Dephosphorization in the Reduction and Melting Separation of High Phosphorus Hematite Carbon Bearing Pellets

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ABSTRACT: The rotary hearth furnace iron nugget process is a new technology with a huge potential to efficiently utilize high phosphorus hematite. In this paper, the influences of the basicity and additives on the phosphorus content and distribution in the iron nuggets and the slag were investigated. At first CaCO3 was added to the pellets and then Na2CO3 and CaF2 were also added in the experiments. The experimental results showed that the increase in the basicity and the addition of Na2CO3 and CaF2 were shown to be effective to inhibit the apatite reduction in high phosphorus iron ores and to reduce the phosphorus content in the nuggets. When the pellets containing 4% Na2CO3 and 4% CaF2 with the basicity at 1.4 were reduced at the temperature of 1400°C for 12 min, the phosphorus content in the iron nuggets was only 0.4% and the dephosphorization rate reached 81.2%.

1. INTRODUCTION

China has 7.45 billion tons of high phosphorus oolitic hematite deposits located in Hubei, Hunan, Yunnan and Sichuan Province [1,2]. Despite the huge reserves, the use of the conventional metallurgy methods is not feasible due to their high phosphorus contents and close intermixed characters between the iron oxides and the fluorapatite. Therefore, it is important and necessary, from the long term prospect for the iron and steel industry in China, to develop a new process to be able to efficiently utilize the high phosphorus hematite contained in those reserves.

The rotary hearth furnace (RHF) iron nugget process is one of the new technologies, which has a huge potential to efficiently utilize the high phosphorus hematite contained in the reserves. In the RHF process, the carbon-bearing pellets, which were made from iron ore fines and reductants, are reduced at a high temperature ranged from 1350°C to 1450°C. After about 15 min, the slag and the iron would be separated from carbon-bearing pellets. The relationship between iron ores and reductants is intimately intermixed and thus a significant reaction is easily achieved. With sharp shortening of the reduction time, however, the element distribution would deviate from the equilibrium state at the separation of the slag and the iron. So far, few studies have been done on the treatment of high phosphorus iron ores by the RHF iron nugget process. In a relevant study, Matinde [3,4] treated a high-phosphorus iron ore by pre-reduction and screening combined with mechanical crushing or air jet milling. Yin et al. [5] proposed a reduction process combined with microwave and magnetic separation. Sun et al. [6] used the process of direct reduction-magnetic separation to treat high-phosphorus iron ore in order to obtain direct reduction iron (DRI). Han [7] and Liu [8] found that certain dephosphorization can be achieved with the RHF iron nugget process. However, additives which can be used as dephosphorization agents were not considered in those studies. Based on the previous studies, the influences of the basicity and dephosphorization agents on the dephosphorization process are investigated in this study.

2. EXPERIMENT

2.1. Raw Materials

High-phosphorus oolitic hematite ore used in this study was obtained from Hubei Province of China and its chemical composition is shown in Table 1. The ore chemical composition shows that the ore has an original basicity at 0.55 and contains high grade Fe at 54.08 wt% and relatively high phosphorus content.
at 1.15 wt%. The high ore phosphorus content is not suitable to be directly used in the blast furnace process.

After fine grinding, the particle size of raw ore is shown in Figure 1. The XRD analysis of high-phosphorus oolitic hematite ore revealed that main crystalline phases contain hematite, quartz and fluorapatite, as shown in Figure 2.

The microstructure of the ore was characterized by the SEM, as shown in Figure 3 and the images are illustrated in Figure 3. It is observed from Figure 3 that the microstructure of the raw ore consists of a typical oolitic structure [9], where Fe, Ca and P show an interphase distribution with clear boundaries while Si and Al are distributed within the hematite. There is a close relationship among the materials disseminated. Ca, P, and F elements distribute as the same ring which forms fluorapatite. Hematite and fluorapatite are distributed around the chamosite core compactly. In addition, little SiO₂ and CaCO₃ are distributed outside the oolitic structure, and a small amount of Si and Al elements are dispersed in hematite.

In the experiment, an analytical grade of CaCO₃, CaF₂ and Na₂CO₃ was used as additives and pulverized coal was used as the reductant. The results from the industrial and ash analyses of the coal are shown in Table 2. It is shown that the coal has high content in fixed carbon and relatively low content in ash, volatile, sulfur and phosphorus.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>TFe</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>P</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>54.08</td>
<td>3.42</td>
<td>73.46</td>
<td>4.26</td>
<td>7.77</td>
<td>5.07</td>
<td>0.74</td>
<td>1.15</td>
<td>0.22</td>
</tr>
</tbody>
</table>

2.2. Experimental Procedure

In the reduction and melting process, a certain amount of high-phosphorus iron ore, pulverized coal, CaCO₃, Na₂CO₃ and CaF₂ were mixed according to the ratio shown in Table 3. The C/O of mixture is 1.0. The mixture was mixed again with 7 wt% water addition. The total mixture weight with added water is 10 g. The mixture was then pressed with a pressure at 16 MPa into a cylindrical pellet with a diameter of 20 mm and a height of about 10 mm. The pellets were placed in a drying oven at 120°C for 12 h.

The reaction process was performed in a laboratory box MoSi₂ muffle resistance furnace, in which the temperature was controlled to within ±3 K. In each experiment, the pellets were put into a graphite crucible, which was pre-heated to the target temperature before the reduction began. Then the crucible was pushed into the furnace at 1400°C for 15 min. Once the separation process of slag and iron nuggets is completed, the samples were taken out of the furnace and cooled to ambient temperature under the protection of nitrogen. The dephosphorization process (η) can be described by the following equation:

\[
\eta = \left(1 - \frac{P\%_{\text{iron}}}{P\%_{\text{tot}}}\right) \times 100\%
\]

where, \(P\%_{\text{tot}}\) is the max phosphorus content in iron...
nuggets, which is 2.12% in this study and \( P^{\%}_{\text{iron}} \) is the phosphorus content in iron nuggets. The phosphorus contents in the slag and iron nuggets were obtained by the chemical analysis. Main crystalline phases of raw ore and slag were analyzed by the X-ray diffraction. The behavior of phosphorus in the process was characterized using the scanning electron microscope-energy dispersive spectrometers (SEM-EDS) analysis.

3. RESULTS AND DISCUSSIONS

3.1. Influence of Basicity on Dephosphorization

Basicity has been found to have a great effect on the smelting separation [10] and dephosphorization [11,12]. In order to identify an appropriate basicity, the basicity range from 0.55 to 1.7 was investigated in this study.

The separation phenomenon of slag and iron could not be observed when the basicity overtopped 1.4 at 15 min. Figure 4 shows the effect of basicity in the range from 0.55 to 1.4 on the phosphorus content in the slag and iron nuggets. It is clear from Figure 4 that, as the basicity increases, the phosphorus content in the iron gradually decreases while the phosphorus content in the slag gradually increases. When the basicity is set to 1.4, the phosphorus content reaches 0.8% in the iron nuggets and 1.24% in the slag.

The distribution of phosphorus in the phases of iron, slag and gas is shown in Figure 5. It is seen from Figure 5 that, as the basicity increases from 0.55 to 1.4, the percentage of phosphorus decreases from 48.18% to 39.15% in the iron phase and increases from 14.04% to 35.88% in the slag, which indicates that the increase of the basicity can inhibit the reduction of apatite. Figure 6 shows the XRD graph of the slag from the pellets with 1.4 basicity. It is observed that CaO has united with SiO\(_2\) and Al\(_2\)O\(_3\) to form Ca\(_2\)Al\(_2\)SiO\(_7\), which is stable enough to entrap SiO\(_2\) and Al\(_2\)O\(_3\). The formation of Ca\(_2\)Al\(_2\)SiO\(_7\) could inhibit the reduction of fluorapatite.

<table>
<thead>
<tr>
<th>CF(_d)</th>
<th>V(_d)</th>
<th>A(_d)</th>
<th>M(_ad)</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>81.40</td>
<td>6.40</td>
<td>11.10</td>
<td>1.10</td>
<td>46.10</td>
<td>32.16</td>
<td>9.51</td>
<td>4.26</td>
<td>0.65</td>
<td>0.032</td>
<td>0.34</td>
</tr>
</tbody>
</table>
3.2. Influence of Na$_2$CO$_3$ on Dephosphorization

With the basicity set at 1.4, the pellets containing different contents of Na$_2$CO$_3$ were reduced at 1400°C for 15 min to investigate the change of the phosphorus content in the iron nuggets and slag. The influence of Na$_2$CO$_3$ on the dephosphorization is shown in Figure 7. As the Na$_2$CO$_3$ content increases, the phosphorus content decrease in the iron nuggets and increases in the slag. When the Na$_2$CO$_3$ content in the pellets is at 4%, the phosphorus contents in the slag and iron reach 0.74% and 1.34%, respectively. Figure 8 shows the comparison in the phosphorus contents with and without Na$_2$CO$_3$. It is shown in Figure 8 that the addition of Na$_2$CO$_3$ results in a 3.14% drop in the phosphorus content in the iron and a 2.55% phosphorus content increase in the slag. Since large amounts of Na$_2$CO$_3$ were volatilized at high temperatures, as observed in this experiment in which the volatilization rate in this experiment reached about 60%, the addition of Na$_2$CO$_3$ can be considered a non-obvious promotion of dephosphorization process.

At high temperatures Na$_2$CO$_3$ is decomposed into CO$_2$ and Na$_2$O·Na$_2$O, which could enlarge the liquid region, improve the liquidity of the slag and thus accelerate the combination of CaO, SiO$_2$ and Al$_2$O$_3$. Meanwhile Na$_2$O could unite with fluorapatite and SiO$_2$ to form Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$ [13,14], which entraps the phosphorus in the slag.

3.3. Influence of CaF$_2$ on Dephosphorization

The pellets with the basicity at 1.4 were heated at 1400°C for 15 min to investigate the effect of the CaF$_2$ on the phosphorus content in the slag and iron. As shown in Figure 9, the phosphorus content in the iron decreases proportionally with the CaF$_2$ content while the phosphorus content in the slag increases with the increase in the CaF$_2$ content. When 4% Na$_2$CO$_3$ and 4% CaF$_2$ were added to the pellets together, the phosphorus content decreased to 0.52% in the iron and increased to 1.46% in the slag. The results of the phosphorus distribution, as shown in Figure 10, show that the percentage of phosphorus contents entering into iron nuggets becomes smaller and smaller as more and

### Table 3. The Experimental Mixed Ratio.

<table>
<thead>
<tr>
<th>R</th>
<th>Raw Ore</th>
<th>Coal</th>
<th>CaCO$_3$</th>
<th>Na$_2$CO$_3$</th>
<th>CaF$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>82.64</td>
<td>17.36</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.0</td>
<td>77.51</td>
<td>16.28</td>
<td>6.21</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.2</td>
<td>75.66</td>
<td>15.89</td>
<td>8.45</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.4</td>
<td>73.89</td>
<td>15.52</td>
<td>10.59</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.4, 2% Na$_2$CO$_3$</td>
<td>72.41</td>
<td>15.21</td>
<td>10.38</td>
<td>2.00</td>
<td>0</td>
</tr>
<tr>
<td>1.4, 4% Na$_2$CO$_3$</td>
<td>70.94</td>
<td>14.90</td>
<td>10.16</td>
<td>4.00</td>
<td>0</td>
</tr>
<tr>
<td>1.4, 2% CaF$_2$</td>
<td>72.41</td>
<td>15.21</td>
<td>10.38</td>
<td>0</td>
<td>2.00</td>
</tr>
<tr>
<td>1.4, 4% CaF$_2$</td>
<td>70.94</td>
<td>14.90</td>
<td>10.16</td>
<td>0</td>
<td>4.00</td>
</tr>
<tr>
<td>1.4, 4% Na$_2$CO$_3$, 4% CaF$_2$</td>
<td>67.98</td>
<td>14.28</td>
<td>9.74</td>
<td>4.00</td>
<td>4.00</td>
</tr>
</tbody>
</table>

![Figure 4](image)

**Figure 4.** The effect of basicity on the phosphorus content in the slag and iron nuggets.

![Figure 5](image)

**Figure 5.** The effect of basicity on the distribution of phosphorus.
more phosphorus contents are entrapped in in the slag. As a result, the proportion of phosphorus contents contained in the iron was 26.01% while the proportion left in the slag was 46.72%.

At high temperatures, the base material CaF₂ could combine with acidic materials, such as SiO₂ and Al₂O₃, to form eutectics with low melting point and the negative ion F⁻ that is entering into the Si-O tetrahedral network could interrupt the Si-O connections. As a result, the tension on the surface of the melting pellets decreases and the liquidity increases, which improves the heat transfer and mass transfer conditions during the process of the reaction [15]. The XRD analysis was conducted on the slag obtained after the reaction of the pellets with the basicity at 1.4 and the CaF₂ content at 4%. The results are shown in Figure 11. When compared to the phenomenon shown in Figure 5, the phase of Ca₄Si₂O₇F₂ appeared in this case because of the combination of CaF₂, CaO and SiO₂.

3.4. Influence of Reaction Time on Dephosphorization

Since an appropriate basicity with the addition of Na₂CO₃ and CaF₂ could shorten the separation time of iron nuggets and slag, the influence of reaction time on the dephosphorization was also investigated in this study. The results are shown in Figure 12. It is seen from Figure 12 that the separation of the slag and iron occurs at 12 min, at which the phosphorus content in the iron is 0.4% with the dephosphorization rate at 81.2%. As the reaction time extends, the phosphorus content in the iron has an upward trend and reaches 0.62% at 21 min. Although increasing basicity and adding additives has a positive effect on the dephosphorization, the reduction reaction of fluorapatite could not be avoided and the reduction amount of fluorapatite increases as the reaction time is prolonged. Therefore, reducing the reaction time within a certain range could lower the phosphorus content in iron nuggets.
Microstructure changes during the reduction and melting process were shown in Figure 13 and Figure 14 with the results from the EDS analysis of the iron and slag at different times were shown in Table 6 and Table 7, respectively. At 0 min, Fe phase within the oolitic was mainly in the form of Fe₂O₃. After 2 min, large number of FeO particles, as presented in light gray points, appeared on the external surface of the oolitic along with some small amounts of the metallic iron, as shown in the brightest points. In the meantime, the dense structures of the oolitic became porous as FeO particles appeared. As the additives were diffused into the oolitic, the slag with gangues started to form. The slag in the oolitic had two regions: the light region was the slag phase with a high Ca content and the dark region was the slag phase with a high Si content. The phosphorous contents were found in the slag but not in the metallic iron. At 4 min, the amounts of the metallic iron increased and they were covered over oolitic but some small amounts of the phosphorous also entered into the metallic iron. At this moment, the slag with a high Ca content was further diffused into the oolitic core and was then integrated into the high Si slag. At 6 min, the oolitic structure started to be disassembled. Meanwhile, metallic iron at the edge of the oolitic started to aggregate and to grow up while the phosphorous content within the iron continued to increase gradually. The oolitic structure completely disappeared at 8 min and at the meantime, the aggregation and growth of the iron proceeded rapidly while the phosphorous content within the metallic iron dramatically increased. At 10 min, big size iron blocks were formed from the metallic iron and the separation of the slag and the iron was about to happen. The phosphorous content in the metallic iron remained the same. The element mapping in Figure 13(f) shows that a large amount of P was entrapped in the slag although some small amounts of P are uniformly distributed in the Fe phase.

Because the Fe-Si-Al slag directly contacted the fluorapatite throughout the entire reaction, the slag composition changes were an important consideration.

**Table 4. Wt. of Chemical Elements at Point 0 through 7 Indicated on the Photos in Figure 13 from the EDS Analysis.**

<table>
<thead>
<tr>
<th>Point No.</th>
<th>Fe</th>
<th>O</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>41.27</td>
<td>58.73</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>52.64</td>
<td>47.36</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>99.99</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>99.98</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>99.95</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>99.86</td>
<td>0</td>
<td>0.14</td>
</tr>
<tr>
<td>7</td>
<td>99.68</td>
<td>0</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Table 4 and Table 5 show EDS quantitative data for fluorapatite and slag in direct reduction process. The content of FeO, SiO$_2$, and Al$_2$O$_3$ was first calculated by the content of Fe, Si, and Al. Depicts composition changes of Fe, Si, and Al elements on the ternary phase diagram of the FeO-SiO$_2$-Al$_2$O$_3$ system. At the beginning of the reaction, slag composition was uneven, and there was more molten Fe$_2$SiO$_4$ and FeSiO$_3$ near SiO$_2$, while there was more FeAl$_2$O$_4$ near the Al$_2$O$_3$. As the reaction continued, the slag was homogeneous more than 10 minutes and the component point of the slag was in the liquid-phase zone, forming stable Fe-Si-Al slag.

4. DEPHOSPHORIZATION MECHANISM DURING THE REDUCTION AND MELTING PROCESS

The dephosphorization process can be described by the following reduction and reactions:

Fluorapatite reduction [16–18]:

\[
\eta 2\mathrm{Ca}_{10}(\mathrm{PO}_4)_6\mathrm{F}_2 + \mathrm{SiO}_2 = 6\mathrm{Ca}_3(\mathrm{PO}_4)_2 + 2\mathrm{CaF}_2 \cdot \mathrm{SiO}_2
\]

(2)

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

(3)

\[
\mathrm{CaO} + \mathrm{SiO}_2 = \mathrm{CaO} \cdot \mathrm{SiO}_2
\]

(4)

\[
\mathrm{FeO} + \mathrm{Al}_2\mathrm{O}_3 = \mathrm{FeAl}_2\mathrm{O}_4
\]

(5)

\[
2\mathrm{FeO} + \mathrm{SiO}_2 = \mathrm{FeSiO}_4
\]

(6)

\[
\mathrm{Fe}_2\mathrm{SiO}_4 + 2\mathrm{Al}_2\mathrm{O}_3 = 2\mathrm{FeAl}_2\mathrm{O}_4 + \mathrm{SiO}_2
\]

(7)

The additives reactions:

\[
\mathrm{CaCO}_3 = \mathrm{CaO} + \mathrm{CO}_2
\]

(8)
Ca$_3$(PO$_4$)$_2$ + SiO$_2$ + 2CaO = Ca$_3$(PO$_4$)$_2$SiO$_4$ (9)

2CaO + SiO$_2$ + Al$_2$O$_3$ = Ca$_2$Al$_2$SiO$_7$ (10)

Na$_2$CO$_3$ = Na$_2$O + CO$_2$ (11)

Na$_2$O + SiO$_2$ + Al$_2$O$_3$ = NaAl$_2$SiO$_6$ (12)

Ca$_3$(PO$_4$)$_2$ + SiO$_2$ + Na$_2$O + CaO
  = Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$ (13)

3CaO + CaF$_2$ + 2SiO$_2$ = Ca$_4$Si$_2$O$_7$F$_2$ (14)

Phosphorus absorption reaction [19]:

$$\frac{1}{2}P_2 = [P]$$ (15)
5. CONCLUSION

1. The basicity and additives have significant effects on the phosphorus behaviour. The fluorapatite reduction can be inhibited by increasing the basicity and adding Na₂CO₃ and CaF₂. For example, the phosphorus content in iron nuggets was reduced to 0.52% when $R = 1.4$, 4% Na₂CO₃ and 4% CaF₂ were used.

2. Prolonging the reaction time has negative effect on the dephosphorization. The separation of the slag and the iron nugget occurs at 12 min and the phosphorus content is at the minimum at 0.4% at that moment.

3. During the reduction and melting process, additives are diffused into the oolitic to combine with SiO₂ and Al₂O₃, which inhibits the reduction of fluorapatite. With the formation and aggregation of the metallic Fe, the phosphorus contents are reduced in the metallic Fe.

6. ACKNOWLEDGEMENT

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7. REFERENCES