Original Article

Systematic study on separation of Mn and Fe from ferruginous manganese ores by carbothermic reduction roasting process: Phase transformation and morphologies

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ABSTRACT

Carbothermic roasting reduction followed by magnetic separation process is reported as an effective technological process to separation and recovery of Fe and Mn from low-grade ferruginous manganese ores (Fe–Mn ores) as an acceptable feed to meet the demands of the developing manganese industry. In this study, the effects of operating variables on the recovery and grade of Fe and Mn are initially investigated during the carbothermic roasting reduction process followed by magnetic separation. Then, the phase transformation and morphologies of spinel (Fe₂Mn₁₋ₓ)Al₂O₄, fayalite Fe₃Mn₂₋ₓSiO₄ and (FeO)(MnO)ₓ are investigated by SEM-EDS, XRD, TG/DTG and thermodynamic analyses. Finally, the stepwise reduction and interfacial reaction of three types of phases are investigated at 700–1100 °C for 10–120 min to clarify the reason for the poor separation of Mn and Fe from Fe–Mn ores. The effect of MnO on the stepwise reduction behavior of Fe₂SiO₄ and FeAl₂O₄ is analyzed in detail. Finally, the tight integration of the MnO phase with a metallic Fe–Mn alloy derived from the stepwise reduction of (FeO)(MnO)ₓ are closely associated with the stepwise reduction of the FeₓMn₂₋ₓSiO₄, (FeₓMn₁₋ₓ)Al₂O₄ and (Fe,Mn)₂O₃ phases. In addition, the formation mechanism and the interfacial reaction reduction of (FeO)(MnO)₁₋ₓ, (FeₓMn₁₋ₓ)Al₂O₄ and FeₓMn₂₋ₓSiO₄ are systematically analyzed to show the effect of the MnO phase on the stepwise reduction of the Fe₂SiO₄ and FeAl₂O₄ phases. Finally, some suggestions were recommended for the carbothermic reduction followed by magnetic separation for utilizing the Fe–Mn ores effectively. The manganese-rich product an acceptable feed containing 53.60 wt.% total Mn with the Mn recovery of 89.38% and mass fraction of Mn/Fe of 5.43 are obtained.

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1. Introduction

Low-grade ferruginous manganese ores (Fe–Mn ores) have received increasing attention as substitutes for high-grade manganese ores, which are one kind of significant manganese resources that can satisfy the demands of the developing manganese industry [1–6]. Unfortunately, Fe–Mn ores with high iron content are unacceptable as feedstocks for smelting ferro-manganese alloys. Therefore, many studies have been carried out to upgrade the mass ratio of Mn/Fe (to over 5) in Fe–Mn ores for use as an acceptable feed in manganese alloy production [7–9]. Carbothermic reduction roasting followed by magnetic separation has been considered as an effective technology for the separation and recovery of Mn and Fe from Fe–Mn ores [7–12].

In the abovementioned technological process, which is satisfactory and acceptable for industrial application, carbothermic roasting reduction is the essential procedure for the recovery and separation of Mn and Fe from Fe–Mn ores [1,7,8,10]. However, Mn and Fe cannot be effectively separated from Fe–Mn ores, and approximately 20% of Mn content was presented in magnetic product by carbothermic roasting reduction process [7–10]. Gao et al. [11] found that during magnetic roasting reduction, the Mn grade in the rich-manganese product was as high as 27–34 wt.%; in this study, the efficiency of the upgrading process was characterized using comprehensive full factorial experiments. Gao et al. focused mainly on the optimization of the technological parameters by comprehensive full factorial experiments but did not clarify why the Mn and Fe were not separated well from Fe–Mn ores. Swamy et al. [13] presented that the mass ratio of Mn/Fe in rich-manganese products to 6.2, while the Mn recovery was only 50 wt.%. Thus, their technique cannot be used to effectively separate and recover Fe and Mn from Fe–Mn ores. Liu et al. [1] clarified the underlying reason for the inferior separation efficiency of Mn and Fe and recommended low temperature (below 800 °C) and prolonged reduction time for the magnetic reduction roasting of Fe–Mn ores. The Fe recovery reached 90.6 wt.%, but the Mn recovery only reached 65.3 wt.%. The formation of spinel manganese ferrite Mn$_x$Fe$_{3-x}$O$_4$ and the olivine phases of Fe$_2$Mn$_{2-x}$SiO$_4$ resulted in the poor separation of Fe and Mn from the Fe–Mn ores. In a direct reduction roasting-magnetic separation process, Huang et al. [14,15] the Fe and Mn was still not separated effectively, and the Mn recovery of non-magnetic product was only 78.46%. Few studies in the literature have investigated the underlying reason for the poor separation of Fe and Mn from Fe–Mn ores. This poor separation may be partially caused by the phase composition of the Mn, Fe, Al and Si constituents in the Fe–Mn ores and the isomorphic substitution of Fe and Mn elements in the mineral lattice structure during the natural mineralization of Fe–Mn oxides in Fe–Mn ores [15–25]. In this paper, the essential features of the carbothermic reduction roasting process for Fe–Mn ores are systematically characterized based on observations of phase transformation and intrinsic morphology evolution.

The objective of the present study is to perform a detailed analysis of the underlying reason for the poor Fe–Mn separation based on observations of phase transformation and morphology evolution. First, the effects of the operating variables on the separation and recovery of Mn and Fe from Fe–Mn ores are investigated. The resulting inference is that the poor separation of Fe and Mn may be related to the phase transformation and intrinsic morphology evolution of composite oxides containing Mn, Fe, Al and Si elements during carbothermic reduction. To further investigate this hypothesis, the phase transformations of spinel (Fe$_x$Mn$_{1-y}$)Al$_2$O$_4$, fayalite Fe$_2$Mn$_{2-y}$SiO$_4$ and (FeO)$_y$(MnO)$_{1-x}$ are examined by SEM-EDS, XRD and thermodynamic analyses. Finally, the stepwise reduction behavior and the interfacial reaction of three types of phases are investigated at 700–1100 °C for 10–120 min to understand the poor separation of Mn and Fe. Recommendations are given for the carbothermic roasting reduction conditions for Fe–Mn ores to obtain credible and reliable experimental results.

2. Experimental

2.1. Raw materials

The Fe–Mn ore samples used in this study were obtained in South Africa. The Fe–Mn ore was a typical high-alumina and low-silicon ferruginous manganese ore that contained 29.50 wt.% TMn (total manganese), 28.28 wt.% TFe (total iron), 3.72 wt.% SiO$_2$ and 7.82 wt.% Al$_2$O$_3$. The manganese mainly comprised manganese MnO(OH) and bixbyite [(Fe,Mn)$_2$O$_3$], and the iron compounds mainly exist in the form of hematite (Fe$_2$O$_3$) and bixbyite [(Fe,Mn)$_2$O$_3$]. The Si, Al and Mg in the Fe–Mn ore, which have an undesirable effect on manganese recovery, were detected in the form of hemicarbonate (Al$_{15.41}$Mg$_{1}$Fe$_{7.18}$O$_{32.00}$) and (Fe,Mn)$_2$SiO$_4$. The reduction coal was obtained from Tianjin province in China. The bituminous coal contained 52.98 wt.% fixed carbon, 40.70 wt.% volatiles, 5.30 wt.% ash and 1.02 wt.% moisture.

2.2. Carbothermic roasting reduction process

The schematic diagram of the industrial recovery and separation of Mn and Fe from Fe–Mn ores by carbothermic reduction roasting process followed by magnetic separation is displayed in Fig. 1(a). In this work, The Fe–Mn ores as a raw material were first crushed to a prescribed range of grain sizes and then subjected to a reduction reaction for Mn and Fe oxide in a rotary kiln; the simulated experiment for the carbothermic reduction was conducted in a vertical resistance furnace that is shown in Fig. 1(b). The raw materials were dried at 105 °C for 3 h in a draft-drying cabinet. The Fe–Mn ores and bituminous coal that were used in this study were crushed by a jaw crusher (PE60 × 100 type) to sizes ranging from 8 to 13 mm and below 3 mm, respectively. Approximately 500 g of raw ores and reduction coal were adequately mixed in a prescribed proportion of FC/O. Noted that, the FC/O is the molar ratio of the fixed carbon in coal to the reducible oxygen of iron and manganese in the Fe–Mn ores. Then, the mixtures were charged into a corundum crucible and placed into the vertical resistance furnace. The mixtures were reduced at a setting temperature for a fixed period of time. Before the carbothermic reduction roasting process, the furnace was preheated to the setting temperature...
at a speed of 10 °C/min. After the reduction roasting process, the reduced samples were cooled to room temperature in an Ar atmosphere. Other detailed descriptions of the carbothermic reduction process were reported in our previous reports [26–28].

2.3. Magnetic separation process

The reduced Fe–Mn ores obtained from carbothermic roasting were ground in a 2-MZ centrifugal grinding machine. Next, approximately 20 g of the reduction product powder was separated in a DTCXG-ZN50 Davies magnetic tube at a prescribed magnetic field intensity to facilitate the separation and recovery of Mn and Fe from the Fe–Mn ores. Subsequently, the resulting magnetic product containing an iron-rich phase and a nonmagnetic product containing a MnO-rich phase were filtered and dried in a vacuum drying oven at 100 °C for 4 h at a negative pressure of 0.06 MPa. The Mn and Fe-grades of the separation products were measured by chemical titration. The chemical analyses were conducted at the Metallurgy Research Institute of Northeastern University, Shenyang, China. Further detailed descriptions of the carbothermic roasting reduction technological process were illustrated in our previous reports [27,28].

2.4. Characterization methods

2.4.1. Instrumental analyses

After the carbothermic roasting reduction process, the main phase identification of the treated Fe–Mn ores was identified using XRD (Almelo, the Netherlands), which was operated under the conditions of copper Kα radiation: Cu Kα, tube current and voltage: 40 mA, 40 kV, scanning range: 5–90° and scanning speed of 0.2°/s.

For the morphology analysis, manganese-rich or iron-rich particles were observed by scanning electron microscopy (SEM, Jena, Germany) with energy dispersive X-ray spectroscopy (EDS). The diffusion coupling method was conducted in conjunction with SEM-EDS to determine the intrinsic morphology evolution during carbothermic roasting reduction.

Thermogravimetric experiments were performed using a Netzsch STA 409 C/CD in an Ar atmosphere (99.99%, volume fraction). The Fe–Mn ores were ground to particle sizes that could pass through a 200 mesh. A sample that weighed approximately 10 mg was heated from room temperature to 1200 °C at a heating rate of 10 °C/min by passing a steady Ar flow (40 mL/min) through the reactor tube.

The particle size distribution (PSD) of the reduced Fe–Mn ore was measured using a laser particle size analyzer (Master size 2000) and corrected with calibration curves to produce the PSD data that are presented in this paper. The equivalent particle sizes (EPS: D10, D20, D40, D60, and D80) and the specific surface areas (SSA) of the reduced Fe–Mn ore were calculated using the software of the laser particle size analyzer.

2.4.2. Separation indexes

The following experimental assessment indicators were chosen: the Mn (rMn) and Fe (rFe) recoveries, the mass ratio of Mn to Fe in the nonmagnetic product (Mn/Fe), the total content of Mn (TMn) and Fe (TFe) in the nonmagnetic product,
and the metallization ratio (MR) of the reduced product [5].
The efficiency of the carbothermic reduction and the magnetic
separation of the Fe–Mn ore were evaluated using the
following equation:

\[ R_{\text{Mn}} = \frac{m_{\text{Mn}} \times \gamma_{\text{Mn}}}{M_{\text{Mn}} \times \gamma_{\text{Mn}}} \times 100 \]  

(1)

where \( R_{\text{Mn}} \) is the recovery of Mn, \%; \( m_{\text{Mn}} \) is the mass of the
nonmagnetic product, \( g \); \( M_{\text{Mn}} \) is the mass of the reduced prod-
tuct, \( g \); \( \gamma_{\text{Mn}} \) is the Mn grade in the nonmagnetic product, wt.\%;
and \( \gamma_{\text{Mn}} \) is the Mn grade in the reduced product, wt.\%. A simi-
lar expression was used to describe how the recovery yield of
iron varied with the composition of the magnetic product.

3. Results and discussion

3.1. Results of the carbothermic reduction
process-magnetic separation of Fe–Mn ores

3.1.1. Effect of carbothermic reduction condition on
separation indexes of Mn and Fe

The effects of the temperature (a, b), the duration time (c, d)
and FC/O (e, f) on the grade and recovery of Mn and Fe from
the Fe–Mn ores are investigated in Fig. 2. As shown in Fig. 2(a),
with the increase of temperature from 1000 to 1100 °C, the Fe
recovery continuously increased from 74.84 to 86.27%, while
the Mn grade increased from 49.02 to 53.30% and then tardily
decreased to 52.15%. This demonstrates that the higher tem-
perature is not favorable to the separation of Mn and Fe. In
Fig. 2(c, d), it can be seen that when the duration time reached
6 h, the Mn and Fe recovery increased from 68.28 to 73.72%;
however, the separation indexes of Mn and Fe decreased when
the duration time exceeded 6 h. That is, increasing the dura-
tion time did not improve the separation and recovery of Mn
and Fe from the Fe–Mn ores. From Fig. 2(e, f), it can be seen that
the FC/O had little influence on the Fe recovery, and the Mn
recovery increased from 70.76 to 78.83% as the FC/O increased
from 1.5 to 3.5. In Fig. 2(g, h), it can be seen that the Fe recovery
decreased from 86.81 to 77.64%, while the Mn recovery increased
from 70.54 to 83.30%, and the particle size of the Fe–Mn ores
increased to 13 mm. It is well known that both the stepwise reduction
reaction of Fe₂O₃ to metallic Fe and the stepwise reduction of
MnO₂ to MnO increase with the duration
time and the temperature [1]. However, the change in
the Mn recovery was different from that of the Fe recovery, and
the variation in the recovery and grade of Mn and Fe are not accor-
dant with the theoretical prediction. Thus, it was deduced that
the phase transformation of Mn may have been related to the
Fe oxide, that is, a complex phase may have formed that pre-
vented the separation and recovery of Mn and Fe from the
Fe–Mn ores during carbothermic roasting reduction.

3.1.2. Effect of grinding time and magnetic intensity on
separation indexes of Mn and Fe

Fig. 3 displays the effects of the grinding fineness and mag-
netic intensity field on Fe–Mn separation efficiency. As the
magnetic intensity increased, the Fe recovery increased from
81.32 to 93.60%, while the Mn recovery decreased from 85.20
to 71.05%, and both the Mn/Fe and Mn grades concurrently
increased. It is obviously found that the recoveries of Mn and
Fe were clearly inversely related. It is concluded that the Mn
oxide may have compounded with Fe oxide or metallic iron to
form a new composite oxide during the carbothermic roasting
reduction process. As shown in Fig. 3(c) and (d), as the grinding
time increased from 1 to 4 min, the Fe recovery decreased from
84.87 to 71.56%, while the Mn recovery increased from 71.24
to 82.16%, and the Mn grade increased from 46.14 to 53.21%.
Thus, prolonging the grinding time improved the separation
of Fe and Mn. Fig. 3(e) shows the effect of the grinding time on
the particle size distribution of the ground samples, as measured
by the particle size analyzer. In Fig. 3(f), the equivalent particle
sizes (EPS; D10, D20, D40, D60, and D80) and the specific surface
areas (SSA) of the reduced Fe–Mn ores are shown for different
grinding times. In this study, the EPS is defined as the particle
size distribution when the cumulative passing of the particles
reaches a prescribed value [29–33]. The EPS decreased while
the SSA increased as the grinding time increased, indicating
that the overall fineness of the Fe–Mn ore powder increased
with the grinding time. The EPS of the Fe–Mn ore powder and
the SSA increased with the grinding time, indicating that fine
particles could upgrade the separation and grade of Mn and
Fe from the Fe–Mn ores.

3.2. Discussion on the carbothermic reduction
behavior of Fe–Mn ores

3.2.1. Phase transformation of Fe–Mn ores during
carbothermic reduction

Fig. 4 displays the XRD patterns of Fe–Mn ore reduced at
1100°C for the duration time of 5–120 min. As illustrated in
Fig. 4(a), the intensity of the diffraction peaks of the Fe-C phase
were detected for 10 min, and the Fe diffraction peaks gradu-
ally decreased with the duration time from 5 to 120 min. It
is observed that the diffraction peaks of the Fe-C group were
observed in the diffraction peaks of the standard substance
of the Fe-C group in Fig. 6(a). Fig. 4(b) displays the diffraction
peaks of (FeO)ₓ(MnO)₁₋ₓ (1 ≥ x ≥ 0) in the Fe–Mn ores. In
particular, it was found that a switching phenomenon for the
characteristic diffraction peaks (2 0 0) of (FeO)ₓ(MnO)₁₋ₓ from
41.802 (FeO, PDF#46-1314) to 40.663 (MnO, PDF#01-0437) was
observed as the x-values increased from 1 to 0 as the dura-
tion time increased from 5 to 120 min. The x-value decreased
as the duration time increased because of the stepwise reduc-
tion of (FeO)ₓ(MnO)₁₋ₓ to Fe and MnO. The intensity of the
diffraction peaks of (FeO)ₓ(MnO)₁₋ₓ remained the same as the
duration time increased. In addition, the diffraction peaks of
the standard substance of the (FeO)ₓ(MnO)₁₋ₓ group are also
shown in Fig. 6(d). Theoretically, the diffraction intensity
peaks of (FeO)ₓ(MnO)₁₋ₓ in the reduced Fe–Mn ores inevitably
descend as the increase of duration time. On the contrary,
the changing rules of x-value in (FeO)ₓ(MnO)₁₋ₓ were not con-
sistent with the theoretical prediction. It was inferred that
the (FeO)ₓ(MnO)₁₋ₓ phase was continually generated via the
phase transformation of an unknown phase or a composites
oxide of Fe oxide and Mn oxide during the carbothermic
reduction process. Fig. 4(c) displays the XRD patterns of
FeₓMn₁₋ₓSiO₄ and the FeₓMn₁₋ₓAl₂O₃ group in the Fe–Mn
ores. As observed, the diffraction intensity peaks of Mn₂SiO₄
and FeMnSiO₄ gradually increased with the reduction time.
Fig. 2 – Effect of (a, b) carbothermic reduction temperature; (c, d) time; and (e, f) FC/O and particle size of Fe–Mn ores on Mn and Fe separation indexes from Fe–Mn ores.
The ionic Fe$^{2+}$ species in fayalite Fe$_2$SiO$_4$ was replaced by ionic Mn$^{2+}$ to form Fe$_y$Mn$_{2-y}$SiO$_4$, which promoted the step-wise reduction of fayalite Fe$_y$Mn$_{1-y}$Al$_2$O$_4$ in the Fe–Mn ores because of the similar ionic radii of Mn$^{2+}$ (0.067 nm) and Fe$^{2+}$ (0.061 nm) [1,34–37]. The diffraction peaks of the standard substance Fe$_y$Mn$_{2-y}$SiO$_4$ are illustrated in Fig. 6(b). Besides, the diffraction intensity peaks of Fe$_y$Mn$_{1-y}$Al$_2$O$_4$ group were little changed with the rising of duration time, indicating that spinel FeAl$_2$O$_4$ was gradually transformed into spinel MnAl$_2$O$_4$. However, it was difficult to determine the $y$-value of the Fe$_y$Mn$_{1-y}$Al$_2$O$_4$ group because there was little change in the two-theta degrees of the characteristic diffraction peaks (3 1 1) of Fe$_y$Mn$_{1-y}$Al$_2$O$_4$. The diffraction peaks of the standard substance of the Fe$_y$Mn$_{1-y}$Al$_2$O$_4$ group are shown in Fig. 6(c). The formation of the Fe$_y$Mn$_{1-y}$Al$_2$O$_4$ phase is a novel means of reducing the spinel FeAl$_2$O$_4$ phase via the phase transformation of FeAl$_2$O$_4$/ Fe$_y$Mn$_{1-y}$Al$_2$O$_4$/ MnAl$_2$O$_4$.

3.2.2. Morphological characteristics of Fe–Mn ores during carbothermic reduction process

It is of great importance to study the microstructure of the samples that were reduced at different reduction time, as described in Fig. 7, to reveal the intrinsic morphology evolution and reduction mechanisms during the carbothermic reduction process. The results displayed an irregular surface structure for the primary particles of the Fe–Mn ores and finer reagent grade iron particles in the matrix of the reacted mate-

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**Fig. 3** Effect of (a, b) magnetic intensity and (c, d) grinding time on separation indexes of Mn and Fe, and effect of grinding time on (e) particle size distribution and (f) equivalent particle size and specific surface area.
rial. Then, as the irregular fragmentation became increasingly apparent, and the initial shape of an iron whisker began to take shape. As the reduction time was increased further, iron particles with different growth orientations of whiskers became interconnected with each other, possibly because of the hooking effects of the iron whiskers. The iron whiskers from Fe$_2$O$_3$ inside the Fe–Mn ores particles facilitated the diffusion of iron atoms, thereby enabling the iron particles to stick together during the fluidization process and promoting the aggregation and growth of iron particles. In addition, when the reduction time exceeded 30 min, the majority of the MnO phase was present on the surfaces of the metallic Fe–Mn particles, and the formation of larger metallic Fe–Mn particles were embedded on the surfaces of the silicates and aluminates. The size of the metallic Fe–Mn particles gradually grew with increasing of duration time.

3.2.3. Carbothermic reduction behavior of Fe–Mn ore during carbothermic reduction process

Based on phase transformation from XRD analysis and SEM of reduced Fe–Mn ores, the thermodynamic and thermogravimetric analysis of Fe–Mn ore during carbothermic reduction process are displayed in Fig. 8. The stepwise reduction reaction equations of the Fe–Mn ores are listed in Table 1. Note that MnO$_2$ was easily reduced to Mn$_2$O$_3$, Mn$_3$O$_4$ and MnO, but could not be further reduced to Mn at low temperatures, whereas Fe$_2$O$_3$ was readily reduced to Fe$_3$O$_4$, FeO and Fe. The stepwise reduction reactions of Fe$_3$SiO$_4$ and FeAl$_2$O$_4$ were considered in the XRD and SEM/EDS analysis. The Fe$_y$Mn$_{2−y}$SiO$_4$ and Fe$_y$Mn$_{1−y}$Al$_2$O$_4$ phases are inevitably generated during the carbothermic reduction of Fe–Mn ores. Therefore, the metallic Fe phases formed from both the direct reduction of Fe$_3$SiO$_4$, FeAl$_2$O$_4$ and Fe$_2$O$_3$ and the stepwise reduction of Fe$_y$Mn$_{2−y}$SiO$_4$, Fe$_y$Mn$_{1−y}$Al$_2$O$_4$ and (FeO)$_y$(MnO)$_{1−y}$. Whereas, there was a clear discrepancy between the CO content and the temperature required for the reduction reaction of FeAl$_2$O$_4$ and Fe$_y$Mn$_{1−y}$Al$_2$O$_4$ or Fe$_3$SiO$_4$ and Fe$_y$Mn$_{2−y}$SiO$_4$. The thermodynamic equilibrium of iron oxide reduction by CO (Fig. 8(a)) and C (Fig. 8(b)) are calculated by FACTSAGE 7.0 Software. The Fe$^{2+}$ in FeAl$_2$O$_4$ and Fe$_2$SiO$_4$ was directly reduced to metallic iron at 841.5 ºC and 815.6 ºC under the CO atmosphere respectively. When MnO was involved in the reduction of FeAl$_2$O$_4$ and Fe$_2$SiO$_4$, the reduction temperature of the FeAl$_2$O$_4$ and Fe$_2$SiO$_4$ was 658.6 ºC and 667.9 ºC under the CO atmosphere respectively. It was demonstrated that the participation of MnO can significantly lower the reduc-

![Fig. 4 – XRD patterns of Fe–Mn ores reduced at 1100 ºC for different reduction time.](image-url)
3.3. Discussion on the interfacial reaction behavior of Fe\textsubscript{y}Mn\textsubscript{2−y}SiO\textsubscript{4} system

Fig. 9 shows the SEM/EDS analysis for the interfacial reaction between Fe\textsubscript{y}Mn\textsubscript{2−y}SiO\textsubscript{4}, (FeO)\textsubscript{x}(MnO)\textsubscript{1−x}, wherein the Fe phase was reduced at 1100 °C for 30 min. As observed, the particles containing (FeO)\textsubscript{x}(MnO)\textsubscript{1−x} and the Fe–Mn alloy were observed to shrink after reduction. It's clearly observed that the metallic Fe–Mn particles were clearly closely wrapped by the fayalite (Fe\textsubscript{y}Mn\textsubscript{2−y}SiO\textsubscript{4}). Numerous small cracks and pits appeared around the elliptical metallic Fe–Mn particles. The SEM for the reduced Fe–Mn ores also provided evidence of the mass motion of liquid Fe–Mn particles through small pellets with lower (FeO)\textsubscript{x}(MnO)\textsubscript{1−x} content and of the motion of the Fe phase towards the larger pellets. Some gaps formed due to particle shrinkage during the reduction of (FeO)\textsubscript{x}(MnO)\textsubscript{1−x} to metallic Fe–Mn and MnO. Thus, it was very easy separate and recover Mn and Fe from the Fe–Mn ores by refining of particles followed by magnetic separation. Hence, the metallic particles with a lower (FeO)\textsubscript{x}(MnO)\textsubscript{1−x} content and the Fe–Mn alloy entered into the magnetic product after magnetic separation.

Fig. 10(a) displays the ternary phase diagram of MnO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3}–20 wt.% SiO\textsubscript{2} system under 60% CO–40% CO\textsubscript{2} by Factsage software during carbothemic reduction process. A stable region of olivine and Fe existed above 915°C. The olivine phase consisted of Fe\textsubscript{2}SiO\textsubscript{4}, Fe\textsubscript{y}Mn\textsubscript{2−y}SiO\textsubscript{4} and Fe\textsubscript{2}MnO\textsubscript{4}. Fig. 10(b) shows the crystal structure of the olivine Fe\textsubscript{2}SiO\textsubscript{4}, Fe\textsubscript{y}Mn\textsubscript{2−y}SiO\textsubscript{4} and Fe\textsubscript{2}MnO\textsubscript{4}. Both the Fe\textsubscript{2}SiO\textsubscript{4} and Fe\textsubscript{2}SiO\textsubscript{4} exhibited similar olivine-type structures. The ionic radii of the Mn\textsuperscript{2+} (0.067 nm) and Fe\textsuperscript{2+} (0.061 nm) are in the
same level [1,34–37]. Thus, Mn$^{2+}$ could easily replace Fe$^{2+}$ in the olivine-type structure, resulting in the formation of intermediate phase Fe$_y$Mn$_{2−y}$SiO$_4$. The XRD results (Figs. 4 and 5) show the phase transformation of Fe$_2$SiO$_4$ to Mn$_2$SiO$_4$ as the duration time or the temperature increased. Fig. 10(c) displays the schematic diagram for the interfacial reaction between Fe$_2$SiO$_4$ and MnO, wherein a diffusion coupling model is applied to illustrate the reaction mechanism between Fe$_2$SiO$_4$ and MnO. Under a reducing atmosphere, a multistep reduction reaction procedure occurred between Fe$_2$SiO$_4$ and MnO. (a) Mn$^{2+}$ ions migrated to the reaction interface of Fe$_2$SiO$_4$ to form an intermediate phase Fe$_y$Mn$_{2−y}$SiO$_4$; some of the Fe$^{2+}$ replaced Mn$^{2+}$ in the olivine-type structure and were directly reduced to metallic iron, whereas the remaining Fe$^{2+}$ combined with free MnO to form an intermediate phase (FeO)$_y$(MnO)$_{1−x}$ that was then further reduced to metallic iron. (b) The reduction reaction of Fe$_2$SiO$_4$ occurred at temperatures above 805 °C. Fig. 10(d) shows the SEM-EDS analysis for the Fe$_2$SiO$_4$ group in Fe–Mn ores that were reduced at 1100 °C for 30 min. The (FeO)$_y$(MnO)$_{1−x}$ and Fe$_y$Mn$_{2−y}$SiO$_4$ were located close to each other, showing that the formation of (FeO)$_y$(MnO)$_{1−x}$ was directly related to the phase transformation of Fe$_y$Mn$_{2−y}$SiO$_4$.

The results of the reaction mechanisms between Fe$_2$SiO$_4$ and MnO were used to calculate the following chemical formulas of the compounds using a valence state balance: Fe$_2$SiO$_4$ of [Fe$^{2+}$]$y$[Si$^{4+}$]$[O^{2−}]_4$, Fe$_y$Mn$_{2−y}$SiO$_4$ of [Fe$^{2+}$]$y$[Mn$^{2+}$]$y$[Si$^{4+}$]$[O^{2−}]_4$ and Mn$_2$SiO$_4$ of [Mn$^{2+}$]$y$[Si$^{4+}$]$[O^{2−}]_4$. In brief, the reduction reaction mechanism between Fe$_2$SiO$_4$ and MnO is summarized by the multistep reactions given in Eqs. (16) and (17). Both Mn$_2$SiO$_4$ and Fe were generated in the reduction product, and the reduction reaction under a reduction atmosphere can be expressed as follows:

\[
[Fe^{2+}]y[Si^{4+}][O^{2−}]_4 + (2 − y)[Mn^{2+}][O^{2−}] \\
= [Fe^{2+}]y[Mn^{2+}]_{2−y}[Si^{4+}][O^{2−}]_4 + (2 − y)[Fe^{2+}][O^{2−}] \\
\text{(16)}
\]

\[
[Fe^{2+}]y[Mn^{2+}]_{2−y}[Si^{4+}][O^{2−}]_4 + y[Mn^{2+}][O^{2−}] \\
= [Mn^{2+}]y[Si^{4+}][O^{2−}]_4 + y[Fe^{2+}][O^{2−}] \\
\text{(17)}
\]

\[
y[Fe^{2+}][O^{2−}] + (1 − y)[Mn^{2+}][O^{2−}] \\
= [Fe^{2+}][O^{2−}]_{1−y}[Mn^{2+}][O^{2−}]_y \\
\text{(18)}
\]

\[
[Fe^{2+}][O^{2−}]_2 + [C^{2+}][O^{2−}]_2 = [Fe] + [C^{2+}][O^{2−}]_2 \\
\text{(19)}
\]

3.4. Discussion on the interfacial reaction behavior of (Fe$_y$Mn$_{1−y}$)Al$_2$O$_4$ system

The corresponding optical microstructure images for the Fe–Mn ores reduced at 1100 °C for 30 min are shown in Fig. 11, showing an enormous quantity of metallic iron particles that appear as bright white. The gray matrix phase primarily consisted of fayalite (Fe$_2$Mn$_{2−y}$SiO$_4$) and spinel (Fe$_y$Mn$_{1−y}$)Al$_2$O$_4$. The metallic particles were a mixture of Fe–Mn, Mn–Fe–C and (FeO)$_y$(MnO)$_{1−x}$ phases and were elliptic in shape, as confirmed by the EDS and XRD analysis. A significant quantity.
Fig. 7 – SEM-EDS analysis of reduction products for different reduction times at 1000 °C: (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 50 min, and (f) 120 min.

of the liquid \((\text{Fe}_y\text{Mn}_{1−y})\text{Al}_2\text{O}_4\) phase appeared around the metallic Fe–Mn particles. The phenomenon of \((\text{FeO})_x(\text{MnO})_{1−x}\) phases wrapped by the metallic Fe–Mn phase was also observed. This phenomenon could be explained using the XRD analysis (Figs. 5 and 6). In addition, a transition phase of a \((\text{Fe}_y\text{Mn}_{1−y})\text{Al}_2\text{O}_4\) product was clearly observed. However, the metallic Fe–Mn particles were closely wrapped by the transition phase product. Additionally, a significant quantity of metallic Fe–Mn particles were also present as spinel \((\text{Fe}_y\text{Mn}_{1−y})\text{Al}_2\text{O}_4\) and the \((\text{FeO})_x(\text{MnO})_{1−x}\) phase, depending on the reduction conditions. The aforementioned results show that the stepwise reduction of \((\text{Fe}_y\text{Mn}_{1−y})\text{Al}_2\text{O}_4\) and \((\text{FeO})_x(\text{MnO})_{1−x}\) inevitably produced a metallic Fe–Mn phase in the reduction of the Fe–Mn ores. The metallic Fe–Mn particles that were wrapped by the \((\text{Fe}_y\text{Mn}_{1−y})\text{Al}_2\text{O}_4\) phase were not conducive to magnetic separation. Particles with composite structures are typically difficult to liberate during ball-milling. The \((\text{Fe}_y\text{Mn}_{1−y})\text{Al}_2\text{O}_4\) phase easily entered into the magnetic product after magnetic separation. This result is one explanation for the poor separation of Fe and Mn from the Fe–Mn ores from carbothermic roasting reduction process followed by magnetic separation.
Fig. 8 – (a) Gas-equilibrium diagram of Mn–Fe–C–O system; (b) $\Delta G^\circ - T$ of FeAl$_2$O$_4$ and Fe$_2$SiO$_4$; (c) TG/DTG of the Fe–Mn ores +5 wt% graphite from room temperature to 1100 ºC at a heating rate of 10 ºC/min in a pure Ar atmosphere.

Table 1 – Reaction equations for reduction of Mn–Fe ore based on the following equation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction equation</th>
<th>No.</th>
<th>Reaction equation</th>
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<tbody>
<tr>
<td>2</td>
<td>Fe$_2$O$_3$ + 4CO = 3Fe + 4CO$_2$</td>
<td>3</td>
<td>FeO + CO = Fe + CO$_2$</td>
</tr>
<tr>
<td>4</td>
<td>Fe$_3$O$_4$ + CO = 3FeO + CO$_2$</td>
<td>5</td>
<td>3Fe$_2$O$_3$ + CO = 2Fe$_2$O$_4$ + CO$_2$</td>
</tr>
<tr>
<td>6</td>
<td>C + CO$_2$ = 2CO</td>
<td>7</td>
<td>FeAl$_2$O$_4$ + CO = Fe + Al$_2$O$_3$ + CO$_2$</td>
</tr>
<tr>
<td>8</td>
<td>FeAl$_2$O$_4$ + MnO + CO = Fe + MnAl$_2$O$_4$ + CO$_2$</td>
<td>9</td>
<td>Fe$_2$SiO$_4$ + 2CO = 2Fe + SiO$_2$ + 2CO$_2$</td>
</tr>
<tr>
<td>10</td>
<td>Fe$_2$SiO$_4$ + 2MnO + 2CO = 2Fe + Mn$_2$SiO$_4$ + 2CO$_2$</td>
<td>11</td>
<td>MnO + C = Mn + CO</td>
</tr>
<tr>
<td>12</td>
<td>Fe$_2$SiO$_4$ + 2C = 2Fe + SiO$_2$ + 2CO</td>
<td>13</td>
<td>Fe$_2$SiO$_4$ + 2MnO + 2C = 2Fe + Mn$_2$SiO$_4$ + 2CO</td>
</tr>
<tr>
<td>14</td>
<td>FeAl$_2$O$_4$ + C = Fe + Al$_2$O$_3$ + CO</td>
<td>15</td>
<td>FeAl$_2$O$_4$ + MnO + C = Fe + MnAl$_2$O$_4$ + CO</td>
</tr>
</tbody>
</table>

**Fig. 12** displays the ternary phase diagram of the crystal structure and phase transformation of FeAl$_2$O$_4$ in a Fe$_2$O$_3$–MnO$_2$–20 wt.% Al$_2$O$_3$ system during carbothermic reduction. As shown in **Fig. 12(a)**, the main phases are a spinel-type phase, the monoxide, and an iron phase. The Al-spinel refers to FeAl$_2$O$_4$ and MnAl$_2$O$_4$. The generation of two types of phases are thermodynamically favored under roasting reduction conditions. **Fig. 12(b)** displays the crystal structure of the spinel FeAl$_2$O$_4$ and MnAl$_2$O$_4$. In the crystal structure of the normal spinel FeAl$_2$O$_4$, Fe$_{2+y}$Mn$_{1-y}$Al$_2$O$_4$ and MnAl$_2$O$_4$, the Al$_{3+}$ atoms form an octahedron, whereas Fe$_{2+}$ or Mn$_{2+}$ atoms form a tetrahedron. High temperatures increase the activity of the cations in the spinels of minerals. The distribution of Fe$_{2+}$ and Al$_{3+}$ atoms in the hercynite is disordered, such that these cations can occupy tetrahedral and octahedral sites [35–37]. In addition, both the FeAl$_2$O$_4$, Fe$_{2+y}$Mn$_{1-y}$Al$_2$O$_4$ and MnAl$_2$O$_4$ have spinel-type structures, and the ionic radii of the Mn$_{2+}$ (0.067 nm) and Fe$_{2+}$ (0.061 nm) are in the same level. These characteristics facilitated the entrance of Mn$_{2+}$ atoms into the crystal lattice and the displacement of Fe$_{2+}$ atoms in the hercynite structure. So it is comfortable to form easily the spinel-type MnAl$_2$O$_4$. **Fig. 12(c)** shows the three types of phase transformation from FeAl$_2$O$_4$ to Fe in the carbothermic reduction reaction. Scenario A is the formation of metallic Fe according to Eqs. (20) and (21). The FeAl$_2$O$_4$ species was converted to Fe$_{2+y}$Mn$_{1-y}$Al$_2$O$_4$ by manganese monoxide and further converted to MnAl$_2$O$_4$. The replaced iron atoms were reduced to metallic iron at approximately 658 ºC under a reducing atmosphere. The XRD results (Figs. 4(c) and 5(c)) demonstrated that the Mn$_{2+}$ easily replaced Fe$_{2+}$ in the spinel-type structure of FeAl$_2$O$_4$, resulting in the formation of Fe$_{2+y}$Mn$_{1-y}$Al$_2$O$_4$. In scenario B, the FeAl$_2$O$_4$ was directly reduced to metallic iron at 841 ºC in a CO atmosphere or at 831 ºC by carbon. In scenario C, Fe$_{2+}$ was replaced by Mn$_{2+}$ in the spinel-type structure and easily combined with free MnO to form the new phase of (FeO)$_x$MnO$_{1-x}$, which was then further reduced to metallic iron at 731 ºC in a CO atmosphere or at 724 ºC by carbon, where the stepwise reduction reactions of (FeO)$_x$MnO$_{1-x}$ are
5.5 Discussion on the interfacial reaction behavior of Fe\textsubscript{y}Mn\textsubscript{2−y}SiO\textsubscript{4} system

The SEM-EDS images and phase transformation of the Fe–Mn ores during the carbothermic reduction process are shown in Fig. 13. During carbothermic reduction process, the formation of (FeO)\textsubscript{y}(MnO)\textsubscript{1−x} was unfavorable to the separation of Mn and Fe from the Fe–Mn ores because metallic Fe–Mn particles were distributed among the (FeO)\textsubscript{y}(MnO)\textsubscript{1−x} phases, and the metallic Fe–Mn particles were wrapped by the (FeO)\textsubscript{y}(MnO)\textsubscript{1−x} particles associated with one another. The tight integration of the MnO phase and metallic Fe–Mn particles derived from the stepwise reduction of (FeO)\textsubscript{y}(MnO)\textsubscript{1−x} were closely

\[ \text{[Fe}^{2+}]\text{[Al}^{3+}]_2\text{[O}^2−]_4 + (1 − y)\text{[Mn}^{2+}]\text{[O}^2−] \]
\[ = \text{[Fe}^{2+}]_y\text{[Mn}^{2+}]_{1−y}\text{[Al}^{3+}]_2\text{[O}^2−]_4 + (1 − y)\text{[Fe}^{2+}]\text{[O}^2−] \] (20)

\[ \text{[Fe}^{2+}]_y\text{[Mn}^{2+}]_{1−y}\text{[Al}^{3+}]_2\text{[O}^2−]_4 + y\text{[Mn}^{2+}]\text{[O}^2−] \]
\[ = \text{[Mn}^{2+}]_y\text{[Al}^{3+}]_2\text{[O}^2−]_4 + y\text{[Fe}^{2+}]\text{[O}^2−] \] (21)
associated with the stepwise reduction of the Fe₉Mn₂₋₂ySiO₄ and (Fe₉,Mn₁₋₂y)Al₂O₄ phases. As observed, the transition phases of Fe₉Mn₂₋₂ySiO₄ and (Fe₉,Mn₁₋₂y)Al₂O₄ are shown in Fig. 13. The metallic Fe–Mn particles were closely wrapped by the transition phase products of the Fe₉Mn₁₋₂yAl₂O₄ and Fe₉Mn₂₋₂ySiO₄ phases, indicating that the formation of the new (FeOₓ)(MnO)₁₋ₓ phase, which resulted from the stepwise reduction process of the two types of phases. With regards to the generation and stepwise reduction behavior of the (FeOₓ)(MnO)₁₋ₓ phase, increasing the reduction temperature and shortening the reduction time could enhance the reduction reaction rate of Fe₉Mn₂₋₂ySiO₄ and (Fe₉,Mn₁₋₂y)Al₂O₄ phase, thereby preventing the generation of the (FeOₓ)(MnO)₁₋ₓ phase to enhance the separation of Mn and Fe from Fe–Mn ores.

**Fig. 10** – (a) Ternary phase diagram of Fe₂O₄–MnO₂–20 wt.% SiO₂ system; (b) crystal structure of fayalite Fe₂SiO₄ and Mn₂SiO₄; (c) phase transformation of Fe₂SiO₄ for carbothermic reduction process; and (d) SEM of Fe–Mn ores reduced at 1100 °C for 30 min.
A schematic diagram of the interfacial reaction between Fe$_2$SiO$_4$, FeAl$_2$O$_4$ and MnO is inferred and described in Fig. 14. The diffusion coupling model [37] was used to determine the interfacial reaction and the mechanism for the formation of the (FeO)$_x$(MnO)$_{1-x}$ phase. The discussion above is summarized in Fig. 14, whereby the reduction reaction between Fe$_2$SiO$_4$, FeAl$_2$O$_4$ and MnO is roughly divided into the following steps: (a) in the main interfacial reaction, the ionic Mn$^{2+}$ species migrated from the reaction interface of the MnO phase to the reaction interface of the Fe$_2$SiO$_4$ phase to form the Fe$_y$Mn$_{2-y}$SiO$_4$ phase on the reaction interface of the Fe$_2$SiO$_4$ phase and the (FeO)$_x$(MnO)$_{1-x}$ phase on the reaction interface of the MnO phase; (b) in the second stage, there was internal diffusion of Mn$^{2+}$ through the product layer of Mn$_2$SiO$_4$/Fe$_y$Mn$_{2-y}$SiO$_4$ phase and external diffusion of Fe$^{2+}$ through the product layer of MnO/(FeO)$_x$(MnO)$_{1-x}$; and (c) the final reduction products of the Mn$_2$SiO$_4$ phase, the (FeO)$_x$(MnO)$_{1-x}$ phase and metallic Fe were obtained. During carbothermic reduction, the CO–CO$_2$ atmosphere played a key role in the stepwise reduction of Fe$_y$Mn$_{1-y}$Al$_2$O$_4$, Fe$_y$Mn$_{2-y}$SiO$_4$, (FeO)$_x$(MnO)$_{1-x}$ and metallic Fe to the final products, which was crucial for the separation and recovery of Fe and Mn by the subsequent magnetic separation processes. Similar expressions can be written for the interfacial reaction between Fe$_2$SiO$_4$ and MnO and the interfacial reaction.
3.6. Recommendations for carbothermic reduction roasting of Fe–Mn ores

The abovementioned results show that the main reason for the poor separation efficiency of Fe–Mn ores was attributed to the formation of the composite oxide phase (FeO)\(_x\)(MnO)\(_{1-x}\) and spinel FeAl\(_2\)O\(_4\) and Fe\(_3\)Mn\(_{2-y}\)SiO\(_4\) during carbothermic reduction roasting. The formation of the (FeO)\(_x\)(MnO)\(_{1-x}\) phase was closely related to the reduction process of (Fe\(_y\)Mn\(_{1-y}\))Al\(_2\)O\(_4\) and Fe\(_3\)Mn\(_{2-y}\)SiO\(_4\). Therefore, to avoid the formation of (FeO)\(_x\)(MnO)\(_{1-x}\) and promote the reduction between FeAl\(_2\)O\(_4\) and MnO.

\[
\begin{align*}
[\text{Fe}^{2+}]_2[\text{Si}^{4+}]_4[\text{O}^{2-}]_4 &+ (3 - y - x)[\text{Mn}^{2+}][\text{O}^{2-}]_4 \\
[\text{Fe}^{2+}]_y[\text{Mn}^{2+}]_{2-y}[\text{Si}^{4+}]_4[\text{O}^{2-}]_4 &+ [\text{Fe}^{2+}][\text{O}^{2-}]_x[\text{Mn}^{2+}][\text{O}^{2-}]_{1-x} \\
[\text{Fe}^{2+}][\text{Al}^{3+}]_2[\text{O}^{2-}]_4 &+ (2 - y - x)[\text{Mn}^{2+}][\text{O}^{2-}]_4 \\
[\text{Fe}^{2+}]_y[\text{Mn}^{2+}]_{1-y}[\text{Al}^{3+}]_2[\text{O}^{2-}]_4 &+ [\text{Fe}^{2+}][\text{O}^{2-}]_x[\text{Mn}^{2+}][\text{O}^{2-}]_{1-x}
\end{align*}
\]

Fig. 12 — (a) Ternary phase diagram of Fe\(_3\)O\(_4\)–MnO\(_2\)–Al\(_2\)O\(_3\) system; (b) crystal structure of the spinel FeAl\(_2\)O\(_4\) and MnAl\(_2\)O\(_4\); and (c) phase transformation of FeAl\(_2\)O\(_4\) in carbothermic reduction process.
rates of \((\text{Fe}_y\text{Mn}_{1−y})\text{Al}_2\text{O}_4\) and \(\text{Fe}_y\text{Mn}_{2−y}\text{SiO}_4\), high temperatures, short reduction times and fine Fe–Mn ores (3–8 mm) particles sizes are recommended. In an attempt to improve separation, the raw ores with particle sizes of 5–8 mm were reduced at 1100 °C for 2 h. Fig. 15 shows that the magnetic separation index for the Fe–Mn ores reduced at 1050 °C for 6 h for particle sizes of 8–13 mm (before) and at 1100 °C for 2 h with particle sizes of 3–8 mm (after). This change in the carbothermic reduction condition resulted in the Mn and Fe recoveries increasing from 83.08 to 89.38% and 75.08 to 80.66%, respectively. In addition, the Mn grade and mass fraction of Mn/Fe in the nonmagnetic product also increased from 51.33 to 53.60% and from 5.16 to 5.42, respectively. The nonmagnetic product is a Mn-rich raw material that can be used as an acceptable feed (Mn/Fe mass ratio over 5) for smelting a ferromanganese alloy product.

4. Conclusions

Carbothermic reduction roasting followed by magnetic separation process is reported an effective technological process to separation and recovery of Mn and Fe from ferruginous manganese ores, which produces an acceptable feed to meet the requirements of the developing manganese industry. Iron-rich products with a Fe recovery of 80.66% and a manganese-rich product with a Mn recovery of 89.38% were obtained at an opti-
Fig. 14 – Schematic diagram for interfacial reaction of \((\text{FeO})_x(\text{MnO})_{1-x}\) in carbothermic reduction process.

Fig. 15 – Magnetic separation index of Fe–Mn ores reduced at 1050°C for 6 h with particle sizes of 8–13 mm (before) and at 1100°C for 2 h with particle sizes of 3–8 mm (after).

The formation mechanism and the interfacial reduction reaction of \((\text{FeO})_x(\text{MnO})_{1-x}\), \((\text{Fe}_y\text{Mn}_{1-y})\text{Al}_2\text{O}_4\) and \((\text{Fe}_y\text{Mn}_{1-y})\text{SiO}_4\) were systematically discussed to illustrate the effect of the MnO phase on the stepwise reduction of the \(\text{Fe}_2\text{SiO}_4\) and \(\text{FeAl}_2\text{O}_4\) phases. The formation mechanism and the stepwise reduction of \(\text{FeAl}_2\text{O}_4\) proceeded as follows: \(\text{FeAl}_2\text{O}_4\) was converted to \(\text{Fe}_2\text{Mn}_{1-y}\text{Al}_2\text{O}_4\) by manganese monoxide and then further converted to \(\text{MnAl}_2\text{O}_4\); \(\text{FeAl}_2\text{O}_4\) was directly reduced to metallic iron in a CO atmosphere, and \(\text{Fe}^{2+}\) replaced \(\text{Mn}^{2+}\) in a spinel-type structure that easily combined with free MnO to form the new phase of \((\text{FeO})_x(\text{MnO})_{1-x}\), which was further reduced to metallic iron. The formation mechanism and stepwise reduction of \(\text{Fe}_2\text{SiO}_4\) proceeded as follows: \(\text{Fe}_2\text{SiO}_4\) was directly reduced to metallic iron in a CO atmosphere; \(\text{Fe}_2\text{SiO}_4\) was converted to \(\text{Fe}_y\text{Mn}_{2-y}\text{SiO}_4\) and further converted to \(\text{Mn}_2\text{SiO}_4\); \(\text{Fe}_2\text{SiO}_4\) was directly reduced to metallic iron in a CO atmosphere; and \(\text{Fe}^{2+}\) replaced \(\text{Mn}^{2+}\) in a fayalite-type structure and easily combined with free MnO to form a new phase \((\text{FeO})_x(\text{MnO})_{1-x}\), which was then further reduced to metallic iron. The formation of the \((\text{FeO})_x(\text{MnO})_{1-x}\) phase resulted from the stepwise reduction of \((\text{Fe}_y\text{Mn}_{1-y})\text{Al}_2\text{O}_4\) and \((\text{Fe}_y\text{Mn}_{1-y})\text{SiO}_4\) phases. Morphology analyses indicated that the presence of \(\text{Fe}_2\text{SiO}_4\), \(\text{FeAl}_2\text{O}_4\) and

Step (a)  Ionic migration of \(\text{Fe}^{2+}\) and \(\text{Mn}^{2+}\) on the interface

Step (b) Internal diffusion of \(\text{Mn}^{2+}\) through \((\text{FeO})_x(\text{MnO})_{1-x}\); External diffusion of \(\text{Mn}^{2+}\) through \(\text{Fe}_2\text{Mn}_{2-y}\text{SiO}_4\) and \((\text{Fe}_y\text{Mn}_{1-y})\text{Al}_2\text{O}_4\)

Step (c) Reduction of iron oxide
The fundamental Natural Conflicts (FeO)\(_x\)(MnO)\(_{1-x}\) as the main reason for the poor separation of Mn and Fe. The high temperature and short reduction time restrained the formation of FeO\(_x\)(MnO)\(_{1-x}\) and promoted the stepwise reduction of the three phases to optimize the separation of Mn and Fe from the Fe–Mn ores.

Conflicts of interest
The authors declare no conflicts of interest.

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