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LABORATORY STUDY ON MAGNETIZATION REDUCTION OF CO

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Abstract

In this study, magnetizing roasting in fluidized bed was employed to separate iron minerals from red mud. The effect of treatment conditions on product quality was investigated. In addition, the phase transformation, changes in magnetism, and microstructures were studied by thermodynamic analysis, chemical analysis, X-ray diffraction technique (XRD), vibrating sample magnetometer (VSM), and optical microscopy. The magnetic concentrates with the total iron grade of 57.65% and recovery of 90.04% were obtained under the optimum conditions. XRD and chemical analysis demonstrated that 92% iron minerals in red mud converted to magnetite. VSM further confirmed that the magnetism of roasting products was strongly enhanced, and the specific susceptibility increased from 1.9×10^{-5} m^3/kg to 2.9×10^{-4} m^3/kg after magnetizing roasting. Hence, fluidized magnetizing roasting is an effective technology for recovering iron minerals from high-iron red mud.

Keywords: *High-iron red mud; Magnetizing roasting; Fluidized bed; Hematite; Magnetite*

1. Introduction

Red mud (bauxite residue) is a solid waste produced in the process of alumina extraction from bauxite [1]. Since the solid waste contains iron oxides that contribute to the characteristic brick red color, it is called “red mud.” Depending on the quality of the raw material processed and the alumina extraction efficiencies, approximately 1–2.5 ton of red mud is generated per ton of produced alumina [2]. More than 70 million ton of red mud is discharged to the environment every year all over the world, leading to the demand for better environmental protection [3].

Many approaches have been reported to utilize the red mud as a resource for environment-friendly application [4-6]. In most of these approaches, the technology applied to separate Fe_2O_3 from red mud is the key. This is because the content of Fe_2O_3 in red mud is about 10–30%, even up to 50–60% in some cases. Many technologies have been proposed for the utilization of iron minerals from red mud, such as separation by high-gradient superconducting magnetic separation (HGSMS) system [7], microwave reductive roasting process followed by wet magnetic separation [8], direct reduction at high temperatures in reducing atmosphere [9-12], reduction-sintering and then magnetic beneficiation [13, 14], leaching iron minerals with acid [3, 15-18], as well as magnetizing roasting with magnetic separation [19, 20]. A comparison of these methods indicates that magnetizing roasting has more advantages. However, it was found that the conventional roasting equipment is inefficient, consumes high energy, and is uneconomical when applied at an industrial scale [21]. In contrast, previous studies showed that the fluidized bed technology provides the advantages of uniform temperature and high efficiency of heat and mass transfer. The hematite in iron ores can be converted to magnetite and magnetic properties will be greatly enhanced by using fludized magnetization raosting [22]. The fluidized bed technology is being widely used in many industries and fields of applications [23-25].

Based on these reports, we developed a fluidized bed reactor for magnetizing roasting of iron minerals in red mud. Under this process, iron minerals can be transformed into magnetite with the help of reducing atmosphere, and then the resulting magnetite can be collected by magnetic separation. In this study, we experimentally investigated the effects of reduction parameters in fluidized bed and the separation factors on product quality. Phase transformation and magnetism changes and the microstructure of red mud and roasting products were studied by thermodynamic analysis, vibrating sample magnetometer (VSM), X-

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ray diffraction technique (XRD), and optical metallographic microscope.

2. Materials and methods

2.1 Raw materials

The red mud samples discharged by the Bayer process were collected from alumina plants in Shandong, China, which were afterwards dried at 110 °C for 4 h before testing. The chemical composition and X-ray diffraction pattern of these red mud samples are shown in Table 1 and Fig. 1, respectively. The results indicate that the iron content in the red mud samples is 44.32%, which is mainly distributed in hematite. Other mineral phases consist of gibbsite, boehmite, and quartz.

Table 1. *Chemical analysis of the main components of red mud (wt%)*

Constituents	TFe	FeO	Al_2O_3	SiO_2	CaO	MgO	P	S	LOI
Content (wt%)	44.32	0.66	13.39	3.23	0.93	0.19	0.1	0.106	11.23

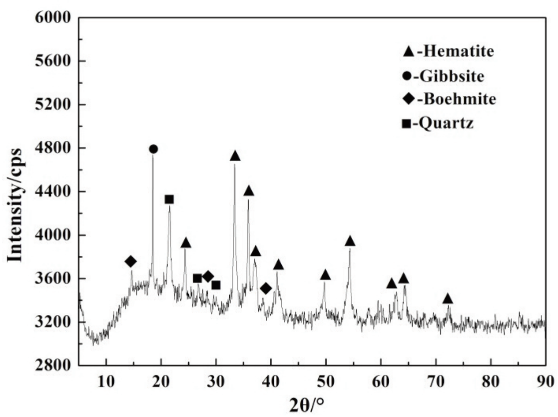

Figure 1*. XRD pattern of raw red mud samples*

2.2 Roasting experiments

The roasting experiments were performed in a customized bench-scale fluidized bed as shown in Fig. 2. This reactor consists of a fluidized bed, an electric furnace, a temperature controller, and a gas supply system. The fluidized bed reactor is made of high-purity quartz glass and is 25 mm in inner diameter. The experiment was initiated by feeding exactly 15 g samples and by heating the reactor to a desired temperature at a rate of 10 °C/min. Then, the mixed gas, including nitrogen and carbon monoxide, was introduced from the gas supply system at a constant flow rate of 500 mL/min.

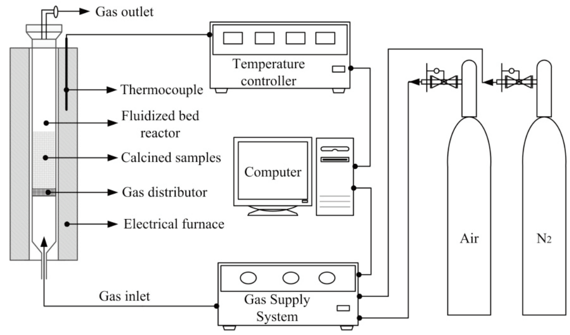

Figure 2*. Schematic diagram of the bench-scale fluidized bed reactor*

2.3 Characterization

The roasted products were milled for a certain particle size by rod mill (XMB-70). Then, these were separated into magnetic concentrates and tailings by a magnetic separator (XCSG-Φ50 mm) with a working magnetic field 80 kA/m. The iron concentrate and tailing were filtered and dried for analyses. The grades and chemical phases of concentrates and tailings were analyzed by chemical method, and the recovery rate of iron was calculated according to the grade and mass balance. For magnetic properties, the magnetic measurement was carried out by a vibrating sample magnetometer (VSM, JDAW-2000D) at room temperature with an applied magnetic field 800 kA/m. Detailed mineralogical phase information of roasted products was detected by an X-ray diffractometer (PANalytical X'pert PW3040) with Cu Kα radiation. A Leica DM4 P optical microscope was used to study the association of hematite with magnetite in the roasted products by examining the polished thin sections.

3. Thermodynamic analysis

With carbon monoxide (CO) introduced to the magnetizing roasting process, the relationships between the temperature and Gibbs free energy of reactions of the main constituents (Fe_2O_3, Al_2O_3, SiO_2, and MgO) in red mud (with CO under standard conditions) are illustrated in Fig. 3. As shown in Fig. 3, Al_2O_3, SiO_2, and MgO in red mud cannot react with CO when the temperature is below 1000 K. However, CO is a good reducing agent and reacts with Fe_2O_3. The probable chemical reactions occurring during Fe_2O_3 reduction are shown through Equations (1)–(4). The equilibrium diagram of reduction of iron oxides by CO is given in Fig. 4. As shown in Fig. 4, the equilibrium curves of reactions given by reactions (1)–(4) divide the ferric oxide equilibrium phase graph into four regions of Fe_2O_3, Fe_3O_4, FeO, and Fe, respectively. Fig. 4 shows that the roasting temperature and CO concentration control are important. When the temperature exceeds 900 K, the curve enters the stable area of FeO with reaction (3), which means that Fe_3O_4 will be reduced to FeO. The curve enters the stable area of Fe with reaction (2), where the concentration of CO exceeds 40%. Once these reactions take place, the ferric minerals have no magnetism after magnetizing roasting, which is not favorable for iron recovery [13, 26]. Therefore, the roasting conditions should be controlled to ensure Fe_2O_3 is reduced adhering to reaction (1) to the maximum extent possible. As shown in the equilibrium phase diagram (Fig. 4), the roasting temperature should be controlled below 600 °C, and the concentration of CO should be controlled below 40% in order to convert ferric compounds to form magnetite.

$$3Fe_2O_3(s)+CO(g)=2Fe_3O_4(s)+CO_2(g) \quad (1)$$

$$1/4Fe_3O_4(s)+CO(g)=3/4Fe(s)+CO_2(g)(T<843K) \quad (2)$$

$$Fe_3O_4(s)+CO(g)=3FeO(s)+CO_2(g)(T<843K) \quad (3)$$

$$FeO(s)+CO(g)=Fe(s)+CO_2(g)\ (T<843K) \quad (4)$$

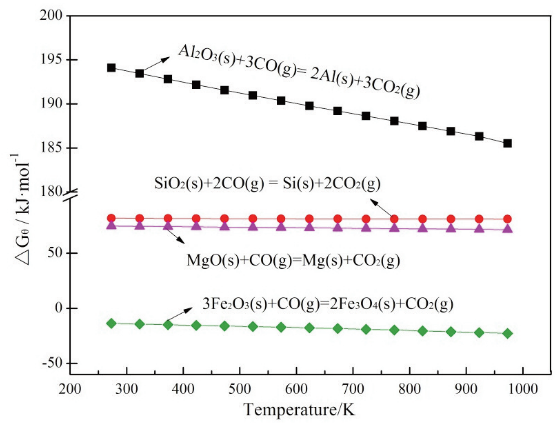

***Figure 3**. Relationship between temperature and Gibbs free energy of reactions*

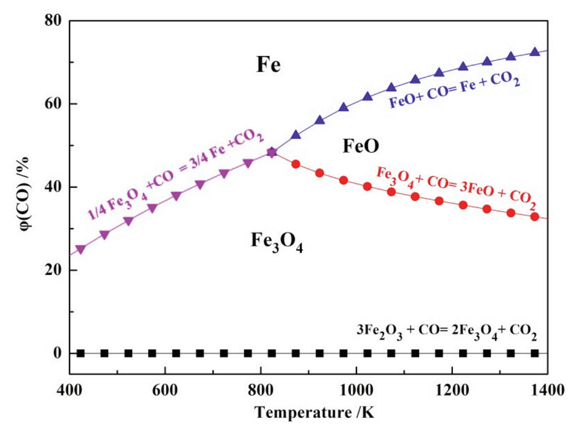

***Figure 4**. Equilibrium phase compositions for reduction of iron oxides by CO*

4. Results and discussion

4.1 Effects of roasting temperature on magnetizing roast

The samples were roasted for 15 min with CO concentration of 30% under different temperatures varying from 500 °C to 600 °C. The roasting products were milled at -38 μm occupying 60%, and then, they were separated by a magnetic separator. The effects of roasting temperatures on the grade and iron recovery of magnetic concentrates are presented in Fig. 5. As shown in Fig. 5, an increase in the roasting temperature from 500 °C to 540 °C results in a significantly improved iron recovery of the magnetic concentrates, from about 87% to 92.72%. In addition, the iron grade increases from about 56% to 56.51%. The recovery and grade present a stable tendency when the temperature is above 540 °C. However, the iron recovery of magnetic concentrates is reduced slightly for temperatures above 600 °C, which may be attributed to FeO formation at high roasting temperatures. Considering the separation performances of the roasting products and the increased energy consumption at higher roasting temperatures, a temperature of 540 °C is recommended in fluidized bed roasting.

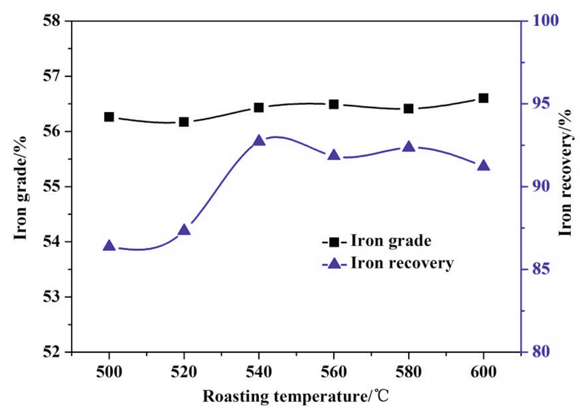

***Figure 5**. Effect of magnetizing roasting temperature on separation performances*

4.2 Effects of CO concentration on magnetizing roast

In order to investigate the effects of CO concentration on the separation performances of the roasting products, different CO concentrations (from 10% to 50%) were studied in the fluidized bed. Other experimental parameters were kept at the following values: roasting temperature at 540 °C, roasting time at 15 min, milled at -38 μm occupying 60% of the roasting products obtained from magnetic separation. The experimental results are shown in Fig. 6. There is a statistically significant change in the iron recovery of magnetic concentrates for an increase in the collector dosage from 79.55% to 93.02% with an increase in the CO concentration from 10% to 30%. It can also be observed that the iron recovery and grade of magnetic concentrates become gradually stabilized after CO concentration is over 30%. It can be inferred that the CO concentration in fluidized bed roasting is about 30%, during which deoxidization reaction of ferrous oxides is mostly completed.

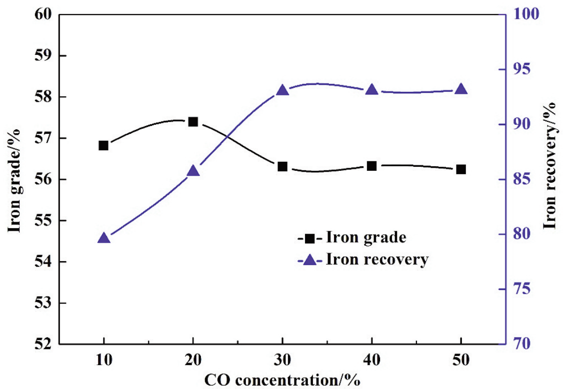

***Figure 6**. Effects of CO concentration on separation performances*

4.3 Effects of roasting time on magnetizing roast

The samples were roasted at 540 °C with a CO concentration of 30% for different durations (from 5 to 25 min). The roasting products were milled at -38 μm occupying 60%, and then, they were separated by a magnetic separator. The effects of roasting times on the grade and iron recovery of magnetic concentrates are presented in Fig. 7. As shown in Fig. 7, there is a nonlinear relationship between the iron recovery and roasting time, where the iron reduction achieves a peak when the roasting time is about 15 min. The iron recovery increases rapidly as the roasting time is extended from 5 min to 15 min. Beyond a reduction time of 15 min, both the iron recovery and the grade

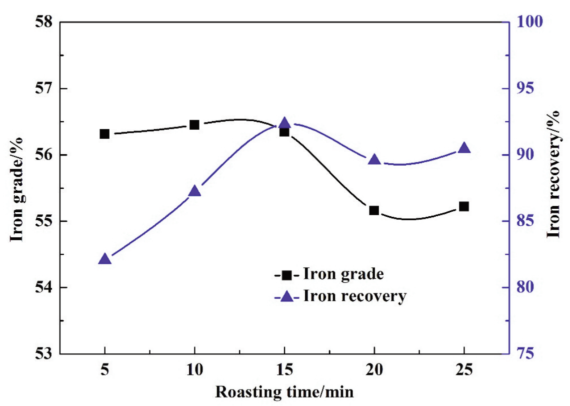

***Figure 7**. Effects of magnetizing roasting time on separation performances*

decline. It indicates that the optimum reduction is 15 min when the reduction reaction of ferrous oxides is mostly completed at 540 °C for 15 min, and the iron grade and iron recovery are 56.35% and 92.32% respectively.

4.4 Effects of grinding fineness on magnetic separation

The grinding fineness of roasting products exerts an important effect on the magnetic separation process to obtain iron concentrates and tailings. When the red mud is roasted at 540 °C for 15 min under a CO concentration 30%, Fig. 8 shows the effects of

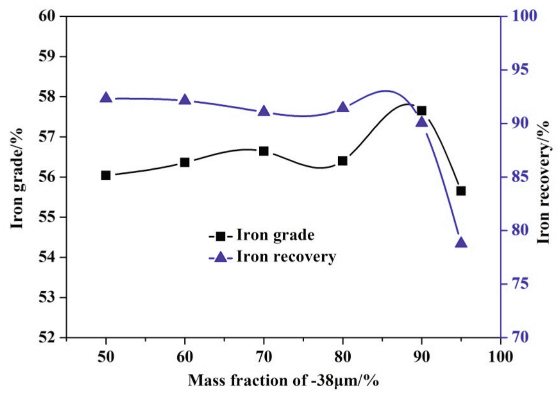

***Figure 8**. Effects of grinding fineness of roasting products on magnetic separation*

grinding fineness on the iron grade and recovery of magnetic concentrates. As shown in Fig. 8, the iron grade increases to 57.65% with 0.11% phosphorus content, and the iron recovery decreases to 90.04% slightly with the increasing fineness contents of -38 μm occupying from 60% to 90%. This is mainly because of the sufficient disaggregation of magnetite and gangue minerals. With the increase of -38 μm contents in the roasting products, over-grinding becomes more severe when these contents comprise more than 95%. During the magnetic separation processes, over-grinding magnetite cannot be collected into concentrates, which reduces the iron recovery and iron grade of the magnetic concentrates. This indicates that the optimum grinding fineness of the roasting products for magnetic separation is -38 μm contents comprising about 90%.

4.5 Phase transformation in magnetizing roasting

The forms of occurrences of iron minerals and gangue minerals in the roasting products and raw materials were investigated by X-ray diffraction (XRD) pattern as shown in Fig. 9. The iron minerals mostly exist in the form of magnetite, while the red

Table 2. *Chemical phases of Fe and its distribution of products before and after roasting (wt%)*

Iron phase		Hematite & limonite	Magnetite	Carbonate	Sulfide	Silicate	Total Fe
Before roasting	Content	42.61	0.59	0.19	0.21	0.79	44.39
	Occupancy	95.99	1.33	0.43	0.47	1.78	100
After roasting	Content	2.39	47.82	0.08	0.11	0.42	50.82
	Occupancy	4.7	94.1	0.16	0.22	0.83	100

mud contains mainly hematite (before roasting). This is confirmed by the previous literature [27]. In addition, the intense peak of gibbsite and boehmite in the red mud completely disappear, and the primary diffraction peak of quartz degrades after roasting. However, the concrete form of iron compounds cannot be clearly identified from the XRD patterns. The changes in the iron chemical phase are presented in Table 2. The iron chemical phase compositions listed in Table 2 show that the iron phase in red mud (before roasting) and the products (after roasting) are clearly different. The magnetite contents increase from 0.59% to 47.82%, and the occupancy increase from 1.33% to 94.10% after magnetizing roasting in the fluidized-bed reactor. When 42.60% hematite in red mud decreases to 2.39% after roasting, this indicates that over 92% of iron mineral has converted to magnetite and can be separated to magnetic concentrates by magnetic separation. Consequently, the magnetic behavior of iron minerals in red mud and roasting products should be investigated in detail to determine the magnetism transformation and separation effects in the magnetic separation process.

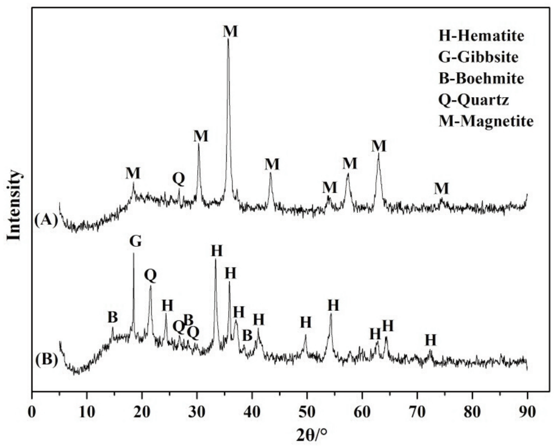

Figure 9. *XRD patterns of (a) red mud and (b) roasting products*

4.6 Changes of magnetism in magnetizing roasting

The specific magnetization and susceptibility of red mud and roasting products were further measured using the vibrating sample magnetometer (VSM). The magnetization curves are shown in Fig. 10. The magnetization curves of red mud exhibit a unique behavior because of its linear relationship with the magnetization and field strength (Fig. 10 (a)). The specific magnetization increases with an increase in the field strength. The specific susceptibility is very low and the maximum is about 1.9×10^{-5} m^3/kg under the applied magnetic field of 700 kA/m. The magnetization curves of red mud with extremely low specific susceptibility demonstrate that the red mud is a weakly magnetic resource, which cannot be efficiently separated by magnetic separation. It can be seen from Fig. 10 (b) that the specific susceptibility of roasting products increases to about 2.9×10^{-4} m^3/kg at a magnetic field of 700 kA/m. The magnetic property

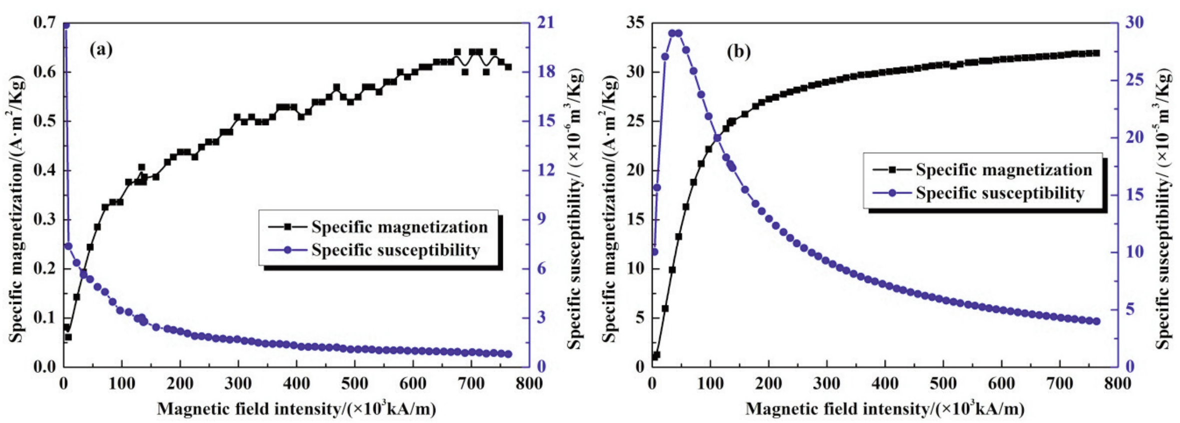

Figure 10. *Magnetization curves of (a) raw red mud sample and (b) roasting products*

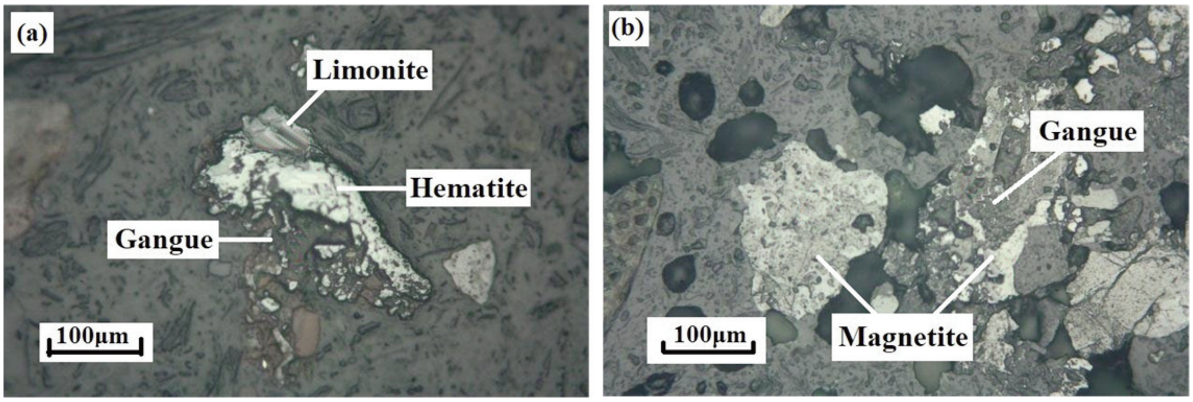

Figure 11*. Optical microstructure images of (a) red mud and (b) roasting products*

of the roasting products is enhanced and it achieves a magnetic saturation. This indicates a degree of ferromagnetism in the sample. This ferromagnetism occurs because most of the mineral hematite in the red mud is reduced to magnetite after magnetizing roasting in the fluidized-bed reactor [28]. These results indicate high efficiency performance of the magnetic separation process for roasting products, which can yield iron recovery of over 92%.

4.7 Microstructure evolution in magnetizing roasting

The morphologies of red mud and roasting products are illustrated in Fig. 11 to verify the association of iron minerals and gangue minerals. The iron minerals in the red mud are mainly hematite and limonite, and form intergrowth with gangue minerals. However, it can be seen that the existed iron minerals are primarily magnetite in the roasting products because of magnetizing roasting in the fluidized-bed reactor. Coarse and fine magnetite particles are found in the roasting products, and there exists a certain amount of intergrowth with gangue minerals. Therefore, the products require reasonable grinding fineness in magnetic separation for realizing adequate mineral dissociation and for preventing over grinding, which is helpful in collecting the magnetite to the concentrates. The above findings are confirmed by the separation results presented in Section 4.5.

5. Conclusions

The performance of a fluidized bed magnetizing roasting process applied in red mud for the recovery of iron minerals was studied. The effects of treatment conditions on the quality of roasting products are detailed. Thermodynamic analysis, chemical analysis, X-ray diffraction technique (XRD), vibrating sample magnetometer (VSM), and optical metallographic microscope were used to analyze the reduction mechanism. Based on the results of this study, the following conclusions have been drawn:

• The fluidized bed is an effective technology for realizing magnetizing roasting and facilitating the conversion of hematite to magnetite. The roasting temperature and CO concentration are the key operational parameters in magnetizing roasting according to thermodynamic analysis.

• Magnetizing roasting and separation tests indicate that the magnetic concentrates with iron grade of 57.65% and recovery of 90.04% can be obtained under the following operating conditions: roasting temperature at 540 °C, roasting time at 15 min, CO concentration at 30%, and grinding fineness of the roasting products at -38 μm comprising 90%.

• The thermodynamic, chemical, XRD, VSM, and microscopy analysis demonstrate that over 90% iron minerals in red mud can be converted to magnetite, and weak magnetism is enhanced to ferromagnetism in the samples with the maximum specific susceptibility increasing from about 1.9×10^{-5} m^3/kg to 2.9×10^{-4} m^3/kg, which are in good agreement with the magnetic separation experiments.

The results indicate that the fluidized bed has good potential for collecting iron minerals from high-iron red mud. This novel technology would allow comprehensive utilization of high-iron red mud.

Acknowledgement

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LABORATORIJSKA STUDIJA O SMANJENJU MAGNETIZACIJE UGLJEN MONOKSIDA

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Apstrakt

U ovom istraživanju primenjeno je fluidizacijsko magnetizaciono prženje za odvajanje minerala gvožđa iz crvenog mulja. Ispitivan je uticaj uslova tokom postupka na kvalitet proizvoda. Pored toga, XRD (rentgenska difrakcija), VSM (magnetometar sa vibrirajućim uzorkom), OM (optička mikroskopija), kao i termodinamička i hemijska analiza su korišćene za ispitivanje fazne transformacije, promena u magnetizmu i promena u mikrostrukturi. Pod optimalnim uslovima, dobijeni su magnetni koncentrati koji sadrže 57,65% gvožđa sa iskorišćenjem od 90,04%. XRD i hemijska analiza su otkrile da se 92% minerala gvožđa konvertovalo u magnetit. VSM analizom se utvrdilo da se magnetizam prženih proizvoda znatno pojačao, a da se specifična susceptibilnost povećala sa 1.9×10^{-5} m^3/kg na 2.9×10^{-4} m^3/kg nakon magnetizacionog prženja. Stoga, fluidizacijsko magnetizaciono prženje se može smatrati efikasnom tehnologijom za dobijanje minerala gvožđa iz crvenog mulja bogatog gvožđem.

Ključne reči: *Crveni mulj bogat gvožđem; Magnetizaciono prženje; Fluidizacijski sloj; Hematit; Magnetit*