Dephosphorization of Iron Ore Bearing High Phosphorous by Carbothermic Reduction Assisted with Microwave and Magnetic Separation

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The integrated process, which combined the carbothermic reduction assisted with microwave irradiation followed by milling and magnetic separation, was investigated as a potential approach for dephosphorization treatment of iron ores bearing high P. Mineralogical Research indicated that the phosphorous in oolitic hematite ores exists in two forms, inter-grew with iron oxide or gather together into a bigger size as gangues. The increase of microwave irradiation time had substantial effect on the reduction of Fe while the influence of carbon dosage was not obvious. As the reduced iron and unreduced P-contained gangues were not efficiently separated, a high iron recovery ratio and a reasonable dephosphorization rate were incompatible under the conditions investigated in this study. This process was successful in the aspect of iron recovery but the dephosphorization rate was unsatisfactory. Microwave-assisted reduction could be a promising pre-reduction process which could be followed by smelting process and dephosphorization treatment.

KEY WORDS: high phosphorous iron ore; microwave irradiation; carbothermic reduction; thermal stress; dephosphorization treatment.

1. Introduction

The crude steel production of China had reached 626 million tons in 2010 which accounted for nearly half of the whole world production. At the same time, the production consumed a large amount of high grade iron ore that imported from Australia and Brazil. As a result, the price of high grade ores consistently increases. Therefore, there’s an urgent need to compensate the raw material cost by using domestic low grade iron ores for the iron and steel plant in China, as China has a large deposit of high phosphorous iron ore with existing reserve of 7.45 billion tons which is unused in any large scale.1

The dephosphorization process for high phosphorous iron ores has been studied for many years all over the world. Typical methods includes beneficiation,2–5) smelting6) and microbial dephosphorization.7,8) Recently, some other approaches were proposed to remove phosphorous economically with respect to various kinds of high phosphorous iron ores. Xue et al.9) used direct reduction followed by magnetic separation to produce low P ferrous powder from high phosphorus oolitic hematite. Tang et al.10) proposed a process that combined the gas-based reduction with smelting of electric furnace. Zeng11) continued the improvement of beneficiation approach. Wu et al.12) put forward a integrated dressing process-Magnetizing roasting, magnetic separation

and reverse flotation dressing considering the influences of temperature, basicity and coal ratio. Matin inde and Hino13,14) investigated the possibility of dephosphorization by using pre-reduction and screening methods combined with mechanical crushing or air jet milling.

To sum up the researches mentioned above, it is a trend to use integrated process rather than single technology to remove the phosphorous. The main obstacle in dephosphorization process is how to separate the phosphorous-contained phase with the ferrous phases at acceptable price. Our study aims at the NingXiang-type oolitic hematite ore, which is characterized by inter-grew or inter-wrapped oolitic hematite grain and phosphorous-contained minerals, and the particle size of oolitic hematite is very fine which makes a very high energy consuming in the process of milling-benefication.12)

Microwave radiation has shown considerable potential for various applications in mineral processing and extractive metallurgy in the past twenty years.15) An important application of microwaves in mineral processing is the induction of thermo-mechanical stresses between the different phases within the treated mineral to reduce grinding energy.16) The characters of selective and rapid heating of microwave were used in this study to generate thermal stress at the interface between ferrous phases and P-contained phases. Besides, the coal was also used as both reductant and auxiliary heating agent. The objective of this study is to use carbothermal-reduction acting as magnetizing roasting, and assisted with microwave radiation generating heat and potential thermal
stress at interface between ferrous phases and P-contained phases which benefits the following milling and magnetic separation processes.

2. Experimental

2.1. Raw Materials
The oolitic hematite used in this study was produced in Wushan region of Chongqing, China. The concentrate were obtained from Chongqing Steel Ltd, China, with a grain distribution of 54.7% <1.25 μm, 39.3% in the range of 1.25–15 μm, and the rest >15 μm. The chemical composition of lump ore and concentrate ore are shown as Table 1.

Figure 1 is the XRD pattern for the sample of concentrate using D/MAX 3C (Cu Kα), suggesting that hematite was in dominate for Fe-containing phase considering the results of chemical analysis as shown in Table 1. The quartz was the main gangue phase while the P existed as hydroxylapatite.

Table 1. Chemical composition of oolitic hematite ores (mass%).

<table>
<thead>
<tr>
<th></th>
<th>TFe</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lump</td>
<td>47.73</td>
<td>18.37</td>
<td>–</td>
<td>6.56</td>
<td>3.45</td>
<td>1.24</td>
<td>1.20</td>
<td>0.12</td>
</tr>
<tr>
<td>Conc.</td>
<td>56.73</td>
<td>12.41</td>
<td>72.09</td>
<td>5.13</td>
<td>1.33</td>
<td>1.36</td>
<td>1.36</td>
<td>0.051</td>
</tr>
</tbody>
</table>

The pulverized coal was milled to below 75 μm. The results of industrial analysis of pulverized coal are shown as Table 2.

2.2. Experimental Procedure
To make the occurrence of phosphorous-contained phase clear, lump ores were used for mineralogical research, scanning electron microscope (SEM), and energy dispersive spectrometer (EDS) analysis. ZEISS Axioskop 40 polarization microscope was used for mineralogical observation. The SEM observation and EDS analysis were carried out with TESCAN VEGA II and OXFORD INCA Energy 350.

In the reduction process, the oolitic hematite concentrate and pulverized coal were mixed and pelletized to samples with a diameter of 25 mm and a thickness of 8 mm. The pellets with total weight of 155 g were put into an alumina crucible. Microwave transparent thermal insulation material was used to prevent heat from emitting, as shown in Fig. 2. The samples were reduced in a commercial microwave oven with a frequency of 2.45 GHz and 1 kW energy supply. The temperature measurement was taken immediately outside of the microwave oven right after the shutting down of microwave radiation, with a K-type thermocouple. Thereafter, the reduced pellets were milled to a particle size under 0.074 mm and followed by magnetic separation process. The XCGS-type magnetic tube was used for the separation, with an exciting current of 3A which correspond to magnetic intensity of 0.278–0.317 T.

The carbothermic reduction under microwave radiation is special in the aspect of reduction temperature, which is always influenced by the dielectric properties of materials and the ongoing reactions occurring in the systems.17) In this study, the microwave irradiation time was chosen as a variable factor rather than the reduction temperature. Nevertheless, the final temperature after microwave irradiation was measured as reference. As shown in Fig. 3, with the increase of the irradiation time, the final temperature increased observably. The temperatures of all the experiments were between 790°C and 970°C.

High carbon dosage were applied as the coal has excellent dielectric properties which is beneficial for the heating process.18) The experimental scheme for the reduction process is shown in Table 3.

3. Results and Discussions

3.1. Mineralogy of Lump Ore
The mineralogy of oolitic hematite ores is shown in Fig. 4, in which ‘a’) presents a oolitic structure observed in this

![Fig. 1. XRD analysis on the sample.](image)

![Fig. 2. Schematic diagram of the experimental apparatus.](image)
study and ‘b)’ illustrates the schematic diagram for typical ‘oolitic’ and ‘inter-grew’ structures. Usually, oolitic structure is composed of one elliptical shape ring (sometimes more than one), ‘inter-grew’ structure consisting of hematite and gangue phases all in tiny size, and a core. The oolitic rings could be hematite, chamosite orapatite (collophane). And the core is mainly composed of quartz, hematite, limonite, chamosite, collophane or their mixture.11) Take Fig. 4(b) for example, the dash lines represent the rings with different colors for different phases. Irregular particles demonstrate how the hematite and gangue phases could be distributed within the oolitic structure. In general, hematite and quartz could form a bigger size. Collophane usually exists in tiny size mixed with hematite as dispersive form, so called ‘inter-grew’ structure. Figure 5 indicates that the existence of phosphorous in the oolitic hematite has two forms, inter-grew with iron oxide or gather together at a bigger size as gangue. Anyway, phosphorous always exists with calcium which confirm the results of XRD patterns shown in Fig. 1. However, most of the P in the high phosphorus iron ore is in the form of oolitic structure. Thus, the separation of Fe and P and the regrowth process are necessary before magnetic separation.

3.2. Characterization of Products

The chemical composition of the sample after magnetic separation are shown in Table 4. According to the research of Ishizaki et al.,19) in the case of magnetite-coal composite pellets irradiated with microwave, Fe3O4 was reduced to FeO at about 800–1 000°C and then FeO was reduced to Fe at about 1 000–1 250°C. However, the metallic iron contents in Table 4 indicate that the transformation of FeO to Fe happened around 800°C. This is mainly due to two reasons. Firstly, the temperature measurement in our study was not

Fig. 3. Comparison of the final temperature after microwave irradiation.

<table>
<thead>
<tr>
<th>Table 3. Experimental scheme.</th>
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<tr>
<td>Radiation time (min)</td>
</tr>
<tr>
<td>Coal dosage (mass%)</td>
</tr>
</tbody>
</table>

Fig. 4. The mineralogy of sample (a, typical mineral morphology for oolitic hematite ores; b, schematic diagram for ‘inter-grew’ structure).

Fig. 5. The distribution of main elements of sample.
online and probably lower than the actual value. For another, the heating rates in Ishizaki’s research were much faster and the reactions were limited by the time to some extent.

Figure 6 is the XRD pattern of samples after magnetic separation, which shows that when the irradiation time increased from 20 min to 30 min, the intensity of diffraction peaks for metallic iron increased dramatically. Combined with the results of chemical analysis (see Table 4), ongoing reaction in this period was supposed to be the reduction of wustite. On the other hand, the hydroxylapatite had been transformed to apatite and its peaks gradually weakened with the increase of reduction time, which suggest that apatite had been reduced to some extent.

The iron recovery ratio and dephosphorization rate were calculated and the results are shown in Fig. 7, the definition of iron recovery ratio and dephosphorization rate were as follows:

\[ \eta_1 = \frac{M_1 \cdot TFe}{M_2 \cdot TFe'} \]  \hspace{1cm} (6)

\[ \eta_2 = \frac{M_1 \cdot P - M_2 \cdot P'}{M_1 \cdot P} \]  \hspace{1cm} (7)

Where, \( \eta_1, \eta_2, M_1, M_2, TFe, P \) and \( P' \) refers to the iron recovery ratio, the dephosphorization rate(\%), the mass of reduced sample, the mass of the sample after magnetic separation, the total iron content of reduced sample (\%), the total iron content of the sample after magnetic separation (%), the phosphorous content in the reduced sample(%) and the phosphorous content of the sample after magnetic separation (%), individually.

Figure 7 indicates that the dephosphorization rate decreased with the increasing of irradiation time while the iron recovery ratio has the opposite tendency. This contradictory relation implied that under the experimental conditions employed in this study, it was impossible to achieve a high iron recovery ratio while maintain a relatively reasonable dephosphorization rate. MATINDE et al. also found the contradictory relation and pointed out the difficulty of P–Fe separation due to the phenomenon that powdery gangue surrounded reduced iron. From this point of view, a integrated process combines pre-reduction (solid state) and mechanical separation methods could not separate the Fe and P-containing phases efficiently.

3.3. Thermodynamic Consideration

As a further understanding of the reduction process and a verification of the output, thermodynamic analysis were carried out as following.

Since quartz is the main gangue phase in the oolitic hematite concentrate (see Table 1). The existence of SiO\(_2\), especially those dispersing along the hematite grain (see Fig. 5), ongoing reaction in this period was supposed to be the reduction of wustite. On the other hand, the hydroxylapatite had been transformed to apatite and its peaks gradually weakened with the increase of reduction time, which suggest that apatite had been reduced to some extent.

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### Table 4: Chemical analysis on the sample before and after magnetic separation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reduced samples</th>
<th>Samples after magnetic separation</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>P(_2)O(_5) (wt%)</td>
<td>TFe (wt%)</td>
</tr>
<tr>
<td>1</td>
<td>1.24</td>
<td>53.91</td>
</tr>
<tr>
<td>2</td>
<td>1.23</td>
<td>53.05</td>
</tr>
<tr>
<td>3</td>
<td>1.24</td>
<td>54.01</td>
</tr>
<tr>
<td>4</td>
<td>1.44</td>
<td>59.63</td>
</tr>
<tr>
<td>5</td>
<td>1.35</td>
<td>58.24</td>
</tr>
<tr>
<td>6</td>
<td>1.45</td>
<td>64.94</td>
</tr>
<tr>
<td>7</td>
<td>1.44</td>
<td>60.7</td>
</tr>
<tr>
<td>8</td>
<td>1.46</td>
<td>62.05</td>
</tr>
<tr>
<td>9</td>
<td>1.51</td>
<td>63.29</td>
</tr>
</tbody>
</table>

Note: x for FeOx was calculated as index for Fe reduction degree (0<x<1.5).
ed that the formation of fayalite (2FeO·SiO₂) is the main hindrance for the rapid reduction of siderite and adding appropriate amount of Na₂CO₃ optimized the reduction. Theoretically, the addition of basic oxide would improve the reduction of FeO because of combining it with the SiO₂. However, the dielectric properties of basic oxide are usually poor, as CaCO₃ for example. Additional research is needed to understand the influence of basicity in the system that microwave involved. The existence of SiO₂ also changed the thermodynamic condition for the reduction of P-containing phases. The difference is shown as below: 20)

\[
\begin{align*}
\text{Ca}_3(\text{PO}_4)_2(s) + 5\text{C}(s) & \rightarrow 3\text{CaO}(s) + \text{P}_2 + 5\text{CO} \\
\text{Fe}_2\text{SiO}_4(s) - 2\text{C}(s) & \rightarrow 2\text{Fe}(s) + \text{SiO}_2(s) + 2\text{CO} \\
\text{Ca}_3(\text{PO}_4)_2(s) + 3\text{SiO}_2(s) + 5\text{C}(s) & \rightarrow 3\text{CaSiO}_3(s) + \text{P}_2 + 5\text{CO}
\end{align*}
\]

The thermodynamic preference for carbothermic reduction of high-P iron ores was illustrated as Fig. 8. It could be seen that with the addition of SiO₂, the reaction temperature decreased from 1418°C to 1161°C. The reduction of calcium phosphate with SiO₂ is more easier when the temperature is beyond 900°C. The XRD patterns indicates that the peak for apatite disappeared in case of 40 min reduction (see Fig. 6). Nevertheless, the highest temperature measured in this study was lower than 1000°C. This is because the temperature measurement was not online and probably lower than the actual temperature. The chemical assay for the product suggested that the reduction process for Fe was around Fe–FeO equilibrium (see Table 4). And mineralogical investigation had showed that hematite and P-containing phases exist in the form of ‘inter-grew’ structure (see Fig. 4). Thus, as the temperature of samples continuously increase with the increase of radiation time, the P would be reduced and move to adjacent metallic Fe as metallic P. As a result, no matter the P was reduced or not, the P still exists accompanied with iron phases. This in turn hampered the separation process thereafter.

3.4. Comparison with Other de-P Methods

The highest dephosphorization rate achieved in this study was 32.5% when the iron recovery ratio was 82.1%. As a comparison, some of the typical dephosphorization methods for high-P iron ores and their outputs were shown in Table 5, which concludes that the chemical leaching and bioleaching were much better in the aspects of dephosphorization and iron recovery. However, the drawbacks were also obvious. Bioleaching is usually time consuming and chemical leaching is uncompetitive for mass production compared with pyrometallurgical methods. The reduction process was proved to be beneficial for iron recovery though, the authors found that it is very difficult to separate the ferrous phase with the P-containing gangue, this phenomenon was also found in other researchers’ work. 13,14) Besides, most of the P exists in the form of inter-grew structure with hematite hampering the mechanical separation. It seems that the smelting process is necessary in order to separate the P from the Fe. According to our study, the energy consuming for a reduction of 1 kg high-P iron ore assisted with microwave radiation (coal 18.47%, 40 min) was about 4.301 kW·h, and the iron recovery ratio was 98.33% (see Fig. 7). Thus, microwave-assisted reduction with low carbon addition could be a promising process which could be followed by smelting process and dephosphorization treatment.

Besides the energy supply, the microwave irradiation was expected to generate thermal stress at interface between ferrous phases and P-contained phases in this study. However, the desired dephosphorization rate did not appear. This is because most of the P-containing phases were in dispersive form with tiny grain size, and possibly there were no substantial grain growth process under such experimental conditions.
4. Conclusion

The integrated process which combined the carbothermic reduction assisted with microwave irradiation and the magnetic separation was investigated as a feasible approach for dephosphorization treatment of high-P iron ores. Particularly, the influences of carbon addition and microwave irradiation time were discussed. Conclusions are summarized as follows:

(1) Phosphorous in oolitic hematite ores exists in two forms, inter-grew with iron oxide or gather together into a bigger size as gangue.

(2) The increase of microwave irradiation time had substantial effect on the reduction of Fe while the influence of carbon addition was not obvious. A high iron recovery ratio and a reasonable dephosphorization rate were incompatible under the conditions investigated in this study.

(3) Microwave irradiation is a promising approach for pre-reduction process benefiting the iron recovery, and could be followed by smelting process and dephosphorization treatment.

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