Journal of Hazardous Materials 174 (2010) 71–77

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Innovative methodology for comprehensive utilization of iron ore tailings Part 1. The recovery of iron from iron ore tailings using magnetic separation after magnetizing roasting

Chao Li[a,*], Henghu Sun[a,b], Jing Bai[c], Longtu Li[a]

[a] State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] School of Engineering and Computer Science, University of the Pacific, Stockton, CA 95211, USA
[c] National Engineering Laboratory of Biohydrometallurgy, General Research Institute for Non-Ferrous Metals, Beijing 100088, China

ARTICLE INFO

Article history:
Received 29 May 2009
Received in revised form 4 September 2009
Accepted 4 September 2009
Available online 11 September 2009

Keywords:
Iron ore tailings
Iron recovery
Magnetizing roasting
Magnetic separation

ABSTRACT

Iron ore tailings have become one kind of the most hazardous solid waste. In order to recycle iron in the tailings, we present a technique using magnetizing roasting process followed by magnetic separation. After analysis of chemical composition and crystalline phase, according to experimental mechanism, the effects of different parameters on recovery efficiency of iron were carried out. The optimum reaction parameters were proposed as the following: ratio of coal: iron ore tailings as 1:100, roasting at 800 °C for 30 min, and milling 15 min of roasted samples. With these optimum parameters, the grade of magnetic concentrate was 61.3% Fe and recovery rate of 88.2%. With this method, a great amount of iron can be reused. In addition, the microstructure and phase transformation of the process of magnetizing roasting were studied.

1. Introduction

With 30 years of reform and opening up, Chinese iron and steel industry has developed rapidly. Meanwhile, a continuous increase of hazardous industrial wastes like iron ore tailings generated by iron steel industry are becoming a serious problem. In China, the total 59.7 billion tons of tailings have been discarded as waste, and the generation of iron ore tailings is estimated to be one third of the total tailings [1]. Iron ore tailings not only cover huge land and pollute environment, but also give rise to security risks. In November 2007, 13 people died in the accident caused by iron ore tailings dam-break in Anshan of Liaoning province, China.

At the same time, iron ore tailings as secondary resources have been of great importance to all countries in the world [2–7]. At present, there are some different ways of utilization of iron ore tailings, as the following: recycling of useful metal, such as Fe, Co, Ni and Cu [8]; producing of building materials directly (including cement clinker and admixture, glass ceramics and wall materials, etc.); filling goaf; and using as soil modifier and magnetization fertilizer [9,10].

In addition, with the continuous exhaustion of mineral resources, iron ore resources in China become increasingly scarce. According to statistics, the annual emission of iron ore tailings is 130 million tons, while every 1 ton of iron ore concentrate should discharge 2.5–3 tons iron ore tailings. Assuming the tailings contain an average of 11% iron, there are 1.41 million tons of metallic iron losses in the tailings [11]. Therefore, the recovery and utilization of iron in iron ore tailings are very important to save iron resources.

At present, magnetizing roasting and direct reduction are the two main ways to recycle iron from tailings or other iron contained wastes [12]. The differences between them are summarized in Table 1.

In our group, the comprehensive utilization of iron ore tailings is the focus of our research, and our final goal is to realize zero-emission of iron ore tailings wastes. Based on the above description of different ways of utilization of iron ore tailings, the cost of only recover iron from tailings is high because of the low content of iron. On the other hand, there is no good economic benefit just using iron ore tailings to produce cementitious materials. So our innovative idea is combining the recovery of iron with reuse of residues to prepare cementitious materials together, which means recovering iron in the process of cementitious materials' preparation using iron ore tailings. The combination point is roasting, by which it can reduce hematite to magnetite and promote the cementitious properties of iron ore tailings at the same time. By this way, the iron ore tailings not only can be comprehensive utilized, but also

---

[*] Corresponding author at: Room 2507, YIFU Science & Technology Building, Tsinghua University, Beijing 100084, China. Tel.: +86 10 62794738; fax: +86 10 62794738.
E-mail address: chao-li07@mails.tsinghua.edu.cn (C. Li).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.09.018

Table 1
The differences between magnetizing roasting and direct reduction.

	Magnetizing roasting	Direct reduction
Object	To produce iron concentrate (Fe_3O_4), used for iron smelting	To produce sponge iron (Fe), used for steel making
Temperature	Usually between 700 and 900 °C	Usually >1000 °C
Production cycle	Short (usually in 1 h)	Long (usually 2–5 h)
Key point	Reducing atmosphere is necessary in order not to be oxidized, because Fe_2O_3 is weakly magnetic and hard to be separated	More reducing agent is needed, and heat consumption is larger than magnetizing roasting

create maximum economic benefit. First of all, the recovery of iron is the first step of the whole technology.

The recovery of iron from low-grade iron ore was investigated by many researchers using froth flotation process [13], reverse anionic flotation of quartz [14], and magnetic separation [15]. As we all know, the most economic and environmental friendly method to recover iron is magnetic separation. Magnetic separation is a method to separate and capture fine magnetic particles by the magnetic force acting on the particles in a gradient magnetic field [16]. The principle of the process is the selective adsorption of the magnetite material on to a mineral surface in a mixed pulp which renders the coated grains amenable to recover by the magnetic separation techniques [6].

Uwadiale [17] gave a thorough review of magnetizing roasting of hematite and concluded that although the roles of temperature, particle size, coal/ore ratio, and catalysts or inhibitors are well established, the mechanism and kinetics of the magnetizing reduction process remain unsolved due to the porous nature of the reduction products. Uwadiale and Whewell [18] reported that a hematite was progressively converted into magnetite, wustite and metallic iron when temperature was increased during reduction roasting.

Considering that the appropriate activation temperature is about 800 °C, so in this paper, the recovery of iron from iron ore tailings using magnetizing roasting was studied, and the reaction process was analyzed.

2. Experiment

2.1. Experimental mechanism

According to the difference of ore property, magnetizing roasting process for the recovery of iron minerals includes reducing roasting, neutral roasting and oxidizing roasting [19]. For hematite, the purpose of magnetizing roasting is reducing hematite to magnetite, and the reducing agents are usually C, CO and H_2. The reaction theory can be expressed with the following equations:

$$3Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO\uparrow \tag{1}$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2\uparrow \tag{2}$$

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O\uparrow \tag{3}$$

Taking Eq. (1) as an example, the relationship between reduction degree and parameters is shown in Eq. (4) [20],

$$t_R = \frac{R'}{[AKM_c \cdot \exp(-E/R^0T)]} + \frac{r'_0\rho_0 \cdot [1/2 - R'/3 - (1-R')^{2/3}/2]}{3D_e} \tag{4}$$

In Eq. (4), t_R is the time of iron oxide reduction (s), A is the reaction constant, R' is the reduction degree of production (%), K is the balance constant of iron reduction equation, M_c is the coal ration (%), E is the activation energy (J mol^{-1} K^{-1}), R^0 is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), r'_0 is the grain radius when reduction degree is R' (m), ρ_0 is the oxygen contain in iron oxide initially (mol m^{-3}), and D_e is the diffuse coefficient in solid phase (m^2 s^{-1}).

Table 2
Chemical composition of iron ore tailings.

Components	SiO_2	Fe_2O_3	CaO	Al_2O_3	MgO	Na_2O	K_2O	LOI
Content (wt%)	47.39	24.82	8.85	7.42	0.097	0.32	0.70	10.40

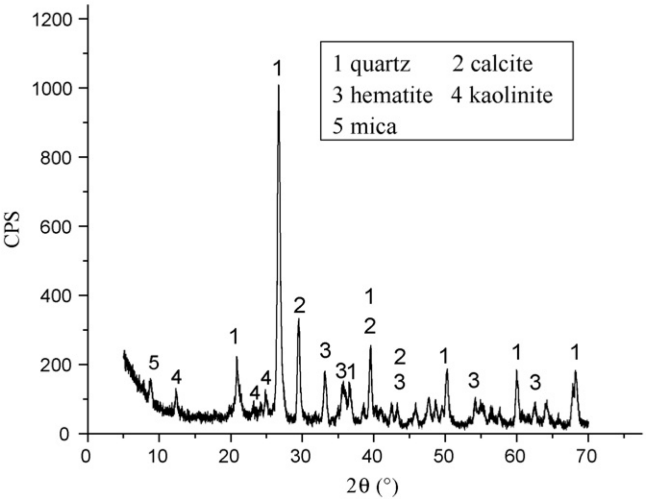

Fig. 1. XRD pattern of iron ore tailings.

From Eq. (4), the parameters that influence reduction reaction of magnetizing roasting are reaction temperature, reaction duration, and ratio of carbon. Meanwhile, the process of milling roasted sample is necessary because of the complicated dissemination characteristics of raw materials (seen Fig. 8) [21].

2.2. Raw materials

Iron ore tailings were sampled from tailing dam of an iron ore dressing plant in Anshan of Liaoning Province, China. Chemical compositions of iron ore tailing samples was analyzed, seen in Table 2. The crystalline phases were investigated by powder XRD technique, using Cu-Kα radiation (40 kV, 30 mA) at the scanning rate of 8°/min from 5° to 70°. Some mineral phases existed, such as quartz, hematite, calcite, mica and kaolinite, shown in Fig. 1.

In the reduction reaction, coal (sampled from Datong of Shanxi Province, China) was used as the reducing agent. The proximate analysis of coal is shown in Table 3.

Table 3
Proximate analysis of coal.

Components	Fixed carbon	Volatile matter	Ash	Water
Content (wt%)	77.70	6.41	8.85	7.42

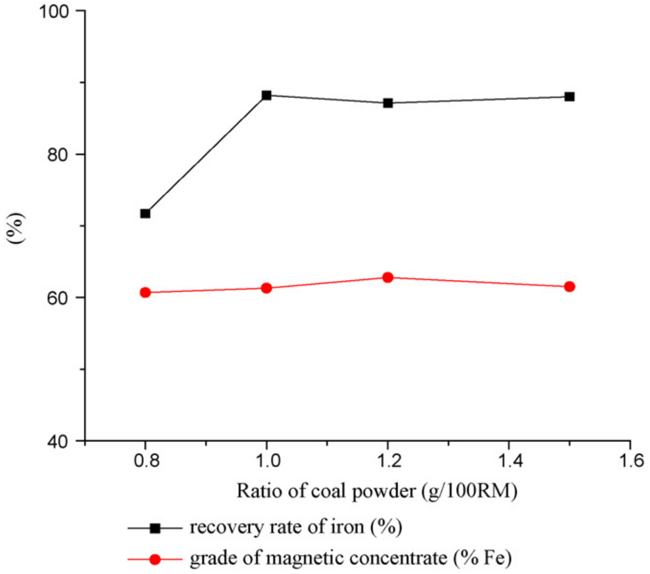

Fig. 2. Effects of ration of coal to iron ore tailings on iron recovery.

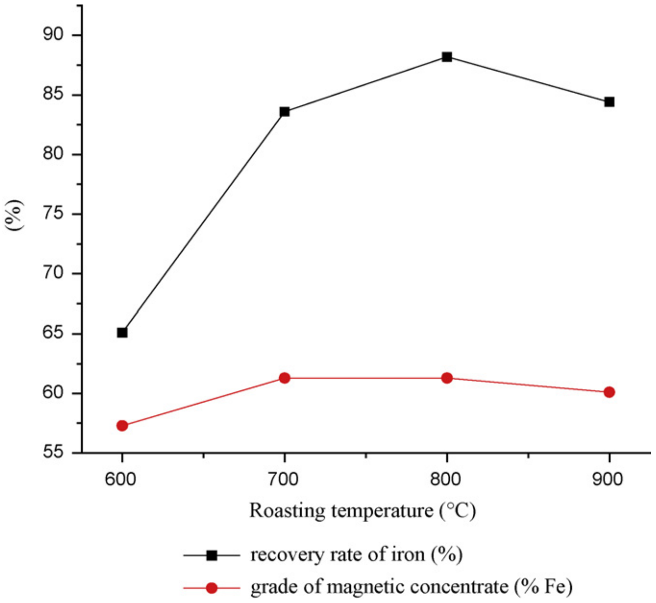

Fig. 3. Effects of roasting temperature on iron recovery.

2.3. Experimental method

Four group experiments were designed to investigate the effects of different parameters on iron recovery from iron ore tailings, such as the ratio of coal to iron ore tailings, roasting temperature, roasting time, and milling time. Iron ore tailings were mixed thoroughly with coal and put in crucible, then roasted at high temperature in furnace (Model: GSL1400, with the atmospheric pressure −0.09 MPa). After a given time, roasted samples were taken out when cooling down to 300 °C in the airtight furnace. Because Stephens et al. [22] observed that if artificial magnetite was quenched in air at temperatures above 500 °C, the magnetite was re-oxidized to weakly magnetic hematite, but if the temperature was below 500 °C the magnetic properties remain unaffected. Products were wet milled in a ball mill then separated by magnetic separator (Model: XCGSφ50), with working electrical current of 1 A (magnetic field intensity 0.08 T). The grades of magnetic concentrate were analyzed by chemistry method. Then the recovery rates of iron (the ratio of the amount of iron minerals in magnetic concentrate to those of in iron ore tailings raw material) were deduced according to mass balance in magnetic separation process.

3. Results and discussion

3.1. Iron recovery

3.1.1. Effects of ratio of coal to iron ore tailings on iron recovery

In order to investigate the optimum content of coal, different ratios of coal to iron ore tailings were studied, respectively. According to Eq. (1), considering the content of Fe_2O_3 in iron ore tailings and fixed carbon in coal, it is known by calculation that the theoretic ratio of coal to raw materials was 0.8%. Therefore, the ratios of coal to iron ore tailings were selected as 0.8:100, 1:100, 1.2:100 and 1.5:100. Other experiment parameters were kept as the following: the roasting temperature of 800 °C for 30 min, milling 15 min. The effects of ratio of coal to iron ore tailings on the grade of magnetic concentrate and iron recovery rate were shown in Fig. 2.

As shown in Fig. 2, by the separation of magnetic separator, the grades of magnetic concentrate were all over 60% Fe, meeting the required standard of iron making. When the ratio of coal to iron ore tailings was over 1:100, the recovery rate of iron kept stable, and the maximum was 88.2%. In case of calculation as only hematite contained in iron ore tailings, 0.8% coal was needed theoretically, which was as much as experimental data. It was indicated that the main crystalline phase was Fe_2O_3, as shown in XRD.

3.1.2. Effects of roasting temperature on iron recovery

Roasting temperature is the main factor that impacts the reaction. Cui et al. [23] reported the lower limit of temperature for magnetic roasting was about 500 °C. In this experiment, roasting temperature were selected as 600, 700, 800 and 900 °C, and samples consisted of coal, iron ore tailings at a proportion of 1:100, roasted 30 min, with the milling time of 15 min. Results were shown in Fig. 3.

From Fig. 3, with the roasting temperature increasing, the reaction between C and Fe_2O_3 was speeded up. While at 600 °C, the temperature was low, and the reaction was incomplete due to the limited reaction rate. But if the temperature was too high (900 °C), the product (Fe_3O_4) may be over-reduced to generate wustite [18], which is weakly magnetic and difficult to recycle. When the temperature was 800 °C, the grade and recovery rate were both high.

3.1.3. Effects of roasting time on iron recovery

Samples were roasted at the temperature of 800 °C for different roasting time, with the same proportion of coal and iron ore tailings at 1:100 and milling time 15 min. Experimental results were shown in Fig. 4.

As shown in Fig. 4, there was non-linear relationship between iron recovery and roasting time. When roasting time was about 30 min, the recovery rate of iron was achieving a peak, with the grade of magnetic concentrate 61.3% Fe. It was inferred that when the roasting temperature was 800 °C, the optimum roasting time was about 30 min, during which reduction reaction of ferrous oxides was mostly completed.

3.1.4. Effects of milling time of roasted samples on iron recovery

Because of the complex dissemination characteristics of roasted samples, making it difficult in magnetic separation, need to be milled before magnetic separation. The conditions of magnetizing roasting were as the following: the roasting temperature of 800 °C for 30 min, with the proportion of coal and iron ore tailings at 1:100. The results were shown in Fig. 5, and the average particle sizes

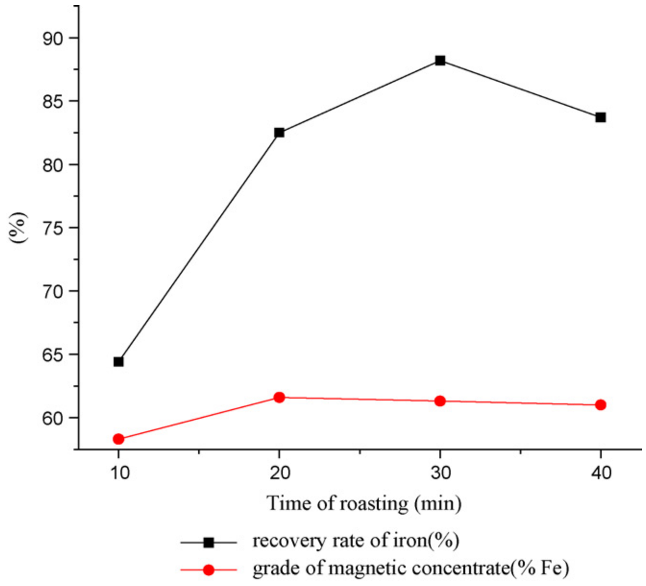

Fig. 4. Effects of roasting time on iron recovery.

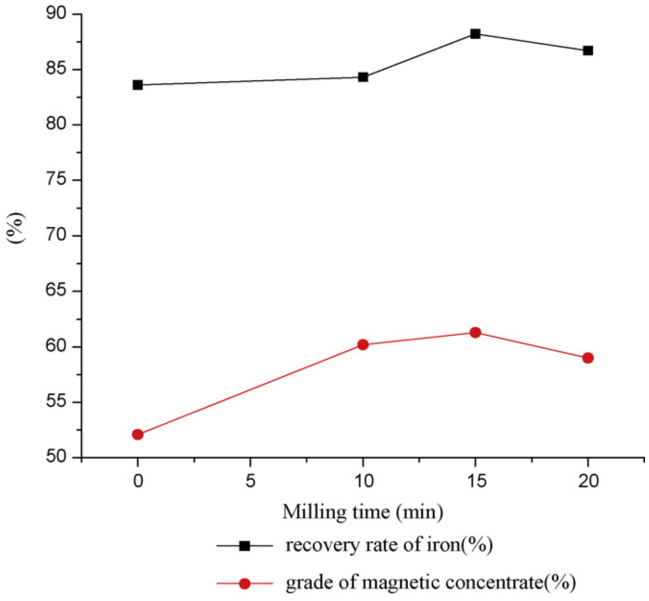

Fig. 5. Effects of milling time on iron recovery.

Table 4
The average particle sizes after different milling time.

Milling time (min)	0	10	15	20
d (0.5) (μm)	16.560	12.243	10.550	9.362

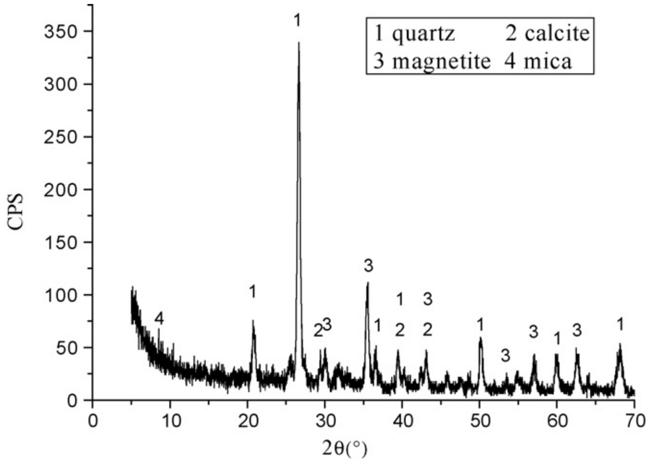

Fig. 6. XRD pattern of roasted sample (800 °C, 30 min, coal/iron ore tailings 1:100).

after different milling time were shown in Table 4, tested by Laser Particle Sizer (Model: MasterSizer 2000).

From Fig. 5, the grade of magnetic concentrate was affected by milling the roasted samples. If the roasted samples were not milled (0 min), the grade was just 52.1% Fe. When milled 15 min, it was 61.3% Fe. However, if the roasted samples were milled too fine (20 min), the particles were agglomerate easily and difficult to be separated in magnetic separator, so the grade was only 59% Fe.

3.2. *Analysis of roasted sample*

3.2.1. *XRD analysis*

Taking the roasted sample for analysis, the experiment conditions were as follows: the roasting temperature of 800 °C for 30 min and the ratio of coal to iron ore tailings of 1:100. Its XRD pattern was shown in Fig. 6.

From the XRD pattern, it can be seen that the hematite had been reduced to magnetite, which made the roasted sample was easy to be separated by low intensity magnetic separation. Meanwhile, in comparison with the XRD pattern of iron ore tailings, the peak of calcite was getting lower; it indicated that $CaCO_3$ in the sample decompounded. Moreover, the pattern of kaolinite disappeared.

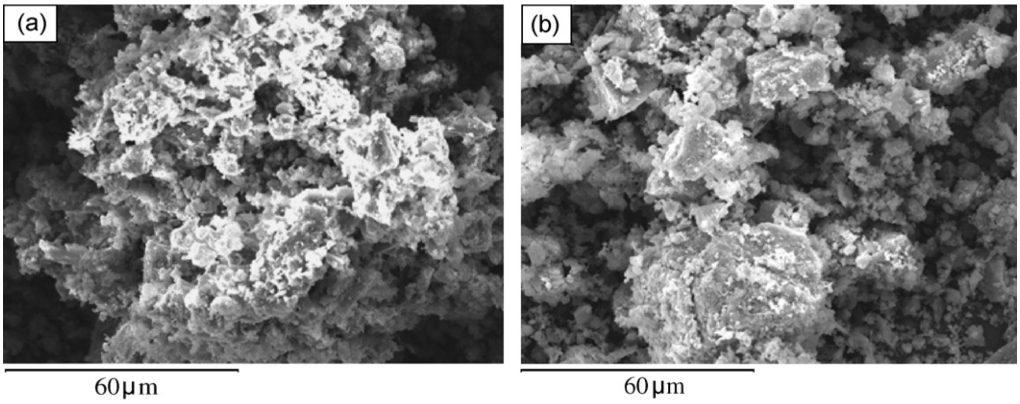

Fig. 7. The SEM images of roasted sample and raw material (a: roasted sample; b: raw material).

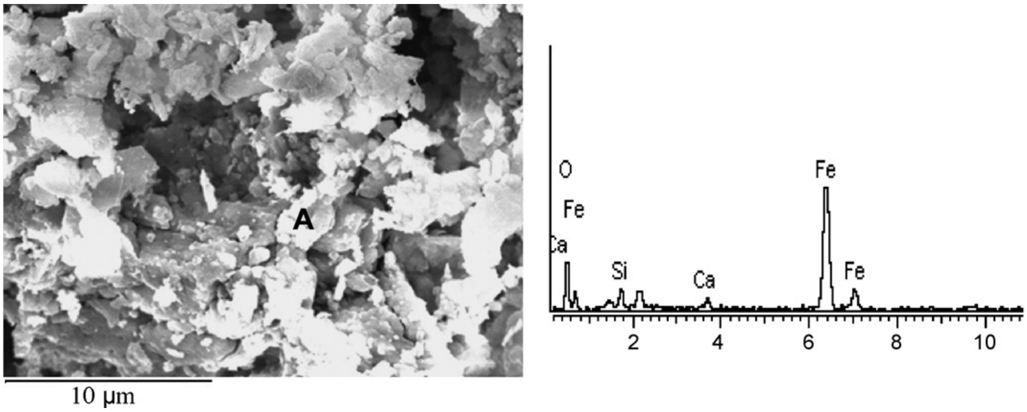

Fig. 8. The SEM image of roasted sample and its energy spectrum of A area.

3.2.2. SEM-EDS analysis

SEM observation was carried out by JSM-6460LV scanning electron microscope equipped with Be4-U92 energy spectrum detector. The SEM images of roasted sample (800 °C for 30 min, coal/iron ore tailings 1:100) and raw material were shown in Fig. 7. Besides, the energy spectrum of some area was shown in Fig. 8.

From Fig. 7, at the temperature of 800 °C for 30 min, the roasted sample was light sintered. With the evaporation of crystal water and volatilization of CO_2 generated in the reaction process, the roasted sample exhibited a porous and granularity increscent appearance, which was proved by the average particle sizes (d (0.5) of roasted sample 16.560 μm while d (0.5) of raw material 14.400 μm).

From the energy spectrum, Fe, Si and Ca were fine-disseminated together, which made them hard to be separated. So the process of milling roasted sample was necessary.

3.3. Analysis of magnetic concentrate

3.3.1. XRD analysis

The concentrated iron ore were separated from the roasted sample as above, and its XRD pattern was shown in Fig. 9.

From Fig. 9, magnetite was the main mineral phase of concentrated iron ore, but quartz also existed, which proved that iron and quartz were fine-disseminated complexly together and it is hard to be separated. In addition, a small amount of hydrogrossular was generated, that was because amorphous SiO_2, CaO (decompounded from calcite) and Al_2O_3 reacted in the water at the process of magnetic separation [24].

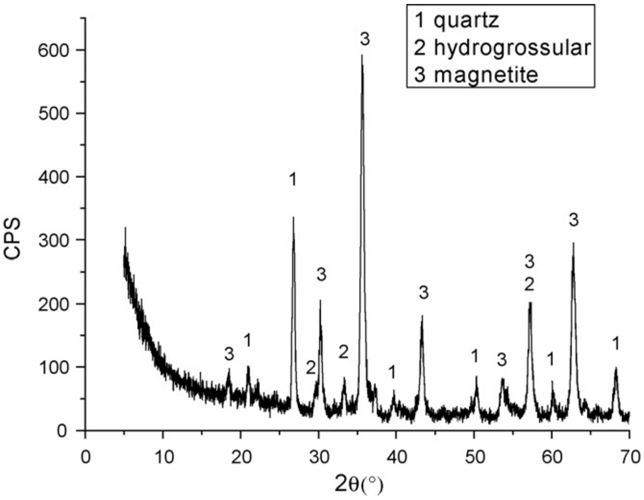

Fig. 9. XRD pattern of magnetic concentrate.

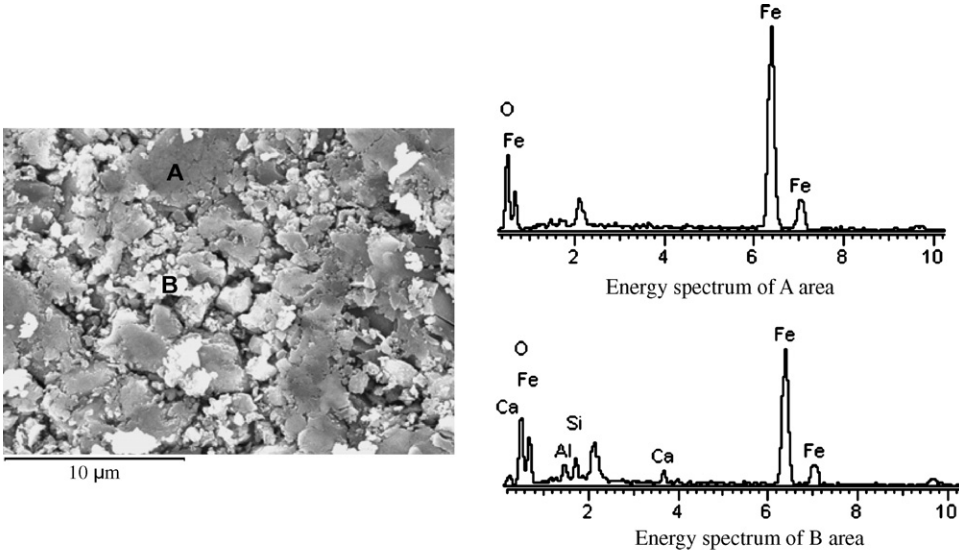

Fig. 10. The SEM image of magnetic concentrate (5000×) and its energy spectrum of A and B areas.

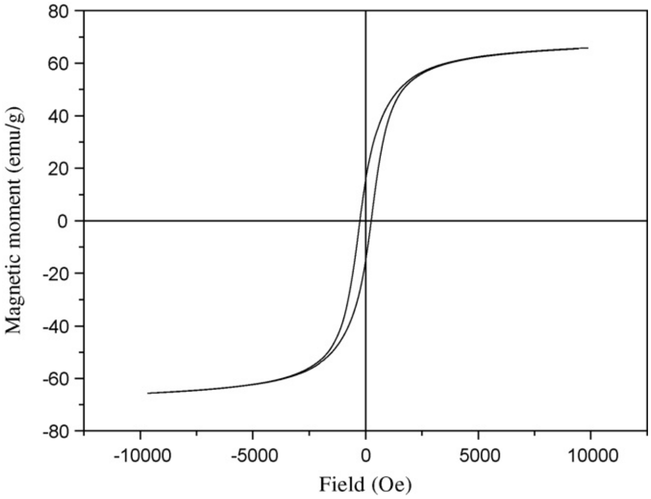

Fig. 11. The magnetic hysteresis loop of concentrated iron ore.

3.3.2. SEM-EDS analysis

The SEM image of magnetic concentrate and its energy spectrum of some areas were shown in Fig. 10.

From Fig. 10, the dark areas were mostly Fe_3O_4 and Si, Ca, Al were included in magnetite at bright areas, which was in accord with XRD analysis.

3.3.3. Magnetic property

The magnetic hysteresis loop of concentrated iron ore was shown in Fig. 11, tested by Vibrating Sample Magnetometer (Model: BHV-50HTI). The saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) were 65.748 emu/g, 15.363 emu/g, 252.43 G, respectively. Because of the high M_r, the problem of magnetic particle aggregation was unavoidable, which influenced the grade of magnetic concentrate.

3.4. Discussion

In this technology, the aim of magnetizing roasting is reducing hematite to magnetite, which is much easier to recover by low intensity magnetic separation method. While the nature of the reduction products is dictated by the roasting conditions. Bitsianes and Joseph [25] identified four phases (iron, wustite, magnetite and hematite) in samples partially reduced in hydrogen at 650 and 850 °C, and three phases (iron, magnetite, and hematite) in samples reduced at 500 °C. Because of the weakly magnetic of wustite which is difficult to recycle, so it has strict reducing conditions. That is why there is little literature about using magnetic roasting method to recycle iron from iron ore tailings, although the technology of magnetic roasting has been widely developed.

Technologies for iron recovery from tailings have already been studied in laboratory, but the industrial application is limited due to the high production cost. Meanwhile, the content of iron in the iron ore tailings is generally very low, making reuse seems valueless. Moreover, the residues after iron recovery are massive, and they also face the problem of storage and secondary pollution. In order to comprehensively utilize iron ore tailings, the best way is to produce building materials using them, and this part of study will be introduced in the next paper Part 2: The residues after iron recovery from iron ore tailings to prepare cementitious material. In a word, if we stand on the innovative idea that recycling iron in the process of using iron ore tailings to prepare cementitious material, it may have good future of industrial application.

4. Conclusions

(1) Major chemical compositions of iron ore tailings were SiO_2, Fe_2O_3, CaO and Al_2O_3. Quartz, hematite, calcite, mica and kaolinite existed in iron ore tailings as main phases, and most of iron and quartz were fine-disseminated complexly together, which was hard to be separated.

(2) The ratio of coal to iron ore tailings, roasting temperature, reduction time, and milling time of roasted samples were four main factors which had effects on recovery of iron minerals. Through corresponding four groups of experiments, optimum reduction reaction conditions were obtained as the following: ration of coal: iron ore tailings as 1:100, roasting at 800 °C for 30 min, and milling 15 min of roasted samples. Under the optimum reaction conditions, the two main parameters of the recovery process of magnetically separated concentration were obtained as the following: the grade of magnetic concentrate of 61.3% Fe and iron minerals recovery rate of 88.2%.

(3) This technology of using magnetizing roasting to recycle iron can be extended to other iron-containing waste, such as red mud, pyrite cinder and so on.

(4) The results demonstrated the feasibility of this technology for iron recovery, and it is a good beginning for comprehensive utilization of iron ore tailings.

Acknowledgments

The authors thank Analytical and Testing Center of Department of Materials Science and Engineering, Tsinghua University, which supplied us the facilities to fulfill the measurement. The authors also would like to thank to teacher Weirui Xu for his help of experiment.

References

[1] S. Zhang, X. Xue, X. Liu, P. Duan, H. Yang, T. Jiang, D. Wang, R. Liu, Current situation and comprehensive utilization of iron ore tailing resources, J. Min. Sci. 42 (2006) 403–408.
[2] K.-K. Kim, K.-W. Kim, J.-Y. Kim, InS. Kim, Y.-W. Cheong, J.-S. Min, Characteristics of tailings from the closed metal mines as potential contamination source in South Korea, Environ. Geol. 41 (2001) 358–364.
[3] M.K. Ghose, P.K. Sen, Characteristics of iron ore tailing slime in India and its test for required pond size, Environ. Monit. Assess. 68 (2001) 51–61.
[4] T.N. Gzogyan, S.L. Gubin, S.R. Gzogyan, N.D. Mel'nikova, Iron losses in processing tailings, J. Min. Sci. 41 (2005) 583–587.
[5] J. Matschullat, R.P. Borba, E. Deschamps, Human and environmental contamination in the Iron Quadrangle, Appl. Geochem. 15 (2000) 193–201.
[6] S. Prakash, B. Das, J.K. Mohanty, R. Venugopal, The recovery of fine iron minerals from quartz and corundum mixtures using selective magnetic coating, Int. J. Miner. Process. 57 (1999) 87–103.
[7] I. Licsko, L. Lois, G. Szebenyi, Tailings as a source of environmental pollution, Water Sci. Technol. 39 (1999) 333–336.
[8] A.A. Sirkeci, A. Gul, G. Bulut, F. Arslan, G. Onal, A.E. Yuce, Recovery of Co, Ni, and Cu from the tailings of Divrigi Iron Ore Concentrator, Miner. Process. Extr. Metall. Rev. 27 (2006) 131–141.
[9] S.K. Das, Sanjay Kumar, P. Ramachandrarao, Exploitation of iron ore tailing for the development of ceramic tiles, Waste Manage. 20 (2000) 725–729.
[10] S. Zhang, X. Xue, Z. Jin, Current situation and comprehensive utilization of iron ore tailings resources in our country, J. Mater. Metall. 4 (2004) 241–245 (in Chinese).
[11] M. Yan, L. Bai, Y. Zhang, J. Zhang, Current situation, problems and countermeasures of comprehensive utilization of iron tailings in China, Exp. Info. Min. Indus. 7 (2008) 9–13 (in Chinese).
[12] H.T. Shen, B. Zhou, et al., Roasting-magnetic separation and direct reduction of a refractory oolitic-hematite ore, Min. Met. Eng. 28 (2008) 30–43 (in Chinese).
[13] K. Hanumantha Rao, K.S. Narasimhan, Selective flocculation applied to Barsuan iron ore tailings, Int. J. Miner. Process. 14 (1985) 67–75.
[14] Y. Wang, J. Ren, The flotation of quartz from iron minerals with a combined quaternary ammonium salt, Int. J. Miner. Process. 77 (2005) 116–122.
[15] S. Song, S. Lu, A. Lopez-Valdivieso, Magnetic separation of hematite and limonite fines as hydrophobic flocs from iron ores, Miner. Eng. 15 (2002) 415–422.
[16] F. Satoshi, Magnetic separation method for continuous separation process, J. Cryog. Soc. Jpn. 37 (2002) 321–327.

[17] G.G.O.O. Uwadiale, Flotation of iron oxides and quartz. A review, Miner. Process. Extr. Metall. Rev. 11 (1992) 129–161.

[18] G.G.O.O. Uwadiale, R.J. Whewell, Effect of temperature on magnetizing reduction of Agbaja Iron Ores, Metall. Trans. B 19 (1988) 731–735.

[19] B. Chen, The Technology of Magnetic Electricity Mineral Processing, China Metallurgical Industry Press, Beijing, 2007 (in Chinese).

[20] Y.K. Liu, X.G. Mei, Study on coal-based direct reduction of high-iron-content red mud, Sintering Pell. 20 (1995) 5–9 (in Chinese).

[21] S. Zhou, J. Liu, Laboratory scale mineral processing research on a complex iron ore with Fe-minerals finely distributed, Nonferrous Met. (Min. Proce. Sec.) 1 (2008) 19–22 (in Chinese).

[22] J.F.M. Stephens, B. Langston, A.C. Richardson, The reduction–oxidation process for the treatment of taconites, J. Met. 5 (1953) 780–785.

[23] Z. Cui, Q. Liu, T.H. Etsell, Magnetic properties of ilmenite, hematite and oilsand minerals after roasting, Mine. Eng. 15 (2002) 1121–1129.

[24] R. Siauciunas, A. Baltusnikas, Influence of SiO_2 modification on hydrogarnets formation during hydrothermal synthesis, Cem. Concr. Res. 33 (2003) 1789–1793.

[25] G. Bitsianes, T.L. Joseph, Solid phase identification in partially reduced iron ore, J. Met. 5 (1953) 1641–1647.