

Direct Reduction of High-phosphorus Oolitic Hematite Ore Based on Biomass Pyrolysis

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Abstract: Direct reduction of high-phosphorus oolitic hematite ore based on biomass pyrolysis gases (CO , H_2 , and CH_4), tar, and char was conducted to investigate the effects of reduction temperature, iron ore-biomass mass ratio, and reduction time on the metallization rate. In addition, the effect of particle size on the dephosphorization and iron recovery rate was studied by magnetic separation. It was determined that the metallization rate of the hematite ore could reach 99.35% at iron ore-biomass mass ratio of 1 : 0.6, reduction temperature of 1100 °C, and reduction time of 55 min. The metallization rate and the aggregation degree of iron particles increase with the increase of reduction temperature. The particle size of direct reduced iron (DRI) has a great influence on the quality of the iron concentrate during magnetic separation. The separation degree of slag and iron was improved by the addition of 15 mass% sodium carbonate. DRI with iron grade of 89.11%, iron recovery rate of 83.47%, and phosphorus content of 0.28% can be obtained when ore fines with particle size of $-10 \mu\text{m}$ account for 78.15%.

Key words: high-phosphorus oolitic hematite ore; direct reduction; biomass pyrolysis; dephosphorization

The oolitic hematite ore is widely distributed in China, especially the Xuanlong-type iron ore in the north and the Ningxiang-type iron ore in the south. It is recognized as one of the most difficult iron ore to use because of its unique oolitic structure, fine iron particle size, and high phosphorus content^[1]. High-phosphorus oolitic hematite ore has been investigated by many researchers due to the development of direct reduction process in recent years. Sun et al.^[2-7] investigated the influence of reductant species, particle size of ore, and dephosphorization agent on coal-based direct reduction, as well as the mechanism of dephosphorization of high-phosphorus oolitic hematite ore. Their results showed that a highly volatile reductant was advantageous to dephosphorization and iron reduction. The developed NCP/NCS dephosphorization agents could react with quartz and phosphate rock in iron ore to de-

stroy the oolitic structure and achieve separation between iron and slag. Zhou^[8] hypothesized that the nucleation of metallic iron particles and growth of the crystal nucleus caused the destruction of the oolitic structure in the oolitic hematite ore during direct reduction. Increasing reduction temperature and extending the reduction time was beneficial for the growth of metallic iron particles. Sun et al.^[9-11] found that hematite with a particle size of $0-20 \mu\text{m}$ was embedded with gangue in the ooid. Besides, they focused on the rule of phosphorus transferring associated with reduction temperature, reduction time, distribution coefficient of carbon, and CaO content in coal-based direct reduction. When the reduction temperature was more than 1200 °C, part of the phosphorite was reduced to phosphorus during direct reduction of iron, and the rest were discharged with the tailing.

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As mentioned above, coal is mainly used as the reductant in the direct reduction process, resulting in several problems caused by the high content of sulfur and ash in the coal. The excessive sulfur content in the direct reduced iron (DRI) reduces its quality and increases the cost of desulfurization. A portion of the sulfur is oxidized to sulfur dioxide (SO_2), causing atmospheric pollution. The iron loss is increased because the ash in coal reacts with the iron oxide to create fayalite and hercynite. Alkali compounds such as CaO , CaCO_3 , and Na_2CO_3 are added into the iron ore to reduce fayalite and hercynite. A large amount of slag generated during the reduction process will hinder the diffusion and growth of the iron grain. Therefore, biomass was used as the reductant to replace coal in this work. Biomass is the most widespread material on earth, including all animals, plants, microorganisms and organic substances generated from derivation, excretion, and metabolism of these living things^[12,13]. Besides, biomass is clean, renewable and carbon neutral^[14], and has been recognized as clean energy^[15]. Through thermal chemistry conversion technology^[16,17] like pyrolysis, biomass can produce a large number of reducing gas, tar, and char that can be used as reductants. According to previous studies on biomass reduction^[18–22], manganese ore can be reduced to MnO upon heating at $400\text{ }^\circ\text{C}$ for 12.5 min.

Hematite can be reduced to Fe_3O_4 while calcining at $650\text{ }^\circ\text{C}$ for 30 min, and to Fe at $1000\text{ }^\circ\text{C}$ after 60 min. In this study, pine sawdust was used as the reductant for the direct reduction of high-phosphorus oolitic hematite ore to investigate the influences of reduction temperature, mass ratio of the iron ore-biomass, and reduction time on the metallization rate.

1 Experimental

1.1 Materials

The high-phosphorus oolitic hematite ore was obtained from west Hubei province in China, with a block size of 2–8 cm. It was pulverized to 0.074 mm using a ND8-4L planetary ball mill, and then dried at $105\text{ }^\circ\text{C}$ in a DHG-9140A electric oven for 24 h to remove moisture. Chemical analysis of hematite samples was conducted using a Shimadzu XRF-1800 spectrometer, and the loss of ignition (LOI) at $1000\text{ }^\circ\text{C}$ was measured by mass loss of a dried sample ($105\text{ }^\circ\text{C}$) using a LECO TGA 601. The TFe (total Fe), FeO, and P contents, shown in Table 1, were examined by the chemical method. The crystalline phases were investigated by powder X-ray diffraction (XRD) technique, using a laboratory Rigaku TTRIII diffractometer with a graphite crystal monochromator to filter the $\text{CuK}\alpha$ radiation, operating at 40 kV and 200 mA , and at a rate of $10\text{ }^\circ/\text{min}$. The mineral composition is shown in Fig. 1.

Table 1 Chemical composition of oolitic hematite ore

| | | | | | | | | | | | mass% |
|-------|------|------|------|-----|----------------|-------------------------|------|----------------------|------|------|-------|
| TFe | FeO | P | S | MnO | SiO_2 | Al_2O_3 | CaO | K_2O | MgO | LOI | |
| 47.87 | 1.71 | 0.99 | 0.02 | 0.1 | 6.43 | 6.32 | 3.68 | 0.35 | 0.50 | 3.12 | |

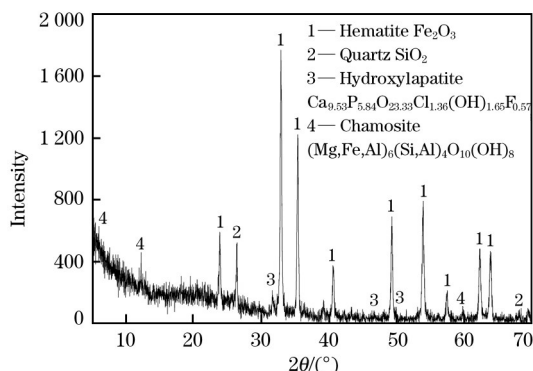


Fig. 1 Mineral composition of oolitic hematite ore

The biomass selected for this experiment was pine sawdust supplied from a local timber shop in Changping District, Beijing, China. It was dried at $80\text{ }^\circ\text{C}$ for 24 h in an electric oven and crushed to sizes

of -0.15 mm . Table 2 shows the properties of the sawdust. The ultimate analysis was carried out according to the Chinese national standards GB/T212-2001 and GB/T214-2001, and the proximate analysis was carried out according to the ASTM E1755-95. High-purity nitrogen with a purity of 99.999% was used in this analysis.

Table 2 Properties of sawdust (dry base) mass%

| Ultimate analysis | | | | | Proximate analysis | | | |
|------------------------|------------------------|------------------------|------------------------|------------------------|--------------------|-------|-------|------|
| C_{ad} | H_{ad} | O_{ad} | N_{ad} | S_{ad} | Water | VM | FC | Ash |
| 43.08 | 6.41 | 32.24 | 0.32 | 0.10 | 13.92 | 62.95 | 19.20 | 3.93 |

Note: ad—Air dried basis; VM—Volatile matter; FC—Fixed carbon.

1.2 Methods

The direct reduction experiment was conducted

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