Experimental Study on the Chemical and Geo-Chemical Properties of a Fe$_3$O$_4$ Dominated Ore

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Dressing iron from the primary ores is the hot topic all the way. In our study, one primary magnetite iron ore was selected to analyze the chemical composition properties, and micro-structures of the minerals. The results show that magnetite is the main iron mineral taking up 25.1% of total, the Fe content in the lattice is 64.45%. Qualified iron ore concentrate would be obtained by using weak magnetic separation and desulfurization. However, the tiny magnetite may form complex dust particle, cloudiness or latticed structure and the close intergrowth with ilmenite, pyrrhotite and gangue minerals would not be fully separated even using fine milling which may definitely affect the grade of iron ore concentrate.

1. Introduction

Magnetite is the main objective mineral to recycle Fe, magnetite generally has two basic types, high-sulfur and low sulfur (Deng et al., 2012; Shang et al., 2015; Chokshi et al., 2016). Mostly, the low-sulfur magnetite has been widely used due to its high grade, the ores could be transport and sell to the market (Valverde et al., 2009; Bodrov and Trotsan, 2014; Dwari et al., 2014). Usually, magnetic separation technique is conducted for the low-sulfur magnetite beneficiation (Arol and Aydogan, 2004; Yavuz et al., 2006). However, the low-sulfur magnetite resources become exhausted after many years exploitation, more attention needs to be paid on high-sulfur magnetite (Zhang et al., 2015). But for high-sulfur magnetite, because pyrrhotite is the main mineral containing sulfur in the ores, the traditional magnetic separation method is not effective to separate iron and sulfur (Zvegintsev and Yakubaliik, 1998; Liu et al., 2013; Lv et al., 2018). Some studies reported that sulfur could be eliminated through burning method, while the result is not satisfactory, there are still about 1% residual sulfur in the ores after burning, and the mine environment would be polluted as well (Vladimir et al., 2006). The flotation could be another method to desulfurization. Now many projects show good results for high-sulfur magnetite ore when removing sulfur (Buswell and Nicol, 2002; Miller et al., 2005; Arvidson et al., 2013). In this study, one high-sulfur iron ore is selected for the process mineralogical study including chemical composition, the occurrence state of the main minerals and the disseminated grain size. The analysis on the factors influencing beneficiation effect would be discussed in this study in order to provide the reference for the further beneficiation design.

2. Chemical composition of the ores

The multielement analysis and chemical phase analysis of iron are shown in Tables 1 and 2. As shown, Fe is the main element could be recycled during beneficiation with a grade at 22.96%; the value of TFe/FeO is 1.45, which indicates a low oxidation level. The alkaline coefficient (CaO+MgO)/(SiO$_2$+Al$_2$O$_3$) is 1.33. In order to enrich the iron minerals, the gangue minerals need to be eliminated are SiO$_2$, Al$_2$O$_3$, CaO and MgO, with the total amount at 38.99%. The detrimental impurities have a low content, but sulfur content can reach up to 3.00%, which shows the typical characteristics of sulfur-rich ores, therefore, the desulfurization operation needs to be conducted during ore processing for the purpose of obtaining good quality of iron ore concentrate.

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The iron occurrence state in the ores appears in two main types: one occurs in magnetite, with a distribution rate at 63.2%, this is the biggest theoretical recycle value of Fe in iron mineral when adopting only weak magnetic separation technique; the other is the Fe in sulfide with a distribution rate at 21.78%. According to the chemical composition characteristics, the ores could be considered as low-phosphorous, sulfur-rich primary low grade magnetite.

**Table 1: Chemical composition of the ores (%)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>TFe</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>22.96</td>
<td>15.82</td>
<td>15.24</td>
<td>2.02</td>
<td>11.57</td>
<td>5.19</td>
<td>5.80</td>
<td>16.43</td>
</tr>
<tr>
<td>Composition</td>
<td>MnO</td>
<td>Na₂O</td>
<td>K₂O</td>
<td>P</td>
<td>S</td>
<td>C</td>
<td>TFe/FeO</td>
<td>Alkaline coefficient</td>
</tr>
<tr>
<td>Content</td>
<td>0.32</td>
<td>0.26</td>
<td>0.42</td>
<td>0.032</td>
<td>3.00</td>
<td>1.65</td>
<td>1.45</td>
<td>1.33</td>
</tr>
</tbody>
</table>

**Table 2: Chemical phase analysis results of iron in the ores (%)**

<table>
<thead>
<tr>
<th>Iron Phase</th>
<th>Magnetite</th>
<th>Limonite (hematite)</th>
<th>Ilmenite</th>
<th>Carbonate</th>
<th>Sulfide</th>
<th>Silicate</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>14.51</td>
<td>0.85</td>
<td>0.83</td>
<td>0.11</td>
<td>5.00</td>
<td>1.66</td>
<td>22.96</td>
</tr>
<tr>
<td>Distribution rate</td>
<td>63.20</td>
<td>3.70</td>
<td>3.61</td>
<td>0.48</td>
<td>21.78</td>
<td>7.23</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**3. The mineral content**

The analysis results, getting from lens-belowed identification, X-ray diffraction, and scanning electron microscope, show that the main metallic minerals in the ores are magnetite, minor pyrrhotite and slight ilmenite. The gangue minerals are mainly feldspar, biotite, serpentine, calcite and minor quartz, hornblende, pyroxene and chlorite. The trace minerals are pyrite, spinel, sphene, talc, flogopite, sercite, zoisite, anatase etc. The weight contents of the main minerals are shown in Table 3.

**Table 3: The weight contents of the main minerals (%)**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Magnetite</th>
<th>Pyrrhotite</th>
<th>Ilmenite</th>
<th>Biotite</th>
<th>Serpentine</th>
<th>Chlorite</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Hornblende</th>
<th>Pyroxene</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>25.1</td>
<td>8.3</td>
<td>1.9</td>
<td>30.5</td>
<td>14.3</td>
<td>14.0</td>
<td>4.9</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**4. The occurrence state of the main minerals**

The widely distributed magnetite is the main objective mineral which could be enriched during beneficiation. They always appear in idiomorphic-hypidiomorphic granular texture, and partly in irregular texture. The three occurrence states of magnetite are as follows: one is closely mosaic with ilmenite, and some ilmenite lamella could also be observed inner the magnetite (Figure 1).

**Figure 1: Granular ilmenite (Il) distributes and fills along the edge and inter-particle of magnetite (M)**

The second type is the intergrowth with pyrrhotite. Part of pyrrhotite shows in dust particle form due to the metasomatism, which results in the difficult identification on the boundary of magnetite and pyrrhotite even under microscope (Figure 2).
Figure 2: Magnetite (M) intergrows with pyrrhotite (Ph), partly in cloudiness structure G-gangue

The third type is the magnetite unevenly distributes in the gangue as tiny dust particle, spiderweb and featheriness structure, the particle size ranges between 0.005 and 0.05mm, part of it are even tiny (Figure 3).

Figure 3: Dust-particled magnetite (M) intergrows with cloudiness gangue (G) Bright color- pyrrhotite

Figure 4: Irregular pyrrhotite (Ph) fills and replaces in the interparticle space of ilmenite (Il) M-magnetite, G-gangue

The ratio of the above three types magnetite is 30:20:50. The disseminated relationship of magnetite is relatively complicated and it widely distributed with tiny particle size and closely embedded with pyrrhotite. Therefore, it is of great difficulty to obtain high grade iron ore concentrate.

Ilmenite occurs in two main states (granular and lamella) with a ratio of 80:20. The granular ilmenite is the main objected mineral when recycling Ti during mineral beneficiation. The three occurrence states are as follows: (1) distributes and fills along the edge and inter-particle of magnetite, the boundary are regular and
straight, the particle size is in the range of 0.04~0.2mm (Figure 1); (2) intergrows with pyrrhotite, granular ilmenite distributes in pyrrhotite matrix in some region in residual form, the particle size ranges between 0.01 and 0.2mm (Figure 4). (3) occurs in worklike or irregular granular structure and unevenly distributes in the gangue in sparse-scattered form, the particle size is generally 0.005~0.3mm (Figure 5). The ratio of three occurrence states ilmenite is 40:45:15. Most ilmenite has tiny particle size and closely intergrows with magnetite, pyrrhotite, therefore, the recycle Ti from ilmenite is of little value.

**Figure 5: Micro-fine wormlike ilmenite (Il) embedded in the gangue (G)**

Ilmenite lamella is the product of solid separation, and always caught in latticed form within magnetite, the width of the lamella is generally in the range of 0.01~0.04mm (Figure 6). However, the lamella is easy to go to iron ore concentrate with magnetite, there is no value to recycle it independently.

**Figure 6: Latticed ilmenite (Il) lamella intergrows with magnetite (M) G-gangue**

Pyrrhotite is the main sulfide in the ores, and generally, the occurrence states are as follows: one is irregular pyrrhotite aggregates distribute along the edge, inter-particle and crack of magnetite and ilmenite. Residual magnetite and ilmenite could be observed in the intensive replacement region. The particle size of pyrrhotite is 0.02~0.5mm, some coarser one reaches up to 1.0mm (Figure 4). The second state is that the micro-tiny booklike, wormlike or irregular pyrrhotite aggregates unevenly embed in the gangue in sparse-scattered form, the cloudiness texture could be observed in some region where the pyrrhotite complicatedly intergrows with gangue, the particle size is generally 0.005~0.2mm (Figure 7). Pyrrhotite is metallic sulfide with strong magnetism, it would go into the iron ore concentrate with magnetite when using weak magnetic separation technique. This is the primary reason why sulfur content is high in iron ore concentrate using weak magnetic separation, floatation desulfurization needs to be conducted in order to obtain iron ore concentrate with low sulfur content.
Figure 7: Pyrrhotite (Ph) intergrowth with needle-like, threadiness gangue (G) forms cloudiness disseminated relationship

The gaugue minerals are primarily feldspar, biotite, serpentine and calcite. Feldspar mainly closely embeds with other gaugue minerals, some suffers chloritization and carbonatation along the edge. Calcite mostly occurs in irregular aggregates and replaces with chlorite, pyroxene, biotite, and hornblende to form the disseminated basement for metallic minerals. The high proportion of low hardness gaugue minerals and developed cleavage in the ores would benefit for the disassociation of metallic minerals, but also may lead to the deteriorated separation environment during grinding process due to the argillization.

5. The disseminated grain size of magnetite

The grain size and the distribution characteristics of the main objective minerals exert great influence on the design of mineral processing flowsheet. The disseminated grain size of magnetite has been counted and the results are shown in Table 4.

Table 4: Disseminated grain size of the magnetite (%)

<table>
<thead>
<tr>
<th>Fraction/μm</th>
<th>830~300</th>
<th>300~150</th>
<th>150~75</th>
<th>75~38</th>
<th>&lt;38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distribution rate</td>
<td>43.1</td>
<td>35.7</td>
<td>15.1</td>
<td>5.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

As shown, the studied magnetite ores are typical fine-micro unevenly distributed. When the grain size is +0.15mm, the positive calculative distribution rate of magnetite is only 78.8%. Therefore, -0.074mm grinding fitness should be selected in order to assure >90% magnetite occurs in monomer form. It's also worth pointing out that the high proportion of low hardness gaugue minerals and developed cleavage in the ores would lead to a coarser grinding fitness during the actual operation than the one selected theoretically.

6. The analysis on the factors influencing beneficiation effect

The magnetite in the ores has Fe content at 64.45%, however, because some magnetite has very fine particle size, high dispersion degree, and complicatedly intergrowth with ilmenite, pyrrhotite and gaugue minerals, especially some ilmenite lamella caught inner the magnetite, it is hard to fully separate magnetite with them even if using fine milling procedure. The low-Fe coenobium would be the main reason leading to the low grade iron ore concentrate and high impurities content; the strong magnetic pyrrhotite going into the iron ore concentrate during weak magnetic separation would result in the high sulfur content in the ore concentrate.

7. Conclusion

The ores are low-phosphorous, sulfur-rich primary low grade, the contents of useful element Fe and harmful element S are 22.96% and 3.00% respectively. The distribution rate of magnetic iron is 63.22%, and magnetite is the main iron mineral taking up 25.1% of total, the Fe content in the lattice is 64.45%. Qualified iron ore concentrate would be obtained by using weak magnetic separation and desulfurization.

The grain size of magnetite is generally 0.03~0.3mm, and mainly distributes in gangue, a little of magnetite disseminates and intergrows with ilmenite and pyrrhotite. The tiny magnetite may form complex dust particle,
cloudiness or latticed structure and the close intergrowth with ilmenite, pyrrhotite and gangue minerals would not be fully separated even using fine milling which may definitely affect the grade of iron ore concentrate.

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