Research Article

Liwei Liu, Guofeng Li*, Yanfeng Li, and Libing Zhao

Dephosphorization behavior of reduced iron and the properties of high-P-containing slag

Abstract: Reduced iron (1.74% P) is produced from oolitic hematite ore by coal-based reduction and magnetic separation. To realize the comprehensive utilization of Fe and P, the dephosphorization behavior of the reduced iron is investigated in the presence of CaO–SiO$_2$–FeO–Al$_2$O$_3$ slag. The P content of the final iron and the P$_2$O$_5$ content of the high-P-containing slag are determined, and the phase composition and P$_2$O$_5$ solubility of the slag are analyzed. The P content can be decreased to 0.2% when the initial slag has a basicity of 3.5 and contains 55% FeO and 6% Al$_2$O$_3$. The phases of the high-P-containing slag are mainly Ca$_3$Al$_2$SiO$_7$, Ca$_2$SiO$_4$, Ca$_5$(PO$_4$)$_2$SiO$_4$, and FeO, and P exists in the form of Ca$_5$(PO$_4$)$_2$SiO$_4$. Excessively high basicity or low content of FeO and Al$_2$O$_3$ results in free CaO, which affects the dephosphorization results. The change rule of the intensity of the Ca$_3$(PO$_4$)$_2$SiO$_4$ diffraction peak agrees well with the dephosphorization indexes, which further verify the accuracy of the dephosphorization experiments. Moreover, the P$_2$O$_5$ content and P$_2$O$_5$ solubility of the high-P-containing slag reached as high as 14.41 and 94.54%, respectively, indicating that it can be used as a phosphate fertilizer.

Keywords: high-P-containing reduced iron, dephosphorization, slag, phosphate fertilizer

1 Introduction

Iron ores are listed as strategic raw materials in the iron and steel industry by some countries. With the consumption of high-quality iron ores, the utilization of refractory iron ores has attracted increased interest [1]. Oolitic hematite ore is regarded as one of the most refractory iron ores because of its layered oolitic texture, fine-grained hematite size, and high P content [2]. It is difficult to obtain a qualified iron concentrate from oolitic hematite ore using traditional processing methods, including fine grinding and froth flotation, gravity separation, and magnetic separation [3–5].

Previous research has shown that coal-based reduction followed by magnetic separation is a promising method to utilize oolitic hematite ore [6,7]. In the reduction process, the hematite is reduced to iron which is then aggregated together to iron particles, which can then be easily recovered by magnetic separation [8,9]. Reduced iron is produced with iron recovery and a metallization ratio above 90%. However, parts of the apatite in oolitic hematite are also reduced to P and migrate into the iron phase. The P content of the reduced iron is considerably higher than that of direct reduced iron [10,11]. Therefore, the reasonable disposition of P is a challenge in this technology.

Some researchers have attempted to decrease the P content of reduced iron because P is deleterious to many steel grades. In normal practice, dephosphorization reagents, such as sodium carbonate, sodium sulfate, and borax, are added to oolitic hematite ore during the reduction process, and the reduction temperature is controlled to not exceed 1,473 K [12–15]. The reduction reaction of apatite is restricted, which effectively decreases the generation of P. Therefore, the P content of the reduced iron is low. For example, Li et al. [13] reported that the P content of reduced iron decreased to 0.09% when an oolitic hematite ore was reduced at 1,323 K and in the presence of 7.5% sodium sulfate and 1.5% borax.

Concurrently, another approach was proposed to enhance P migration into the reduced iron. The high-P-containing reduced iron could be converted to molten...
iron and high-P-containing slag by a dephosphorization process [16,17]. This method was expected to realize the comprehensive utilization of Fe and P in oolitic hematite ore because the high-P-containing slag could be used as a phosphate fertilizer. Li et al. [16] and Han et al. [18] found that increasing the temperature or C/O molar ratio (the molar ratio of fixed C in coal to O in the iron oxides of the ore) was beneficial for promoting the reduction of apatite and improving the P content of the reduced iron. When the oolitic hematite ore with a C/O molar ratio not lower than 2.0 was reduced at temperatures exceeding 1,523 K, approximately 80% apatite was reduced to P, and the P content of the reduced iron reached approximately 2%. However, the dephosphorization of reduced iron with a high P content has not been systematically studied.

This study focuses on the dephosphorization behavior of high-P-containing reduced iron in the presence of the CaO–SiO2–FeO–Al2O3 slag. The effect of the chemical composition of the initial slag on the P content of the final metal and high-P-containing slag was investigated in detail. Meanwhile, the phase compositions of the high-P-containing slag and the solubility of P2O5 in the slag were analyzed, which will boost the comprehensive utilization of Fe and P in the oolitic hematite ore.

2 Experimental

2.1 Materials

The reduced iron was produced from an oolitic hematite ore, which contained 1.31% P and 42.21% Fe. First, the oolitic hematite ore was reduced in a unidirectional heating furnace at a 1,548 K reduction temperature, 2.0 C/O molar ratio, and 60 min reduction time. The ore sample used for each test was 3 kg. The reduction products were ground to 85% passing 74 μm using a Φ460 mm × 500 mm ball mill. Then, the grinding products underwent a two-stage magnetic separation by a Φ240 mm × 120 mm low-intensity magnetic separator with the magnetic field intensities of 79.62 kA/m and 47.77 kA/m, respectively. The magnetic concentrates were the reduced iron. The chemical composition of the reduced iron is listed in Table 1.

As shown in Table 1, the reduced iron contained 92.27% total Fe, of which metallic Fe accounted for 84.34%. The P content of the reduced iron was 1.74%. The impurities were mainly 10.19% FeO, 2.12% SiO2, and 1.19% Al2O3, which will become part of the CaO–SiO2–FeO–Al2O3 slag in the dephosphorization process.

| TFe | MFe | FeO | P  | C   | SiO2 | Al2O3 |
|-----|-----|-----|----|-----|------|-------|
| 92.27| 84.34| 10.19| 1.74| 0.19| 2.12 | 1.19  |

Table 2 shows the particle sizes of the reduced iron. Most of the iron particles were <0.1 mm and accounted for 87.24% of the Fe content.

The materials used for slag-making included analytically pure CaO, SiO2, Al2O3, and FeO reagents.

2.2 Experimental method

The dephosphorization experiments were conducted at 1,873 K, and the mass ratio of slag to reduced iron was fixed at 0.2. Based on the designed basicity (wCaO/wSiO2) and the FeO and Al2O3 contents, the amounts of CaO, SiO2, FeO, and Al2O3 to be added could be calculated. The oxides in the reduced iron were also considered in the calculation because the oxides were present in the slag phase after melting the reduced iron.

About 40 g of reduced iron and 8 g of initial slag were loaded in a 50 mm-diameter corundum crucible. The crucible was then placed in an MXGL1700-80 vertical tube-type furnace at 1,873 K. The dephosphorization reaction started when the reduced iron and slag were melted under the protection of an N2 atmosphere. After 2 to 30 min of dephosphorization, the corundum crucible was removed from the furnace. The final metal and high-P-containing slag were obtained after cooling the crucible to room temperature under an N2 atmosphere. The P content of the final metal and the P2O5 content of the high-P-containing slag were determined by chemical analysis. The dephosphorization ratio of the reduced iron was calculated using equation (1):

\[ \eta_p = \frac{w_{IP} - w_{IP}}{w_{IP}} \times 100\% \]

where \( \eta_p \) (%) is the dephosphorization ratio, \( w_{IP} \) (%) is the initial P content of the reduced iron, and \( w_{FP} \) (%) is the P content of the final iron.

Furthermore, the high-P-containing slag produced under suitable dephosphorization conditions was ground to different particle sizes using an XPM-Φ120 × 3 three-head grinder. The P2O5 in the ground product was insoluble in water but was soluble in a 2% citric acid solution. Therefore, the soluble P2O5 content was determined by chemical analysis according to the national standard GB
The solubility of $P_2O_5$ was calculated using equation (2):

$$\alpha = \frac{\omega_{SP}}{\omega_{P}} \times 100\%,$$

where $\alpha$ (%) is the solubility of $P_2O_5$, $\omega_{SP}$ (%) is the soluble $P_2O_5$ content in the ground product, and $\omega_{P}$ (%) is the $P_2O_5$ content in the ground product.

### 2.3 Characterization

The phase compositions of the high-P-containing slag were analyzed using a PANalytical X’pert PW3040 X-ray diffraction analyzer (XRD). The sample was scanned at a voltage of 40 kV and a current of 40 mA, while the diffraction angle ranged from 10 to 90°.

### 2.4 Dephosphorization process

The dephosphorization process can be described by the theoretical model of molten slag ions, given by equation (3) [20]:

$$2[P] + 5[O] + 3(O^{2-}) = 2(PO_4^{3-}).$$

If the $[O]$ is provided by the FeO in the slag, then

$$5(Fe^{2+}) + 5(O^{2-}) = 5[O] + 5Fe_{(l)}.$$

The overall process can be written as equation (5):

$$2[P] + 5(FeO) + 3(O^{2-}) = 2(PO_4^{3-}) + 5Fe_{(l)}.$$

### 3 Results and discussion

#### 3.1 Dephosphorization behavior of reduced iron

#### 3.1.1 Determination of dephosphorization time

Before investigating the effect of the slag composition on the dephosphorization indexes, a suitable dephosphorization time needed to be determined. Figure 1 shows the $P$ content of the final metal and the $P_2O_5$ content of the high-P-containing slag as a function of time where the initial slag composition was 55% FeO and 6% Al$_2$O$_3$ content with 3.5 basicity.

![Figure 1](image-url)

Figure 1: Effect of the dephosphorization time on the $P$ content of the final metal and the $P_2O_5$ content of the high-P-containing slag: (a) $P$ content and dephosphorization ratio and (b) $P_2O_5$ content.
Figure 1 shows that as the dephosphorization time increased from 2 to 5 min, the P content of the final metal decreased to 0.23% from 0.88% and the dephosphorization ratio increased from 49.43 to 86.78%, while the P$_2$O$_5$ content of the high-P-containing slag increased from 7.58 to 13.90%. With a further extension of the dephosphorization time from 10 to 30 min, the P content of the final metal slightly decreased to 0.20 ± 0.01%, and the P$_2$O$_5$ content of the high-P-containing slag was approximately 14.4%. The dephosphorization reaction was considered to be almost complete after 10 to 30 min because the experiments were not thermodynamic equilibrium tests. Therefore, the dephosphorization time was determined to be 20 min in follow-up studies.

### 3.1.2 Effect of basicity

Figure 2 shows the effect of basicity on the dephosphorization results at a FeO content of 55% and an Al$_2$O$_3$ content of 6%.

Figure 2 shows that the basicity considerably affected the dephosphorization of the reduced iron. The P content of the final metal decreased from 0.29 to 0.20% and the dephosphorization ratio increased from 83.33 to 88.51% as the basicity increased from 3.0 to 3.5. The corresponding P$_2$O$_5$ content of the high-P-containing slag increased from 13.12 to 14.41%. However, a further increase in basicity was unfavorable for dephosphorization. The P content of the final metal and the P$_2$O$_5$ content of the high-P-containing slag were 0.34 and 12.37%, respectively, at a basicity of 5.0. This is because high basicity increases the CaO content in the slag system, which reduces the activity of P$_2$O$_5$ in the molten slag and improves the phosphorus storage capacity of the molten slag. However, the excess CaO did not melt completely, which was not conducive to dephosphorization.

### 3.1.3 Effect of FeO content

Figure 3 plots the effect of the FeO content on the P content of the final metal and the P$_2$O$_5$ content of the high-P-containing slag at a basicity of 3.5 and an Al$_2$O$_3$ content of 6%.

Figure 3 shows that the P content of the final metal decreased from 0.45 to 0.20% as the FeO content increased from 40 to 55%, while the dephosphorization ratio increased from 74.14 to 88.51%. The corresponding P$_2$O$_5$ content of the high-P-containing slag increased from 7.88 to 14.41%. However, when the FeO content reached 60%, the P content of the final metal increased to 0.31%. This may be attributed to an excess FeO content that decreases the CaO content of the slag system, reducing the P storage capacity of the molten slag. Furthermore, excess FeO reduced the stability of phosphate and deteriorated the dephosphorization effect.

### 3.1.4 Effect of Al$_2$O$_3$ content

The basicity and FeO content were fixed at 3.5 and 55%, respectively. Figure 4 shows the effect of the Al$_2$O$_3$ content on the dephosphorization indexes.
Figure 4 shows that as the Al₂O₃ content increased from 4 to 6%, the P content of the final metal decreased from 0.26 to 0.20%, the dephosphorization ratio increased from 85.06 to 88.51%, and the P₂O₅ content of the high-P-containing slag increased from 11.66 to 14.41%. A further increase in the Al₂O₃ content resulted in a higher P content in the final metal and a lower P₂O₅ content in the high-P-containing slag. This phenomenon occurs because an appropriate amount of Al₂O₃ can generate low melting point materials with other oxides in the slag, which is favorable for reducing the melting point of the slag and improving the rheological properties of the molten slag. However, the high-melting-point substances may be formed when the Al₂O₃ content exceeds 6% [21].

3.2 Phase compositions of high P-containing slag

3.2.1 Effect of basicity

Figure 5 shows the XRD patterns of the high-P-containing slag at different initial basicity. The basicity affected the
3.2.2 Effect of FeO content

The effect of the FeO content on the phase composition of the high-P-containing slag was analyzed at basicity of 3.5. The XRD patterns are shown in Figure 6.

Figure 6 shows that the diffraction peak of free CaO was visible at a 40% FeO content but decreased gradually and even disappeared with a further increase in FeO. The intensities of the Ca₃SiO₄ and FeO diffraction peaks exhibited an increasing trend, while the intensity of the Ca₃Al₂SiO₇ diffraction peaks decreased with an increase in the FeO content. Furthermore, the intensity of the Ca₅(PO₄)₂SiO₄ diffraction peaks increased as the FeO content increased from 40 to 55% but decreased slightly at a 60% FeO content.

3.2.3 Effect of Al₂O₃ content

The effect of the Al₂O₃ content on the phase composition of the high-P-containing slag was investigated at a basicity of 3.5 and FeO content of 55%. The XRD patterns are shown in Figure 7.

Figure 7 shows that the diffraction peak of free CaO appeared at a 4% Al₂O₃ content but disappeared when the Al₂O₃ content reached 6%. Meanwhile, the presence of free CaO resulted in low-intensity Ca₃SiO₄ diffraction peaks. The intensity of the Ca₃Al₂SiO₇ diffraction peaks did not increase with increasing Al₂O₃ content, while the intensity of the FeO diffraction peaks decreased slightly. This phenomenon may be attributed to the formation of Fe aluminates, which were present in small quantities.
and were not detected by the XRD analyzer. Moreover, the intensity of the Ca$_5$(PO$_4$)$_2$SiO$_4$ diffraction peaks increased with increasing Al$_2$O$_3$ content from 4 to 6% but decreased with an Al$_2$O$_3$ content above 6%.

In summary, the change rule of the intensity of the Ca$_5$(PO$_4$)$_2$SiO$_4$ diffraction peaks with basicity, FeO content, and Al$_2$O$_3$ content was consistent with the P$_2$O$_5$ content of the high-P-containing slag in Section 3.2. This further verifies the accuracy of the dephosphorization tests.

3.3 P$_2$O$_5$ solubility of high-P-containing slag

The slag was ground to different particle sizes, and the effect of particle size on the specific surface area and P$_2$O$_5$ solubility of the high-P-containing slag is shown in Figure 8.

Figure 8 shows that the specific surface area and the P$_2$O$_5$ solubility were affected by the fineness of the high-P-containing slag. When the particle size decreased from $d_{90} = 92.4$ to 38.7 μm, the specific surface area of the slag increased from 682.1 to 1,606 m$^2$/kg, but the P$_2$O$_5$ solubility changed slightly and ranged from 87.59 to 87.65%. Moreover, the specific surface area of the slag increased to 2,373–2,677 m$^2$/kg when the particle size further decreased to $d_{90} = 23.8$–20.7 μm, while the P$_2$O$_5$ solubility reached 93.81–94.54%. This can be attributed to the lattice energy of the slag increasing during the grinding process, which resulted in the breakage of chemical bonds and a decrease in the degree of crystallinity on the particle surface [22]. The solubility of P$_2$O$_5$ in the slag was then improved.

4 Conclusion

The dephosphorization of high-P-containing reduced iron was investigated in the presence of CaO–SiO$_2$–FeO–Al$_2$O$_3$ slag. The properties of the high-P-containing slag, including phase composition and P$_2$O$_5$ solubility, were also analyzed. The following conclusions were drawn from the experimental results:

(1) The composition of the initial slag affected the dephosphorization of the reduced iron. Higher basicity, FeO content, and Al$_2$O$_3$ content favored dephosphorization to a certain extent. The P content of the final iron was decreased from 1.74 to 0.2% with a basicity of 3.5, FeO content of 55%, and Al$_2$O$_3$ content of 6%. The dephosphorization ratio reached 88.51%.

(2) The high-P-containing slag was obtained apart from the final iron, which was composed of Ca$_2$Al$_2$SiO$_7$, Ca$_2$SiO$_4$, Ca$_5$(PO$_4$)$_2$SiO$_4$, and FeO, and P existed in the form of Ca$_5$(PO$_4$)$_2$SiO$_4$. The intensity of the Ca$_5$(PO$_4$)$_2$SiO$_4$ diffraction peaks changed with the initial slag composition, and the change rule was in accordance with the indexes of dephosphorization.

(3) The P$_2$O$_5$ content of the high-P-containing slag was 14.41% under suitable dephosphorization conditions, while the P$_2$O$_5$ solubility of the slag reached approximately 94%, which indicates that the slag could be used as a phosphate fertilizer.

Acknowledgments: The authors gratefully acknowledge financial support from the the National Natural Science Foundation of China (No. 51804123) and the Natural Science Foundation of Hebei Province, China (No. E2018209089).

Funding information: This research was supported by the National Natural Science Foundation of China (No. 51804123) and the Natural Science Foundation of Hebei Province, China (No. E2018209089).

Author contributions: Liwei Liu: writing the original draft, conducting the experiments; Guofeng Li: methodology, reviewing the document; Yanfeng Li: phase composition analysis of the high-P-containing slag; Libing Zhao: project administration.
Conflict of interest: The authors state that there are no conflicts of interest.

Data availability statement: All authors can confirm that all data used in this article can be published the Journal “High Temperature Materials and Processes”.

References

[1] Gao, P., G. F. Li, X. T. Gu, and Y. X. Han. Reduction kinetics and microscopic properties transformation of boron-bearing iron concentrate–carbon-mixed pellets. Mineral Processing and Extractive Metallurgy Review, Vol. 41, No. 3, 2020, pp. 162–170.

[2] Cao, Y. Y., D. P. Duan, E. Zhou, and T. C. SUN. The function of blast furnace dust as reductant on simultaneous reduction of high-phosphorus oolitic hematite. Iron & Steelmaking, Vol. 47, No. 5, 2018, pp. 520–530.

[3] Wu, J., Z. J. Wen, and M. J. Cen. Development of technologies for high phosphorus oolitic hematite utilization. Steel Research International, Vol. 82, No. 5, 2011, pp. 494–500.

[4] Yu, K. P., Y. F. Yu, and X. Y. Xu. Separation behavior and mechanism of hematite and collophane in the presence of collector RFP-138. Transactions of Nonferrous Metals Society of China, Vol. 23, No. 2, 2013, pp. 501–507.

[5] Nunes, A. P. L., C. L. L. Pinto, G. E. S. Valadão, and P. R. D. M. Viana. Floatability studies of wavellite and preliminary results on phosphorus removal from a Brazilian iron ore by froth flotation. Minerals Engineering, Vol. 39, 2012, pp. 206–212.

[6] Sun, Y. S., Y. X. Han, P. Gao, Z. H. Wang, and D. Z. Ren. Recovery of iron from high phosphorus oolitic iron ore using coal-based reduction followed by magnetic separation. International Journal of Minerals, Metallurgy and Materials, Vol. 20, No. 5, 2013, pp. 411–419.

[7] Yu, W., T. C. Sun, Q. Cui, C. Y. Xu, and J. Kou. Effect of coal type on the reduction and magnetic separation of a high-phosphorus oolitic hematite ore. ISIJ International, Vol. 55, No. 3, 2015, pp. 536–543.

[8] Li, Y. F., Y. X. Han, Y. S. Sun, P. Gao, Y. J. Li, and G. C. Gong. Growth behavior and size characterization of metallic iron particles in coal-based reduction of oolitic hematite–coal composite briquettes. Minerals, Vol. 8, No. 5, 2018, id. 177.

[9] Sun, Y. S., P. Gao, Y. X. Han, and D. Z. Ren. Reaction behavior of iron minerals and metallic iron particles growth in coal-based reduction of an oolitic iron ore. Industrial & Engineering Chemistry Research, Vol. 52, No. 6, 2013, pp. 2323–2329.

[10] Li, Y. L., T. C. Sun, A. H. Zou, and C. Y. Xu. Effect of coal levels during direct reduction roasting of high phosphorus oolitic hematite ore in a tunnel kiln. International Journal of Mining Science and Technology, Vol. 22, No. 3, 2012, pp. 38–43.

[11] Sun, Y. S., Y. F. Li, Y. X. Han, and Y. J. Li. Migration behaviors and kinetics of phosphorus during coal-based reduction of high-phosphorus oolitic iron ore. International Journal of Minerals, Metallurgy, and Materials, Vol. 26, No. 8, 2019, pp. 938–945.

[12] Zhao, Y. Q., T. C. Sun, H. Y. Zhao, X. H. Li, and X. P. Wang. Effects of CaCO3 as additive on coal-based reduction of high-phosphorus oolitic hematite ore. ISIJ International, Vol. 58, No. 10, 2018, pp. 1768–1774.

[13] Li, G. H., S. H. Zhang, M. J. Rao, Y. B. Zhang, and T. Jiang. Effects of sodium salts on reduction roasting and Fe-P separation of high-phosphorus oolitic hematite ore. International Journal of Mining Processing, Vol. 124, 2013, pp. 26–34.

[14] Rao, M. J., C. Ouyang, G. H. Li, S. H. Zhang, Y. B. Zhang, and T. Jiang. Behavior of phosphorus during the carbothermic reduction of phosphorus-rich oolitic hematite ore in the presence of Na2SO4. International Journal of Mining Processing, Vol. 143, 2015, pp. 72–79.

[15] Han, H., D. Duan, P. Yuan, and S. Chen. Recovery of metallic iron from high phosphorus oolitic hematite by carbothermic reduction and magnetic separation. Iron & Steelmaking, Vol. 42, No. 7, 2015, pp. 542–547.

[16] Li, G. F., Y. X. Han, P. Gao, and Y. S. Sun. Enrichment of phosphorus in reduced iron during coal-based reduction of high phosphorus-containing oolitic hematite ore. Iron & Steelmaking, Vol. 43, No. 3, 2016, pp. 163–170.

[17] Sun, Y. S., Q. Zhang, and Y. X. Han. Comprehensive utilization of iron and phosphorus from high-phosphorus refractory iron ore. JOM, Vol. 70, 2018, pp. 144–149.

[18] Han, Y. S., G. F. Li, P. Gao, and Y. S. Sun. Reduction behaviour ofapatite in oolitic haematite ore using coal as a reductant. Iron & Steelmaking, Vol. 44, No. 4, 2017, pp. 287–293.

[19] Standardization Administration of the People’s Republic of China. Calcium magnesium phosphate: GB 20412-2006. Standards Press of China, Beijing, 2006.

[20] Tian, Y. W., X. J. Zhai, K. R. Liu. A concise course of metallurgical physical chemistry. Beijin, Chemical Industry Press, 2011.

[21] Diao, J., X. Liu, T. Zhang, and B. Xie. Mass transfer of phosphorus and iron in high-phosphorus hot-metal refining. International Journal of Minerals, Metallurgy and Materials, Vol. 22, No. 3, 2015, pp. 249–253.

[22] Zhao, F. T., G. S. Gai, D. W. Jing, Y. F. Yang, and C. S. Liu. Ultrafine grinding activations of phosphate rock and their dynamic phosphorus releases. Plant Nutrition and Fertilizer Science, Vol. 15, No. 2, 2009, pp. 474–477.