Desulfuration Behavior of Low-grade Iron Ore-coal Briquette during the Process of Direct Reduction Followed by Magnetic Separation

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The process of coal-based direct reduction followed by magnetic separation was employed to produce direct reduction iron powder (DRIP) from a refractory low-grade iron ore. The desulfuration behavior of the composite briquettes during this process was studied. Experimental results showed that this process presents advanced sulfur removal ability. The sulfur contained in the composite briquette was almost reserved in the form of troilite at the advanced sulfur removal ability. Experimental results showed that this process presents advanced sulfur removal ability. The sulfur contained in the composite briquette was almost reserved in the form of troilite at the reduction stage; however, after grinding and magnetic separation the sulfur was removed efficiently into the tailing, and the DRIP with low content of sulfur was obtained.

KEY WORDS: iron ore-coal briquette; direct reduction; magnetic separation; desulfuration.

1. Introduction

Recently, a considerable attention has been devoted to the production of DRIP from refractory iron ores, red mud, and iron-rich metallurgical slags by the process of coal-based direct reduction followed by magnetic separation. In this process, the iron containing compounds were prior reduced to metallic iron, and then the reduced products were ground to liberation size and concentrated by magnetic separation. The iron product obtained by this process generally contains more than 90 mass% Fe, and was expected to be a substitute of steel scrap in electric arc furnaces (EAF) for steelmaking. It is well known that the sulfur content of the feed stock for steelmaking must be strictly controlled because too high concentration of sulfur will cause hot shortness of steel. One of the flaws of the DRI, resulted from several new ironmaking processes such as FASTMET, ITmk3, and HiQIP which all charge coal-bearing pellets, was of high level sulfur. Reductant was one of the most important sulfur resources, and therefore its sulfur content should be strictly controlled in these processes.

In the process of coal-based direct reduction followed by magnetic separation, a physical separation technique was involved. Therefore the desulfuration of this process may differ from those noted above, and may have a higher receptivity on coal type from the viewpoint of its sulfur content.

In the present work, a difficult-to-process iron ore was treated with coal-based direct reduction followed by magnetic separation process, the desulfuration behavior of this process was investigated.

2. Experimental

2.1. Materials

The iron ore used was obtained from Hubei province, China. It contained 43.58 mass% Fe, 17.1 mass% SiO2, 9.28 mass% Al2O3, 3.58 mass% CaO, and 0.071 mass% S. Two kinds of coal with different sulfur content were used as reductants. The proximate analysis results and sulfur contents of these two coals were shown in Table 1. The iron ore and coal used in the experiments were crushed to 100% passed 1 mm.

2.2. Experimental Procedure

Before submitting to roasting experiments, the mixture of iron ore and coal was fully mixed with an appropriate amount of water (8 mass% to 12 mass%), and pressed to briquettes in a steel die (30 mm in diameter) with a hydraulic press. 20 g iron ore used in one run. The coal dosages were calculated based on the mole ratio of the fixed carbon to removable oxygen of the iron oxides (C/O ratio), in all the experiments the C/O ratio was fixed at 0.82 according to the previous study.

Reduction roasting was performed in a muffle furnace after the briquettes were dried. The reduced briquettes were ground and wet separated in a magnetic tube. The methods of roasting, grinding and magnetic separation have been described elsewhere. The Fe content of magnetic products was chemical analysed and the sulfur content of the samples were analyzed by a carbon and sulfur Analyzer (CS-2800). The iron recovery refers to the percentage of the total iron metal contained in the ore that is recovered into the DRIP. The desulfuration ratios of reduction stage and whole stage were calculated as follows:

\[
D_{s1} = \frac{m_0s_0 - m_1s_1}{m_0s_0} \times 100\%
\]

\[
D_{s2} = \frac{m_0s_0 - m_2s_2}{m_0s_0} \times 100\%
\]

Where, \(D_{s1}\) and \(D_{s2}\): desulfuration ratio of reduction stage and whole stage, respectively; \(m_0, m_1\) and \(m_2\): mass of the unreduced briquette, reduced briquette, and magnetic product, respectively; \(s_0, s_1\), and \(s_2\): mass% of sulfur content of the unreduced briquette, reduced briquette, and magnetic product, respectively.

Table 1. The proximate analysis and sulfur content of coals (mass%).

<table>
<thead>
<tr>
<th>Coal code</th>
<th>Moisture (%)</th>
<th>Ash (%)</th>
<th>Volatiles (%)</th>
<th>Fixed carbon (%)</th>
<th>Sulfur content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>11.77</td>
<td>17.56</td>
<td>24.86</td>
<td>45.80</td>
<td>1.77</td>
</tr>
<tr>
<td>C2</td>
<td>6.55</td>
<td>14.40</td>
<td>24.13</td>
<td>54.92</td>
<td>0.13</td>
</tr>
</tbody>
</table>

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3. Results and Discussion

3.1. Reduction and Separation Results

The reduction experiments were conducted at the temperature of 1200°C with the reduction time of 40 min. The roasting conditions were decided according to the previous study. The experimental results in the sulfur removal of carbon-bearing briquettes during roasting and the beneficiation process were shown in Table 2.

Table 2 shows that, the desulfuration ratios of C1 based briquettes and C2 based briquettes were just 9.99 mass% and 12.56 mass%, respectively, in the reduction stage. These results were agreed with other researchers’ that most of sulfur remained in the reduced coal containing pellets during reduction. However, after grinding and magnetic separation, the sulfur content of DRIP obtained from C1 based briquettes and C2 based briquettes were 0.113 mass% and 0.060 mass% with the corresponding desulfuration ratios were up to 93.05 mass% and 77.57 mass%, respectively. These results illustrate that the process of coal-based direct reduction followed by magnetic separation presents good sulfur removal ability on treating low-grade iron ore. Moreover, the sulfur content of the DRIP highly depends on the sulfur content in the reductant. In addition, the iron content of the DRIP derived from the C1 based briquettes and C2 based briquettes were up to 95.29 mass% and 94.84 mass% with corresponding recoveries of 87.14 mass% and 90.01 mass%, respectively.

3.2. XRD Analysis

In order to study the desulfuration mechanism of this process, the reduced briquettes with C1 as reductant and the two products obtained from this briquette during magnetic separation were analyzed by X-ray diffraction (XRD), respectively. The results were given in Fig. 1.

It can be seen from Fig. 1 that sulfur occurred in the form of troilite (FeS) in the reduced briquette, and most of the troilite was rejected into the tailing after magnetic separation. The diffraction peaks of troilite were not observed in the concentrate. This is because troilite is non-magnetic.

Table 2. Experimental results in the sulfur removal of carbon-bearing briquettes (mass%).

<table>
<thead>
<tr>
<th>Briquette code</th>
<th>S content of the unreduced briquette</th>
<th>S content of the reduced briquette</th>
<th>Ds1</th>
<th>S content of the DRIP</th>
<th>Ds2</th>
<th>Fe content of the DRIP</th>
<th>Fe recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 based briquette</td>
<td>0.514</td>
<td>0.696</td>
<td>9.99</td>
<td>0.113</td>
<td>93.06</td>
<td>95.29</td>
<td>87.14</td>
</tr>
<tr>
<td>C2 based briquette</td>
<td>0.091</td>
<td>0.118</td>
<td>12.56</td>
<td>0.060</td>
<td>77.57</td>
<td>94.84</td>
<td>90.01</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of the roasted briquette, DRIP, and tailing.

Fig. 2. SEM image and EDS results of the roasted C1 based briquette.
material and thus can be removed from metallic iron via grinding and magnetic separation techniques.

3.3. SEM Observation

The distribution of sulfur in the reduced C₁ based briquette was observed by scanning electron microscope (SEM) with energy dispersive spectrum (EDS).

Figure 2 illustrates that the troilite grains were enclosed by metallic iron in the reduced briquette. From the viewpoint of mineral processing, these troilite particles can be liberated from metallic iron via ground and hence be removed with other non-magnetic components by magnetic separation. On the other hand, some of troilite grains generated were just several microns which are difficult to be removed completely. Therefore the sulfur content of the magnetic product depends on the sulfur content of the reducing agent used. Moreover, as shown in Table 2, the desulfuration ratio of the low-sulfur coal based briquettes was lower than that of the high-sulfur coal based briquettes in the whole stage, this may contribute to that toilet particles formed in the former were smaller than that in the latter.

4. Conclusions

The process of coal-based direct reduction followed by magnetic separation presents good ability of desulfurization for treating low-grade iron ore-coal composite briquettes. During the reduction of composite briquettes, most of the sulfur remained in the roasted products in the form of troilite. However, most of the troilite was rejected into the tailing after grinding and magnetic separation. Furthermore, the sulfur content of the DRIP highly depends on the sulfur content in the reductant.

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