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Carbothermic Reduction of Ferruginous Manganese Ore for Mn/Fe Beneficiation: Morphology Evolution and Separation Characteristic

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Abstract: In the present paper, beneficiation of Fe and Mn elements from a ferruginous manganese ore via carbothermic reduction followed by magnetic separation process was investigated in detail. The effects of the experimental parameters were systematically discussed. Iron-rich products with an Fe grade of 62.3% and 88.2% of Fe recovery, and manganese-rich product with a Mn grade of 63.7% of and 70.4% of Mn recovery were obtained, respectively, at an optimal temperature of 1100 °C, with a roasting time of 100 min, anthracite addition of 25%, milling fineness of 90% passing 0.074 mm, and a magnetic intensity of 140 A/m. Furthermore, the morphology evolution and phase transformation laws along with reduction process were revealed by optical microscope, scanning electron microscope equipped with energy dispersive X-ray detector (SEM-EDX), X-ray diffraction (XRD), and chemical phase analysis. The results demonstrated that the ferruginous manganese ore reduction can be described as follows: plate-like Fe-Mn symbiotic phase decomposition \rightarrow granular MnO phase formation \rightarrow fine metallic iron formation \rightarrow aggregation of metallic iron \rightarrow boundary development between Fe and Mn phases.

Keywords: ferruginous manganese; carbothermic reduction; morphology evolution; phase transformation; Mn/Fe beneficiation; magnetic separation

1. Introduction

Manganese is an important element and is widely used in metallurgy, chemistry, paints, and batteries. About 95% of Mn is consumed in the iron and steel manufacture for its alloying, deoxidizing, and sulfur-fixing properties [1–3]. So far, there is no satisfactory substitute in its major applications related to ferrous or nonferrous alloy production. However, global lack of high-grade manganese ore has failed to meet the rising demand of manganese ferroalloys [4]. For example, China demands most of the manganese resources due to its large crude steel production. However, almost no rich ore (manganese grade higher than 44 wt %) has been found in its total reserves of 40 million tons [5]. Moreover, manganese minerals are mostly found associated with iron oxides, which are unsuitable for either iron or ferrous alloy-making [6,7].

The manganese and iron minerals separation process always shows low efficiency for their homogeneous characteristics. Numerous studies have been conducted to upgrade the low-grade ferruginous manganese ore resources more efficiently. Gravity separation, magnetic separation, and even flotation are always applied in ferruginous manganese ore processing [8,9]. Only poor targets could be achieved for the high similarity in density and magnetic susceptibility of manganese and iron minerals. Additionally, their extremely fine, but intergrowth occurrence state, also obstructs

the effective beneficiation [10–12]. Reduction-leaching processes are proposed to recover manganese from manganese oxide ores [10–14]. Sulfite, ammonium chloride, H_2O_2 , and biomass are usually used as reductants. However, impurity elements are simultaneously leached with manganese, especially in ferruginous manganese ore treatment. Another approach, reduction-magnetic separation, is also developed for iron and manganese beneficiation from ferruginous manganese ore [6,15–21]. In this process, iron minerals are transformed to ferromagnetic substance (Fe₃O₄ or Fe) for magnetic separation purposes. However, the separation performance affected by many factors (reduction degree, ferromagnetic substance size, minerals occurrence state, etc.) is always unfavorable.

It is noteworthy that manganese minerals are used more and more in the area of chemical looping combustion (CLC) as an oxygen carrier [22–25]. CLC is an emerging technology for high-efficiency fuel conversion with inherent carbon capture. Researchers have proved its higher reactivity with syngas and gasification rate for char, which made this cheap, but environmental material, become the focus. It may be a potentially-important future market for manganese ore utilization.

However, using it as an oxygen carrier could not solve the global demand for manganese. The objective of the current study is the beneficiation of manganese and iron, respectively, from a ferruginous manganese ore.

2. Experimental

Ferruginous manganese ore was treated via a carbothermic reduction followed by a magnetic separation process. Raw materials, reduction behavior, separation treatment, and products' characteristics were systematically researched. The experimental procedure can be described as follows: The mixture of ferruginous manganese ore (<5 mm) and reducing coal (<2 mm) with various proportions were prepared for carbothermic reduction. Roasting of the mixtures was carried out in a muffle furnace. Reduced samples were then cooled to room temperature in a nitrogen atmosphere. The metallization ratio of the reduced samples was measured after each roasting experiment. The metallization ratio (M_R) was evaluated with Equation (1):

$$M_{\rm R} = M_{\rm Fe} / T_{\rm Fe} \times 100\% \tag{1}$$

where M_{Fe} was the weight of metallic iron and T_{Fe} was the weight of total iron in the reduced samples. The commonly used FeCl₃-K₂Cr₂O₇ and TiCl₃-K₂Cr₂O₇ volumetric methods were applied to M_{Fe} and T_{Fe} measurement, respectively [26].

Milling (with a fineness of 90% passing 0.074 mm), followed by magnetic separation of the reduced samples, was carried out subsequently for the beneficiation of manganese and iron. The magnetic separation was treated by a high-gradient magnetic separator (SLon-1000, SLon Magnetic Separator Ltd., Ganzhou, China) at intensity range of 80–230 A/m. Grade and recovery of beneficiation products were calculated by Equations (2) and (3), respectively:

$$Grade = m_1/m_0 \times 100\%$$
⁽²⁾

$$Recovery = m_1/m_2 \times 100\%$$
(3)

where m_1 was the weight of iron or manganese in beneficiation product and m_0 was the weight of beneficiation product. The m_2 was the weight of iron or manganese in reduced sample.

Phase transformation of the reduced samples was analyzed by X-ray diffraction (D/Max 2500, RIGAKU, Tokyo, Japan) and chemical phase dissolution measurement. The elements occurrence state and morphology evolution were investigated by optical microscopy (DMRXP, Leica Microsystems Inc, Lake County, IL, USA) and scanning electron microscope (Quanta-200, FEI, Hillsboro, OR, USA) equipped with EDX.

3. Results and Discussion

3.1. Chemical Composition and Characterization of Feed Materials

A ferruginous manganese ore from Hunan Province, China was investigated in this work. The elemental composition of this ferruginous manganese ore was shown in Table 1. It was characterized by high manganese grade (35.26 wt %) and high iron content (21.28 wt %).

Table 1. Chemical composition of ferruginous manganese ore.

Composition	Mn _{total}	Fe _{total}	FeO	SiO ₂	CaO	Al ₂ O ₃	MgO	LOI *
wt %	35.26	21.28	0.13	4.79	1.93	0.83	0.33	4.70
* LOI: loss on ignition.								

The XRD pattern of the ferruginous manganese ore was shown in Figure 1. It can be identified that manganese mainly existed in the form of oxide, as $(Mn, Fe)_2O_3$ (bixbyite). In addition to bixbyite, hematite was investigated as another prominent phase in this ferruginous manganese ore.



Figure 1. X-ray diffraction pattern of ferruginous manganese ore.

The SEM-EDS and elemental map analysis were carried out as given in Figure 2 for the further understanding of this ore. Two phases could be roughly distinguished from Figure 2a. Firstly, the dark gray platy zone with high manganese, but low iron (spots 2 and 4), constituted the main phase of this ore. In addition, the light white granules with relatively high iron but low manganese (spots 1 and 3, about 5 μ m) embedded dispersedly in the substrate of the gray phase. Elemental map patterns (Figure 2b,c) also approximately showed a complementary distribution state for manganese and iron minerals, while oxygen distributed uniformly in each mineral phase of the ore. All of these characteristics brought great difficulty to the beneficiation for this ferruginous manganese ore resource.

A more accurate measure for manganese and iron phase distribution in this ore was carried out via chemical phase dissolution. The Fe/Mn content and its distribution ratio in iron mineral phase/manganese mineral phase were examined, respectively, as presented in Table 2. As can be seen, hematite accounts for 89.76% of the total iron mineral list, followed by ferrosilite and magnetite. Meanwhile, manganese associated with iron minerals account for 49.53% of the total being the main existing form for manganese minerals. In addition to that, manganese oxide (48.78%) and carbonate almost constituted the rest.



Spot	0	Mn	Fe	Mg	Al	Si	K	Ca
1	26.73	20.01	51.38	0.19	0.26	0.53	0.47	0.42
2	27.14	56.05	13.81	0.33	0.25	1.09	0.33	1.00
3	26.42	17.97	54.02	0.21	0.22	0.49	0.34	0.33
4	30.71	52.21	13.06	0.37	0.45	1.06	1.29	0.85

Figure 2. SEM-EDS (a) and elemental map patterns ((b)-Fe; (c)-Mn; (d)-O) of ferruginous manganese ore.

Table 2. (nemical phase analysis of the ferruginous manganese ore (wt	%).
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Mineral	Iron Mineral Phase						
Species	Hematite *	Ferrosilite	Magnetite	Pyrites	Total		
Content of Fe Distribution	19.1 89.8	1.9 9.0	0.2 1.1	0.1 0.1	21.3 100.0		
Minoral	Manganese Mineral Phase						
Species	Mn in Iron Minerals	Manganese Oxide	Manganese Carbonate	Manganese Silicate	Total		
Content of Mn Distribution	19.3 49.5	19.1 48.8	0.6 1.6	0.1 0.1	39.1 100.0		

* Hematite: total of substantive and symbiotic (with manganese mineral) hematite phase.

Typical anthracite, bituminous coal, and lignite were used as reducing coal in this work and their compositions are given in Table 3.

Reducing Coal	Fixed Carbon	Ash	Volatilization	Moisture
Anthracite	77.46	7.58	11.54	3.41
Bituminous coal	52.12	31.41	4.49	11.98
Lignite	36.63	30.11	22.27	10.99

Table 3. Proximate analysis of the reducing coal (wt %).

3.2. Factors Affecting Metallization

3.2.1. Effect of Temperature

Chemical reactions that may take place during the carbothermic reduction process in the experimental temperature range (600–1200 $^{\circ}$ C) are listed in Table 4. An Ellingham diagram for these key reactions is shown in Figure 3.

Table 4. Key chemical reactions may take place during the carbothermic reduction process.

Equation	Chemical Reaction	Delta G/J∙mol ⁻¹
(1)	$3Fe_2O_3 + C = 2Fe_3O_4 + CO$	120,000 — 218.46 T
(2)	$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$	-52,131 - 41.0 T
(3)	$Fe_3O_4 + C = 3FeO + CO$	207,510 — 217.62 T
(4)	$Fe_3O_4 + CO = 3FeO + CO_2$	35,380 — 40.16 T
(5)	FeO + C = Fe + CO	158,970 — 160.25 Т
(6)	$FeO + CO = Fe + CO_2$	-13,175 + 17.24 T
(7)	$C + CO_2 = 2CO$	166,550 — 171 Т
(8)	$Mn_2O_3 + C = 2MnO + CO$	68,239 — 192.67 T
(9)	$Mn_2O_3 + CO = 2MnO + CO_2$	—100,824 — 18.93 Т
(10)	MnO + C = Mn + CO	249,717 — 191.27 T
(11)	$3Fe + C = Fe_3C$	15,083 — 13.6 T



Figure 3. Ellingham diagram of chemical reactions listed in Table 4.

As is known from Figure 3, iron oxides can be reduced to metallic iron above 800 °C. Iron carbide also forms at temperatures higher than 800 °C. The Mn_2O_3 transforms to MnO spontaneously at this experimental condition. However, elemental manganese forms until the temperature reaches higher than 1400 °C. Therefore, except for reaction 10, the others listed in Table 4 are actually taking place in the carbothermic reduction process.

The metallization ratio of reduced samples obtained at different temperatures is given in Figure 4. It can be seen from the line chart that, as ferruginous manganese ore is roasted at 600 °C, almost no reduction occurred. Then, the reduction improves greatly with the temperature rising up to 1000 °C. The improvement showed a prominent increase in the metallization ratio of reduced samples. This value reached 75.7% at 1000 °C and increased by 75%, as compared to 600 °C. A further temperature rise only led to a slight increase of the metallization ratio. It finally attained 90.4% at 1200 °C and topped within experimental range in this paper.



Figure 4. Effect of roasting temperature on the metallization ratio of the reduced sample.

Samples reduced at different temperatures for 100 min were characterized by X-ray diffraction, as presented in Figure 5, to understand the phase transformation law with temperature. The XRD pattern showed the major phase Fe₂O₃ and Mn₂O₃ coexisted with minor (Mn, Fe)₂O₃ and MnO in sample reduced at 600 °C indicating that the decomposition of (Mn, Fe)₂O₃ (main phase in raw ore) occurred at this temperature. Meanwhile, a very small amount of MnO was also identified due to the reduction of Mn₂O₃. Temperature rise improved this reduction as an obvious increase of MnO was identified in samples reduced between 800 °C and 1200 °C. The diffraction peak corresponding to iron phase was observed in sample obtained between 1000 °C and 1100 °C. It can be inferred that the reduction of iron oxide to metallic iron occurred at this temperature range. A further temperature rise to 1200 °C led to the formation of carbide (Fe_{2.7}Mn_{0.3}C), which inevitably hindered the separation for Fe and Mn elements. Thus, the phase transformation of ferruginous manganese ore reduction with temperature could be summarized as follows: Fe-Mn symbiotic phase decomposition \rightarrow carbide (Fe_{2.7}Mn_{0.3}C) formation.



Figure 5. X-ray diffraction pattern of reduced sample obtained at different temperatures: 1: Fe₂O₃; 2: (Mn, Fe)₂O₃; 3: Mn₂O₃; 4: MnO; 5: Fe; and 6: Fe_{2.7}Mn_{0.3}C.

The microstructure (cross-section) of raw ore and samples reduced at 600 °C to 1200 °C (for 100 min) were characterized, as shown in Figure 6, to reveal the intrinsic morphology evolution. A compact platy structure could be widely observed in unroasted ore, as presented in Figure 6a. It was mainly composed of iron or manganese-rich minerals identified by EDX. Then, the fragmentary structure generated as a sample was reduced at $600 \,^{\circ}$ C (shown in Figure 6b). Decomposition of the (Fe, Mn)₂O₃ phase (as discussed in Figure 5) at this temperature may be the inducement. At 800 °C the fragmentation became more and more apparent. It was accompanied by the reduction of high-valence manganese oxides to the MnO phase according to EDX (spot 3), which also coincided well with the XRD analysis. From Figure 6d fine iron particles began to form, but still dispersed in the substrate of the MnO phase as the sample was reduced at 1000 °C. Then, much more iron formed and aggregated as the temperature further rose to 1100 °C and 1200 °C. The iron phase gradually separated from the manganese-rich phase and eventually formed a distinct boundary between metallic iron, MnO, and the manganese-rich slag phase, as shown in Figure 6e,f. Especially for samples roasted at 1200 °C, there was evidence of a liquid phase formation, which would have enhanced the aggregation of the metallic iron-based phase (Figure 6f). From the XRD analysis result presented in Figure 5, low eutectic carbide generated at 1200 °C may be the main inducement for liquid phase formation and the distinct boundary development, consequently. Thus, the morphology evolution of ferruginous manganese ore reduction with temperature could be probably summarized as follows: plate-like structure fragment \rightarrow granular MnO phase formation \rightarrow fine metallic iron formation \rightarrow aggregation of metallic iron \rightarrow boundary development between phases.



Spot	0	Mn	Fe	Mg	Al	Si	Ca
1	26.73	20.01	51.38	0.19	0.26	0.53	0.42
2	27.14	56.05	13.81	0.33	0.25	1.09	1.00
3	20.02	66.79	10.15	0.90	0.24	1.27	0.62
4	4.03	9.69	83.50	0.48	0.60	1.32	0.37
5	24.66	41.35	10.31	1.11	0.27	14.86	7.44

Figure 6. SEM images of reduced sample obtained at different temperatures: (**a**) raw ore; (**b**) 600 °C; (**c**) 800 °C; (**d**) 1000 °C; (**e**) 1100 °C; and (**f**) 1200 °C.

3.2.2. Effect of Roasting Time

The metallization ratio of samples reduced (1100 $^{\circ}$ C) for different times is presented in Figure 7. It can be seen from the line chart that the metallization ratio showed an obvious increase with prolonged time. As ferruginous manganese ore was roasted for 10 min only 2.5% of metallization ratio could

be obtained. However, this value sharply rose to 72.1% as the roasting time lengthened to 50 min. After this, the upward trend gradually slowed down and the metallization ratio stabilized at 80.2% as the sample was reduced for 100 min. Thus, it can be inferred that the drastic reduction occurred within 50 min, but about 100 min was required for maximum reduction.



Figure 7. The effect of roasting time on the metallization ratio of the reduced sample.

Samples reduced for different times were characterized by X-ray diffraction, as presented in Figure 8, to understand the phase transformation law with roasting time.



Figure 8. X-ray diffraction pattern of samples reduced for different times: 1: Fe₂O₃; 2: (Mn, Fe)₂O₃; 3: Mn₂O₃; 4: MnO; and 5: Fe.

The XRD pattern shows that the major phase $(Mn, Fe)_2O_3$ in raw ore almost disappeared when reduced for 10 min. Instead, the new phases Mn_2O_3 and MnO were identified, which indicate that decomposition of $(Mn, Fe)_2O_3$ and fractional reduction of Mn_2O_3 had completed within 10 min. After 30 min of reduction, the characteristic diffraction peaks that represent Mn_2O_3 faded away, while peaks of MnO intensified correspondingly. The new iron phase began to form as well. It can be inferred that the transformation of manganese oxides with high valence to MnO had mainly accomplished within 30 min. Lengthening the time further brought about an obvious increase of metallic iron without any other phase extinction or regeneration. From the iron phase transformation aspect, it showed good agreement with the metallization ratio trend, as displayed in Figure 7. Thus, the phase transformation of ferruginous manganese ore reduction with time could be summarized as follows: Fe-Mn symbiotic phase decomposition \rightarrow reduction of manganese oxides with high valence to MnO \rightarrow reduction of iron oxides to metallic iron.

The microstructure (cross-section) of raw ore and samples reduced for 10 min to 150 min (at 1100 °C) were characterized, as shown in Figure 9, to reveal the intrinsic morphology evolution. It can be observed that the compact platy structure in raw ore had fragmented to be several bulky cakes when the sample was reduced for 10 min. Decomposition of Mn-Fe associated minerals may have caused this variation as compared with its phase transformation (as discussed in Figure 8). This fragmentation appeared to be more serious with time prolonged to 30 min and 50 min for its drastic reduction in the meantime. A fine iron phase began to form beside the cracks and pores at 30 min, as shown in Figure 9c, which coincided well with the XRD analysis. Then, more iron formed and aggregated as the time was further lengthened to 100 min, and even to 150 min. Iron oxides dispersed in the MnO phase were also fully reduced to iron and separated with the manganese phase gradually. Thus, the morphology evolution with time could be probably summarized as follows: plate-like structure fragment \rightarrow granular MnO phase formation \rightarrow fine metallic iron formation \rightarrow aggregation of metallic iron \rightarrow separation of iron and manganese phase.



Figure 9. SEM images of sample reduced for (a) raw ore; (b) 10 min; (c) 30 min; (d) 50 min; (e) 100 min; and (f) 150 min; 1: hematite; 2: Mn-Fe-associated mineral; 3: MnO; 4: MnO with iron oxide; and 5: iron.

3.2.3. Effect of the Reducing Agent

In this part, anthracite with relatively high fixed carbon was chosen to study the effect of reductant dosage as presented in Figure 10. As can be seen from the line chart, the metallization ratio gradually rose to be stable with reductant dosage. The metallization ratio of the reduced sample reached 45.2% with 15 wt % of anthracite addition. This was the stoichiometric amount that was required for a complete reaction (Fe₂O₃ \rightarrow Fe and Mn₂O₃ \rightarrow MnO) of this ferruginous manganese ore. An obvious upward trend as anthracite dosage increased to 25% was observed. Further anthracite dosage increased to 30% had little effect on the reduction degree. The metallization ratio of the reduced sample still remained at about 82% as 25% of anthracite was added. On one hand, the reductant increase could enhance the reduction potential in the reaction system and, therefore, promoted the metallization ratio. On the other hand, too much may turn into a barrier for full reduction because of its obstruction effect on the aggregation of newly-formed iron grains. Thus, anthracite dosage of 25% was appropriate for this reduction process.



Figure 10. The effect of the anthracite ratio on the metallization ratio of the reduced sample.

From the metallization ratio, phase evolution aspects of reduced samples discussed above, and also from a cost perspective, the optimal temperature of 1100 °C, a roasting time of 100 min, and anthracite addition of 25% were selected for the ferruginous manganese ore reduction process.

3.3. Beneficiation of Reduced Samples

3.3.1. Effect of the Reduction Temperature

The magnetic separation results of reduced samples obtained at different temperatures (ranging between 800 °C and 1200 °C) are shown in Figure 11. As can be seen from the line chart, the magnetic separation index of samples reduced at 800 °C was undesirable, as the recovery of Fe and Mn in magnetic substance were only 11.8% and 5.1%, respectively. The corresponding Fe and Mn grades were 59.6% and 17.8%, respectively. About 90% of iron and 95% of manganese distributed in the non-magnetic substance without effective separation.



Figure 11. The effect of reduction temperature on the beneficiation index of the magnetic product: 1: iron grade; 2: iron recovery; 3: manganese grade; and 4: manganese recovery.

With respect to Fe, its grade and recovery improved continuously as the temperature rose to 1100 °C. Compared with those at 800 °C, Fe recovery in the magnetic substance increased significantly by 80.8%, with only a slight grade drop to 56.6%. Meanwhile, the recovery and grade of Mn in the magnetic substance also showed a minor increase maybe due to the inevitable entrainment during

separation process. However, further temperature rise to 1200 °C caused a both decline of Fe grade and recovery to 52.9% and 83.6%, respectively. However, an increase of Mn grade and recovery for the magnetic substance occurred simultaneously. The Mn content rise in the metallic iron phase induced by ferromanganese compound formation at this temperature (as discussed in the Section 3.2.1) may lead to this undesirable change.

3.3.2. Effect of the Reduction Time

Figure 12 presents the magnetic separation indices of samples reduced at 1100 °C as a function of roasting time in the range of 30–150 min. Results showed that a prolonged reduction time was favorable for the Fe recovery in the magnetic substance. In consideration of the Fe grade, it approximately stabilized at the level of 56% as reducing time varied from 30 min to 100 min. Further prolonging the time led to an obvious Fe grade drop to about 47%. Meanwhile, the Mn recovery showed a rapid rise at 120 min with little variation of Mn grade in magnetic substance. This could be attributed to more manganese minerals being entrained into the iron phase for the iron grains' aggregation enhancement with prolonged time (as shown in Figure 9).



Figure 12. The effect of reduction time on the beneficiation index of the magnetic product: 1: iron grade; 2: iron recovery; 3: manganese grade; and 4: manganese recovery.

3.3.3. Effect of Reducing Agent

Taking the fixed carbon content of 25% anthracite dosage (discussed in Section 3.2.3) as a reference (mol(C/Fe) = 4.2), 37.2% of bituminous coal and 52.9% of lignite with an equivalent ratio of fixed carbon to Fe₂O₃ were adopted for reduction roasting, respectively. The effect of reducing the agent species on the separation indices were compared in Figure 13. It can be seen from the column graph, anthracite roasting facilitated the beneficiation of iron in the magnetic product. The Fe grade and recovery reached 56.1% and 92.6%, respectively, which was superior to the cases of bituminous coal and lignite roasting. Meanwhile, the Mn grade and recovery was 62.4% and 76.5%, respectively, in the non-magnetic product obtained by anthracite roasting. Thus, the Fe and Mn elements in ferruginous manganese ore had been separated and enriched effectively. However, the lower Mn grades and recoveries obtained by bituminous coal or lignite roasting may be attributed to their high ash (>30%) introduction into reduced samples. Therefore, anthracite with high carbon and relative lower ash was optimal for this process.



Figure 13. The effect of the reducing agent on the Fe and Mn beneficiation index: (**a**) magnetic product; (**b**) non-magnetic product.

3.3.4. Effect of Milling

Milling was applied to liberate iron grains formed in reduced sample for the following separation of iron and manganese. The magnetic separation results of reduced sample with variable milling fineness (passing 0.074 mm ranged between 40 wt % and 95 wt %) are shown in Table 5. The reduction experimental conditions were fixed at temperature of 1100 °C, time of 60 min and anthracite dosage of 25%.

10.074	Magnet	ic Product	Non-Magnetic Product		
<0.074 mm	Fe Grade	Fe Recovery	Mn Grade	Mn Recovery	
40	43.2	84.1	60.8	54.4	
80	50.0	91.5	64.1	68.0	
90	56.1	92.6	62.4	78.5	
95	63.7	84.3	61.0	80.1	

Table 5. Effect of milling fineness on separation index (wt %).

As can be seen from Table 5, the Fe grade and recovery in the magnetic product rose to 56.1% and 92.6%, respectively, as milling fineness improved to 90% passing 0.074 mm. The Mn recovery in the non-magnetic product also showed a sharp increase simultaneously. Further milling of the sample could more fully liberate the iron grains with other minerals, which caused a higher Fe grade of 63.7% on one hand; however, it also brought about an over-grinding problem and, therefore, part of the iron grain loss during separation on the other. This part of iron grain transferred to the non-magnetic product and unfavorably led to a decline in Fe recovery (84.3%) and Mn grade (61.0%). The milling

fineness of 90% passing 0.074 mm was optimal in consideration of the separation objective (maximize Fe recovery, but minimize Mn recovery in the magnetic concentrate) and milling energy consumption.

3.3.5. Effect of the Magnetic Intensity

The separation results obtained at different magnetic intensities (ranging between 80 A/m and 230 A/m) were presented in Figure 14. As can be seen from the line chart, the magnetic intensity variation influenced the separation index slightly. Recoveries of Fe and Mn in the magnetic product remained almost at 90% and 30%, respectively. A relative peak of the Fe grade (62.3%) was observed at 140 A/m. Meanwhile, a Mn grade of 23.3% also showed a corresponding low point. Thus, the magnetic intensity of about 140 A/m was optimal for Fe, Mn beneficiation.



Figure 14. The effect of magnetic intensity on the beneficiation index of the magnetic product; 1: iron recovery; 2: iron grade; 3: manganese recovery; and 4: manganese grade.

3.4. Products Characterization

3.4.1. Reduced Product

The reduction product obtained at 1100 °C and roasted for 100 min with 25% of anthracite addition was examined with SEM-EDS and map analysis, as shown in Figure 15.



Figure 15. SEM-EDS (a) and elemental map patterns ((b)-Fe; (c)-Mn; and (d)-O) of the reduction product.

Two phases with distinctive features can be distinguished from Figure 15a. Firstly, the light white granules (about 20 μ m, spot 1) were observed embedded in the gray substrate. It could be identified as a metallic iron phase mingled with some MnO for its main composition of 83.71% Fe, 4.88% O, and 9.98% Mn. The other, dark gray substrate (spot 2) was identified to be MnO associated with the unreduced FeO phase. Elemental map patterns (Figure 15b,c) also show Fe and Mn beneficiated in the light white and dark gray phases, respectively. Moreover, these two phases presented complementary, but clear, boundaries. Most of the O (as displayed in Figure 15d) distributed in the gray substrate, which also proved the full reduction of iron minerals as compared with that of ferruginous manganese ore in Figure 2d. All of these characteristics created favorable mineralogy conditions for the consequent Fe/Mn separation process.

3.4.2. Beneficiation Products

The chemical compositions of beneficiation products obtained at the optimal experimental conditions (a temperature of 1100 °C, a roasting time of 100 min, anthracite addition of 25%, milling fineness of 90% passing 0.074 mm and magnetic intensity of about 140 A/m) was analyzed and given in Table 6. Finally, 88.2% of Fe and 29.6% of Mn in the raw ore were recovered into iron-rich product. This product with 62.3% and 23.3% of Fe and Mn grade, respectively, can be well used in a blast furnace (BF) for iron and manganese-rich slag manufacture [27]. Meanwhile, a manganese-rich product with a Mn grade of 63.7% (recovery of 70.4%), but Fe-lean (only 3.7%), is superior to most current high-grade Mn ores, and is a favorable material for alloy manufacturing by electric arc furnace (EAF) smelting.

Table 6. Chemical compositions of beneficiation products (wt %).

Compositions	Fe _{total}	Mn _{total}	SiO ₂	CaO	MgO	Al ₂ O ₃	Р
Iron-rich product	62.31	23.26	0.86	0.62	0.50	0.37	0.006
Manganese-rich product	3.74	63.65	8.23	4.16	1.03	0.25	0.015

4. Conclusions

In the present paper, beneficiation of Fe/Mn from a ferruginous manganese ore via carbothermic reduction followed by magnetic separation process was investigated in details. Optical microscope, SEM, and XRD analysis were carried out to understand the phase transformation mechanisms. Following conclusions can be drawn from this work:

- (1) The ferruginous manganese ore mainly exists in the forms of (Fe, Mn)₂O₃ and Fe₂O₃. Part of iron phase granules (<5 μm) embed dispersedly in the substrate of manganese-rich phase. The rest scatter as mixed isomorphisms in manganese minerals.</p>
- (2) The morphology evolution laws, along with reduction process of ferruginous manganese ore, can be described as plate-like Fe-Mn symbiotic phase decomposition → granular MnO phase formation → fine metallic iron formation → aggregation of metallic iron → boundary development between Fe and Mn phases.
- (3) Fe and Mn elements are beneficiated effectively at the optimal temperature of 1100 °C, with a roasting time of 100 min, anthracite addition of 25%, and milling fineness of 90% passing 0.074 mm, with a magnetic intensity of 140 A/m. Iron-rich concentrate with 62.3% grade and 88.2% recovery for Fe, and manganese-rich concentrate with 63.7% grade and 70.4% recovery for Mn are obtained, respectively. The beneficiation products can be further processed in blast furnace (BF) or electric arc furnace (EAF) smelting with no waste production.

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