Effects of reductant type on coal-based direct reduction of iron ore tailings

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ABSTRACT. This paper explores the effects of reductant type, flux, reduction temperature, and reduction time on coal-based direct reduction of iron ore tailings. A series of tests were designed and implemented on ore tailing samples containing 14.51% of iron. The results show that the most ideal coal reductant for the direct reduction of iron ore tailings should be rich in fixed carbon and poor in volatile matters; with anthracite as reductant and CaO as flux, the tailing samples roasted and magnetically separated for 180 min at 1,300 °C yielded high iron content (90.12%) and iron recovery rate (72.21%). Then, the components of the product was analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). According to the XRD, SEM and EDX spectra, the product consists of lots of metallic irons and a few α-cristobalite and magnetite. The metallic irons were obtained through direct reduction, while the α-cristobalite and magnetite came from the secondary oxidization of metallic iron. The research findings shed new light on the reduction and recovery of iron in iron ore tailings.

RÉSUMÉ. Cet article explore les effets du type de réducteur, du fondant, de la température de réduction et du temps de réduction sur la réduction directe à base de charbon des résidus de minerai de fer. Une série de tests ont été conçus et mis en œuvre sur des échantillons de résidus miniers contenant 14,51% de fer. Les résultats montrent que le réducteur de charbon le plus idéal pour la réduction directe des résidus de minerai de fer devrait être riche en carbone fixe et pauvre en matières volatiles; avec l’anthracite en tant que réducteur et le CaO en tant que fondant, les échantillons de résidus grillés et séparés de manière magnétique pendant 180 minutes à 1300°C ont donné une teneur en fer élevée (90,12%) et un taux de
La récupération du fer (72,21%). Ensuite, les composants du produit ont été analysés par diffraction des rayons X (XRD), microscopie électronique à balayage (SEM) et spectroscopie des rayons X à dispersion d'énergie (EDX). Selon les spectres XRD, SEM et EDX, le produit est composé de beaucoup de fers métalliques et quelques α-cristobalites et de magnétites. Les fers métalliques ont été obtenus par réduction directe, tandis que l'α-cristobalite et la magnétite provenaient de l'oxydation secondaire du fer métallique. Les résultats de la recherche ont offert une nouvelle perspective sur la réduction et la récupération du fer dans les résidus de minerai de fer.

**KEYWORDS:** iron ore tailings, coal-based direct reduction, reductant type, roasting.

**MOTS-CLÉS:** résidus de minerai de fer, réduction directe à base de charbon, type de réducteur, grillage.

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**1. Introduction**

The rapid development of China’s steel industry has sped up the depletion of domestic iron ore resources. Many large steel enterprises have to purchase large quantities of iron ores from overseas for blast furnace smelting (Xu et al., 2011; Zhu et al., 2008; Li et al., 2012; Yang et al., 1999). The increasing demand of iron ores and the growing dependence on import have posed a major threat to the economic security of China’s steel industry. Against this backdrop, China must develop techniques to fully utilize the existing iron ore tailings, which are widely regarded as a key secondary resource around the world (Licskó et al., 1999; Gzogyan et al., 2005; Matschullat et al., 2000; Kim et al., 2004; Ghose & Sen, 2011).

The iron minerals have extremely fine dissemination size, due to the rich content of silicate minerals in iron ore tailings. As a result, the conventional beneficiation methods (e.g. magnetic separation, segmental grinding + magnetic separation, and magnetic separation + flotation) cannot achieve a high iron recovery rate, despite the extensive research by domestic institutes and plants (Zhu et al., 2008; Chen et al., 2007; Wang et al., 2009; Zhu et al., 2012; Wang et al., 2009). Focusing on refractory iron ores, most of the existing roasting reduction approaches convert the iron in iron ores into magnetite (Li et al., 2010) or metal iron (Gu et al., 2008; Liu et al., 2012), turning the micro fine structure of iron into a massive granular structure, with the aim to facilitate iron separation and recovery. However, there is no report on iron recycling through roasting reduction of iron ore tailings.

In the current methods of direct reduction, the reductant is either gas or coal. The gas-based method can achieve sufficient contact between mineral and gas, but its reductant (natural gas) is a scarce resource and its utilization rate is as low as 65%. The coal-based method uses non-catalytic coke as reductant, which is readily available, thanks to the huge coal reserve in China. Considering the abundance of China’s refractory iron ore tailings, it is very promising to develop a coal-based direct reduction method for the utilization of iron ore tailings (Zhang et al., 1997; Xu et al., 2010).

This paper deals with the iron ore tailings (Fe content: 14.51%) of Shanxi Lingqiu Haoyang Mining Co., Ltd. The iron ore tailings were selected because they
belong to silicon-rich, Anshan-type magnetic quartzite iron ores, which are the dominant type of iron ore deposit in China. After analysing the mineralogical features of the tailings, the iron was extracted via a coal-based direct reduction method. Then, the law of iron reduction was studied under different factors, including reductants, flux contents, calcination temperatures and roasting durations. X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were adopted to detect the iron minerals in magnetic iron concentrates, aiming to extract high purity iron concentrates from iron ore tailings rich in silicon and iron silicates. The research findings shed new light on the development and utilization of iron ore tailings in China.

2. Materials and Methods

2.1. Raw materials

(1) Iron ore tailings

The test sample was magnetite iron ore tailings collected from a tailings dam with uniform distribution. These iron ore tailings are hereinafter referred to as the “original tailings”. The chemical compositions of the original tailings are listed in Table below.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>TFe</th>
<th>P</th>
<th>S</th>
<th>C</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>K₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>14.51</td>
<td>0.048</td>
<td>0.63</td>
<td>0.051</td>
<td>54.41</td>
<td>7.99</td>
<td>5.06</td>
<td>0.43</td>
<td>2.90</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from Table 1 that the iron content of the original tailings is only 14.51%, the silica content is as high as 54.41%, the phosphorus content is quite low (0.048%), while the sulphur content is fairly high (0.63%). No metal element other than iron can be recycled.

The iron occurrence of the original tailings was determined through a chemical phase analysis. The analysis results are presented in Table 2.

As shown in Table 2, the iron in the original tailings mainly exists in the form of iron silicate. The distribution rate of iron in iron silicate iron is 81.39%, followed by that in magnetic iron (7.37%) and carbonate iron (3.38%).

The original tailings facies were identified by electron microscopy and scanning electron microscopy, and semi-quantitative analysis of each mineral was performed using X-ray diffraction data (see Figure 1).
Table 2. Chemical phase analysis results of the original tailings (%)

<table>
<thead>
<tr>
<th>Type</th>
<th>Magnetite</th>
<th>Pyrrhotite</th>
<th>Carbonate iron</th>
<th>Sulphide iron</th>
<th>Hematite and limonite iron</th>
<th>Silicate iron</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron content</td>
<td>1.07</td>
<td>0.35</td>
<td>0.49</td>
<td>0.39</td>
<td>0.40</td>
<td>11.81</td>
<td>14.51</td>
</tr>
<tr>
<td>Iron distribution rate</td>
<td>7.37</td>
<td>2.41</td>
<td>3.38</td>
<td>2.69</td>
<td>2.76</td>
<td>81.39</td>
<td>100</td>
</tr>
</tbody>
</table>

As shown in Figure 1, the original tailings mainly consist of the following minerals: quartz (43%), hornblende (21%), grunerite (21%), plagioclase (11%), chlorite (1%), biotite (1%), and dolomite (2%). The iron content of hornblende (Al$_3$Ca$_3$$_2$Fe$_{4.02}$K$_{0.6}$Mg$_6$NaSi$_{12.8}$O$_{44}$(OH)$_4$) is 12.73%, and that of grunerite (Fe$_7$Si$_8$O$_{22}$(OH)$_2$) is 39.03%. The irons contained in these two minerals make up for 10.87% of the total iron content in the original tailings. Considering the silicate iron content (11.81%) in the original tailings, it can be seen that most irons in the tailings exist in amphibole, with only a few presents in chlorite and biotite. Hence, it is difficult to recover iron from the original tailings by conventional beneficiation methods.

(2) Reductants

Three types of coals were selected as reductants for our test, namely, lignite, anthracite and stone coal. According to the industrial analysis results in Table 3, these reductants differ slightly in moisture and volatile contents and have a low
presence of the harmful element sulphur. However, there are huge differences in ash content and fixed carbon content among these reductants. Anthracite has lots of fixed carbon but few ashes.

<table>
<thead>
<tr>
<th>Name</th>
<th>Moisture</th>
<th>Ash</th>
<th>Volatile</th>
<th>Fixed carbon</th>
<th>Total sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bone coal</td>
<td>12.68</td>
<td>8.01</td>
<td>49.66</td>
<td>45.84</td>
<td>0.11</td>
</tr>
<tr>
<td>Anthracite</td>
<td>1.40</td>
<td>7.99</td>
<td>11.34</td>
<td>78.79</td>
<td>0.41</td>
</tr>
<tr>
<td>Lignite</td>
<td>10.75</td>
<td>18.93</td>
<td>27.31</td>
<td>53.64</td>
<td>2.01</td>
</tr>
</tbody>
</table>

2.2. Methodology

The coal, the original tailings and the flux CaO (analytically pure) were crushed to the size of -2mm before mixing at a certain ratio. Then, the mixed sample was relocated to a graphite crucible and placed into a D-1400X muffle furnace for reduction roasting. To prevent re-oxidation, the calcined product was water quenched and cooled to room temperature.

After that, the cooled calcined product was ground on an XMB-70 lab rod mill into the fineness of -0.074 mm (92.58%) at the grinding concentration of 60%, and magnetically separated in a 0~200kA·m⁻¹ type weak magnetic tube at the magnetic field strength of 111.5 kA·m⁻¹. The grinding and magnetic separation processes belong to two independent sections.

The microstructure of the calcined product was analysed on German Zeiss SUPRA™55 field emission scanning electron microscopy (FE-SEM), the changes of mineral composition in the calcined product were analysed on Japanese Rigaku D/MAX-RC 12KW rotating anode diffractometer (target: Cu; wavelength: 1.5406nm; working current: 150mA; working voltage: 40kV; scanning range: 5°-90°).

In addition, the mass percentage of coal or flux CaO added to the original tailings were recorded as the coal content or the flux CaO content, and the selective reduction effect is based on the iron content and iron recovery rate in the iron concentrate.

3. Results and discussion

3.1. Effects of reductants on iron selective reduction

Different amounts of the three reductants were added to the direct reduction test, aiming to disclose their impacts on iron selective reduction. The test was conducted under the following conditions: the calcination temperature was 1,200°C, the
calcination time was 120min and the flux CaO content was 16.2%. The test results are illustrated in Figure 2 below.

![Figure 2](image-url)

*Figure 2. Effects of reductants on iron content and recovery rate*

Figure 2 shows that the type and amount of reductants had a major impact on the content and recovery rate of directly reduced iron. With the growing coal consumption, the iron content of iron concentrates continued to decline and the iron recovery rate first increased and then decreased. This is because the iron in the ore tailings was not completely reduced when the blending ratio of coal was insufficient. The iron content in the concentrates remained at a low level, for the FeO could react easily with Al\(_2\)O\(_3\) and SiO\(_2\) in iron tailings at high temperature and the iron concentrates were mingled with complex compounds like iron spinel (FeO·Al\(_2\)O\(_3\)) and fayalite (2FeO·SiO\(_2\)). At a high blending ratio of coal, the amount of whole slag liquid phase increased, such that the impurities were stuck onto the reduced metal iron and gangue minerals. As a result, the iron and gangue minerals were difficult to dissociate in subsequent grinding. Thus, the iron recovery rate grew less rapidly and even started to decrease.

As shown in Figure 2, the iron grade obtained through direct reduction with anthracite was generally higher than that obtained with lignite and stone coal, so did the iron recovery rate. When the blending ratio of coal was 4.5%, the stone coal-based method achieved an iron recovery rate of 49.58%, higher than that of lignite-based method (48.43%) and that of anthracite-based method (47.03%). This means volatile content is a key driver of iron reduction of high silicon iron ore tailings at a low blending ratio of coal. That is why the stone coal (with relatively high volatile content) was more reactive than lignite and anthracite.

When the blending ratio of coal surpassed 4.5%, the iron recovery rate increased
under the effect of sufficient reductants. In this case, anthracite displayed better reduction effect than the other two reductants. The edge of anthracite can be attributed to the high fixed carbon content. At a high calcination temperature, the solid reduction of iron and carbon are intense thanks to the sufficient carbon gasification reaction.

When the blending ratio of coal was higher than 7.5%, the iron recovery rate continued to decrease. The anthracite-based method (6%) led to a greater decline than the anthracite-based method (4%) and stone coal-based method (2%). A possible reason for these trends goes as follows. The fixed carbon of each reductant had been substantially consumed with the elapse of the calcination time, and the reduction activity of volatiles in stone coal slowed down the disappearance of the reducing atmosphere created by fixed carbon.

The above comparison reveals the major impact of reductant type on the direct reduction roasting effect. The anthracite boasts the strongest reduction effect, followed by lignite and stone coal. The blending ratio of anthracite was recommended as 7.5% because the corresponding iron content and iron recovery rate are as high as 64.01% and 78.37%, respectively.

3.2. Anthracite-based selective reduction tests

3.2.1. Effects of flux content

To disclose the effects of flux CaO on the reduction results, selective reduction tests were carried out at the blending ratio of anthracite at 7.5% and the flux CaO content at 5.4%, 16.2%, 21.6%, 32.4% and 43.2%, respectively. The other test conditions were the same as those in Section 3.1. The test results are presented in Figure 3 below.

![Figure 3. Effects of flux content on iron content and recovery rate](image-url)
It can be seen from Figure 3 that, with the increase of the flux content, the iron grade grew rapidly before a slight decline, while the iron recovery rate surged up before a deep plunge. At the flux content of 21.6%, the iron recovery rate peaked at 82.93% and the iron content stood at 63.23%. Below is a detailed explanation of these trends.

In the initial phase, compound like CaO·SiO₂, 2CaO·SiO₂ were formed preferentially because CaO has a greater affinity than FeO to SiO₂ (Shivaramakrishna et al., 1996). Owing to the high contents of Al₂O₃ and SiO₂ impurities in the ore tailings, a solid phase reaction occurred in the presence of a reduction phase (Fe₂O₃ → Fe), producing complex oxides like iron spinel (FeO·Al₂O₃) and fayalite (2FeO·SiO₂). After a proper amount of flux CaO was added, the temperature to initiate the reduction of these complex oxides was lowered, the reactivity was improved and the FeO in the metal oxides was replaced, forming free FeO. Thus, the FeO→Fe reaction was completed (Ni et al., 2010).

After the CaO content surpassed 21.6%, the iron content changed slightly because the excess CaO suppressed the fluidity of the whole slag, making it impossible for the iron particles to aggregate into large particles. Thus, the iron recovery rate in the grinding process was reduced. Through comprehensive consideration, the optimal flux CaO content was determined as 21.6%.

3.2.2. Effects of reduction temperature

In deep reduction reaction, the reduction system must be provided with sufficient heat to fully reduce the iron oxides. The calcination temperature directly bears on the reduction rate and effect of the iron tailings, the connection of iron grains, and the growth of iron crystal grains. In light of these, the effects of reduction temperatures on the reduction of iron ore tailings were investigated through selective reduction tests at different temperatures (i.e. 1,000°C, 1,050°C, 1,100°C, 1,150°C, 1,200°C, 1,250°C, 1,300°C and 1,350°C). In the tests, the flux CaO content is 21.6%, and the other conditions are the same as those in 3.2.1. The test results are displayed in Figure 4 below.

![Figure 4. Effects of reduction temperature on iron content and recovery rate](image-url)
As shown in Figure 4, the iron recovery rate increased significantly from 11.54% to 82.93%, while the iron content dropped sharply, as the reduction temperature grew from 1,000°C to 1,100°C. This is because the iron was not sufficiently reduced under the weak reduction atmosphere at a low temperature.

By contrast, as the temperature increased from 1,100°C to 1,300°C, both the iron recovery rate and iron content were on the rise. The iron recovery rate peaked at 63.23% and the iron content stood at 63.23% at 1,200°C. This is because the amount of slag liquid phase increased with the reduction temperature; when the iron particles aggregated to a suitable size, the iron and gangue monomers could be dissociated more effectively in subsequent grinding; when the iron particles became too large, it was difficult for monomer dissociation in the grinding process.

When the temperature continued to grow after 1,300°C, the iron recovery rate started to drop, reaching 51.12% at 1,350°C. At this temperature, the iron ore tailings underwent a semi-melting reduction reaction, resulting in relatively large iron particles in the calcined product. The product is hard to break or grind, adding to the difficulty in grinding and magnetic separation. Thus, the iron content and iron recovery rate were both slightly reduced.

3.2.3. Reduction time

In deep reduction reaction, the iron is gradually reduced from iron oxides through a series of complex reactions. Fully reduction of the iron requires sufficient reaction time. However, the reaction time should not be too long. Otherwise, the reduced iron may suffer from secondary oxidization, melting, sintering or impurity encapsulation, making it difficult for grinding or magnetic separation (Fruehan,
1977). Therefore, the effects of reduction time on the reduction of iron ore tailings were investigated through selective reduction tests with different reduction times (i.e. 90min, 120min, 150min, 180min, 210min and 240min) at 1,300°C. The other conditions were the same as those in 3.2.1. The test results are shown in Figure 5 below.

It can be seen from Figure 5 that the iron recovery rate exhibited a significant upward trend with the increase of reduction time. When the reduction time was 60min, iron content was 81.17% and the iron recovery rate was 47.76%. When the reduction time grew to 120min, the iron content and iron recovery rate reached 92.15% and 63.34%, respectively. The sharp growth is attributed to the thoroughness of reduction after a long reaction.

The iron content changed gradually between 120min and 180min and dropped markedly after 180min. The change of iron recovery rate (91.78%~90.12%) was less violent than that of iron content (65.24%~72.21%) between 120min and 180min. After 180min, the iron recovery rate started to decline while the iron content continued to rise, because the iron particles were tightly mixed with the gangue after a long reaction, reducing the degree of dissociation.

### 3.3. Product analysis

Figures 6 and 7 are the SEM and XRD patterns of the iron concentrate produced in our tests. The irregular particles in Figure 6 are reduced iron particles, which are well developed and large in mean particle size. The long-axis direction of individual particles could reach 40μm or more, and the short-axis direction could reach about 20μm. As shown in Figure 7, the main phase in the iron concentrate was iron. The few weak magnetite peaks are possibly caused by the partial oxidation of iron before preparation or analysis. Quartz, the main component of the ore, was turned into α-cristobalite through crystal transformation under 1,300°C, and was mixed in the iron concentrate.

![Figure 6. SEM pattern of iron ore concentrate](image)
Figure 7. XRD pattern of iron ore concentrate

Figure 8 show the EDX spectra of particles 1 and 2 in Figure 6. As shown in Figure 8(1), particle 1 mainly contains high-purity metallic iron, which agrees with the 90.12% iron content and XRD spectrum in Figure 7. As shown in Figure 8(2), the two particles mainly contain Fe, plus a small amount of Si, Ca, O and Al. The iron content of the two particles was 90.12%, while the total content of the other impurities amounted to 9.88%.

Figure 8. EDX spectra of particles 1 and 2 in the SEM pattern

4. Conclusions

This paper studies quartzite iron ore tailings rich in iron silicate magnets, whose fine grain size makes it difficult to optimize the sorting indices by conventional methods. In light of the mineralogical features of the tailings, the author put forward
a brand-new coal-based direct reduction method capable of enriching the iron in the tailings. The method sheds new light on the development and utilization of secondary resources like ore tailings in China.

Comparative tests show that the reductant anthracite can lead to higher iron content than the same amount of lignite or stone coal. When the blending ratio of coal reductant falls in the interval of 4.5% and 6%, the calcination reduction of iron ore tailings is dominated by the direct reduction of solid carbon. In this case, the content of fixed carbon in the reductant has considerable impacts on the reduction effect. When the blending ratio of coal was below or above the said interval, the volatile matter in the coal can maintain a good reduction effect. Therefore, it is recommended to roast and reduce iron ore tailings with a reductant with a fixed carbon content and a small amount of volatiles.

The optimal conditions for roasting and magnetic separation are determined as follows: the blending ratio of anthracite should be 7.5%, the amount of CaO flux should be 21.6%, the roasting should be conducted at 1,300°C for 180min, the grain size for grinding should be -0.074mm (92.58%), the magnetic field strength should be 111.5kA/m. Under these conditions, the produced iron concentrate has a total iron content of 90.12% and an iron recovery rate of 72.21%. The XRD, SEM and EDX analyses show that the product mainly contains high-purity elemental iron and a very limited amount of harmful impurities.

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