

Manganese extraction from high-iron-content manganese oxide ores by selective reduction roasting-acid leaching process using black charcoal as reductant

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Abstract: Reduction roasting-acid leaching process was utilized to process high-iron-content manganese oxide ore using black charcoal as reductant. The results indicate that, compared with the traditional reductant of anthracite, higher manganese extraction efficiency is achieved at lower roasting temperature and shorter residence time. The effects of roasting parameters on the leaching efficiency of Mn and Fe were studied, and the optimal parameters are determined as follows: roasting temperature is 650 °C, residence time is 40 min, and black charcoal dosage is 10% (mass fraction). Under these conditions, the leaching efficiency of Mn reaches 82.37% while that of Fe is controlled below 7%. XRD results show that a majority of MnO₂ and Fe₂O₃ in the raw ore are reduced to MnO and Fe₃O₄, respectively.

Key words: manganese ore; reduction roasting; acid leaching; black charcoal

1 Introduction

As a strategically important ferrous element, manganese (Mn) is widely used for the steel production, ferromanganese, non-ferrous alloys, dry cell batteries, paint and other chemicals [1–2]. Acid leaching is a common process to dissolve bivalent Mn. When Mn exists as an insoluble form (e.g. MnO₂) in the raw ores, the high valence Mn oxides must be firstly reduced to MnO and then leached in a dilute acid solution. Up to now, hydro-reduction at room or heated temperature using various reducing agents in acid solution environment [3–6] and pyro-reduction followed by acid leaching [7–10] are two kinds of commonly known approaches to extract Mn from the manganese oxide ores.

Coals (general anthracite) are traditional reductants in the pyro-reduction processes for manganese oxide ores [11–13]. However, the industrial practice shows that the coal-based pyro-reduction processes are characterized by high roasting temperature, high energy consumption and serious gaseous pollutant emission (NO_x, SO₂, etc). Recently, biomass, such as cornstalk and straw, has been used as a substitute of coal in the pyro-reduction processes [14–17]. Biomass has a lower density and still contains a small amount of sulfur and nitrogen, which

likely brings about adverse impact on the future industrial production. Moreover, a relatively long residence time (>1 h) is commonly required when the biomass is applied.

For the manganese oxide ores containing high content of Fe₂O₃, simple hydro-reduction is not desirable since Fe₂O₃ is easily dissolved in an acid solution, leading to an increase of acid consumption. On the other hand, the dissolved iron ionic is unfavorable to the subsequent purification of Mn²⁺ solution. The utilization of high-iron-content manganese oxide ores and the dissolution behavior of iron oxides have been less discussed in the previous investigations. Generally, Fe₂O₃ is reduced step by step according to Fe₂O₃→Fe₃O₄→FeO→Fe while MnO₂ is reduced to MnO during the reduction process. In comparison with Fe₂O₃, FeO and Fe, Fe₃O₄ is more difficult to be dissolved in the dilute sulfuric acid solution. Therefore, it is feasible to extract Mn from high-iron-content manganese oxide ores with a lower iron dissolution by controlling the phase composition of Mn/Fe oxides in the roasted products.

Black charcoal is the carbonization product of biomass, which has a lower sulfur and nitrogen content compared to the biomass. As reported, the reducibility of black charcoal is higher than that of anthracite. In the present work, one lean manganese oxide ore containing high content of Fe₂O₃ was handled by a selective

reduction roasting process using black charcoal as a reductant. The effects of roasting parameters on the leaching efficiency of Mn and Fe were examined. XRD was applied to determine the phase transformation of manganese and iron oxides in the roasted products.

2 Materials and methods

2.1 Manganese oxide ore

The manganese oxide ore sample was taken from a certain plant in China. The main chemical composition of the sample is listed in Table 1. It can be seen that, the sample, belonging to a typical lean manganese ore, contains 17.90% total Mn, 12.72% total Fe, 28.12% SiO₂ and 11.89% Al₂O₃. Figure 1 presents the XRD pattern of the sample, indicating that manganese in the ore mainly exists as the form of todorokite and the predominant gangue minerals include limonite, quartz and kaolinite.

Table 1 Main chemical composition of raw ore (mass fraction, %)

Total Mn	Total Fe	Al ₂ O ₃	SiO ₂	
17.90	12.72	11.89	28.12	
CaO	MgO	K ₂ O	P	S
0.34	0.44	0.54	0.13	0.094

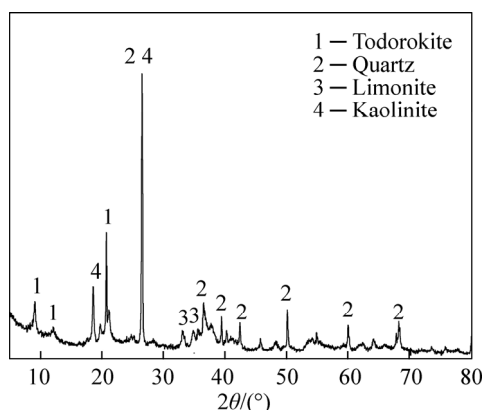


Fig. 1 XRD pattern of manganese oxide ore

Table 2 presents the chemical phases of Mn in the sample identified by chemical dissolution method. As seen from Table 2, 82.07% of Mn exists as manganese oxide. In addition, 14.41% Mn exists as the form of ferromanganese oxide. In addition, Fe phases in the raw ore were particularly detected prior to reduction roasting. The results show that 93.95% of total iron exists in the

form of hematite (or limonite), and the rest are 3.61% ferrous silicate and 2.44% iron carbonate.

Table 2 Phase composition of manganese in raw ore (mass fraction, %)

Manganese oxide	Ferromanganese oxide	Manganese carbonate	Manganese silicate	Total
82.07	14.41	2.79	0.73	100

2.2 Reducing agents

Two kinds of reducing agents were used in this work. One was black charcoal purchased from the local market and the other was anthracite taken from Guangxi province in China. The proximate analysis and elemental analysis results of reducing agents are given in Table 3. Compared to anthracite, black charcoal has less fixed carbon, more volatile matter and less ash content. Nitrogen and sulfur contents in the black charcoal are approximately one tenth of those in the anthracite, indicating that the emission of NO_x and SO₂ during the reduction roasting can be significantly declined when black charcoal is used as reductant.

TG-DSC analysis was conducted for both black charcoal and anthracite, which is shown in Fig. 2. Obvious mass loss occurs at 350 °C for black charcoal and at 500 °C for the anthracite. When the temperature reaches around 550 °C, the black charcoal almost combusts completely while only about 20% anthracite combusts, showing that the black charcoal possesses a better combustibility and reactivity. From the DSC curves, it can be seen that black charcoal combusts much faster than anthracite as the DSC curve decreases sharply to approximately zero at 550 °C.

2.3 Procedure

Manganese ore sample and reductants were firstly crushed, ground and screened to obtain raw materials with particle size below 74 μm, respectively. Then, the ground manganese ore was mixed with a certain amount of reducing agents to prepare green pellets with a diameter of 10–12 mm. The green pellets were desiccated at (105±5) °C for 4 h to obtain dry pellets. Next, the dry pellets were placed into a corundum crucible and roasted at given temperature for certain period in an electrically heated muffle furnace. The experimental schematic diagram is presented in Fig. 3.

Table 3 Proximate and elemental analysis results of reducing agents (mass fraction, %)

Reductant	Proximate analysis				Element analysis				
	Fixed carbon	Volatile constituent	Moisture	Ash	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
Black charcoal	75.92	19.08	1.99	3.01	77.60	3.76	17.23	0.09	0.08
Anthracite	82.45	2.75	2.66	12.14	83.84	2.46	7.23	0.94	0.82

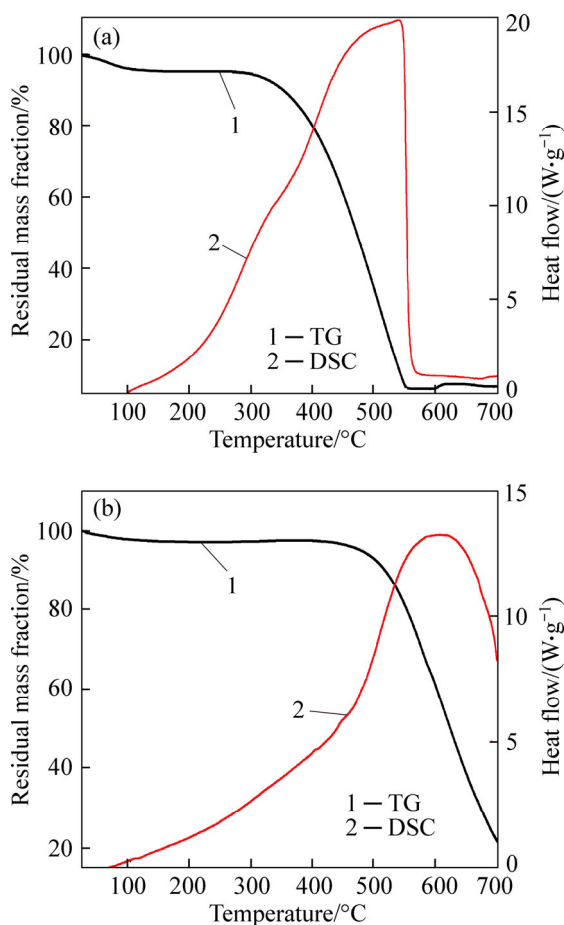


Fig. 2 TG-DSC analysis of black charcoal (a) and anthracite (b)

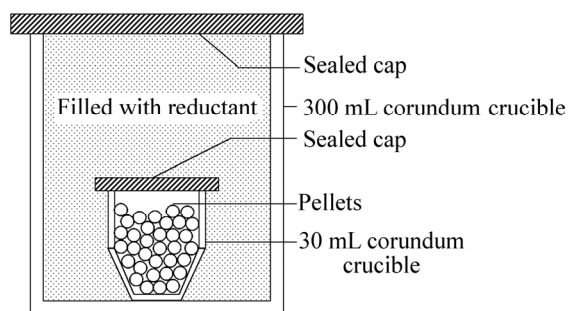


Fig. 3 Schematic diagram of reaction apparatus

After roasting, the pellets staying in the sealed reactor were cooled to room temperature. Finally, the cooled samples were discharged from the reactor.

The leaching experiment was carried out in a 400 mL beaker. In each leaching test, 10.0 g of the roasted sample was precisely weighed and leached in the beaker in a water bath. The leaching solution was then filtered after the leaching process was finished. The filter cake was subsequently washed for three times with distilled water and dried for further chemical analysis. All of the leaching solution was prepared for ICP analysis to evaluate the Mn balance. Leaching efficiency is the evaluation index in this work, which is calculated according to

$$\gamma = \left(1 - \frac{m_1 \times \beta}{m_0 \times \alpha}\right) \times 100\% \quad (1)$$

where γ is the leaching efficiency (%); m_1 is the mass of filter cake (g); m_0 is mass of roasted sample (g); α is grade of Mn/Fe in roasted ore (%); β is grade of Mn/Fe in filter cake (%).

Process parameters of reduction roasting-acid leaching are numerous. The optimal leaching conditions have been acquired in our previous report [10], which are sulfuric acid concentration of 2.0 mol/L, liquid-to-solid ratio of 5, leaching temperature of 25 °C, leaching time of 20 min and stirring speed of 400 r/min. This work mainly concerns about acquiring optimal parameters of reduction roasting, and the leaching conditions were fixed unless specified otherwise.

Iron phase is reported to have a great effect on the leaching efficiency of Fe in acid environment. Therefore, chemically pure FeO and Fe₃O₄ were firstly used to compare the solubility in dilute sulfuric acid solution. Figure 4 shows that the solubility of FeO is much higher than that of Fe₃O₄ at the same leaching temperature. As a result, it is essential to avoid the formation of FeO phase during the reduction roasting. Furthermore, the leaching temperature should be controlled below 60 °C to obtain a lower Fe leaching efficiency of Fe₃O₄.

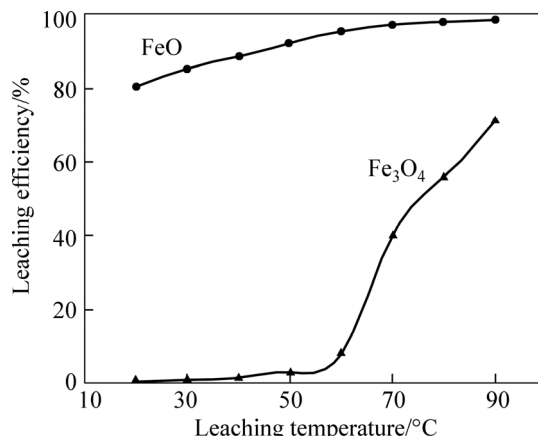


Fig. 4 Leaching efficiency of pure FeO and Fe₃O₄ as a function of leaching temperature

3 Results and discussion

3.1 Effect of reductants

Black charcoal and anthracite were used as reductants in the reduction roasting process. The residence time was 40 min, reductant dosage was 25% (mass fraction) and roasting temperature was chosen as 600 °C, 700 °C and 800 °C. Under these parameters, reduction roasting-acid leaching of manganese oxide ore was conducted and results are shown in Fig. 5.

As observed from Fig. 5, leaching efficiencies of Mn and Fe increase with the increase of roasting

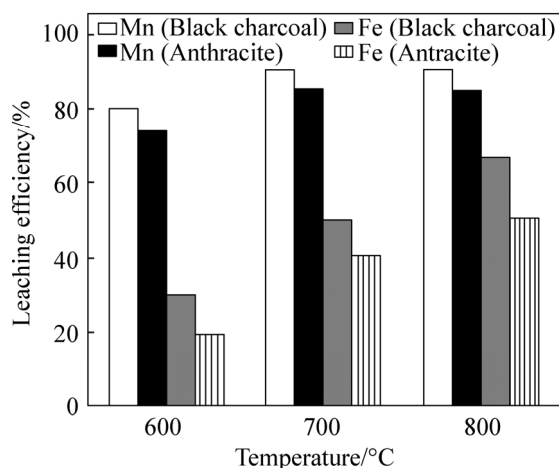


Fig. 5 Leaching efficiency of Mn and Fe from roasted ore reduced by two reductants

temperature. At all temperature levels, the extraction efficiency of Mn and Fe using black charcoal is better than that using anthracite. From the perspective of Mn extraction, extraction efficiency of black charcoal at 600 °C is close to that of anthracite at 700 °C. Comparatively, high extraction efficiency can be achieved at lower roasting temperature and shorter roasting time when black charcoal is used as reductant. Therefore, the following tests are carried out using black charcoal as reductant.

3.2 Effect of roasting temperature

The effect of roasting temperature on leaching efficiency of Mn and Fe was carried out at roasting temperature ranging from 600 °C to 850 °C at residence time of 40 min and black charcoal dosage of 25% (mass fraction). The obtained results given in Fig. 6 show that leaching efficiency of Mn improves from 79.88% at 600 °C to 90.56% at 700 °C and then flattens as the temperature further increases. The leaching efficiency of Fe increases substantially with the roasting temperature,

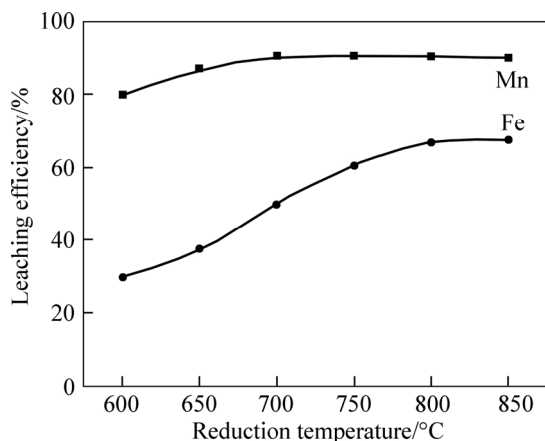


Fig. 6 Effect of roasting temperature on leaching efficiency

from 29.73% at 600 °C to 49.82% at 700 °C and then slowly increases.

Figure 7 shows the XRD patterns of roasted samples at different roasting temperatures. It can be observed that the diffraction peaks of MnO_2 disappear and those of MnO emerge at all temperature levels, indicating that MnO_2 is easily reduced to MnO . On the other hand, diffraction peak of metallic iron appears above 800 °C, indicating that reduction temperature should be controlled below 800 °C. Another iron phase, FeO , emerges once the temperature exceeds 600 °C. Since FeO is easily dissolved in the subsequent acid leaching, its formation should be avoided and the roasting temperature should not exceed 600 °C. However, the leaching efficiency of Mn at this temperature is not satisfied from Fig. 6. Considering the above results, optimal roasting temperature is chosen as 650 °C, at which the leaching efficiency of Mn is appropriate while the leaching efficiency of Fe is relatively low.

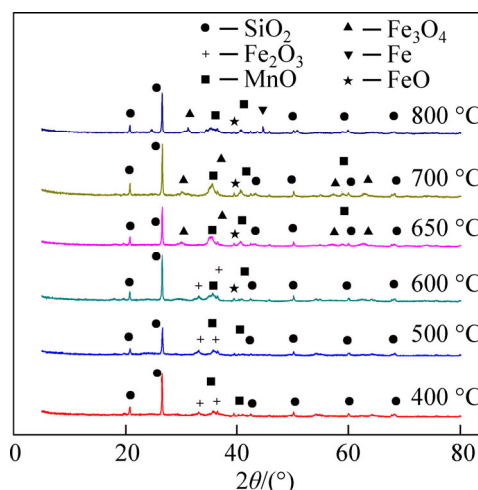


Fig. 7 XRD patterns of roasted products at different roasting temperatures

3.3 Effect of residence time

The effect of residence time on leaching efficiency of Mn and Fe was carried out at roasting temperature of 650 °C and charcoal dosage of 25% (mass fraction). The residence time was ranged from 20 min to 100 min. Figure 8 shows that the leaching efficiency of Mn almost reaches a maximum at the residence time of 40 min. Moreover, as the residence time further goes up, the leaching efficiency of Fe also increases.

Figure 9 shows the XRD patterns of roasted samples at different residence time. It can be seen from Fig. 9 that the diffraction peaks of MnO_2 have already disappeared and diffraction peaks of MnO occur. When the residence time reaches 40 min, diffraction peaks of Fe_2O_3 disappear and diffraction peaks of Fe_3O_4 occur, indicating that Fe_2O_3 is reduced to Fe_3O_4 .

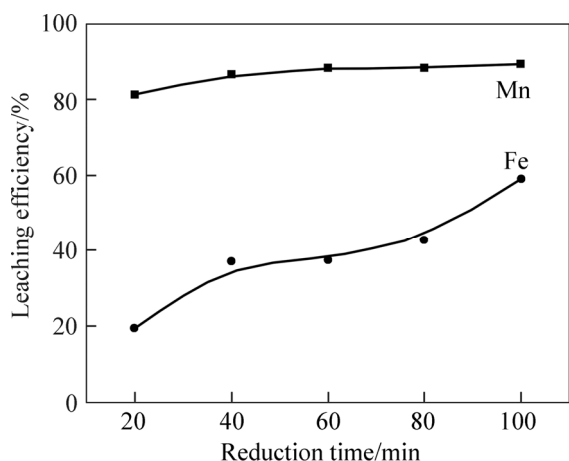


Fig. 8 Effect of reduction time on leaching efficiency

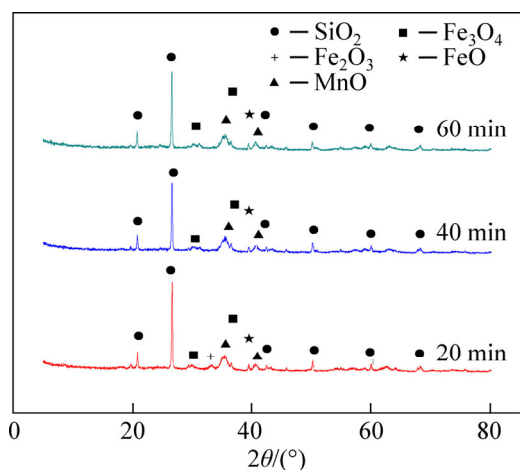


Fig. 9 XRD patterns of roasted products at different reduction time

3.4 Effect of black charcoal dosage

The effect of black charcoal dosage on leaching efficiencies of Mn and Fe was carried out at reductant dosage ranging from 5% to 25% (mass fraction) at roasting temperature of 650 °C and residence time of 40 min. Figure 10 shows that the leaching efficiency of Mn improves from 50.88% to 82.37% when black charcoal

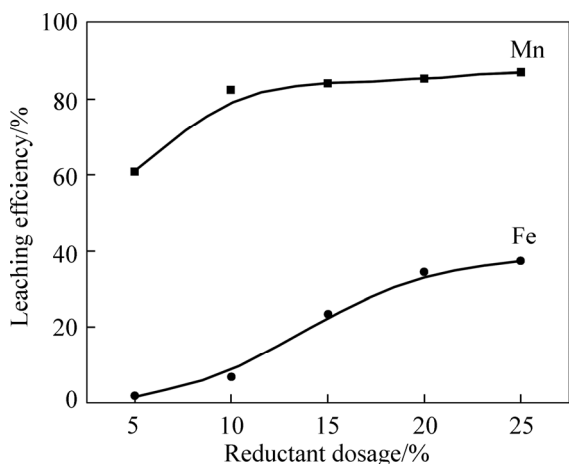


Fig. 10 Effect of black charcoal dosage on leaching efficiency

dosage increases from 5% to 10% (mass fraction) and then remains almost constant as the dosage further increases. Leaching efficiency of Fe is greatly affected by the black charcoal dosage.

Figure 11 shows the XRD patterns of roasted ore at different charcoal dosages. After being reduced at 5% (mass fraction) black charcoal, MnO₂ is reduced to MnO and diffraction peaks of MnO are strengthened as the black charcoal dosage increases. Fe₂O₃ still exists in roasted ores at 5% (mass fraction) charcoal dosage. As the charcoal dosage increases, the diffraction peaks of Fe₃O₄ become more obvious. From the above results, the optimal charcoal dosage is chosen as 10% (mass fraction).

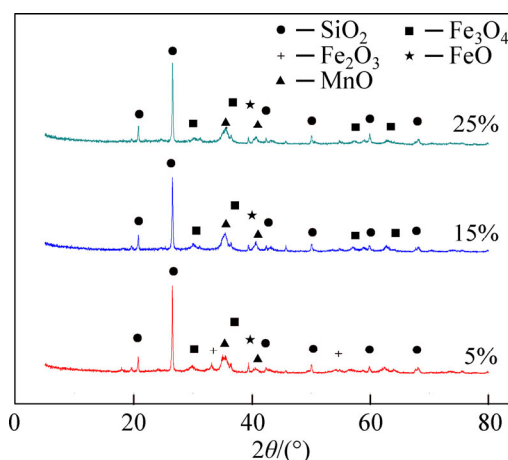


Fig. 11 XRD patterns of roasted products at different black charcoal dosages

Considering the results mentioned above, the optimal roasting parameters are as follows: reduction temperature is 650 °C, residence time is 40 min and charcoal dosage is 10% (mass fraction). Under these optimal conditions, the leaching efficiency of Mn reaches 82.37% while that of Fe is controlled below 7%.

4 Conclusions

1) When black charcoal is used as a substitute of anthracite, a higher leaching efficiency of Mn can be achieved at lower roasting temperature and shorter residence time.

2) Reduction roasting conditions can be controlled to facilitate the formation of Fe₃O₄ to realize a low iron leaching efficiency during the extraction of Mn from high-iron-content manganese oxide ores.

3) The optimal roasting parameters based on black charcoal are: roasting temperature of 650 °C, residence time of 40 min and charcoal dosage of 10% (mass fraction). Under these conditions, leaching efficiency of Mn reaches 82.37% while that of Fe is controlled below 7%.

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