Gasification and Migration of Phosphorus from High-phosphorus Iron Ore during Carbothermal Reduction

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The effect of different gangue oxides (Al₂O₃, SiO₂ and Fe₂O₃) on the gasification and migration of phosphorus during the carbothermal reduction of fluorapatite has been investigated. The vaporization of phosphorus during the carbothermal reduction of synthesized model sample demonstrating a high-phosphorus iron ore was analyzed by gas mass spectrometry. Results revealed that the dephosphorization of fluorapatite was promoted by Al₂O₃ and SiO₂ to form CaAl₂O₄ and CaSiO₃, respectively. The promotion effect of SiO₂ was larger than that of Al₂O₃. With the increase in the addition of gangues, the thermodynamic conditions for the reduction of fluorapatite were continuously optimized, thereby accelerating the dephosphorization of fluorapatite. At a C/O (O originated from fluorapatite and Fe₂O₃) of larger than 1 in molar ratio, P₂ was the the dephosphorization product. Whereas, at a C/O of less than 1, the dephosphorization product turn to PO. With the addition of Fe₂O₃ to fluorapatite, a large amount of phosphorus was absorbed by liquid iron, resulting in a decrease of the amount of volatilized P₂, leading to the slow increase or decrease in the dephosphorization ratio of the pellets. Phosphorus was absorbed by liquid iron as P₂, whereas PO gas was completely volatilized. Gasification dephosphorization mainly occurred from 10 min to 25 min at 1 200°C. These findings leads to a new idea on the dephosphorization of a high-phosphorous iron ore, that is, decreasing the reduction temperature to retard melting of iron and simultaneously adding the additives to promote the dephosphorization of fluorapatite.

KEY WORDS: high-phosphorus iron ore; fluorapatite; dephosphorization; reaction mechanism.

1. Introduction

High-phosphorus oolitic hematite is a potential iron ore resource. China and Europe have 4–5 billion tons and more than 14 billion tons of iron reserves, respectively.1–4) Corresponding resources have also been reported in the United States and Egypt.5) On account of the high content of phosphorus in the iron ore, which adversely affects the quality of pig iron and steel, phosphorus and iron combine to form Fe₃P, thereby forming a binary eutectic Fe₃P–Fe with iron and causing steel to exhibit a “cold and brittle” phenomenon; this phenomenon limits the use of the High-phosphorus iron ore in industry.6–9) The development of this mine constitutes considerable economic importance. The high-phosphorus oolitic hematite ore is embedded with extremely fine grains, with an uneven distribution and a high content of harmful impurities. Iron oxides are intercalated with gangue minerals, which cause iron and phosphorus to be difficult to separate. High-phosphorus iron ore is a world-recognized complex refractory iron ore.10) On account of the above-mentioned difficulties, in recent years, experiments using the high-phosphorus iron ore have been carried out to improve the iron grade while considering dephosphorization. Domestic and international researchers have carried out several experiments, among which physical mineral separation, leaching, magnetization roasting, and magnetic separation constitute the main processing methods.11–15)

Direct reduction is short and simple, and the metallization rate can be controlled, with low requirements for the iron ore and reducing agent. This method can be employed as efficient pretreatment for the treatment of the high-phosphorus iron ore.16–19) Several studies have reported the mechanism for the carbothermal reduction of iron oxides. Fluorapatite is the major constituting phosphorus-bearing mineral in a high-phosphorous iron ore.20) In contrast, on account of the difficult preparation of fluorapatite and the incomplete thermodynamic data, few studies have reported the mechanism for the carbothermal reduction of fluorapatite. Only the mechanism of the carbothermal reduction of iron oxides and fluorapatite in the high-phosphorous iron ore can be identified to achieve the purpose of improving iron grade and dephosphorization.

In this study, according to the mineral composition characteristics of the high-phosphorus iron ore, the evolution of fluorapatite during the direct reduction of gangue was examined. The rule for the migration of phosphorus during direct reduction was clarified, which provided the theoretical basis for the separation of iron and phosphorus from the high-phosphorus iron ore. The laws for the vaporization of
phosphide during carbothermal reduction were investigated as well. To permit gasification dephosphorization, a concept of a new method of utilizing the high-phosphorus iron ore was proposed.

2. Experimental

2.1. Experimental Materials

In this experiment, the effect of gangues on the evolution of phosphorus-containing minerals in the high-phosphorus iron ore during carbothermal reduction was predominantly investigated. Table 1 summarizes the chemical composition. On account of the complex composition and structure of the high-phosphorus iron ore, in this study, pure materials were used to simulate the composition of the high-phosphorus iron ore, for highlighting the evolution of phosphorous-containing minerals. Experimental materials included analytical pure Fe₂O₃, SiO₂, Al₂O₃, and homemade high-purity fluorapatite (Ca₁₀(PO₄)₆F₂). Fluorapatite was prepared by solid phase reaction of Ca₃(PO₄)₂ with CaF₂. Homemade fluorapatite was detected by XRD and Raman analysis. The results are shown in Fig. 1. The peak position of the homemade fluorapatite and the standard sample corresponded well, indicating that the fluorapatite has a complete lattice and a very high purity. High-purity graphite (w% > 99.9%) was used as the reducing agent. To decrease the effect of factors, a less than 1% mass fraction of the materials (i.e., CaO and MgO) was ignored. Ingredients were based on the composition of the equilibrium reaction and the raw material ratio scheme (Table 2). The ratio of each substance in Exp. 1–5 was determined according to the mass ratio of each substance in the equilibrium equation of the reaction. For example, in Exp. 1, when the phosphorus in the fluorapatite is all reduced to P₂, the mass ratio of fluorapatite to carbon is 5.5:1. In Exp. 3, the Ca₁₀(PO₄)₆F₂ is all reacted to form CaSiO₃ and SiF₄, the mass ratio of SiO₂ is 3.5. In Exp. 4, when the phosphorus in the fluorapatite is all converted into P₂ and Fe₃P, the mass ratio of Fe₂O₃ is 0.75. Exp. 6 and 7 were conducted to understand the effect of carbon content on phosphorous gasification. When Fe₂O₃ and Ca₁₀(PO₄)₆F₂ are completely reduced, the molar ratio C/O should be 0.7 (O from Fe₂O₃ and Ca₁₀(PO₄)₆F₂), considering that the reduced metallic iron is carburized, the molar ratio C/O should be larger than 0.7 (O originated from Fe₂O₃ and Ca₁₀(PO₄)₆F₂). So the content of carbon in Exp. 6 was selected as the molar ratio C/O = 1 (O originated from Fe₂O₃ and Ca₁₀(PO₄)₆F₂). In order to understand the gasification of phosphorus when carbon is insufficient, the carbon content of Exp. 7 was selected as the molar ratio C/O = 0.4 (O originated from Fe₂O₃ and Ca₁₀(PO₄)₆F₂).

### Table 1. Chemical composition of the high-phosphorus iron ore (mass%).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fe₂O₃</th>
<th>Ca₁₀(PO₄)₆F₂</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition of raw ore</td>
<td>73.46</td>
<td>6.23</td>
<td>7.77</td>
<td>5.07</td>
<td>0.79</td>
<td>0.74</td>
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<tr>
<td>Approximate ratio</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

### Table 2. Raw material mixing ratio of fluorapatite during carbothermal reduction experiments (mass ratio and mass%).

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Ca₁₀(PO₄)₆F₂ mass ratio</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>C</th>
<th>Ca₁₀(PO₄)₆F₂ mass%</th>
<th>Ca</th>
<th>P</th>
<th>F</th>
<th>O</th>
<th>Al₂O₃ mass%</th>
<th>SiO₂ mass%</th>
<th>Fe₂O₃ mass%</th>
<th>C</th>
<th>C/O molar ratio</th>
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<tr>
<td>1</td>
<td>5.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>84.6</td>
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<td>3.2</td>
<td>32.2</td>
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<td>0.0</td>
<td>15.4</td>
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<td>2</td>
<td>5.5</td>
<td>5.9</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>44.4</td>
<td>17.6</td>
<td>8.2</td>
<td>1.7</td>
<td>16.9</td>
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<td>3.5</td>
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<td>1</td>
<td>55.0</td>
<td>21.9</td>
<td>10.1</td>
<td>2.1</td>
<td>20.9</td>
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<td>35.0</td>
<td>10.0</td>
<td>0.6</td>
<td>0.6</td>
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<tr>
<td>4</td>
<td>4.7</td>
<td>0</td>
<td>0</td>
<td>0.75</td>
<td>1</td>
<td>72.9</td>
<td>29.0</td>
<td>13.4</td>
<td>2.7</td>
<td>27.7</td>
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<td>0.0</td>
<td>11.6</td>
<td>15.5</td>
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<td>5</td>
<td>6.3</td>
<td>6.5</td>
<td>7.7</td>
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<td>1.4</td>
<td>27.5</td>
<td>10.9</td>
<td>5.1</td>
<td>1.0</td>
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<td>6</td>
<td>1</td>
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<td>1</td>
<td>10</td>
<td>2.6</td>
<td>6.4</td>
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<td>2.4</td>
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<td>6.4</td>
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<td>16.7</td>
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<td>7</td>
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<td>1</td>
<td>1</td>
<td>10</td>
<td>1</td>
<td>7.1</td>
<td>2.8</td>
<td>1.3</td>
<td>0.3</td>
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<td>7.1</td>
<td>7.1</td>
<td>7.1</td>
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<td></td>
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</tbody>
</table>

Fig. 1. Homemade fluorapatite compared with the standard material (a) XRD pattern, (b) Raman spectra. (Online version in color.)
2.2. Experimental Methods

According to the mixing ratio shown in Table 2, raw materials were uniformly mixed, and 50 mg of the mixture was pressed into cylindrical pellets and subsequently dried for use in experiments. The quadrupole mass spectrometry (QMS) was used to detect the gas species during the reduction process. When the furnace temperature was constant at 1200°C, Ar gas was introduced at a rate of 100 mL/min. After five minutes, the sample was placed in a constant temperature zone of the quartz reactor, and the reactor was rapidly connected to the quadrupole mass spectrometer. The vacuum conditions of the QMS system were maintained at 3×10^{-6} torr. The gas species were determined by detecting the ionic masses, and Table 3 shows the molecular ions and their masses ionic analyzed in this experiment. Figure 2 shows the schematic of the experimental apparatus.

SEM-EDS was employed to investigate the changes occurring during the reduction of fluorapatite for the purpose of determining the type of products obtained. Thermogravimetric analysis (TGA) and chemical analysis were employed to determine whether dephosphorization occurs, and the dephosphorization ratio was calculated by the following formula. To better understand the evolution of phosphorus-containing minerals in the high-phosphorus iron ore during direct reduction, the mechanism for the reduction and gasification of fluorapatite was discussed.

\[
\eta = \frac{P_{0\text{min}} \times m_{30\text{min}}}{P_{0\text{min}} \times m_{0\text{min}}}
\]

In the formula, \(\eta\) represents the dephosphorization rate. \(P_{0\text{min}}\) and \(P_{30\text{min}}\) represent the content of P in the pellet before and after the reaction, respectively. \(m_{0\text{min}}\) and \(m_{30\text{min}}\) represent the mass of the pellet before and after the reaction, respectively.

Table 3. Detected the molecular ions and their masses.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Ionic Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>31 P⁺</td>
<td>124 P⁺</td>
</tr>
<tr>
<td>47 PO⁺</td>
<td>142 P₂O⁺</td>
</tr>
<tr>
<td>62 P₂⁺</td>
<td>284 P₃O₁₀⁺</td>
</tr>
<tr>
<td>63 PO₂⁺</td>
<td>84 AlF₃⁺</td>
</tr>
<tr>
<td>78 P₂O⁺</td>
<td>104 SiF₄⁺</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Macroscopic Analysis for the Carbothermal Reduction of Fluorapatite and Gangue

Figure 3 shows the thermogravimetric analysis results obtained for the carbothermal reduction of fluorapatite and gangue. First, fluorapatite and graphite were mixed and calcined at 1200°C (Experiment 1): The sample barely lost weight. However, samples exhibited different degrees of weight loss after the mixing and calcination of fluorapatite and gangue. Without iron oxide, gentle weight loss curves attaining 5–12% weight loss at 30 min were observed (Experiment 2, 3). With the addition of Fe₂O₃, the sample rapidly lost weight in the first 10 min, and the weight loss curve gradually became flat, indicating a more rapid reduction of iron oxides compared to fluorapatite (Experiment 4). With the addition of only Fe₂O₃, the reduction of iron oxide followed as Fe₂O₃ → FeO → Fe, whereas with the addition of SiO₂ and Al₂O₃ (Experiment 5), the iron oxide reduction pathway was changed. Some FeO mostly reacted with gangue minerals to form hard-to-reduce intermediates, Fe₂SiO₄ and FeAl₂O₄, leading to slower weight loss.

To determine the relationship between weight loss and dephosphorization, the dephosphorization of different samples was summarized (Fig. 4). With the addition of only carbon, the content of phosphorus in the pellets was almost the same as the theoretical phosphorus content, indicating that the fluorapatite is not reduced. With the addition of gangue, fluorapatite was dephosphorylated to varying degrees. With the addition of Al₂O₃ or Fe₂O₃, the dephosphorization ratio of the sample reached 20%, and the dephosphorization ratio of SiO₂ in the fluorapatite-containing carbon pellets reached 30%. SiO₂ exhibited the strongest effect on the dephosphorization of fluorapatite. With the simultaneous addition of SiO₂, Al₂O₃, and Fe₂O₃, the dephosphorization ratio did not correspond to those of the three gangues because during carbothermal reduction, a large amount of intermediate products were generated by three gangues. Comparing the results obtained from Experiments 6 and 7, the dephosphorization ratio decreased with increasing carbon content (7.1 to 16.7 mass%) because reduced iron underwent carburization to increase the amount of liquid iron, and a large amount of
phosphorus was absorbed.

From Figs. 3 and 4, with the simultaneous addition of three gangue oxides, the sample underwent a violent reaction, but the dephosphorization ratio of carbon-containing pellets was low possibly because of the following reasons. First, reduced phosphorus was absorbed by the iron phase; Second, fluorapatite was reduced and decomposed, generating intermediate phosphorous products that were retained in the pellets, leading to a low dephosphorization ratio.

3.2. Effect of Gangue Oxides on the Evolution of Phosphorus-containing Minerals

To reasonably explain the above experimental phenomena, SEM-EDS analysis was employed to microscopic ally analyze the carbothermal reduction of fluorapatite with each of the gangue oxides. Figure 5 shows the microanalysis of the reduced pellets under different conditions, and Table 4 summarizes the result obtained from EDS point scanning. Ca was separated from P and distributed with Al in overlapped (1, 4), indicating that fluorapatite was decomposed and reduced to form a new gangue phase, and EDS analysis revealed that the new gangue product was determined to be CaAl\(_2\)O\(_4\) (Fig. 5(a)). However, P and F were not detected from the products obtained by the decomposition and reduction of fluorapatite, suggesting that P and F were volatilized as gas.

Some new gangue was formed in the contact part between fluorapatite and SiO\(_2\) (Fig. 5(b)). The reaction was a typical soli-solid reaction, and SiO\(_2\) was gradually consumed. Products were wrapped around the SiO\(_2\) surface to hinder the progress of the reaction, leading to the incomplete reaction of fluorapatite. Results of EDS analysis revealed that

![Fig. 4. Standardized phosphorous content and dephosphorization ratio of carbon-bearing pellets. (Online version in color.)](image)

![Fig. 5. SEM-EDS analysis of the reduced pellets (a-Experiment 2, b-Experiment 3, c-Experiment 4, d-Experiment 5). (Online version in color.)](image)
CaSiO$_3$ is generated by the reaction. Similarly, phosphorus was not obtained as a reaction product from fluorapatite, indicating that the phosphorus produced by the reduction of fluorapatite is released as gas.

A new gangue phase was formed at the contact interface between fluorapatite and metallic iron (Fig. 5(c)). EDS quantitative analysis revealed the presence of Ca and O in the new gangue phase, indicating that the dephosphorization of fluorapatite leads to the formation of CaO, and a majority of P is volatilized as gas. However, with the progress of the reaction, a part of the phosphorus was absorbed by the iron phase because metal iron undergoes carburization to form liquid iron, which exhibits a strong ability to absorb phosphorus. P$_2$ gas was absorbed to form an Fe–P alloy in the iron phase as indicated by the overlapping areas of Fe and P shown in Fig. 5(c). CaO wrapped around the unreacted fluorapatite surface hindered the further reaction of fluorapatite.

With the simultaneous addition of three gangue oxides, the result obtained from the carbothermic reduction of fluorapatite is shown in Fig. 5(d). Fluorapatite particles underwent complete reaction. In the gangue phase, black-striped Ca–Si–Al and gray Ca–Fe–Si–Al–P gangue phases were observed. Some of the unreduced phosphorus and iron to form Fe–P–O phase exist in the gray phase. EDS analysis revealed that Ca–Si–Al gangue is determined as CaAl$_2$Si$_2$O$_8$. The melting point of the newly generated gangue phase was low; hence, a liquid phase is formed, which improves the mass transfer conditions of the system, and the unreacted graphite particles traction to the fluorapatite surface to increase the contact area of graphite and fluorapatite to facilitate easy reduction.

### 3.3. Effect of Gangue Oxides on the Gasification of Phosphorus

During carbothermal reduction, fluorapatite was reduced, phosphorus was not observed in the reduction product by EM-EDS analysis, and reduced phosphorus was presumed to be volatilized as gas. To determine the vaporization of phosphorus, the gas phase volatiles during reduction were detected by quadrupole mass spectrometry. P$_2$, PO, SiF$_4$, and AlF$_3$ were observed. Figure 6 shows the results. Fluorapatite was not considerably reduced in the absence of gangue oxides. With the addition of gangue oxides, fluorapatite was reduced to varying degrees. Results revealed that a shorter time is required to generate P$_3$, and the formation of P$_2$ gas from pellet with SiO$_2$ was more rapid than that from pellet with Al$_2$O$_3$ and Fe$_2$O$_3$. The promotion of SiO$_2$ on the gasification and dephosphorization of fluorapatite is stronger than that of Al$_2$O$_3$ and Fe$_2$O$_3$. In the presence of Fe$_2$O$_3$ in the sample, the P$_2$ volatilized during the later period of the reaction decreased possibly because the reduced phosphorus is absorbed by the pellets, leading to the decrease in the amount of the volatilized P$_2$ gas. With the coexistence of Al$_2$O$_3$, SiO$_2$, and Fe$_2$O$_3$, the reaction of fluorapatite was more severe; the time required for the generation of P$_2$ was the shortest; and the increase of P$_2$ was more rapid. At this
time, fluorapatite was easily dephhosphorized reductively. PO gas was generated in the later stage of reduction (Fig. 6(b)). With the progress of the reaction, a large amount of the reducing agent was consumed, leading to the partial reduction of fluorapatite. Some of the phosphorus was present as oxide, PO. In the presence of Fe\textsubscript{2}O\textsubscript{3}, the generated PO curve did not exhibit a decreasing trend as that observed for the P\textsubscript{2} gas curve. This observation is possibly related to the fact that phosphorus in fluorapatite entered into iron as elemental phosphorus, and PO was not absorbed by iron. The generated PO gas was completely discharged from the sample, which was advantageous for depromotion. The generation of phosphorus-containing gas was accompanied by the formation of a fluorine-containing gas (Fig. 6(c)). The defluorination of fluorapatite was promoted by Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}, generating more easily reduced Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{3}, and promoting the gasification of phosphorus. At a C/O (O originated from fluorapatite and Fe\textsubscript{2}O\textsubscript{3}) of greater than 1 in molar ratio, fluorapatite was completely reduced, and P\textsubscript{2} was the phosphorization product (Fig. 7). At 25 min, the P\textsubscript{2} gas curve tended to decrease. This result could be explained as follows. Metal iron began to melt as a result of carburization, leading to higher absorption of phosphorus due to a higher solubility compared with it to solid iron. At a C/O of less than 1, phosphorus was not completely reduced. PO was the phosphorization product, and the PO curve did not exhibit a decreasing trend, indicating that liquid iron can only absorb elemental phosphorus and cannot absorb phosphorus oxide.

3.4. Change in the Dephosphorization Ratio and Migration of Phosphorus

According to the variation in the curve of P\textsubscript{2} in Fig. 7, phosphorus was absorbed by iron after a reduction time of 25 min. To further verify this result, the phosphorization of carbon-containing pellets (Experiment 6) was investigated by chemical analysis during reduction. Figure 8 shows the results. Dephosphorization slowly increased in the first 10 min, indicating that only a small amount of fluorapatite is reduced during this time, and the reduced P is volatilized as P\textsubscript{2} gas. The phosphorization ratio rapidly increased from 10 min to 25 min, indicating that the phosphorization of fluorapatite mainly occurs during this period, and a large amount of phosphorus-containing gas generated by reduction is volatilized, leading to the increase in the phosphorization ratio of pellets. However, the phosphorization ratio decreased at 30 min possibly because reduced P\textsubscript{2} was absorbed by the iron phase. To further verify this result, the distribution of P and Fe was investigated by SEM. Figure 9 shows the distribution of P and Fe at different times. At 15 min, the metallic iron particles were smaller, with a dispersed distribution; a large amount of phosphorus was still retained in fluorapatite; the distribution of P and Fe did not overlap; and the reduced phosphorus-containing gas was completely volatilized. At 20 min, the overlap area of Ca and P was extremely small, indicating that a large amount of fluorapatite is reduced. The size of the iron particles increased, P was gathered on the iron particle surface, and a small amount of P was absorbed by iron. At 25 min, P was diffused into the interior of the iron phase, and the content of phosphorus in the iron phase increased. At 30 min, the content of phosphorus in the iron phase increased further, and a large amount of phosphorus was absorbed by iron. SEM analysis was consistent with the above experimental results. Before 20 min, the content of carbon in the metal was low, the metal was not melted, and the solubility of phosphorus in the solid-phase iron was particularly small; hence, phosphorus is completely volatilized during this period. At 20 min, metallic iron was subjected to carburization, leading to the appearance of liquid iron. On account of the higher solubility of phosphorus in liquid iron, phosphorus was absorbed by the iron phase. With the progress of the reaction, the content of iron gradually increased promote liquid iron formation; hence, the content of phosphorus in the iron phase increases. The most effective time range was 10–25 min. After 25 min, a large amount of reduced P\textsubscript{2} was absorbed by the iron phase, leading to the increased content of P in metallic iron.

3.5. Phosphorus Gasification Mechanism

Phosphorus mainly exists as fluorapatite in high-phosphorus iron ore. In addition, iron oxide and various gangues (such as Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, etc.) are also present in the high-phosphorus iron ore. These iron oxides and gangues have an impact on the migration and gasification of phos-
Therefore, the carbothermal reduction of fluorapatite, which is extremely complicated, comprises different stages. TGA and QMS results only indicated whether the fluorapatite is reduced and the species of gas-phase products in the presence of different components; however, the reaction mechanism of fluorapatite has not been established thus far. To clarify the carbothermal reduction of fluorapatite, the thermodynamics of this reaction was discussed in detail.

(1) Carbothermal reduction reaction of Ca$_{10}$(PO$_4$)$_6$F$_2$. The equations for the possible dephosphorization is expressed as follows:

\[
\text{Ca}_{10} \text{(PO}_4\text{)}_6\text{F}_2(s) + 15\text{C}(s) = \text{CaF}_2(s) + 15\text{CO}(g) + 3\text{P}_2(g) + 9\text{CaO}(s) \quad \ldots (1)
\]

\[
2\text{Ca}_{10} \text{(PO}_4\text{)}_6\text{F}_2(s) + 30\text{C}(s) = 2\text{CaF}_2(s) + 30\text{CO}(g) + 6\text{PO}(g) + 9\text{CaO}(s) \quad \ldots (2)
\]

\[
\text{Ca}_{10} \text{(PO}_4\text{)}_6\text{F}_2(s) + 9\text{C}(s) = \text{CaF}_2(s) + 9\text{CO}(g) + 3\text{PO}(g) + 9\text{CaO}(s) \quad \ldots (3)
\]

\[
\text{Ca}_{10} \text{(PO}_4\text{)}_6\text{F}_2(s) + 3\text{C}(s) = \text{CaF}_2(s) + 3\text{CO}(g) + 6\text{PO}_2(g) + 9\text{CaO}(s) \quad \ldots (4)
\]

Figure 10 shows the relationship between the Gibbs free energy and temperature for the above four equations. Thermodynamic calculations revealed that in the case of only carbon, fluorapatite is reduced to temperatures greater than 1 400°C. According to the calculation results, it is easier for fluorapatite to be reduced to generate P$_2$ and P$_4$ than to generate the phosphorus-containing oxide at temperatures above 1 200°C. At high temperatures without oxygen, P$_4$ is unstable and prone to homologous transformation into P$_2$, and P$_2$ was a small molecule; hence, it can be easily volatilized. Therefore, the following thermodynamic calculation was based on P$_2$ as the phosphorus gasification product.

(2) Carbothermal reduction of Ca$_{10}$(PO$_4$)$_6$F$_2$ with Al$_2$O$_3$ and SiO$_2$. Al$_2$O$_3$ and SiO$_2$ in gangue can react with Ca$_{10}$(PO$_4$)$_6$F$_2$ to form CaAl$_2$O$_4$ and CaSiO$_3$, respectively. The independent reaction between Ca$_{10}$(PO$_4$)$_6$F$_2$ and gangue is expressed as follows:

\[
\text{Ca}_{10} \text{(PO}_4\text{)}_6\text{F}_2(s) + 15\text{C}(s) + 9\text{Al}_2\text{O}_3(s) = \text{CaF}_2(s) + 15\text{CO}(g) + 3\text{P}_2(g) + 9\text{CaAl}_2\text{O}_4(s) \quad \ldots (5)
\]

\[
3\text{Ca}_{10} \text{(PO}_4\text{)}_6\text{F}_2(s) + 45\text{C}(s) + 3\text{Al}_2\text{O}_3(s) = 2\text{AlF}_3(g) + 45\text{CO}(g) + 9\text{P}_2(g) + 30\text{CaAl}_2\text{O}_4(s) \quad \ldots (6)
\]
liquid iron exhibited a strong absorption capacity for P and promoted the dephosphorization of CaO was different from that of Al2O3 and SiO2, and the reduced liquid iron exhibited a strong absorption capacity for P2 and promoted the dephosphorization of CaO. The equation for the possible reaction between Ca10(PO4)6F2 and Fe2O3 is expressed as follows:

$$\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2(s) + 18\text{C}(s) + \text{Fe}_2\text{O}_3(s) = \text{CaF}_2(s) + 18\text{CO}(g) + 3\text{P}_2(g) + 9\text{CaSiO}_3(s) \quad \quad (7)$$

$$2\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2(s) + 30\text{C}(s) + 21\text{SiO}_2(s) = \text{SiF}_2(g) + 30\text{CO}(g) + 6\text{P}_2(g) + 20\text{CaSiO}_3(s) \quad \quad (8)$$

(3) Carbothermal reduction of Ca10(PO4)6F2 with Fe2O3. The mechanism for the reduction of Ca10(PO4)6F2 by Fe2O3 was different from that of Al2O3 and SiO2, and the reduced liquid iron exhibited a strong absorption capacity for P2 and promoted the dephosphorization of Ca10(PO4)6F2. The equation for the possible reaction between Ca10(PO4)6F2 and Fe2O3 is expressed as follows:

$$\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2(s) + 18\text{C}(s) + \text{Fe}_2\text{O}_3(s) = \text{CaF}_2(s) + 18\text{CO}(g) + 3\text{P}_2(g) + 9\text{CaO}(s) + 2\text{Fe}(s) \quad \quad (9)$$

$$\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2(s) + 18\text{C}(s) + \text{Fe}_2\text{O}_3(s) = \text{CaF}_2(s) + 45\text{CO}(g) + 2\text{P}_2(g) + 9\text{CaO}(s) \quad \quad (10)$$

$$+2\text{Fe}_2\text{P}(s) + 14\text{Fe}(s)$$

$$\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2(s) + 45\text{C}(s) + \text{Fe}_2\text{O}_3(s) = \text{CaF}_2(s) + 45\text{CO}(g) + 9\text{CaO}(s) + 6\text{Fe}_2\text{P}(s) + 2\text{Fe}(s) \quad \quad (11)$$

(4) Carbothermal reduction of Ca10(PO4)6F2 with three gangues. The dephosphorization of Ca10(PO4)6F2 is expressed as follows:

$$2\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2(s) + 36\text{C}(s) + 41\text{SiO}_2(s) + 2\text{Al}_2\text{O}_3(s) + 2\text{Fe}_2\text{O}_3(s)$$

$$= 20\text{CaAl}_2\text{Si}_2\text{O}_6(s) + 4\text{Fe}(s) + 36\text{CO}(g) + 6\text{P}_2(g) + \text{SiF}_2(g) \quad \quad (12)$$

Table 5 summarizes the main thermodynamic data obtained from reactions (1)–(12).25) The Gibbs free energy for the reduction of Ca10(PO4)6F2 was decreased by the addition of gangue oxides, promoting the gasification dephosphorization of fluorapatite (Table 5). The initial reaction temperature (temperature at $\Delta G^\theta = 0$) for reactions (6), (8), and (10)–(12) was less than 1,200°C, but the initial reaction temperature of reactions (1)–(5), (7), and (9) was greater than 1,200°C. At this point, the dephosphorization of fluorapatite was hindered.

First, from thermodynamic calculations, at a C/O (O originated from fluorapatite) of greater than 1, the initial temperature (temperature at $\Delta G^\theta = 0$) for the dephosphorization of fluorapatite was lower; fluorapatite was completely reduced; and phosphorus was mainly volatilized as P2. At a C/O of less than 1, the initial temperature (temperature at $\Delta G^\theta = 0$) of fluorapatite was relatively high, and fluorapatite was not completely reduced. The reduced phosphorus was predominantly volatilized as oxides. With the increase in the amount of C, the contact area of fluorapatite with C and the porosity of pellets increased, and the thermodynamic and kinetic conditions favorable for the reductive dephosphorization of fluorapatite were obtained. Second, the addition of Al2O3 and SiO2 was known to improve the thermodynamic conditions of the system, and the temperature at which fluorapatite started to undergo dephosphorization was reduced. In particular, at a high content of Al2O3 and SiO2, adequate Al2O3 or SiO2 allowed for more close contact with fluorapatite to improve the diffusion conditions. Fluorapatite was defluorinated to generate fluorine-containing gas; the partial pressure of phosphorus-containing gas decreased; the volatilization of phosphorus was promoted; a low-melting point slag phase was formed; the reaction kinetics was improved; the dephosphorization of fluorapatite was promoted; and the reduction temperature is reduced, which was favorable for the dephosphorization of fluorapatite. The promotion effect of SiO2 is stronger than that of Al2O3.

Secondly, the mechanism for the reduction of fluorapatite by Fe2O3 was different from that of Al2O3 and SiO2, and liquid iron exhibited a strong ability to absorb phosphorus to form Fe3P, thereby promoting the dephosphorization of Ca10(PO4)6F2. In the reduction of a high-phosphorus iron ore, the phosphorus absorption of metal iron should be avoided as much as possible; hence, focus on methods to effectively suppress this behavior is crucial for future research. With the simultaneous presence of three gangue oxides, the reaction of fluorapatite was extremely complicated; hence, only the total reaction equation is given. The dephosphorization of fluorapatite was easier at this time because the gangue phase was transformed to form low-melting FeAl2O4 and Fe2SiO4 during carbothermal reduction. Thermodynamic and kinetic conditions for the dephosphorization of fluorapatite were improved for the promotion of the dephosphorization of fluorapatite.

In summary, during the carbothermal reduction of a high-phosphorus iron ore, the migration and gasification of phosphorus is gradually clarified A new idea was proposed for the dephosphorization of the high-phosphorus iron ore. That is, reducing the temperature at which the melting of the iron, and the reduction of fluorapatite was promoted by the addition of the dephosphorization additive via the vaporization of phosphorus.

Table 5. Thermodynamic data obtained from reactions (1)–(12).25)

<table>
<thead>
<tr>
<th>Reaction formula</th>
<th>$\Delta G^\theta$(kJ mol $^{-1}$))</th>
<th>$t_B$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>4.75385E6 $-3$ 311.45T</td>
<td>1 435</td>
</tr>
<tr>
<td>(2)</td>
<td>8.95862E6 $-6$ 182.49T</td>
<td>1 449</td>
</tr>
<tr>
<td>(3)</td>
<td>4.98221E6 $-2$ 859.53T</td>
<td>1 742</td>
</tr>
<tr>
<td>(4)</td>
<td>4.17455E6 $-1$ 909.04T</td>
<td>2 187</td>
</tr>
<tr>
<td>(5)</td>
<td>4.54327E6 $-3$ 588.68T</td>
<td>1 266</td>
</tr>
<tr>
<td>(6)</td>
<td>1.67425E7 $-15$ 945.22T</td>
<td>1 050</td>
</tr>
<tr>
<td>(7)</td>
<td>3.93131E-3 269.56T</td>
<td>1 202</td>
</tr>
<tr>
<td>(8)</td>
<td>7.14216E-7 7 002.12T</td>
<td>1 019</td>
</tr>
<tr>
<td>(9)</td>
<td>5.09075E-3 821.93T</td>
<td>1 331</td>
</tr>
<tr>
<td>(10)</td>
<td>7.68721E-8 8 212.36T</td>
<td>935</td>
</tr>
<tr>
<td>(11)</td>
<td>6.81645E-7 7 804.43T</td>
<td>873</td>
</tr>
<tr>
<td>(12)</td>
<td>3.92757E-4 5 509.26T</td>
<td>871</td>
</tr>
</tbody>
</table>

Note: $\Delta G^\theta$—standard Gibbs free-energy variable; $t_B$—thermodynamic temperature.
4. Conclusion

(1) With the addition of Al₂O₃ and SiO₂, CaAl₂O₄ and CaSiO₃ were generated by the reaction between gangues and fluorapatite, respectively, which promoted the dephosphorization of fluorapatite. The promotion effect of SiO₂ was larger than that of Al₂O₃. With the increase in the addition amount of gangues, the thermodynamic conditions for the reduction of fluorapatite were continuously optimized, thereby accelerating the dephosphorization of fluorapatite.

(2) During the initial stage of reduction, P₂ was obtained from the gasification and dephosphorization of fluorapatite because the surrounding carbon of fluorapatite was relatively abundant, fluorapatite was completely reduced, and the Gibbs free energy required to generate P₂ was lower. With the progress of the reaction, carbon was continuously consumed; carbon around fluorapatite was not sufficient; fluorapatite was not completely reduced; and PO gas was generated.

(3) With the addition of Fe₂O₃, after the metal iron was melted, a large amount of phosphorus was absorbed by the iron, and volatilized P₂ was reduced, leading to the slow increase or even decrease in the dephosphorization ratio of the pellets. Phosphorus was absorbed by iron as P₂, and PO gas was completely volatilized.

(4) Gasification dephosphorization mainly occurred from 10 min to 25 min at 1200°C. A large amount of phosphorus was volatilized as gas. After 25 min, P₂ was absorbed by the liquid phase, leading to the decrease in the dephosphorization ratio.

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