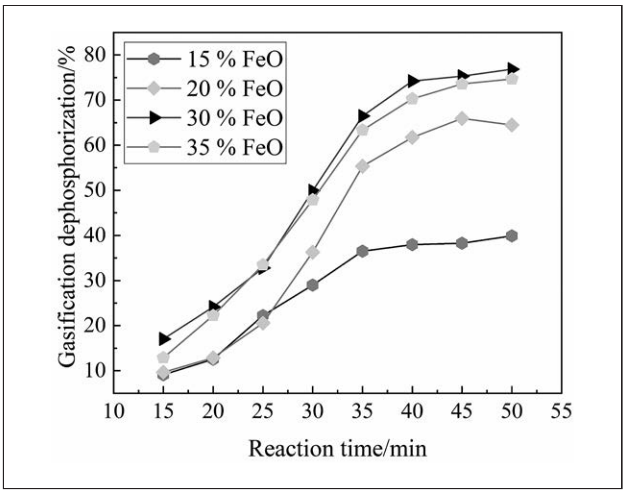


Figure 2 The influence of FeO content on the dephosphorization rate of gasification

The actual P_2O_5 in the slag exists in the form of $3CaO·P_2O_5$, and the C reduced $3CaO·P_2O_5$ and FeO Gibbs free energy are calculated by equations (2) - (5) in the standard state. 1 823 K, The composition of the furnace subslag with FeO content of 20 % is shown in Figure 3.

$$3CaO\cdot P_2O_5(s)+5C+3(CaO\cdot SiO_2)_{(s)}$$
$$=P_{2(g)}+5CO_{(g)}+3(2CaO\cdot SiO_2)_{(s)}$$
$$\Delta G^{\theta}=1\,662\,900-1\,026,75T \quad (2)$$

$$\Delta G_{3CaO\cdot P_2O_5}=\Delta G^{\theta}{}_{3CaO\cdot P_2O_5}+RT\ln\frac{P_{P_2}P^5{}_{CO}\alpha^3{}_{CaO\cdot P_2O_5}}{\alpha_{P_2O_5}\alpha_C\alpha^3{}_{2CaO\cdot P_2O_5}} \quad (3)$$

$$FeO_{(l)}+C_{(s)}=Fe_{(l)}+CO_{(g)}$$
$$\Delta G^{\theta}=141\,660-139,45T \quad (4)$$

$$\Delta G_{FeO}=\Delta G^{\theta}{}_{FeO}+RT\ln\frac{P_{CO}\alpha_{Fe}}{\alpha_{FeO}\alpha_C} \quad (5)$$

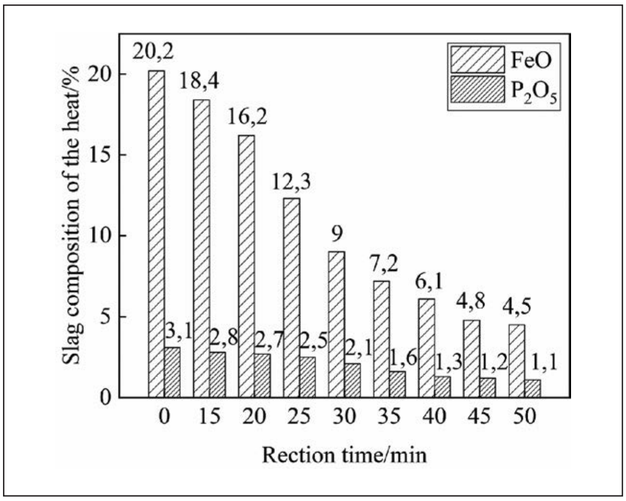


Figure 3 Slag composition of some heats after the test

By calculating the variation of the reduction Gibbs free energy of $3CaO\cdot P_2O_5$ and FeO with the reaction time, as shown in Figure 4. It can be seen from Figure 5 that the Gibbs free energy of $3CaO\cdot P_2O_5$ is less than that of FeO. As the reaction time increases, the Gibbs free energy of $3CaO\cdot P_2O_5$ is closer to the Gibbs free energy of FeO. This shows that under high FeO conditions, The reaction driving force of $3CaO\cdot P_2O_5$ is greater, and the Gibbs free energy is smaller. This also indirectly indicates that the high FeO content is favorable for the gasification dephosphorization reaction to proceed.

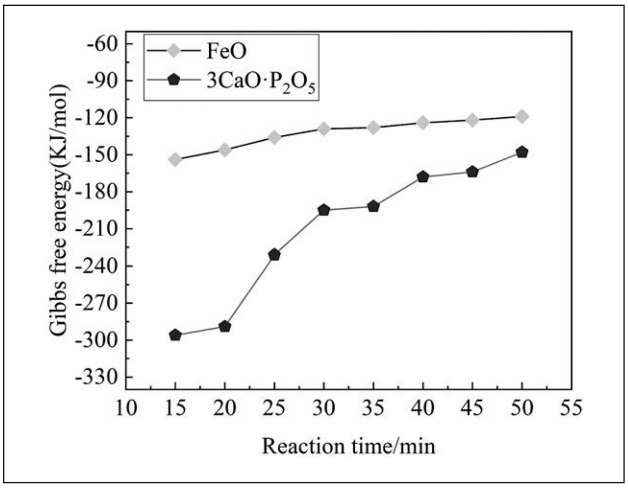
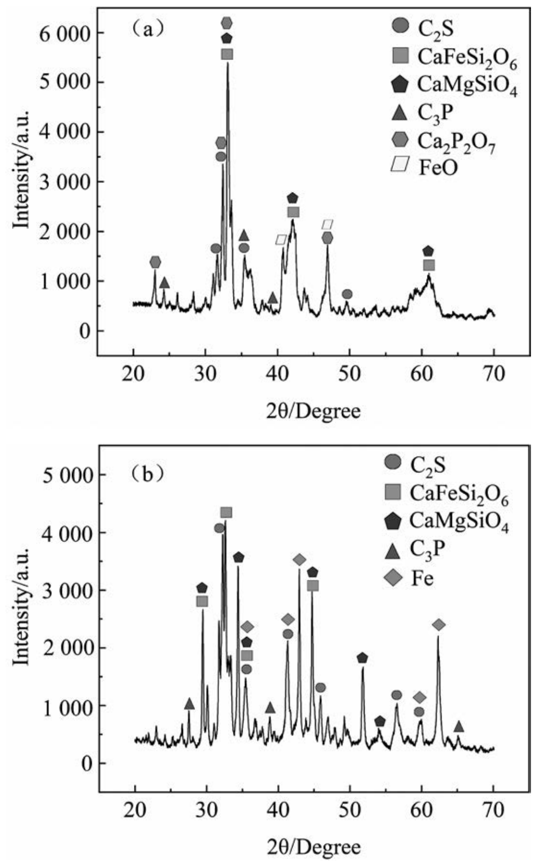


Figure 4 The reduction of Gibbs free energy of $3CaO\cdot P_2O_5$ and FeO with reaction time

Slag phase analysis before and after gasification dephosphorization

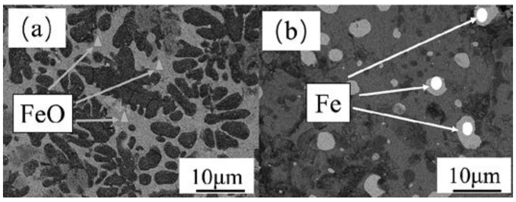
The converter final slag and gasification dephosphorization slag were examined and analyzed using X-Ray Diffraction(XRD), Scanning Electron Eicroscope(SEM) and Energy Dispersive Spectrometer (EDS), as shown in Figures 5 and 6. The converter final slag is composed of $CaFeSi_2O_6$, $CaMgSiO_4$, FeO phase, C_2S phase, $Ca_2P_2O_7$, and C_3P. The gasification dephosphorization slag is mainly composed of $CaFeSi_2O_6$, $CaMgSiO_4$, Fe phase, and C_2S phase. The peak intensity of the C_3P phase in the gasification dephosphorization slag is significantly weakened, and the C_2S phase is significantly enhanced, indicating that the C_3P phase is reduced and the C_2S phase has an enhanced ability to enrich P during the C reduction of converter slag. The FeO phase in the final slag was reduced to a bright white large-diameter granular Fe phase with the dispersed distribution.

During the EDS analysis, it was found that a large number of P elements were present in all the Fe phases,



a. Converter final slag
b. Reduced gasification dephosphorization slag

Figure 5 XRD patterns before and after the converter slag gasification and dephosphorization reaction



a. Converter final slag
b. Reduced gasification dephosphorization slag

Figure 6 SEM before and after the converter slag gasification and dephosphorization reaction

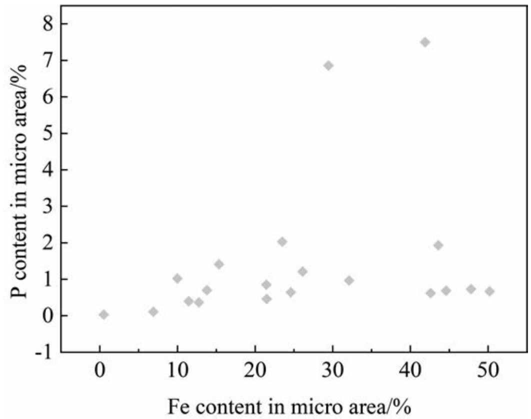


Figure 7 The relationship between P content and Fe content in Fe phase microdomains

because the behavior of P cannot be captured at high temperature, the Fe phase detection was performed on 20 micro-regions of the gasified dephosphorization slag. The relationship between P content and Fe content in the microzones is shown in Figure 7.

From Figure 7, it shows that the P content in the Fe phase microzone of the gasification dephosphorization slag is in the range of 0,15 – 7,5 %, and the Fe element content is in the range of 0 - 50 %. Overall, the P content fluctuates little, and when the Fe content is less than 30 %, the P content is densely distributed, mainly in the range of 0 - 2 %; when the Fe content is greater than 30 %, the P content has a decreasing trend with the increase of Fe content, but there will still be high P microregions. The Fe phase microzone of gasification dephosphorization slag contains P elements, indicating that the gasification dephosphorization product P_2 gas will be endowed in the Fe phase while discharging out of the furnace, and the P content also has a tendency to increase with the increase of Fe content. Since the presence of FeO will increase the activity coefficient of P_2O_5, maintaining a reasonably high FeO content in the final slag will facilitate the gasification and dephosphorization reaction. However, if the FeO content is too high, a large number of FeO reduction by C will generate Fe phase and endowed with more P, there will certainly be back phosphorus phenomenal, directly leading to lower steel quality.

CONCLUSION

To investigate the effect of different FeO content on gasification dephosphorization experiments, respectively, the FeO content of 15 %, 20 %, 30 %, 35 % of the converter slag coke reduction gasification dephosphorization experiments, to obtain the following conclusions:

(1) With the increase of FeO content in the final slag, the gasification dephosphorization rate showed a trend of increasing first and then decreasing. With the increase of reaction time, the Gibbs free energy of $3CaO·P_2O_5$ slowly approaches the FeO Gibbs free energy, so the high FeO content is beneficial to the gasification dephosphorization reaction.

(2) Compared with the final slag, the C_3P phase in the gasification dephosphorization slag is reduced, and the small granular and elongated FeO phase in the final slag is reduced to large diameter granular Fe phase, and in the process of gasification dephosphorization, the gasification dephosphorization product P_2 will be partially endowed in the Fe phase, which will produce the phenomenon of back phosphorus. In a comprehensive view, the converter slag gasification dephosphorization should maintain the final slag FeO content between 20 % - 30 %.

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Note: The responsible translator for English language is Y. Zhang - North China University of Science and Technology, China