Phosphorus Gasification during the Carbothermic Reduction of Medium Phosphorus Magnetite Ore by Adding Na$_2$CO$_3$

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For medium phosphorus magnetite ore, effects of carbon mixing ratio, reduction temperature and basicity on phosphorous gasification and iron metallization during carbothermic reduction were investigated using XRD, SEM-EDS and FactSage software, as well as the existing status of Fe and P in the Bayan Obo raw ore and the appropriate addition of Na$_2$CO$_3$. The obtained results show that magnetite grains and phosphorous containing minerals (apatite and monazite) are finely disseminated and closely associated with gangue minerals of carbonate, silicate and aluminosilicate. Moreover, adding 5 mass% Na$_2$CO$_3$ is capable of breaking the abovementioned gangue mineral weaved structure and promoting the reduction of phosphorous ores. Furthermore, the optimum condition for phosphorus gasification is carried out at reduction temperature of 1 050°C, with the carbon mixing ratio and basicity of 15 mass% and 0.5, respectively. The corresponding dephosphorization and iron metallization are 31.61% and 96.35%, respectively. Both of the increased carbon mixing ratio and reduction temperature lead that the reduced phosphorous gas tends to migrate in the metallic iron phase. Besides, thermodynamic analysis demonstrates that the presence of SiO$_2$ not only promotes the dephosphorization but reacts with FeO resulting in the formation of fayalite, which prevents FeO from deeper reduction to metallic iron. Meanwhile, the combination of CaO, CaF$_2$ and SiO$_2$ produces cuspidine and decreases the quantity of liquid phase, consequently increasing the dephosphorization more or less.

KEY WORDS: Bayan Obo iron ore; carbothermic reduction; phosphorus gasification; carbon mixing ratio; reduction temperature; basicity.

1. Introduction

The rapidly increasing product of iron and steel in China leads to the seriously short supply of iron ore and it becomes urgent and necessary to explore the high and medium phosphorus mineral resources which accounts for billions ton of reserves. Among them, the Bayan Obo iron ore is typically characterized by polymetallic symbiosis (which is acknowledged for its rare earth and niobium resources), low total iron grade (mainly in the form of magnetite) and medium content of phosphorus (0.8–1.0 mass%). This medium phosphorus magnetite ore is one of the most refractory iron ore resources and rather difficult in the removal of phosphorus because the iron and phosphorus containing ores are finely disseminated and closely encompassed by gangue minerals. The conventional physical and chemical approaches of removing phosphorus have been proved less effective and cost-saving due to poor dephosphorization, low iron metallization, large environmental pollution and great consumption, such as beneficiating method including gravity separation,$^{19}$ magnetic separation$^{9}$ and flotation separation,$^{9}$ gas-based reduction,$^{10}$ microwave method,$^{11,12}$ chemical leaching$^{13}$ and bioleaching$^{14}$ individually or in combination.

Comparing with the abovementioned approaches, the direct reduction roasting followed by mechanical crushing-screening and magnetic separation methods exhibited better beneficiation performance in recovering metallic iron and removing phosphorus.$^{15}$ Li et al. reported that a metallic iron concentrate with 85.1 mass% Fe and 0.97 mass% P was obtained from an oolitic hematite ore bearing 49.0 mass% Fe and 1.61 mass% P by using this method,$^{16,17}$ which has been further improved in the presence of sodium salts.$^{18–22}$ In order to decrease energy consumption and emission of CO$_2$, a novel process of pre-reducing sinter production characterized by high carbon mixing ratio, strong reduced atmosphere, high temperature and negative pressure has been proposed by JFE.$^{23,24}$ On the one hand, it could remarkably relieve the burden of ironmaking in blast furnace, coupled with decreasing coke usage and CO$_2$ emission. On the other hand, it provides favorable thermodynamic and kinetic condition for phosphorus gasification, which could remarkably improve the quality of iron and steel, decreasing the production cost and promoting the circulative utilization of steel slag resources. Comparing with the direct reduction roasting followed by grinding and magnetic separation, the pre-reducing sinter process largely shortens flow procedure and saves energy and cost.

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In this work, effects of carbon mixing ratio, reducing temperature and basicity on phosphorus gasification and iron metallization during carbothermic reduction in the presence of sodium carbonate and with 0.9 negative pressure were systematically investigated, to elucidate the mechanism of phosphorus removal by analyzing phase transformation and distribution of phosphorus, which lay the foundation for the further study on pre-reducing sinter process. Moreover, the optimization for the condition of dephosphorization and iron metallization is conducted on the raw ore based on the existing status of Fe and P in the Bayan Obo iron ore of which the experimental results are more applicable than pure reagents (could not reflect the effect of embedded features of minerals).

2. Experimental

2.1. Materials

2.1.1. Medium Phosphorous Magnetite Ore

The medium phosphorus magnetite ore (hereafter referred as raw ore) used in this work was provided by the Bayan Obo iron ore in Baotou, China. The main chemical composition is listed in Table 1. The total iron grade is as low as 31.70 mass% and phosphorus content is as high as 0.91 mass%. The valuable minerals are magnetite and a small amount of hematite. The main composition of gangue minerals includes 14.90 mass% CaO, 10.97 mass% SiO2.

2.1.2. Reductant

Coke was used as the reductant, and its composition is presented in Table 2.

2.1.3. Sodium Carbonate

The sodium carbonate was used as dephosphorization agent or addictive which is of analytical reagent grade (> 99.8 mass%).

2.2. Methods

2.2.1. Experimental Procedure

The experimental process includes tableting and reduction roasting. The medium phosphorus magnetite ore and coke were crushed and ground to pass through a 0.074 mm sieve and then mixed with a certain amount of sodium carbonate and 8 mass% water thoroughly. Tablets with 20 mm diameter were prepared by compressing the mixture with a pressure of 5 MPa and then dried in a drying oven at 105°C for 4 h. The reduction roasting was carried out in a graphite tube resistance furnace under vacuum condition with a negative pressure of 0.9 atm, as shown in Fig. 1. The prepared tablets were heated from room temperature to reaction temperature at 15°C/min and then held for 60 min. After that, the roasted tablets were taken out of the furnace and cooled to room temperature. In terms of the effect of reduction temperature on phosphorus gasification and iron metallization, the reaction temperature is 950°C, 1000°C, 1050°C, 1100°C and 1150°C, respectively. For effects of carbon mixing ratio and basicity, the reaction temperature is 1050°C.

2.2.2. Thermodynamic Calculation

FactSage software was used to calculate the relationship between standard Gibbs free energy change and temperature (ΔG°−T) of the reactions during carbothermic reduction process.

2.2.3. XRD Analysis

The powder (less than 0.074 mm) of raw ore and roasted tablets were prepared to analyze phase composition by using X-ray diffraction (XRD, Rigaku, MiniFlex600, Japan) which was conducted on a Cu Kα X-ray source, with a scanning angle 2θ in the range from 10° to 90° and step size of 0.02°. The applied voltage and current were 40 kV and 15 mA, respectively.

2.2.4. SEM-EDS Analysis

To investigate the microstructure and composition of iron, phosphorus containing minerals and impurities in raw ore and reduced tablets, the polished lump ore and tablets whose cross sections were embedded in epoxy resin were observed using Field emission scanning electron microscope (Zeiss Sigma 500, Germany) in conjunction with Energy Disperse spectroscopy (Bruker, Germany) and an advanced mineral identification and characterization system (AMICS).

2.3. Evaluation Indexes

The content of metallic iron and phosphorus in reduced tablets were measured and the dephosphorization and iron metallization during carbothermic reduction process can be calculated by Eqs. (1) and (2).

\[
\eta = \left(1 - \frac{m_{P_2}}{m_{P_1}}\right) \times 100\% \quad \text{(1)}
\]

Table 1. Main chemical composition of raw ore (mass fraction, mass%).

<table>
<thead>
<tr>
<th>Fe</th>
<th>CaO</th>
<th>SiO₂</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>F</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.70</td>
<td>14.90</td>
<td>10.97</td>
<td>1.97</td>
<td>1.00</td>
<td>0.35</td>
<td>0.49</td>
<td>4.50</td>
<td>1.72</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Table 2. The proximate analysis of coke (mass fraction, mass%).

<table>
<thead>
<tr>
<th>Fixed carbon</th>
<th>Ash</th>
<th>Volatile matter</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.84</td>
<td>11.90</td>
<td>1.21</td>
<td>0.96</td>
<td>0.74</td>
<td>6.77</td>
<td>2.67</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of the experimental apparatus.
where $\eta$ is the dephosphorization of total reduction process, $\%$; $m_0$ is the weight of dried tablet, g; $m_1$ is the weight of reduced tablet, g; $p_0$ is the phosphorus content of dried tablet, mass%; $p_1$ is the phosphorus content of reduced tablet, mass%; $M$ is the iron metallization of reduced tablet, $\%$; $\delta$ is the metallic iron content of reduced tablet, mass%; $\alpha$ is the total iron grade of reduced tablet, mass%.

3. Results and Discussion

3.1. Minerals Composition and Distribution in the Raw Ore

The phase composition and distribution of Fe and P in the raw ore were determined by XRD, SEM, EDS and AMICS, as presented in Table 3 and Figs. 2–5. It can be concluded that phosphorus exists in apatite (including fluorapatite) and monazite while iron mainly exists in the form of magnetite. Besides, the main gangue minerals are in type of cerium fluorocarbonate, carbonate of calcium and magnesium, aluminosilicate and silicate. The distribution of minerals in different fields exhibits that the finely disseminated magnetite, apatite and monazite are closely surrounded and encompassed by gangue. The considerably complex mineralogical relationship among iron, phosphorus containing minerals and other gangue minerals makes it rather difficult to achieve mineral liberation as well as to remove phosphorus from magnetite ore by physical processing methods.

3.2. Effect of Sodium Carbonate Dosage

According to the existing status of phosphorus in raw ore, sodium carbonate and/or sodium sulfate are commonly used to remove the gangue closely encircling phosphorus containing minerals to improve the kinetic condition for phosphorous gasification. Because they could react with gangue minerals such as $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$, resulting in the formation of nepheline ($\text{NaAlSiO}_4$) and destroy the wrapping structure, as shown in reactions 1 and 2.

$$\text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 = 2\text{NaAlSiO}_4 + \text{CO}_2(g) \quad \ldots \quad (1)$$

$$\Delta G^0 = -182.8T + 3516$$

$$\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + \text{CO} = 2\text{NaAlSiO}_4$$

$$+ \text{SO}_2(g) + \text{CO}_2(g) \quad \ldots \quad (2)$$

$$\Delta G^0 = -210.9T + 67937$$

Fig. 2. XRD pattern of medium phosphorus magnetite ore (Cu-Kα).

Fig. 3. SEM image of raw ore and EDS spectrums of the representative particles.

| Table 3. Main phase composition of raw ore (mass fraction, mass%). |
|----------------------|------------------|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Magnetite Fe$_3$O$_4$ | Pyrite FeS$_2$   | Fluorite CaF$_2$ | Bastnaesite CeFCO$_3$ | Dolomite CaMg(CO$_3$)$_2$ | Mica KAl$_2$(SiAl$_3$O$_{10}$)(OH)$_2$ | Quartz SiO$_2$ | Apatite Ca$_5$(PO$_4$)$_3$ | Monazite CePO$_4$ |
| 45.40                | 2.11             | 11.98           | 6.12              | 3.30              | 2.81              | 2.11             | 3.04             | 2.31             |
Fig. 4. (a) SEM image of raw ore and representative elements mapping: (b) Fe; (c) Ca; (d) Ce; (e) O; (f) P; (g) Al; (h) Si. (Online version in color.)

Fig. 5. Typical SEM images of minerals distribution in raw ore (Ap-Apatite; Amp-Amphibole; Bio-Biotite; Dol-Dolomite; Mag-Magnetite; Mnz-Monazite; RE-Bastnaesite).

Fig. 6. SEM images of raw ore with different sodium carbonate dosage and EDS maps of Al, P and Si: (a) 3 mass%; (b) 5 mass%; (c) 8 mass%; (d) 10 mass%. (Online version in color.)
From the $\Delta G^0 - T$, it is evident that both of sodium salts are easily reacted with the gangue of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$. The product is nepheline and the gas phase of $\text{CO}_2$ and $\text{SO}_2$. As $\text{SO}_2$ is the poisonous gas and the reaction of sodium sulfate needs $\text{CO}$ (consuming the reductant), sodium carbonate was selected to be the additive or dephosphorization agent to remove the gangue package.

For the purpose of obtaining the optimal dosage of sodium carbonate, the different content of sodium carbonate (3 mass%, 5 mass%, 8 mass% and 10 mass%) was added into the ground raw ore and mixed with 8 mass% water. Tablets were roasted at 1 050°C for 60 min.

Figure 6 shows SEM images and EDS maps of Al, P and Si of the raw ore roasted with various additions of sodium carbonate. When the sodium carbonate dosage is 3 mass%, the phosphorous containing mineral is locked in the core and encompassed by the gangue as seen in Fig. 6(a). In Figs. 6(b)–6(d), with the increased dosage of sodium carbonate, it is obvious that the gangue package is broken and the phosphorous containing mineral is separated from the gangue. Notably, the excessive addition of sodium carbonate causes the generation of sodium phosphate which is rather more difficult to be reduced than apatite. Therefore, the optimal dosage of sodium carbonate is 5 mass%.

3.3. Characteristics of the Reduced Raw Ore

3.3.1. Effect of Coke Mixing Ratio on Dephosphorization and Iron Metallization

Under the reducing condition that the reaction temperature and time were 1 050°C and 60 min, respectively, different content of coke (5 mass%, 10 mass%, 15 mass%, 20 mass% and 25 mass%), 5 mass% sodium carbonate, 8 mass% water and the balanced raw ore were mixed and tableted. The effect of coke mixing ratio on dephosphorization and iron metallization is presented in Fig. 7. As the carbon mixing ratio increases from 5 mass% to 15 mass% and from 15 mass% to 25 mass%, the dephosphorization of reduced tablet first sharply increases from 9.76% to 25.23% and then slowly increases to 30.82%. The iron metallization first rises from 78.54% to 98.87% and then reaches 100%.

As shown in Fig. 8, the $\Delta G^0 - T$ of the related reactions was calculated by FactSage software. It is obvious that the difficulty for direct reduction follows the sequence of $\text{Fe}_3\text{O}_4 < \text{FeO} < \text{Ca}_3(\text{PO}_4)_2$. Namely, the reduction of iron oxide is prior to happening during roasting process.

$$\text{Fe}_3\text{O}_4 + \text{C} = 3\text{FeO} + \text{CO}(g) \quad \text{(3)}$$

$$\text{FeO} + \text{C} = \text{Fe} + \text{CO}(g) \quad \text{(4)}$$

$$\text{Ca}_3(\text{PO}_4)_2 + 5\text{C} = 3\text{CaO} + \text{P}_2(\text{g}) + 5\text{CO}(g) \quad \text{(5)}$$

With different amount of carbon mixing ratio, the phase transformation of raw ore after reduction at 1 050°C for 60 min was analyzed, and the XRD pattern (including the detected products), SEM images and EDS maps are shown in Fig. 9, Table 4 and Fig. 10.

As can be seen in Fig. 9 and Table 4, metallic iron, wustite ($\text{FeO}$) and fayalite ($\text{Fe}_2\text{SiO}_4$) are observed in the reduced tablet with 5 mass% carbon mixing ratio, suggesting that a portion of $\text{FeO}$ has not been reduced and was existed in separated phase or combined with $\text{SiO}_2$. In the presence of 10 mass% carbon mixing ratio, the diffraction intensity of metallic iron is obviously increased, which indicates...
that more iron oxide was reduced to metallic iron with the increased addition of coke. When the carbon mixing ratio exceeds 15 mass%, the peak of metallic iron is decreased and the Fe₃P phase appears, which reveals that a portion of apatite has been reduced to phosphorus gas and it entered into metallic iron leading to the formation of Fe₃P. Besides, the nepheline (NaAlSiO₄) is observed in all reduced samples which was produced by the reaction between SiO₂, Al₂O₃ and Na₂CO₃.

The SEM images and EDS maps of the roasted tablets reduced with different carbon mixing ratio are shown in Fig. 10. In Fig. 10(a), metallic iron in white grey and gangue minerals in dark grey are weaved together. From the EDS maps of Ca and P, they have the same distribution character indicating that a portion of phosphorus has not been reduced yet and exists in the form of apatite, as well as shown in the typical EDS spectrum. According to the thermodynamic calculation, it is probably due to the reduction priority of iron oxides, which consumes the major carbon and yields the reduction of phosphorus bearing minerals. When the carbon mixing ratio increases to 15 mass%, the apatite has been reduced and a part of phosphorus gas was entered into the reduced iron phase (Fig. 10(b)). Meanwhile, there still exist some iron oxides as shown in EDS maps of Fe and O, coupled with the typical EDS spectrum. With the increase of carbon mixing ratio, the iron oxides is basically vanished and the elements of Fe and P are totally overlapped, as illustrated in Fig. 10(c), which is in good consistent with XRD patterns.

From the abovementioned analysis, the increasing carbon mixing ratio from 5 mass% to 15 mass% leads phosphorous phase transformed from phosphate to the reduced phosphorous gas and consequently accelerates dephosphorization. As carbon mixing ratio further increases to 25 mass%,

<table>
<thead>
<tr>
<th>Samples</th>
<th>Products after reduction roasting from XRD patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon mixing ratio</td>
<td>A</td>
</tr>
<tr>
<td>5 mass% C</td>
<td>✓</td>
</tr>
<tr>
<td>10 mass% C</td>
<td>✓</td>
</tr>
<tr>
<td>15 mass% C</td>
<td>✓</td>
</tr>
<tr>
<td>20 mass% C</td>
<td>✓</td>
</tr>
<tr>
<td>25 mass% C</td>
<td>✓</td>
</tr>
<tr>
<td>Reduction temperature</td>
<td>950°C</td>
</tr>
<tr>
<td>1 000°C</td>
<td>✓</td>
</tr>
<tr>
<td>1 050°C</td>
<td>✓</td>
</tr>
<tr>
<td>1 100°C</td>
<td>✓</td>
</tr>
<tr>
<td>1 150°C</td>
<td>✓</td>
</tr>
<tr>
<td>Basicity</td>
<td>B = 0.5</td>
</tr>
<tr>
<td>B = 0.8</td>
<td>✓</td>
</tr>
<tr>
<td>B = 1.1</td>
<td>✓</td>
</tr>
<tr>
<td>B = 1.4</td>
<td>✓</td>
</tr>
<tr>
<td>B = 1.7</td>
<td>✓</td>
</tr>
</tbody>
</table>

Note: The “✓” represents the detected product after reduction roasting from XRD analysis, and the blank stands for the undetected product.

![Fig. 10. Typical SEM images and EDS maps of raw ore reduced with different carbon mixing ratio at 1 050°C for 60 min: (a) 5 mass%; (b) 15 mass%; (c) 25 mass%. (Online version in color.)](image-url)
the reduction of iron oxide is enhanced and the reduced phosphorous gas obviously tends to combine with metallic iron. Therefore, the carbon mixing ratio is selected to be 15 mass%.

3.3.2. Effect of Reduction Temperature on Dephosphorization and Iron Metallization

For reduction experiment, 15 mass% coke, 5 mass% sodium carbonate, 8 mass% water and the balanced raw ore were mixed and tableted. Tablets were roasted at different temperature of 950°C, 1 000°C, 1 050°C, 1 100°C and 1 150°C for 60 min. The effect of reduction temperature on dephosphorization and iron metallization is presented in Fig. 11. It is clear that the dephosphorization of the reduced tablet first increases from 16.80% to 25.23% and then decreases to 10.58% with reducing temperature rises from 950°C to 1 150°C, as well as the tendency of iron metallization versus reducing temperature. The maximum value is obtained at 1 050°C.

To better understand the phase transformation of phosphorus during the carbothermic reduction, XRD and SEM-EDS were carried out to analyze the mineral phases after reduction. In Fig. 12 and Table 4, the phase of Fe3P was newly generated in the reduced product at the temperature high than 1 000°C. Moreover, a decreasing diffraction intensity of metallic iron in the samples reduced at 1 050°C–1 150°C was observed in comparison with that corresponding to 950°C and 1 000°C. The more phosphorus volatilization entering into metallic iron phase causes the increased amount of Fe3P as reduction temperature increases. Besides, the reaction between dephosphorization agent, quartz and Al2O3 in the raw ore generated nepheline which damaged the package structure, resulting in the improved liberation degree of minerals in the roasted products.

Fig. 13 shows SEM images and EDS maps related to the phase transformation in the reduced ore. As seen in Fig. 13(a) corresponding to the reduction temperature of 950°C, the metallic iron is enwrapped by gangue minerals and gangue minerals in the roasted products contained Ca, P and O, which was identified to be apatite. In addition, the typical EDS spectrum of Point A also indicates that a portion of apatite has not been reduced and the elements of Fe and P are scarcely overlapped. When the temperature increases to 1 050°C, the iron oxides is encircled by metallic iron and a portion of P is overlapped with the element of Fe, as well as shown in the typical EDS spectrum of Point B (Fig. 13(b)). From Fig. 13(c), the metallic iron seen from the SEM image and EDS maps is closely associated with the gangue minerals. Besides, the distribution character of Fe and O is totally different while the overlapped area (the dark grey contrast in the iron distribution area) of Fe and P is evidently increased as the reduction temperature increased from 1 050°C to 1 150°C.

The reduction of phosphorous is endothermic reaction (Eq. (5)) and thus elevating temperature enhances dephosphorization. However, once the temperature exceeds 1 050°C, the reduced phosphorous gas easily migrates into the metallic iron phase, which is caused by the increased liquid phases. The optimal carbothermic reduction is suggested conducting at 1 050°C.

![Fig. 11. Effect of reduction temperature for 60 min on dephosphorization and iron metallization of raw ore. (Online version in color.)](image1)

![Fig. 12. XRD patterns of raw ore reduced at different reaction temperature ranging from 950°C to 1 150°C for 60 min (D-CaF2; E-Fe3P; F-Fe; N-NaAlSiO4; O-Ca4Si2O7(F,OH)2; S-Na2CaSi3O8). (Online version in color.)](image2)

3.3.3. Effect of Basicity on Dephosphorization and Iron Metallization

In order to investigate the effect of basicity (0.5, 0.8, 1.1, 1.4 and 1.7) on dephosphorization and iron metallization, tablets with a mixture of different content of SiO2, 15 mass% coke, 5 mass% sodium carbonate, 8 mass% water and the balanced raw ore were prepared. The reducing roat was conducted at 1 050°C for 60 min. The result is presented in Fig. 14. As the basicity increases from 0.5 to 1.1, the dephosphorization of reduced samples decreases from 31.61% to 28.25% and the iron metallization increases from 96.35% to 100%. When the basicity exceeds 1.1, the dephosphorization is slightly increased and there are no obvious changes in iron metallization.

According to the relationship of ΔG°– T for the following reactions (Fig. 15), it is obvious that reaction between FeO and SiO2 easily takes place resulting in the formation of fayalite, which prevents FeO from deeper reduction to metallic iron, thus the dephosphorization is increased and the phosphorus gas entering into iron phase is inhibited. In addition, the thermodynamic calculation of Ca3(PO4)2–SiO2–
C system with and without Na$_2$CO$_3$ calculated by FactSage software is shown in Figs. 16 and 17. It indicates that adding SiO$_2$ promotes the dephosphorization in the absence or presence of Na$_2$CO$_3$. Therefore, with the decrease of basicity, the dephosphorization of reduced samples is increased.

\[ \text{FeO} + C = \text{Fe} + \text{CO}(g) \] ........................(4)

\[ 2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4 \] ...........................(6)

\[ \text{Fe}_2\text{SiO}_4 + 2C = 2\text{Fe} + \text{SiO}_2 + 2\text{CO}(g) \] ............(7)

\[ \text{Ca}_3(\text{PO}_4)_2 + 5C = 3\text{CaO} + \text{P}_2(g) + 5\text{CO}(g) \] ............(5)

\[ 2\text{Ca}_3(\text{PO}_4)_2 + 10C + 3\text{SiO}_2 = 3\text{Ca}_3\text{SiO}_4 + 2\text{P}_2(g) + 10\text{CO}(g) \] .................................(8)

\[ \text{Ca}_3(\text{PO}_4)_2 + 5C + 2\text{SiO}_2 = \text{Ca}_3\text{Si}_2\text{O}_7 + \text{P}_2(g) + 5\text{CO}(g) \] ... (9)

\[ \text{Ca}_3(\text{PO}_4)_2 + 5C + 3\text{SiO}_2 = 3\text{CaSiO}_3 + \text{P}_2(g) + 5\text{CO}(g) \] ... (10)

Fig. 13. Typical SEM images and EDS maps of raw ore reduced at different reaction temperature for 60 min: (a) 950°C; (b) 1 050°C; (c) 1 150°C. (Online version in color.)

Fig. 14. Effect of basicity on dephosphorization and iron metallization of raw ore at 1 050°C for 60 min. (Online version in color.)

Fig. 15. Plots of standard Gibbs free energy variation versus temperature of the reduction reactions (Eqs. (4), (6) and (7)). (Online version in color.)
To make clear the effect of basicity on the mineral phase transformation of phosphorus during reduction, XRD and SEM-EDS analysis were applied and the results are shown in Figs. 18, 19 and Table 4. In Fig. 18 and Table 4, some new diffraction peaks attributed to calcium silicate in the roasted product appear when the basicity is above 0.8. Meanwhile, the stronger diffraction intensity of cuspidine \((\text{Ca}_4\text{Si}_2\text{O}_7(\text{F},\text{OH})_2)\) with the increase of basicity can be observed, which is probably due to the combination of CaO, CaF\(_2\) and SiO\(_2\). The reactions can be described as:

\[
\text{Ca}_3(\text{PO}_4)_2 + \text{Na}_2\text{CO}_3 + 6\text{C} = 3\text{CaO} + \text{Na}_2\text{O} + \text{P}_2(\text{g}) + 7\text{CO}(\text{g})
\]

\[
\text{Ca}_3(\text{PO}_4)_2 + \text{Na}_2\text{CO}_3 + 6\text{C} + 6\text{SiO}_2
\]

\[
\text{Ca}_3(\text{PO}_4)_2 + \text{Na}_2\text{CO}_3 + 13\text{C} + 9\text{SiO}_2
\]

\[
2\text{Ca}_3(\text{PO}_4)_2 + 3\text{Na}_2\text{CO}_3 + 8\text{C} + 15\text{SiO}_2
\]

From Eq. (11) to Eq. (15), it shows the changes of calcium silicate and phosphorus gas during the reduction process.

Figure 19 presents the micrographs of reduced samples with different basicity of 0.5 and 1.7, respectively. The metallic iron grains have not been combined with each other fully and are still associated with gangue minerals closely. Moreover, it also indicates that not only the iron bearing minerals are reduced to metallic iron during the reduction roasting but the high melting point phase of cuspidine also forms, thus the phosphorus gas entering into metallic iron is suppressed more or less. Therefore, the dephosphorization of raw ore is slightly increased when the basicity increases from 1.1 to 1.7.

### 3.3.4. Effect of Fluorine on Phosphorus Gasification

As raw ore contains a relatively large amount of fluorine, the NaF and SiF\(_4\) will form and vaporize with the addition of sodium carbonate. Their obvious vaporization happens at the temperature higher than 900°C and 1 200°C, respectively.\(^{25}\) The phosphorus gas mostly forms when temperature reaches 1 050°C during the process of carbothermic reduction. Therefore, the vaporization of NaF is basically earlier than the formation of phosphorus gas. Besides, the reaction temperature in this work was controlled in the range of 950°C–1 150°C which is insufficient for the large vaporization of SiF\(_4\). Combined with the vacuum condition of 0.9 atm negative pressure (accelerating gas discharge), the vaporization of fluorine gas phases does not have obvious effect on the phosphorus gasification.
4. Conclusion

The phosphorus gasification during the carbothermic reduction of medium phosphorus magnetite ore in the presence of Na₂CO₃ was investigated in this work. The conclusions can be drawn as follows:

1. The existing status of Fe and P indicates that the finely disseminated magnetite, apatite and monazite are closely surrounded and encompassed by gangue minerals, which makes it rather difficult to achieve mineral liberation as well as to remove phosphorus from magnetite ore by physical processing methods.

2. Comparing EDS maps of Ca, P, Al and Si of roasted products in the presence of various dosage of sodium carbonate, adding 5 mass% Na₂CO₃ is capable of breaking products in the presence of various dosage of sodium carbonate, which makes it rather difficult to achieve mineral liberation as well as to remove phosphorus from magnetite ore by physical processing methods.

3. An increase of carbon mixing ratio from 5 mass% to 15 mass% leads phosphorous phase transformed from phosphate to the reduced phosphorous gas and consequently accelerates dephosphorization. As carbon mixing ratio further increases, the reduced phosphorous gas enters into metallic iron, resulting in the formation of Fe₃P and decrease of dephosphorization.

4. Elevating reduction temperature from 950°C to 1 050°C enhances the phosphorus gasification because the reduction of phosphorus is endothermic reaction. However, once the temperature exceeds 1 050°C, the reduced phosphorous gas easily migrates into the metallic iron phase, which yields phosphorus gasification.

5. As the basicity decreases from 1.1 to 0.5, the dephosphorization of reduced samples is increased because the quartz not only prevents forming Fe₃P phase but also enhances the dephosphorization. But there is a slight increase with basicity varying from 1.1 to 1.7 due to the formation of cuspidine.

6. The optimal carbothermic reduction is conducted at 1 050°C with 15 mass% carbon mixing ratio and 5 mass% Na₂CO₃, as well as controlling the basicity of 0.5. The corresponding dephosphorization and iron metallization are 31.61% and 96.35%, respectively.

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