

Article

Reaction Behavior of Phosphorus in Coal-Based Reduction of an Oolitic Hematite Ore and Pre-Dephosphorization of Reduced Iron

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Abstract: Coal-based reduction followed by magnetic separation is an effective way to recover iron from high phosphorus-containing oolitic hematite ore. Given that high quantities of dephosphorization agent are needed to obtain low phosphorus reduced iron, a novel approach is proposed by the authors. Without prior phosphorus removal, the phosphorus was enriched in the reduced iron during a reduction process, then high-phosphorus reduced iron was refined to low phosphorus molten iron and high phosphorus dephosphorization slag to be used as a phosphate fertilizer. The influences of various parameters, including the reduction temperature, the reduction time, and the C/O molar ratio, on the reaction behavior of phosphorus during reduction process were studied. Experimental results indicate that a higher reduction temperature, a longer reduction time, or a higher C/O molar ratio was favorable for the reduction of apatite to phosphorus and the enrichment of phosphorus in reduced iron. X-ray diffraction (XRD) analysis demonstrated that the apatite was reduced to phosphorus and Ca_2SiO_4 (or $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$) in the presence of SiO_2 and Al_2O_3 , whilst the phosphorus enriched in reduced iron formed Fe_3P . The migration behavior of phosphorus was investigated using line scanning analysis of reduction products at different reduction times. The results show that the phosphorus primarily existed in the slag phase 10 min before reduction, and a large amount of phosphorus migrated into iron phase from slag phase with a reduction time of 40 min. The phosphorus content in the iron phase only slightly changed after 50 min. The pre-dephosphorization of reduced iron was performed at 1873 K, indicating a higher basicity or Fe_tO content of CaO-based slag was beneficial to dephosphorization of the reduced iron.

Keywords: oolitic hematite ore; reduction; phosphorus; migration behavior; pre-dephosphorization

1. Introduction

Due to the depletion of high quality iron ores with the rapid development of the iron and steel industry, the utilization of refractory iron ores has recently attracted increased attention [1–3]. Oolitic hematite ore, a standard type of refractory iron ore, is mainly distributed in America, France, Russia, Pakistan, China, and other countries [4–6]. In China, the explored reserves of oolitic hematite ores reached 3.72 billion tons, which accounts for approximately 1/9 of total iron ore resources [7]. The oolitic hematite ore is characterized by high phosphorus content (0.4%–1.8%), and micro-fine grained hematite disseminates with gangue minerals and forms special concentric and layered oolitic textures [8,9]. It is difficult to obtain high iron grade concentrates with low phosphorus content using conventional magnetic separation or froth flotation methods following fine grinding of oolitic hematite ores [10–12].

The acid leaching or bio-leaching is used for the dephosphorization of high phosphorus-containing iron ore. It was reported that acid leaching of high phosphorus-containing iron ores could dramatically reduce the phosphorus content in concentrates [13–16]. For example, the hydrochloric acid leaching of an iron ore containing 1.16% phosphorus removed 98% phosphorus at a particle size of 100% passing 0.147 mm. However, the acid-leaching method causes equipment corrosion and environmental pollution in addition to high operation cost. Bio-leaching is another method for removal of phosphorus from high phosphorus iron ores [17–19]. For example, more than 80% phosphorus was removed from iron ore containing 1.04% phosphorus after 21 days of leaching using sulfur-oxidizing bacteria with a particle size +0.074–0.1 mm. Nevertheless, collection, separation, culture, and domestication of leaching bacteria are time-consuming, which restricts its application in the mineral industry.

In recent years, magnetic roasting and coal-based reduction of oolitic hematite ores followed by magnetic separation have received considerable attention [20,21]. In the case of magnetic roasting, the hematite can be reduced to magnetite. However, the oolitic texture is unlikely to be destroyed at low temperatures ranging from 973 to 1173 K, which results in an unsatisfactory recovery of magnetite from gangue minerals in the magnetic separation process [10]. In coal-based reduction, the hematite is reduced in the following sequence: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. The final product, Fe, then grows into particles of a certain size at temperatures higher than those in magnetic roasting. The iron particles can be readily recovered by magnetic separation with high recovery [22]. Previous studies have revealed that the reduced iron with metallic degree >90% and iron recovery >90% can be obtained under optimal reduction conditions [23,24]. However, a considerable amount of phosphorus, a deleterious element in most steel grades, obtrudes into the reduced iron from gangue minerals during the reduction process [25,26]. Many researchers focus on the dephosphorization of high phosphorus-containing oolitic hematite ore by adding a large amount of additive during the reduction process [27,28]. For example, reduced iron with <0.07% phosphorus was obtained by magnetic separation following the coal-based reduction of an oolitic hematite ore containing 0.83% phosphorus with the addition of 15% $\text{Ca}(\text{OH})_2$ and 3% Na_2CO_3 .

Zhang *et al.* [29] reported a reduction of hot metal containing 1.3% phosphorus to less than 0.1% at 1673 K using 20% slag with 40% CaO , 8% SiO_2 , 8% Al_2O_3 , 10% FeO , 30% Fe_2O_3 , and 4% CaF_2 . Meanwhile, when the phosphorus content of the hot metal was about 0.2%, the P_2O_5 content in the dephosphorization slag increased above 10%, which could be used as a phosphate fertilizer [30].

Based on the above-mentioned findings, a novel approach is proposed to enhance phosphorus enrichment in the reduced iron during coal-based reduction of high phosphorus-containing oolitic hematite ore. The reduced iron is then refined by a dephosphorization process. High phosphorus dephosphorization slag is obtained and used as a phosphate fertilizer apart from molten iron.

As the reduction of hematite and its mechanism was studied in detail, this research focused on the reaction behavior of phosphorus during the reduction process. The phosphorus in the oolitic hematite ore exists as apatite, which is a double salt formed by $\text{Ca}_3(\text{PO}_4)_2$ and CaF_2 , CaCl_2 , or $\text{Ca}(\text{OH})_2$. The reduction of apatite to phosphorus, the enrichment of phosphorus in reduced iron, the corresponding phase transformation, and the migration behavior of phosphorus were analyzed. In addition, the pre-dephosphorization of the reduced iron was investigated at different conditions.

2. Materials and Methods

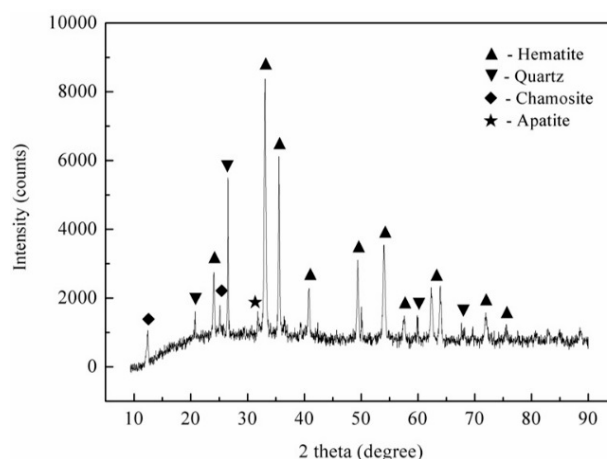
2.1. Materials

A high phosphorus-containing oolitic hematite ore was collected from Enshi, China. Table 1 displays the chemical composition of the ore sample, which contains 42.21% total iron and some impurities, including 21.80% SiO_2 , 5.47% Al_2O_3 , 4.33% CaO , and 1.31% phosphorus.

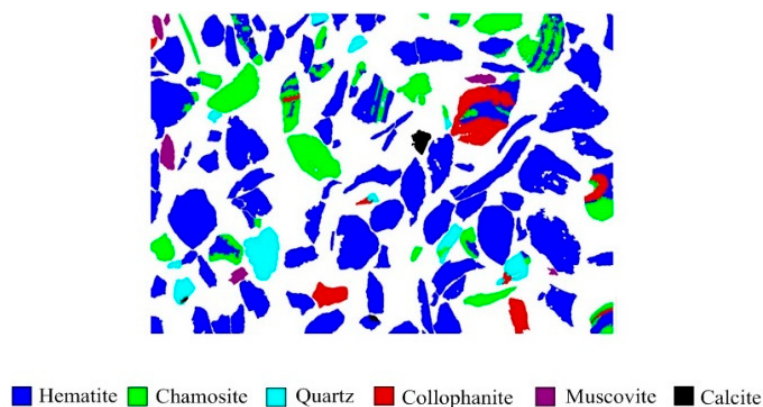
Table 1. Chemical composition of high phosphorus-containing oolitic hematite ore (wt. %).

Constituents	TFe	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S	TiO ₂	K	Mn
Content	42.21	4.31	21.80	5.47	4.33	0.59	1.31	0.13	0.19	0.41	0.20

The X-ray diffraction analysis indicates that the ore consists of hematite and gangue minerals including quartz, chamosite, and apatite (Figure 1). The results indicate that the phosphorus existed in the form of apatite.

**Figure 1.** X-ray diffraction pattern of the ore sample.

The mineral distribution of the ore sample were investigated using a mineral liberation analyser (MLA, FEI Co., Canberra, Australia), and the result is presented in Figure 2.

**Figure 2.** The mineral liberation analyser (MLA) automatic detection image of the ore sample.

It can be seen that the hematite particles were uniformly distributed in the ore. The collophanite closely associated with hematite, chamosite, or quartz apart from some single collophanite particles. Meanwhile, parts of hematite, chamosite, and collophanite formed layered textures.

The occurrence state of phosphorus in oolitic hematite ore was further analyzed by a polarizing microscope (Olympus Optical Co., Ltd., Tokyo, Japan). Figure 3 shows the optical image of the collophanite particles, which is formed by colloidal and cryptocrystalline apatite. The apatite is composed of 54.57% CaO, 41.38% P₂O₅, 1.23% F, 2.26% Cl, and 0.56% H₂O.

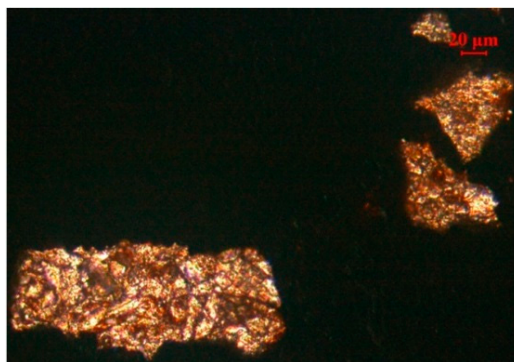


Figure 3. Collophanite particles under the polarizing microscope.

A coal sample sourced from Baishan, China was used as a reductant. The proximate analysis results show that the coal was mainly composed of 67.83% fixed carbon, 18.45% volatile matter, 12.02% ash, and 1.48% moisture. The phosphorous content in the coal was as low as 0.004%, which did not need to be counted as a source of phosphorus in experiments.

Analytical grade reagents CaO and Fe₂O₃ from Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China were employed to pre-dephosphorize the reduced iron.

2.2. Reduction and Dephosphorization Experiments

Prior to use, the high phosphorus-containing oolitic hematite ore and coal were crushed down to 100% passing 2.0 mm using a MPG-Φ200 × 125 double rollers crusher (Wuhan Exploring Machinery Factory, Wuhan, China). The mix of 80 g of the ore and coal at a pre-determined C/O molar ratio (the molar ratio of fixed carbon in the coal to oxygen in iron oxides in the ore) was placed in a corundum crucible. The reduction reaction was then conducted at various temperatures for different duration by placing the corundum crucible in a KSL-1400X orbital box-type furnace (Shenyang Kejing Auto-instrument Co., Ltd., Shenyang, China) after the furnace was heated to a pre-determined temperature. The temperature of the furnace was measured with Pt-10 Rh/Pt thermocouples and maintained by an automated 708P temperature controller. The temperature fluctuation was controlled to within 1.0 K. After reduction, the products were taken out of the furnace and immediately quenched in water and dried in a vacuum oven at 353 K before weighing. The reduction products were ground to 85% passing 74 μm at a pulp density of 70 wt. % using a Φ200 × 200 mm ball mill and separated by XCSG-Φ50 mm magnetic tube (Wuhan Exploring Machinery Factory, Wuhan, China) with a magnetic intensity of 89 kA·m⁻¹. The P₂O₅ content of non-magnetic material and the phosphorus content of magnetic material (reduced iron) were determined. The reduction degree of apatite, which was expressed by the reduction degree of P₂O₅, is defined in Equation (1), and the phosphorus enrichment ratio in reduced iron is given by Equation (2).

$$\alpha = \left(1 - \frac{m \times \gamma_1 \times \omega_{P_2O_5}}{m_{P_2O_5}}\right) \times 100 \quad (1)$$

$$\varepsilon = \frac{m \times \gamma_2 \times \omega_P}{m_P} \times 100 \quad (2)$$

where α (%) is the reduction degree of apatite; ε (%) is the phosphorus enrichment ratio in reduced iron; m (g) is the mass of a reduction product; γ_1 (dimensionless) and γ_2 (dimensionless) are the mass ratios of non-magnetic material and reduced iron to the reduction products, respectively; $\omega_{P_2O_5}$ (%) is the P₂O₅ content in non-magnetic material; ω_P (%) is the phosphorus content in reduced iron; and $m_{P_2O_5}$ (g) and m_P (g) are the masses of P₂O₅ and phosphorus in the high phosphorus-containing oolitic hematite ore, respectively.

An enlarged experiment of coal-based reduction followed by magnetic separation of 100 kg high phosphorus-containing oolitic hematite ore was performed on an AMITEC, $\Phi 460 \times 500$ mm ball mill (Wuhan Exploring Machinery Factory, Wuhan, China), and $\Phi 240 \times 120$ mm low intensity magnetic separator (LONGi Magnet Co., Ltd., Fushun, China). The reduction was carried out at 1548 K for 60 min using C/O molar ratio at 2.5. The dephosphorization of a reduced iron sample containing 1.79% P, 0.19% C, 2.15% SiO_2 , 1.21% Al_2O_3 , and 10.32% FeO was tested using a SP-25 induction furnace (Shenyang Kejing Auto-instrument Co., Ltd., Shenyang, China) at 1873 K. An argon gas flow was used to purge the furnace. The reduced iron was mixed with CaO (CaO and Fe_2O_3) at a pre-determined mass ratio. The CaO (CaO and Fe_2O_3) combined with SiO_2 , Al_2O_3 , and FeO in reduced iron and formed CaO-based slag at high temperatures. The mix was placed in a corundum crucible and then in an induction furnace at room temperature. The timing of pre-dephosphorization of the reduced iron was initiated after the induction furnace was heated to 1873 K, which was measured with a GQ-330 infrared thermometer (Nanjing Solid March Analysis instrument manufacturing Co., Ltd., Nanjing, China). After pre-dephosphorization, the phosphorus content of molten iron and the P_2O_5 content of dephosphorization slag were determined.

2.3. Analysis and Characterization

The mineral compositions of the reduction products and reduced iron were investigated using X-ray diffraction analysis (PANalytical X'pert PW3040, PANalytical B.V., Almelo, Holland) with Cu K α radiation source. The operating voltage and current were 40 kV and 40 mA, respectively. The diffraction angle was scanned from 10° to 90° .

The microstructure and the elemental distribution of reduced samples were analyzed with a scanning electron microscope (Hitachi S-3400N, Hitachi Ltd., Tokyo, Japan) integrated with an energy dispersive spectroscope (SEM-EDS, Horiba Ltd., Kyoto, Japan); the acceleration voltage was 20 kV.

3. Results and Discussion

3.1. Reaction Behavior of Phosphorus

3.1.1. Effect of Reduction Temperature

The effect of reduction temperature on the reaction behavior of phosphorus at the C/O molar ratio of 2.0 and after 50 min reduction time is shown in Figure 4.

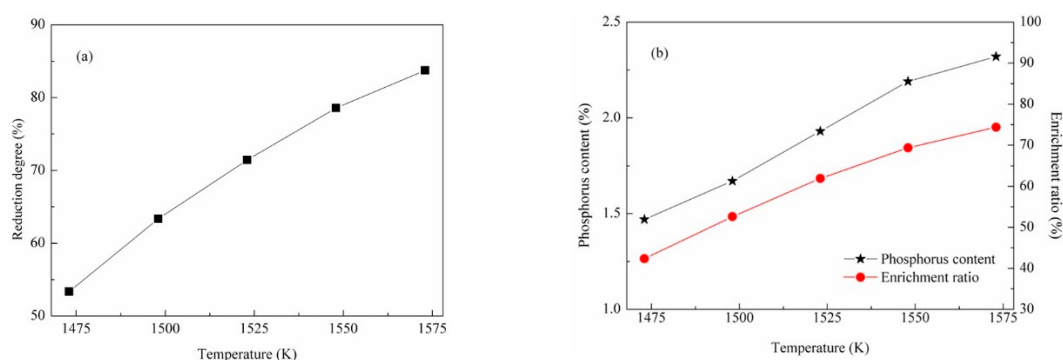


Figure 4. Effect of reduction temperature on the reaction behavior of phosphorus: (a) reduction of apatite to phosphorus; and (b) phosphorus enrichment in reduced iron.

It can be seen that when the reduction temperature was increased from 1473 to 1573 K, the reduction degree of apatite was raised to 83.72% from 53.35%. The phosphorus content and the phosphorus enrichment ratio in reduced iron were increased from 1.47% and 42.34% to 2.32% and 74.37%, respectively. The results indicate that a higher reduction temperature was favorable for

the apatite reduction and the phosphorus enrichment in reduced iron, which is plausible since the reduction of apatite to phosphorus is an endothermic reaction. A higher temperature also improved the thermal diffusion motion of phosphorus molecules in the reduction process by accelerating the enrichment of reduced phosphorus towards iron phase [31].

3.1.2. Effect of Reduction Time

Figure 5 shows the effect of reduction time on the reaction behavior of phosphorus at the C/O molar ratio of 2.0 and 1548 K.

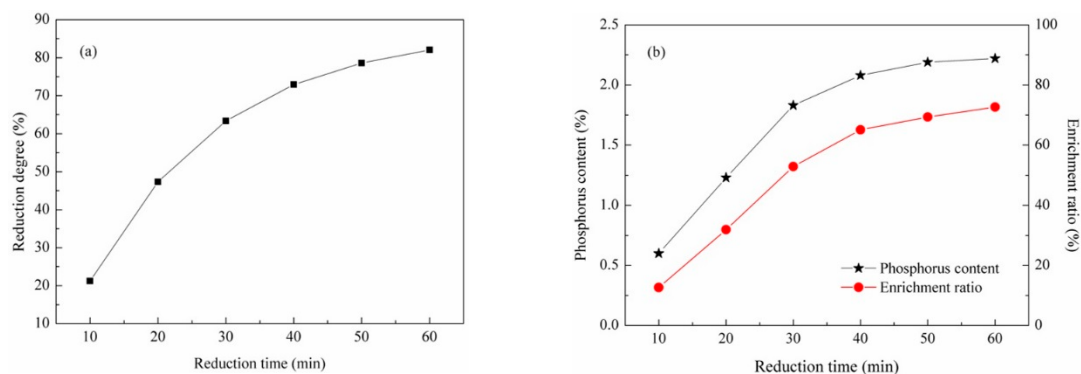


Figure 5. Effect of reduction time on the reaction behavior of phosphorus: (a) reduction of apatite to phosphorus; and (b) phosphorus enrichment in reduced iron.

It is evident that a longer reduction time led to a greater reduction degree of apatite and a higher enrichment ratio of phosphorus into reduced iron. With the reduction time increasing from 10 to 60 min, the reduction degree of apatite was increased from 21.24% to 82.05%, whilst the phosphorus content and the phosphorus enrichment ratio in reduced iron was increased from 0.60% and 12.62% to 2.22% and 72.68%, respectively. This is attributed to a prolonged reduction time that enhanced the reduction of apatite towards completion and the diffusion of reduced phosphorus into reduced iron. The enrichment of phosphorus into reduced iron nearly approached a plateau between 50 and 60 min reduction times.

3.1.3. Effect of C/O Molar Ratio

Under the conditions of 1548 K reduction temperature and 60 min reduction time, the effect of C/O molar ratio on the reaction behavior of phosphorus is plotted in Figure 6.

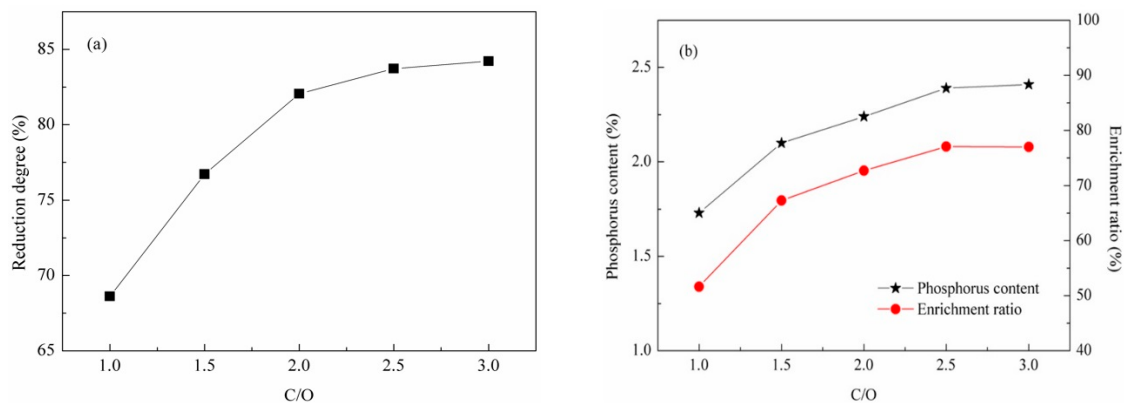


Figure 6. Effect of C/O molar ratio on the reaction behavior of phosphorus: (a) reduction of apatite to phosphorus; and (b) phosphorus enrichment in reduced iron.

As shown, the reduction degree of apatite, phosphorus content, and phosphorus enrichment ratio into reduced iron were increased as the C/O molar ratio increased up to 2.5. At the C/O molar ratio above 2.5, the reduction degree of apatite, phosphorus content, and phosphorus enrichment ratio into reduced iron plateaued at 84%, 2.4%, and 77%, respectively. This is because a higher C/O molar ratio promoted the reduction of apatite, which benefited the enrichment of reduced phosphorus in reduced iron.

3.2. Phase Transformation of Phosphorus

3.2.1. Phase Compositions of Reduction Products

The phase transformation of high phosphorus-containing oolitic hematite after reduction at 1548 K for 60 min with a C/O molar of 2.5 was identified, and the X-ray diffraction pattern is shown in Figure 7.

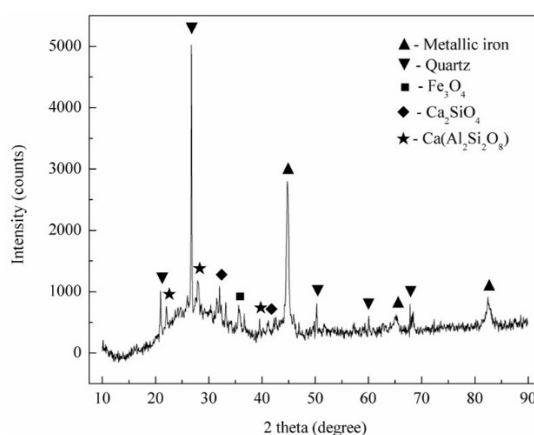
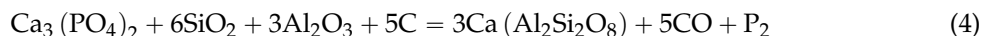
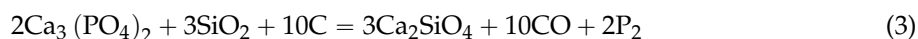


Figure 7. X-ray diffraction pattern of the reduction products.

As seen in Figure 7, the hematite in ore sample was reduced to metallic iron apart from a little Fe_3O_4 . The diffraction peaks of apatite and chamosite disappeared and that of the quartz became smaller compared to the X-ray diffraction pattern of ore sample (as shown in Figure 1). Moreover, the peaks of Ca_2SiO_4 and $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ were observed in the reduction products. The results indicate that with the reduction of iron oxides, the apatite was also reduced to Ca_2SiO_4 and $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ in the presence of SiO_2 and Al_2O_3 . Meanwhile, previous studies have revealed that the phosphorus reduced from apatite mainly existed in the form of P_2 in a temperature range of 1273 to 1700 K [32]. Therefore, the reduction of apatite during the reduction process of high phosphorus-containing oolitic hematite ore is expressed by Equations (3) and (4):



3.2.2. Phase Compositions of Reduced Iron

Separation of reduction products via magnetic tube was needed since the phosphorus content in the reduction products was less than the limit required for X-ray diffraction detection. The X-ray diffraction pattern of the reduced iron is shown in Figure 8.

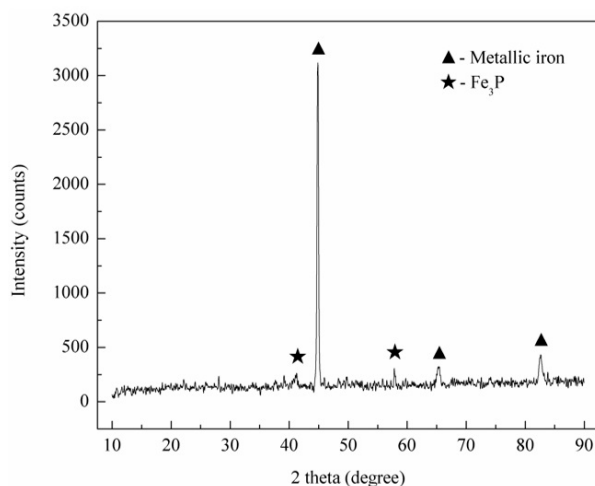


Figure 8. X-ray diffraction pattern of the reduced iron.

The peaks of metallic iron with high intensity are observed in Figure 8. Meanwhile, the peaks of Fe_3P appeared in the X-ray diffraction pattern of the reduced iron. The results show that the reduced phosphorus reacted with iron phase and formed Fe_3P , as described by Equation (5):



3.3. Migration Behavior of Phosphorus

The microstructure and line scanning analysis of P-K α of reduction products under the conditions of 1548 K reduction temperature, 2.5 C/O molar ratio, and different reduction times are shown in Figure 9.

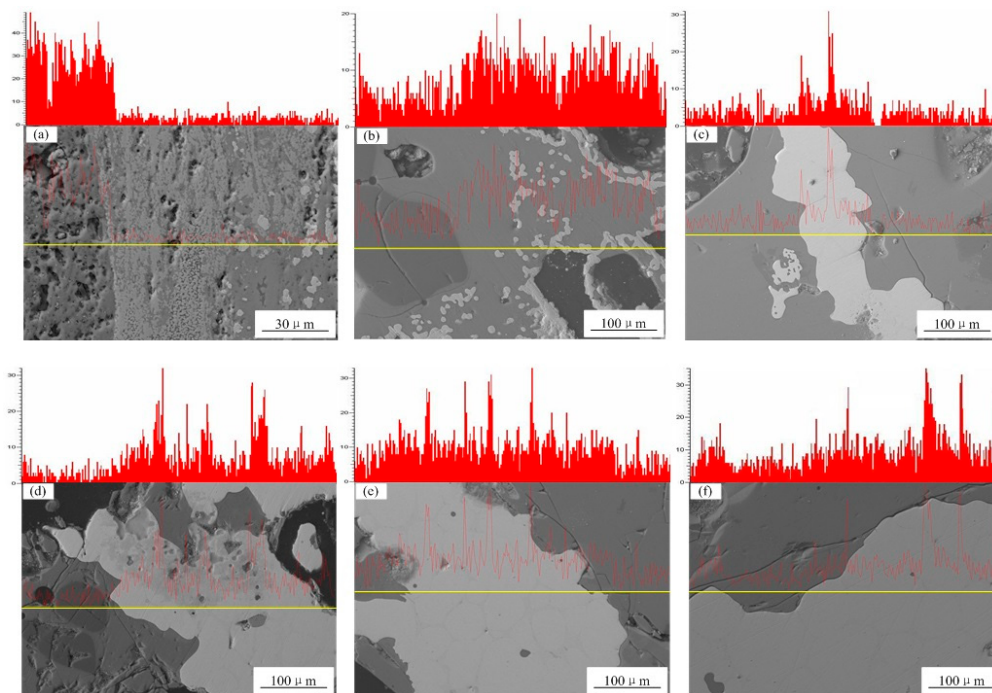


Figure 9. Line scanning analysis of P-K α of ore samples after reduction for: (a) 10; (b) 20; (c) 30; (d) 40; (e) 50; and (f) 60 min.

It can be seen that, the oolitic texture was not completely destroyed, and a small amount of fine iron particles (grey-white) appeared in the reduction products at reduction time less than 10 min. As shown in the line scanning result for phosphorus, the peak intensity of phosphorus was weak in iron particles but strong in part of slag phase (Figure 9a). These results indicate that the phosphorus enriched area existed in slag phase.

At the reduction time of 20 min, the oolitic texture was destroyed, and more iron oxides were reduced to micro-sized iron particles, which migrated to together and formed chains (Figure 9b). The phosphorus content in iron particles and slag phase was similar as indicated by its similar peak intensity distributions in the both phases. This demonstrated that some phosphorus migrated from slag phase into iron phase when the reduction time reached 20 min.

When the reduction time was increased to 40 min, the chain-like iron particles further migrated and merged together to form much larger iron particles (Figure 9c,d). The peak intensity of phosphorus became much stronger in iron phase than in the slag phase. This indicated that more phosphorus migrated into iron phase from slag phase with a prolonged reduction time.

At the reduction time of 50 min and greater, the effect of reduction time on the size of iron particles was minimal. Changes in the peak intensity of phosphorus were also negligible with further increasing reduction time, indicating that the phosphorus content in iron phase changed insignificantly at a reduction times of 50 min and greater (Figure 9e,f).

3.4. Pre-Dephosphorization of Reduced Iron

3.4.1. Effect of Basicity

The effect of basicity ($R = \text{CaO}/\text{SiO}_2$) of CaO-based slag on the pre-dephosphorization of the reduced iron at 1873 K and 3–12 min is shown in Figure 10.

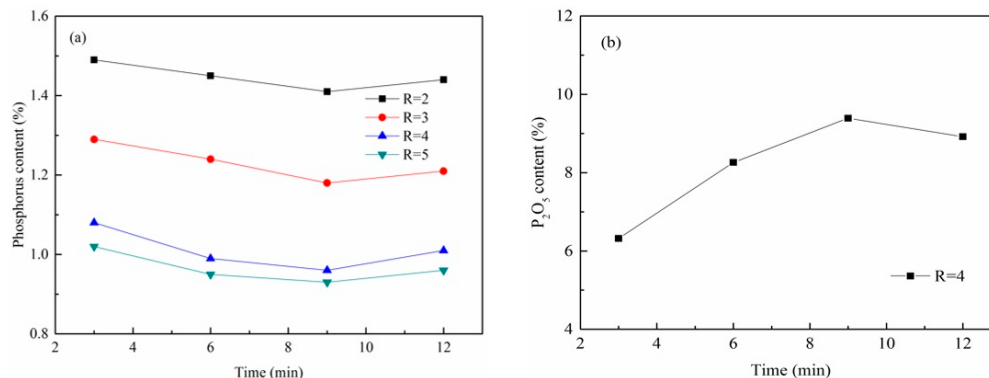


Figure 10. Effect of basicity on the dephosphorization of the reduced iron: (a) phosphorus content of the molten iron; and (b) P₂O₅ content of the dephosphorization slag.

It is evident that higher basicity was favorable for the dephosphorization of the reduced iron. For example, at a treating-time of 9 min, the phosphorus content of the molten iron decreased from 1.41% to 0.93% with the basicity increasing from 2 to 5. This is attributed to the CaO that reacts with P₂O₅ and forms stable phosphate. A basicity of 4 was recommended because the phosphorus content of the molten iron only changed slightly with basicity above 4. At this point the FeO content of CaO-based slag was 43%. The P₂O₅ content of the dephosphorization slag at this basicity was analyzed, indicating that the P₂O₅ content reached 9.39%.

It also can be seen that the phosphorus content of the molten iron increased with increasing reaction time from 9 min to 12 min. This is because the oxidability of slag was weakened, which led to the phenomenon of molten iron rephosphorization. Take a basicity of 4 for example, the FeO content of slag phase decreased to 5.48% after 12 min reaction.

3.4.2. Effect of Fe_tO Content

The Fe_2O_3 reagent was used to adjust the mass ratio of FeO and Fe_2O_3 to slag (the Fe_tO content). Figure 11 shows the effect of Fe_tO content of CaO -based slag on the dephosphorization of the reduced iron with a basicity of 4 at 1873 K and 3–12 min.

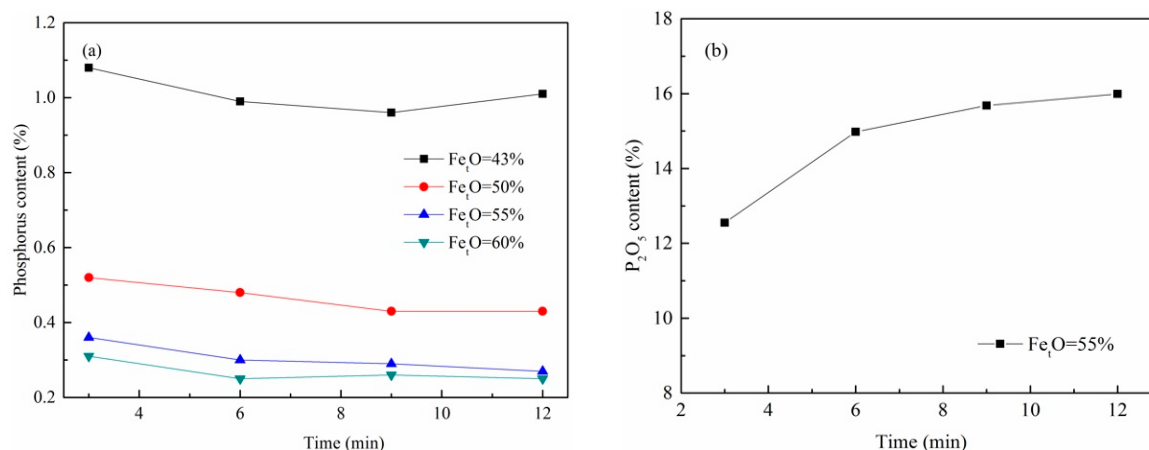


Figure 11. Effect of Fe_tO content on the dephosphorization of the reduced iron: (a) phosphorus content of the molten iron; and (b) P_2O_5 content of the dephosphorization slag.

It can be seen that the phosphorus content of the molten iron decreased with increasing Fe_tO content. For example, the phosphorus content of the molten iron decreased from 0.96% to 0.26% with an increase in Fe_tO content from 43% to 60% at a treating-time of 9 min, whilst the phosphorus content of the molten iron only marginally changed when the Fe_tO content was above 55%. This is because the oxidability of slag increased with increasing Fe_tO content, which improved the dephosphorizing capacity of slag. The P_2O_5 content of the dephosphorization slag with 55% Fe_tO content was also analyzed. The results show that the dephosphorization slag contained above 15% P_2O_5 at 9–12 min treating-time, which conformed to the requirement of the phosphate fertilizer.

4. Conclusions

A high phosphorus-containing oolitic hematite ore was reduced in the presence of coal in consideration of apatite reduction and phosphorus enrichment in reduced iron. The phase transformations, migration behavior of phosphorus, and the dephosphorization of reduced iron were analyzed. According to the present investigation, the following statements are concluded:

- (1) The reduction of apatite to phosphorus and the phosphorus enrichment in reduced iron were enhanced by a higher reduction temperature, longer reduction time, and higher C/O molar ratio. The reduction degree of apatite, phosphorus content, and enrichment ratio of phosphorus in reduced iron were about 84%, 2.4% and 77%, respectively, at 1548 K with a C/O molar ratio 2.5 and reduction time of 60 min.
- (2) During the reduction process, the apatite in high phosphorus-containing oolitic hematite ore was reduced to phosphorus and Ca_2SiO_4 (or $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$) in the presence of SiO_2 and Al_2O_3 . Most of the reduced phosphorus was enriched in reduced iron and existed in the form of Fe_3P .
- (3) Line scanning results showed that phosphorus primarily existed in slag phase at a reduction time less than 10 min. When the reduction time increased to 40 min from 10 min, increased amounts of phosphorus migrated into iron phase from slag phase. The enrichment of phosphorus in reduced iron was negligible at reduction times 50 min and greater.
- (4) The phosphorus content of the molten iron decreased with increasing basicity or Fe_tO content of the CaO -based slag. The phosphorus content was decreased below 0.3% at 1873 K with a

basicity of 4 and 55% Fe_2O_3 content after 9–12 min dephosphorization. Meanwhile, the P_2O_5 content of dephosphorization slag increased above 15%, suggesting its use as a phosphate fertilizer. The results of our research indicate that the comprehensive utilization of high phosphorus-containing oolitic hematite ore is possible. It should be noted that the molten iron with less than 0.3% phosphorus is still higher than market specifications. The further dephosphorization of the molten iron will be studied by designing a suitable slag system.

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Author Contributions: P.G. and G.-F. L. designed the experimental procedure and conducted the experiments and line scanning analysis of reduction products; Y.-X. H. provided valuable comments on a first draft; and Y.-S. S. performed the XRD analysis.

Conflicts of Interest: The authors declare no conflict of interest.

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