Upgrading Iron and Removing Phosphorus of High Phosphorus Oolitic Iron Ore by Segregation Roasting with CaCl$_2$+Ca(ClO)$_2$

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(Received 22 July 2018; accepted 15 May 2019)
Abstract

The iron-bearing ore, existing in the form of oolite, was mainly composed of hematite, limonite, daphnite and collophane. Harmful element phosphorus content was 1.56%, belonging to high phosphorus oolitic iron ore in western Hubei. In this study, segregation roasting and low intensity magnetic separation techniques were applied to upgrading iron and removing phosphorus. The ores, chlorinating agent and reducing agent were mixed into the roasting furnace for segregation roasting. After being transferred from weak magnetic minerals to the strong ones, the iron was recovered by low intensity magnetic separation. During segregation roasting, new ore phases, metallic iron (Fe), small amount of ferroferric oxide (Fe$_3$O$_4$) and ferrous oxide (FeO) can be observed. Results showed that iron concentrate with Fe content of 90.3%, phosphorus content of 0.15%, iron recovery of 92.9% were obtained under segregation roasting temperature 1273 K, roasting time 90 min, CaCl$_2$ (calcium chloride) 20%, Ca(ClO)$_2$ (calcium hypochlorite) 3%, dosage of coke 20%, low intensity magnetic separation field intensity 0.12 T.

Keywords: Low intensity magnetic separation; ferroferric oxide; calcium chloride; calcium hypochlorite
1 Introduction

The available reserves of high phosphorus oolitic iron ore [1] located in western Hubei are above 2 billion tons. The ore is considered as chemical sedimentary iron ore, mainly composed of oolite and detritus. Specifically, oolite consists of oolite core (quartz or iron material), collophane girdle, hematite, and limonite girdles. Detritus is composed of fine-grained hematite and quartz feldspar. Generally, the iron concentrate consists of iron-rich oolite and some amount of hematite, with an iron grade of up to 55%. The phosphorus in the ore is mainly in the form of collophane, where the grain sizes of collophane girdle and monomer quartz are relatively small. The sizes of hematite and limonite in chilimonite are small and difficult to separate. Meanwhile, the low grade of aggregate iron makes it difficult to upgrading iron and removing phosphorus [2].

Conventionally, direct utilization of oolitic iron ore without any pre-treatment [3-5] is not suitable, since its iron minerals, e.g., Fe$_2$O$_3$, had weak magnetic characteristic which cannot distinguish them from other gangue minerals. Meanwhile, due to its low Fe content, poor liberation and complicated composition, satisfactory processing method with acceptable cost that can effectively utilize the ore is still lack. However, it is feasible and sometimes necessary to modify the properties before direct beneficiation using various roasting methods [6-9], e.g., microwave roasting [10], salt roasting [11, 12], sulfur-fixed roasting [13] and sintering roasting modelling [14], and sulphating roasting [15-17]. Segregation roasting, a technology that applies to the theory of chlorination metallurgy, shows excellent performance in extracting valuable compositions and removing harmful ones from complex refractory iron ore. The methods that applied to processing high phosphorus oolitic iron ore are mainly magnetic roasting [18], direct reduction [19], deep reduction and suspension roasting, and so on [20, 21].

However, emphasize by segregation roasting on high phosphorus oolitic iron ore was rarely investigated. Hereby in this study, calcium chloride as chlorinating
reagent, calcium hypochlorite as auxiliary, and coke as reducing agent were applied, to treat the sedimentary high phosphorus oolitic iron ore in western Hubei by segregation roasting. This work was to gain a better understanding of the detailed characteristics of the iron phase change and microstructures under various conditions, e.g., segregation roasting temperature and coke dosage. The final chemical composition of iron concentrate with magnetic separation was also examined. The present study aims at providing a basis on upgrading iron and removing phosphorus for the commercial utilization of such oolitic iron ores.

2 Experimental

2.1 Materials and reagents

The sedimentary high phosphorus oolitic iron ore in western Hubei was sampled and processed to size of -1 mm. The hematite and limonite in the samples exist in the form of oolite, concentric and ellipsoidal structures, taking up 64.26% of total ores. The iron-bearing minerals in the oolite were mainly hematite, limonite, daphnite and collophane. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS) images of oolite are shown in Fig. 1. SEM and EDS images of collophane are shown in Fig. 2. The main chemical composition of high phosphorous oolitic iron ores is shown in Table 1, and the iron phase analysis results of sample are shown in Table 2.

![Fig. 1. SEM and EDS images of oolite iron ore.](image-url)
Fig. 2. SEM and EDS images of collophane.

Table 1 Main chemical composition of high phosphorous oolitic iron ores (mass, %).

<table>
<thead>
<tr>
<th>TFe</th>
<th>P</th>
<th>S</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>C</th>
<th>H₂O⁻</th>
<th>V₂O₅</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.70</td>
<td>1.56</td>
<td>0.05</td>
<td>13.58</td>
<td>6.56</td>
<td>5.63</td>
<td>0.40</td>
<td>0.071</td>
<td>0.86</td>
<td>2.89</td>
<td>0.091</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Table 2 Iron phase analysis results of sample (mass, %).

<table>
<thead>
<tr>
<th>TFe</th>
<th>Magenite</th>
<th>Hematite and limonite</th>
<th>Pyrite</th>
<th>Siderite</th>
<th>Ferrosilite</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.70</td>
<td>0.086</td>
<td>42.39</td>
<td>0.11</td>
<td>0.69</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The segregation reagents are presented in Table 3. All reagents are of analytical grade. Fineness of coke was -0.5 mm. Quality analysis of coke is listed in Table 4.

Table 3 Roasting reagents used in segregation roasting.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Chemical formula</th>
<th>Purity (%)</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium chloride</td>
<td>CaCl₂</td>
<td>98</td>
<td>Chlorinating agent</td>
</tr>
<tr>
<td>Calcium hypochlorite</td>
<td>Ca(ClO)₂</td>
<td>95</td>
<td>Auxiliaries</td>
</tr>
</tbody>
</table>

Table 4 The whole quality analysis of coke.

<table>
<thead>
<tr>
<th>Mad</th>
<th>Ad</th>
<th>Vad</th>
<th>FCd</th>
<th>Characteristic of char residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56</td>
<td>2.19</td>
<td>1.13</td>
<td>94.22</td>
<td>2</td>
</tr>
</tbody>
</table>


2.2 Material characterization

SDTQ600 differential thermal analyzer (TG-DTA) was used to characterize the thermal decomposition behaviors of the ore.
In this experimental study, advanced equipment including X-ray photoelectron spectroscopy (XPS)-EDS, SEM-EDS and electron probe EDS analyzer made by EDAX Inc, USA, were used to analyze the mineral morphology and mineral compositions.

2.3 Segregation roasting and low intensity magnetic separation

The ores were crushed to a certain particle size, then the chlorinating agent and reducing agent were mixed and put into the roasting furnace. These mixtures were heated to a certain temperature under the neutral or weak reducing atmosphere, where the chlorinating agent was used to form volatile metal chlorides. The products after roasting were ground to a suitable fineness then separated to produce magnetic products and non-magnetic ones through a XCGS-13 magnetic tube under certain magnetic field intensity. Then, the two products were filtered, dried, weighed, sampled and tested for further evaluation based on the iron grade, phosphorus content and iron recovery in magnetic products.

3 Results and discussion

3.1 Thermal analysis

TG-DTA of high phosphorous oolitic iron ores were conducted from 35 to 900°C in air at a heating rate of 10°C/min, and the results are presented in Fig. 3. It can be seen that the total heat absorption was 313.8 J/g with the temperature increase from ambient temperature 35°C to 900.0°C. The absorption process was mainly divided into three stages, of which the second and third stages are more pronounced.
In the first stage, the temperature increased from 169.5°C to 307.3°C, and the endothermic peak was 265.9°C, the heat absorption occupies 6.6% of the total heat absorption. It could be observed that a small amount of heat absorption occurred at this stage, and the process was relatively mild, which might be due to the moisture evaporation in the ore. For the second stage from 307.3°C to 588.8°C, the endothermic peak was 469.7°C, and the heat absorption was about 60% of the total heat absorption.

In the third stage, the temperature increased from 588.8°C to 721.9°C. The endothermic peak at this phase was 687.0°C, which was one of the important endothermic peaks. It was speculated that the hematite and limonite was converted into hematite and magnetite by absorbing heat [22]. At the temperature above 721.9°C, the reaction almost stopped and the heat absorbed by the minerals turned to be little.

3.2 Effect of segregation roasting temperature

At the experimental condition of segregation roasting time of 90 min, dosage of calcium chloride of 15%, dosage of calcium hypochlorite of 5%, dosage of coke of 15%, the SEM analysis and the iron phase analysis results of different segregation roasting temperatures are shown in Fig. 4 and Fig. 5, respectively.
Fig. 4. SEM images after roasting at various segregation roasting temperatures.

Fig. 5. Iron phase after roasting at different segregation roasting temperatures (mass, %).

It was found from Fig. 4 and Fig. 5 that the segregation roasting temperature is one of the key factors that determine whether the chlorinating agent can be decomposed and whether the Fe can be chlorinated to form volatile metal chloride. With the increase of temperature, the content of magnetite decreases dramatically. The content of magnetite increases slightly after the temperature exceeds 1270 K. The change trend of metallic iron is negatively correlated with the change trend of magnetite. An increase in the segregation roasting temperature has a significant effect on the generation of Fe and magnetite within the segregation roasting process [23, 24]. When the segregation roasting temperature exceeded 1273 K, the proportion of Fe has a small range of fluctuations [25]. At 1173 K, the SEM spectra showed a dispersed granular shape, which became more concentrated when the
temperature rose to 1223 K. At 1273 K, the dispersed granules disappeared and the maps showed large aggregates. Fig. 5 can clearly know that this is the time when the metal iron content is the largest, and the bulk morphology is mainly the embodiment of metal iron at this time. Meanwhile, the SEM images showed that the content of Fe was also in well degree at segregation roasting temperature of 1273 K. It can be concluded that segregation roasting temperature of 1273 K can be a suitable condition, under which Fe 32.67% and magnetite 5.68% could be obtained.

3.3 Effect of coke dosage

SEM imagines of products using various coke dosages are shown in Fig. 6, and the iron phase analysis results are shown in Fig. 7. These results were obtained at conditions of segregation roasting temperature of 1273 K, roasting time 90 min, dosage of calcium chloride 15%, dosage of calcium hypochlorite 5%.

Fig. 6. SEM imagines after roasting with various coke dosages.

![SEM images of products with various coke dosages](image)

![Graph showing Fe and Fe₂O₃ content](image)
During the segregation roasting process (Fig. 6 and Fig. 7), the coke reacted with water vapor to form H₂ and CO, and volatile FeCl₂ could be reduced to Fe particles by H₂ over the coke surface, as shown in Eq. (1) and Eq. (2).

\[ C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_2(g) \]  \hspace{1cm} (1)

\[ FeCl_2(s) + H_2(g) \rightarrow Fe(s) + 2HCl(g) \]  \hspace{1cm} (2)

As the coke dosage increased, the Fe content in the segregation roasting ore gradually increased. Under the condition that the coke dosage reached 20% or above, the increasing of Fe stopped. For Fe₃O₄ (Fig. 7, red line), when the coke dosage was below 20%, the smaller coke dosage could lead to the increased amount of magnetite in the roasting ore. Taking into account costs, excessive or insufficient coke dosage was not beneficial, coke dosage 20% could be a choice.

### 3.4 Effect of calcium chloride

At condition of segregation roasting temperature 1273 K, roasting time 90 min, calcium hypochlorite 5%, and coke dosage 20%, the SEM imagines and iron phase analysis with that of calcium chloride are shown in Fig. 8 and Fig. 9.

**Fig. 8.** SEM imagines after roasting with different calcium chloride dosages.
Fig. 9. Iron phase results after roasting with different calcium chloride dosages.

Fe content increased significantly firstly than decreased slightly (Fig. 8 and Fig. 9) with increasing calcium chloride dosage in the segregation roasting process. Along with the gradually decreased generation amount of magnetite, which indicates that increasing the amount of calcium chloride in a certain range will promote the formation of iron, but after exceeding a certain limit, the amount of calcium chloride is increased, and the formation of iron is not changed much and tend to be stable. During the segregation roasting process, the calcium chloride reacted with the acidic oxides in the ore (e.g., SiO₂, Al₂O₃) and H₂O, forming hydrogen chloride, as shown in Eq. 3 and Eq.4 [26].

\[
CaCl_2(s) + SiO_2(g) + H_2O(g) \rightarrow CaSiO_3(s) + 2HCl(g) \tag{3}
\]

\[
CaCl_2(s) + Al_2O_3(g) + H_2O(g) \rightarrow CaAl_2O_3(s) + 2HCl(g) \tag{4}
\]

If calcium chloride reached an excessive content, the amount of hydrogen chloride generated in the system would increase. FeCl₂ could be generated by chlorination reaction between the Fe and hydrogen chloride. FeCl₂ was easily reduced by H₂ to metal particles and then adsorbed on the surface of the coke, due to its instability [27, 28]. However, if calcium chloride is not sufficient, the amount of hydrogen chloride generated would be reduced, which is not conducive to the
formation of Fe in the segregation roasting process. It showed that the dosage of calcium chloride 20% could be a good choice.

3.5 Effect of calcium hypochlorite

SEM imagines, and iron phase analysis results after segregation roasting with various calcium hypochlorite dosages, are shown in Fig. 10 and Fig. 11, at the conditions of segregation roasting temperature of 1273 K, roasting time 90 min, calcium chloride 20%, and coke 20%.

![Fig. 10. SEM imagines with various calcium hypochlorite dosages.](image)

![Fig. 11. Iron phase analysis results with various calcium hypochlorite dosages.](image)

With the increasing of calcium hypochlorite dosage, a gradual increase of Fe content and a reduction of magnetite in segregation roasting process (Fig. 10, Fig. 11) can be found. Chemical reaction between calcium hypochlorite (an auxiliary) and
hydrogen chloride in the system occurred, forming calcium chloride and chlorine, as shown in Eq. 5 [29].

\[ \text{Ca(ClO)}_2(s) + 4\text{HCl}(g) \rightarrow 2\text{Cl}(g) + \text{CaCl}_2(s) + 2\text{H}_2\text{O}(g) \] (5)

With the increased dosage of calcium hypochlorite, the chlorine generated by the reaction accelerated the chlorination reaction of Fe to a certain extent, contributing to the formation of FeCl2. In addition, it can be found that excessive calcium hypochlorite might lead to excessive consumption of hydrogen chloride. On the other side, hydrogen chloride involved in the chlorination reaction during the segregation roasting process [30] is the most important chemical reaction.

3.6 Effect of segregation roasting time

At the condition of segregation roasting temperature of 1273 K, calcium chloride 20%, calcium hypochlorite 3%, and coke of 20%, SEM analysis and the iron phase analysis results of different segregation roasting time are shown in Fig. 12 and Fig. 13, respectively.

![Fig. 12. SEM imagines with various segregation roasting time.](image-url)
Fig. 13. Iron phase results with various roasting time.

Extending segregation roasting time was effective for the formation of Fe (Fig. 12, Fig. 13), but when the roasting time was increased to 120 min, the increasing of Fe stopped and decreased slightly. The segregation roasting process had multiple chemical reactions occurring over time, e.g., the decomposition, chlorination and reduction reactions; it also involved complex phase change. Shorter roasting time will result in insufficient and non-effective chemical reaction progress [30].

3.7 Low intensity magnetic separation

At condition of roasting temperature 1273 K, roasting time 90 min, calcium chloride 20%, calcium hypochlorite 3%, and coke 20%, 36.18% Fe and 1.89% magnetite were in the roasted ore (total was 38.07%), which accounts for 91.29% of all the iron. It is known that the factors affecting low intensity magnetic separation for the roasted ore are mainly grinding fineness and magnetic field intensity. Under the above conditions involved in the segregation roasting process, with the low intensity magnetic separation field intensity of 0.10T, the effect of grinding fineness of low intensity magnetic separation is presented in Table 5.

<table>
<thead>
<tr>
<th>Grinding fineness</th>
<th>Products</th>
<th>Productivity</th>
<th>Grade</th>
<th>Recovery</th>
</tr>
</thead>
</table>

Table 5 Effect of grinding fineness on low intensity magnetic separation (mass, %).
From the data in Table 5, with the increase of the grinding fineness, a regular increase of the iron grade and reduction of phosphorus content in iron concentrate can be observed. Due to the increased grinding fineness, the difficulty in the liberation of mineral monomer increased. However, excessively higher grinding fineness may lead to reduction of iron recovery in iron concentrate, along with the significantly increased grinding costs. The effect of field intensity is shown in Fig.14, with grinding fineness less than 0.019 mm accounting for 98%.

![Fig. 14. Effect of field intensity on low intensity magnetic separation.](image)

From Fig. 14, with the increased magnetic field intensity, a regular decrease of the iron grade and increase of both phosphorus content and iron recovery can be
observed. With the decreased magnetic field intensity, the materials will undergo combined action by mechanical and magnetic forces during the separation process. Under the condition of the magnetic field intensity 0.12T, the iron grade of iron concentrate decreased to 86.54%, the phosphorus content increased to 0.27%, while the iron recovery was 96.0%, which indicated that the increasing magnetic field intensity has a positive influence on the increase of overall iron recovery. But it was not beneficial to improve the iron grade of the concentrate.

3.8 Chemical composition of iron concentrate

The effects of CaCl$_2$ and Ca(ClO)$_2$ on upgrading iron and removing phosphorus of high phosphorus oolitic iron ore in western Hubei by segregation roasting were tested. The iron concentrate with Fe content of 90.3%, phosphorus content of 0.15%, iron recovery of 93.0% were obtained under the segregation roasting temperature of 1273 K, segregation roasting time of 90 min, dosage of calcium chloride of 20%, dosage of calcium hypochlorite of 3%, dosage of coke of 20%, low intensity magnetic separation field intensity of 0.12 T. To further investigate the final quality of the iron concentrate, chemical composition analysis, phase analysis, SEM, and electronic probe composition analysis were performed. The results are shown in Table 6 to Table 8, and Fig. 15.

Table 6 Main chemical compositions of iron concentrate (mass, %).

<table>
<thead>
<tr>
<th>TFe</th>
<th>P</th>
<th>S</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.25</td>
<td>0.15</td>
<td>0.02</td>
<td>4.12</td>
<td>0.06</td>
<td>1.25</td>
<td>0.08</td>
<td>0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 7 Iron phase results of iron concentrate (mass, %).

<table>
<thead>
<tr>
<th>TFe</th>
<th>Fe</th>
<th>Ferrous oxide</th>
<th>Ferroferric oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.26</td>
<td>86.91</td>
<td>1.22</td>
<td>2.13</td>
</tr>
</tbody>
</table>
Fig. 15. SEM (a)-EDX image (b), and SEM image (c) (10 μmscale) of iron concentrate.

Table 8 Electronic probe composition analysis results of iron concentrate (mass, %).

<table>
<thead>
<tr>
<th>Position</th>
<th>Composition</th>
<th>Fe</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>P₂O₅</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td>91.60</td>
<td>1.65</td>
<td>0.95</td>
<td>0.36</td>
<td>4.33</td>
<td>1.11</td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>93.01</td>
<td>1.87</td>
<td>0.87</td>
<td>0.28</td>
<td>2.89</td>
<td>1.08</td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>92.42</td>
<td>2.22</td>
<td>1.06</td>
<td>0.31</td>
<td>2.67</td>
<td>1.32</td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>89.77</td>
<td>1.08</td>
<td>1.54</td>
<td>0.37</td>
<td>6.13</td>
<td>1.11</td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>e</td>
<td></td>
<td>90.72</td>
<td>0.96</td>
<td>1.73</td>
<td>0.28</td>
<td>5.33</td>
<td>0.98</td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>91.97</td>
<td>1.06</td>
<td>0.89</td>
<td>0.33</td>
<td>4.87</td>
<td>0.88</td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>91.59</td>
<td>1.47</td>
<td>1.17</td>
<td>0.32</td>
<td>4.37</td>
<td>1.08</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

It could be seen (Table 6, Table 7) that the new ore phases dominated by Fe (86.91%), a small amount of FeO and Fe₂O₃. The iron phase has changed comparing with the iron phase of the crude ore, which changed from limonite (Fe₂O₃, Fe₂O₃·nH₂O) to a new iron phase dominated by metallic iron. Based on the SEM images and electronic probe composition analysis in Fig. 15 and Table 8, remarkable changes on the iron phases of high phosphorus oolitic iron ore after segregation roasting process can be observed.

4 Conclusions

High phosphorus oolitic iron from western Hubei, China, was investigated using segregation roasting and low intensity magnetic separation method to upgrade iron and remove phosphorus. The iron-bearing ore in in the oolite are mainly hematite, limonite, chlorite and collophanite. Detailed behaviors of the iron phase change and microstructures during segregation roasting were examined at various
conditions, including effect of roasting temperature, effects of various roasting reagents, e.g., coke, calcium chloride, and calcium hypochlorite. Low intensity magnetic separation after segregation roasting showed that iron content of 90.3%, phosphorus content of 0.15%, iron recovery of 93.0% were obtained for the iron concentrate under the segregation roasting temperature of 1273 K, segregation roasting time of 90 min, dosage of calcium chloride of 20%, dosage of calcium hypochlorite of 3%, dosage of coke of 20%, low intensity magnetic separation field intensity of 0.12 T and 98% grinding fineness of less than 0.019 mm. The chemical composition analysis, iron phase analysis, SEM, electron probe analysis and EDS of iron concentrate, showed that new ore phases dominated by Fe (86.9%), small quality of FeO and Fe$_3$O$_4$ from the original hematite and limonite (i.e., Fe$_2$O$_3$, Fe$_2$O$_3$·nH$_2$O) were generated.

**Acknowledgments**

This work was supported by Open Foundation of the State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology (ZR201801), Doctoral Foundation of Southwest University of Science and Technology (17zx7161 and 17LZXT05).

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