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A novel process for extraction of iron from a refractory red mud

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Abstract: Red mud is a kind of solid waste produced during alumina extraction from bauxite. To extraction valuable iron from red mud, the technology of adding sodium sulfate-segregation roasting-magnetic separation to treat red mud was developed. During the paper, the effects of various process parameters on the extraction of iron by segregation roasting-magnetic separation were studied, and the phase transformation behavior and microstructure of iron are explored. Repeated test results showed that magnetic concentrate (mass percent), T_{Fe} of 80.29 % and overall iron recovery of 92.08 %was obtained. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) results indicated that after the segregation roasting, the hematite was transformed into a new metal phase consisting mainly of metallic iron and magnetite. The addition of sodium sulfate during the segregation roasting can obviously improve the efficiency of segregation roasting-magnetic separation for iron extraction.

Keywords: red mud, sodium sulfate, segregation roasting, magnetic separation, iron recovery

1. Introduction

Red mud is a residue generated during alumina production. According to the Bayer process and the composition of bauxite, approximately 1.0-1.5 tonnes of red mud is produced for each ton of alumina recovered (Paramguru et al., 2004). At present, China's emissions of red mud exceed 30 million tonnes/year, and it is estimated that over 120 million tons of red mud are produced every year worldwide (Zhao et al., 2010). Due to the high alkalinity of red mud, long-term open-air accumulation of red mud will pollute the water supplies, air, and soil, which is one of the principal factors restricting sustainable development of the aluminum industry. Moreover, the treatment methods of red mud generally include building materials (Liu et al., 2009; Kim et al., 2019), environmentally friendly raw materials (Chen et al., 2019), auxiliary additives (Liu et al., 2019) and filling materials (Li et al., 2019), but these treatments account for only 30% of the total red mud produced each year. Meanwhile, Red mud is rich in a variety of valuable elements, including Fe, Al, Sc and Ti, so it is a useful secondary polyvalent metal resource. For major iron-bearing minerals such as hematite and goethite in red mud, if efficient and reasonable utilization processes are developed, they will add economic value to the utilization of red mud. Therefore, numeric studies have been conducted to recycle iron from red mud worldwide.

Hematite and goethite are the main components of red mud, and magnetic separation is the basic method for iron recovery from red mud. However, direct magnetic separation is considered to be inefficient due to the diffusion of fine iron oxide. In addition, Different metallurgical methods such as the following have also been proposed, such as the iron nugget process (Archambo, 2020) was used to extract iron from iron minerals in red mud. Hardwood and softwood were used as the reducing agent. The iron nugget process can reduce iron oxides to metallic iron in a single step and separate it from gangue minerals. The iron grade of the produced iron nuggets is equivalent to that of blast furnace pig

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iron. the technology of direct reduction--magnetic separation was developed to treat red mud (Fan et al., 2015). The reduction of Fe_2O_3 in red mud to magnetic product (Fe) by direct reduction, while low-intensity magnetic separation is the most extensive way for concentrating the magnetized ores. Zhu etc. (2012) develop the technology of adding sodium carbonate reduction roasting magnetic separation to treat high-iron red mud. In the final concentrate obtained by this process, the grade of iron reached 90.87%, and the total iron recovery rate was 95.76%. The microwave reduction method was used to extract iron from iron minerals in red mud (Shrey et al, 2018; Xiao et al. 2020). Research shows that microwave reduction of red mud at 1000 ℃for 10 minutes, an iron concentrate with 48.5 wt.% iron content and 95% iron recovery rate can be achieved. The magnetic property of the red mud was significantly enhanced by microwave. Liu etc. (2016) adopted the reduction roasting-magnetic separation process to recover ferric oxide from red mud. The experimental results indicated that the iron recovery and the grade of total iron were 91% and 60%. Jayasankar etc. (2012) adopted plasma smelting using thermal plasma technology to produce pig iron from red mud. However, the research on the preparation of metal iron powder by chlorination separation after mixing red mud, chlorinating agent and reducing agent has not been reported yet.

At the same time, the high-grade iron concentrates obtained by adding additives in red mud roasting-magnetic separation process is a research hotspot in recent years. Sodium salts were proved to be favorable for the magnetic separation of metallic iron, through facilitating the reduction of iron oxides and the growth of metallic iron grains, during the roasting process. This is consistent with the findings of Li etc. (2014) on red mud roasting. Chun etc. (2014) research indicates, during the reduction roasting, additives (Na_2SO_4 and CaO) reacted with SiO_2 and Al_2O_3 of red mud, forming $Na_2Al_2(SiO_4)_2$, $Ca_2Al_2SiO_7$, $CaAl_2O_4$ and Ca_2SiO_4, which ameliorates the separation between iron and alumina during magnetic separation.

Herein, the novelty of this process, the segregation roasting method is a one-step replacement for the reduction roasting method that simultaneously separates metallic iron from the red mud. Segregation roasting can avoid the in-situ reduction of iron oxide in reduction roasting and improve the efficiency of iron extraction. The sodium salt is used to intensify the reduction of iron oxide, promote the growth of metal iron particles, and improve the magnetic separation efficiency. The effects of different process parameters on the final product quality and phase transition of iron ores during the segregation roasting process are discussed in detail, which provided a new avenue for the comprehensive utilization of red mud resources.

2. Materials and methods

2.1. Sample characteristics

The test red mud sample was derived from an alumina refinery in Yunnan Province, China. Red mud sampled from the red mud deposits had a higher moisture content. Therefore, it is necessary dried into blocks and grind it to a certain particle size of 0.15 mm to obtain its representative sample as an experimental material. The Sichuan coke was used as reductant (passing 0.25 mm), with fixed carbon of 84.4 wt.%, ash of 14.1 wt.% and volatile matter of 1.5 wt.%.

The samples were subjected to X-ray fluorescence spectrometry analysis (XRF), XRD and particle size composition analysis. The total iron concentration (T_{Fe}) of the samples was determined by XRF. Chemical analysis results show that compositions of red mud comprise Fe_2O_3, Al_2O_3, SiO_2, CaO, and Na_2O (as shown in Table 1), the metals that can be recycled from red mud are iron and titanium. The diffractogram of red mud is shown in Fig.1, Mineralogically, red mud has mainly phases of hydrogrossular ($Ca_3Al_2SiO_4(OH)_8$), hematite (Fe_2O_3) and quartz (SiO_2). See Table 2, 91.24 wt.% of the red mud passes through 0.074 mm. One of the typical characteristics of the red mud from Bayer process is the extremely fine size.

2.2. Methods

The red mud, chlorinating agent, reducing agent, water and additives were uniformly mixed in a certain proportion. It is processed into a briquette in balling press and placed in a corundum crucible (Φ = 75 mm × 68 mm), and then dried in a constant temperature drying oven. The capped corundum crucible

Table 1. Chemical composition of red mud (mass percent, %)

T_{Fe}	Al_2O_3	SiO_2	CaO	Na_2O	TiO_2	MgO	S	P
19.86	17.17	13.70	16.33	6.86	4.40	0.47	0.37	0.125

Table 2. Size analysis of red mud (mass percent, %)

Size fraction	<6.76 μm	6.76~38.00 μm	38.00~74.00 μm	>74.00 μm
Content	53.17	30.04	8.03	8.76

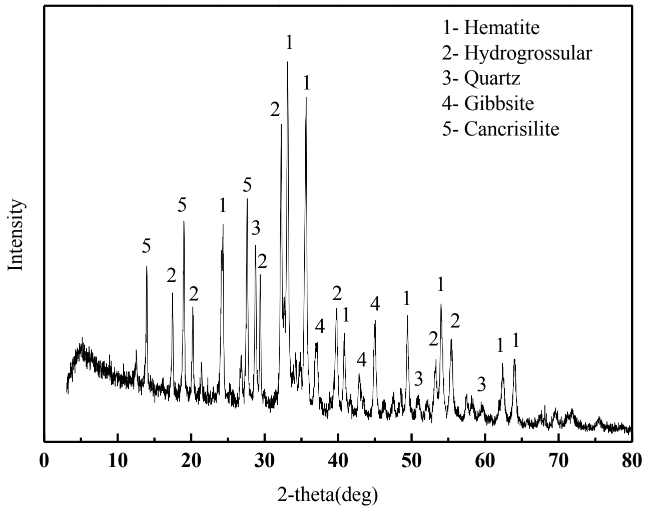

Fig. 1. XRD phase analysis of red mud

containing the sample was placed in a pre-heated box type resistance furnace. These mixtures were roasted to a certain time under the neutral or weak reducing atmosphere. The roasted ore were quenched with water, dried, was used in this study. 40g of roasted ore were finely ground in the cone ball rail of XMQ-Φ150×50, and then separated to produce magnetic +concentrate and tailings through a XCGS-13 magnetic tube under certain magnetic field intensity.

Finally, the roasted ore、 magnetic concentrate and tailings was performed by XRF analysis (PANalytical, Axios type), XRD analysis (Cu, X Pert pro, Panaco, Netherlands), SEM (Sigma300, Carl Zeiss, Germany) equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector (Ultra55, Carl zeissNTS GmbH, Germany) .The potassium chloride (KCl), sodium chloride ($NaCl$), barium chloride ($BaCl_2$), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), calcium oxide (CaO), calcium fluoride (CaF_2), sodium carbonate (Na_2CO_3), and sodium sulfate (Na_2SO_4) used in the study were of chemical grade. A flowchart of the process sees Fig. 2.

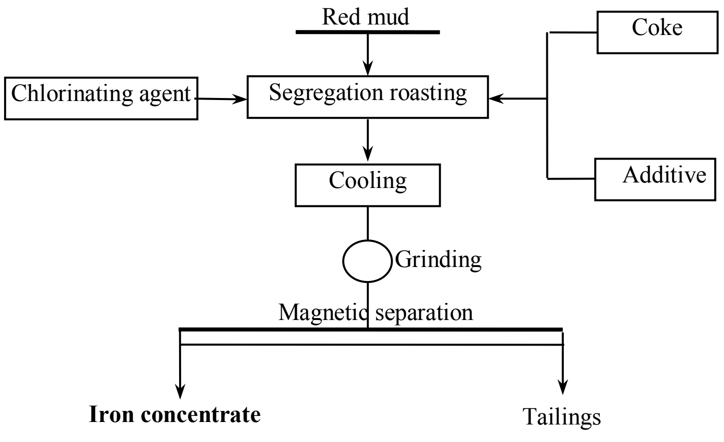

Fig. 2. Segregation roasting- magnetic separation test flow sheet

3. Results and discussion

3.1. Chlorinating agent types

The effect of the type of chlorinating agent on extraction of iron under the following conditions: red mud/chlorinating agent/reducing agent (coke) mass ratio of 100:15:15, were roasted 90 min at 1000 ℃, and the roasted ore by grinding up to 90 %passing 0.045 mm, and magnetic separation was performed at magnetic field intensity of 0.22 T (Fig. 3(a)).

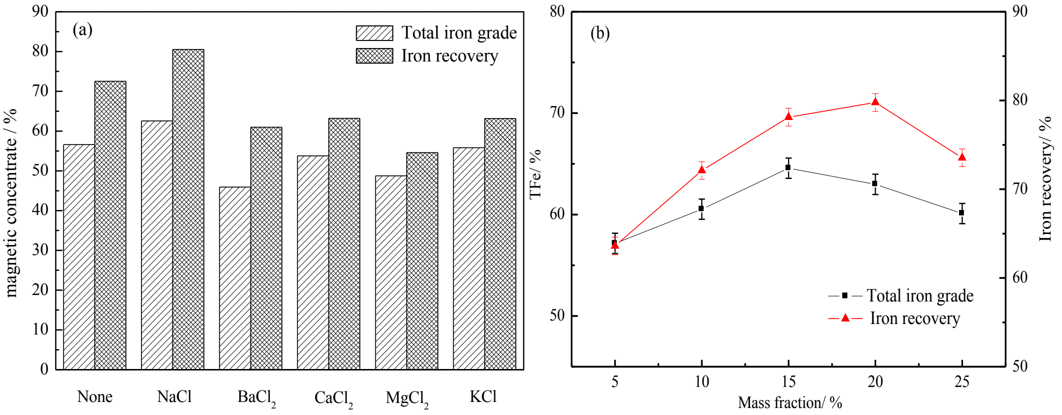

Fig. 3. Effects of the type of chlorination agent (a) and dosage of sodium chloride (b) on extraction of iron

The chlorinating agent was a critical component in the segregation roasting process. Under high temperature conditions, the solid chlorinating agent reacted with the water vapor, silica, and alumina to produce chlorine gas and hydrogen chloride(g). Hydrogen chloride gas reacted with the iron oxide in the red mud to transform into gaseous iron chloride (Xiao et al., 2019; Xiao et al., 2020). Experiments have shown that water vapor is a necessary condition for the decomposition of NaCl, and silica with alumina promote the reaction. From Fig. 3(a), different chlorination agents had different effects on the results of the segregation roasting. This is attribute to the inconsistent standard Gibbs free energies for the reaction of different chlorinating agents with silicon-aluminum compounds. The decomposition reactions of magnesium chloride, barium chloride and potassium chloride are easier to proceed at low and medium temperatures. Hydrogen chloride(g) reacts with iron oxide to produce ferric chloride(s), but it cannot be volatilized due to the low temperature, which reduces the reduction efficiency of ferric chloride. (Sui et al., 2015).

When sodium chloride was used as a chlorinating agent, the iron concentrate grade and recovery were the highest, 62.57% and 80.53% respectively. Compared with the reduction roasting (no chlorination agent was involved), the grade of iron concentrate exhibited an improvement, from 56.60% to 62.57%, and the recovery rate has also been improved. Therefore, high quality iron concentrate can be produced using the segregation roasting, sodium chloride was considered to be the most suitable chlorinating agent.

3.2. Chlorinating agent dosage

In this part of the study, the mass fraction of sodium chloride of 5, 10, 15, 20, 25 w.% and red mud/ reducing agent (coke) mass ratio of 100: 15 were to explore the effect of sodium chloride dosage on extraction of iron. The parameters of roasted 90 min at 1000 ℃, and the magnetic separation conditions are consistent with 3.1 (Fig 3(b)).

From Fig. 3(b), as the mass fraction of the sodium chloride increased, the T_{Fe} and iron recovery rate first increased and then decreased. When the mass fraction of sodium chloride was 15%, the maximum value of the iron grade was 64.57%; when the mass fraction of sodium chloride was 20%, the maximum value of the iron recovery was 79.77%, but the iron grade has dropped slightly. This occurred because an appropriate increase in the amount of sodium chloride is beneficial for the increase in the amount of hydrogen chloride and chlorine generated during the segregation roasting, which correspondingly increase the amount of ferric chloride formed (Pomiro et al., 2013). However, other elements such as magnesium, aluminum, sodium, etc. can also react with hydrogen chloride gas to produce magnesium chloride, aluminum chloride, and sodium chloride. This leads to a decrease in the subsequent reduction efficiency of ferric chloride and an increase in the cost of the chlorination agent (Xiao et al., 2020). Overall, the mass fraction of sodium chloride is 15 wt.%.

3.3. Reducing agent dosage

The influence of the mass fraction of coke on extraction of iron under the following conditions: red mud/ sodium chloride mass ratio of 100:15, were roasted 90 min at 1000 °C, and the magnetic separation conditions are consistent with 3.1 (Fig. 4).

From Fig. 4, as the mass fraction of coke increased, the iron grade and recovery rate first increased and then decreased. When the mass fraction of coke was 15%, the maximum amount of the iron grade was 65.00%, the maximum value of iron recovery was 80.49%. As reducing agent, coke plays a dual role of providing a reducing atmosphere and providing a metal chloride reduction carrier during the segregation roasting process (Halmann et al., 2012). Excessive reductants will cause the reaction between C and H_2O to generate excessive H_2 and CO, which will cause the in-situ reduction of iron oxide, thus affecting the effect of segregation roasting (Li et al., 2020). Considering these results, a coke mass fraction of 15% was determined to be the most appropriate.

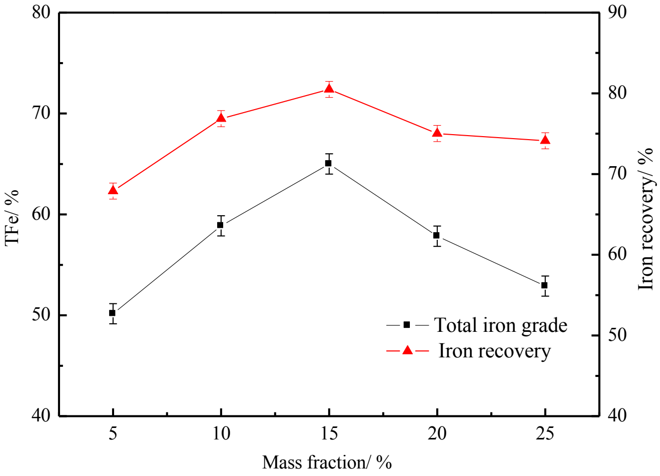

Fig. 4. Effects of the mass fraction of coke on extraction of iron

3.4. Segregation roasting time

Fig. 5(a) shows the effect of roasting time on extraction of iron under the following conditions: red mud/coke/sodium chloride mass ratio of 100:15:15, roasted at the temperature of 1000 °C for different roasting time.

When roasting time was 60 min, each iron reduction parameter achieving a peak. It was speculated that the optimum roasting time was 60 min, during which the reduction reaction of ferric chloride was mostly completed. When the roasting time was extended, iron concentrate grade and iron recovery rate are gradually decreasing. This is due to with the increase of the segregation roasting time, the reaction is relatively complete, but some of the generated metallic iron will react with silica, alumina, etc. to form fayalite and spinel, which affects the extraction effect of iron. Considering these results, segregation roasting time of 60 min was chosen. At this time, the grade and recovery of iron in the concentrate are 65.13% and 84.78%, respectively.

3.5. Segregation roasting temperature

The influence of the segregation roasting temperature on extraction of iron under the following conditions: red mud/coke/sodium chloride mass ratio of 100:15:15, were roasted 60 min at different temperatures of 800, 900, 1000 ,1100 and 1200 °C, and the magnetic separation conditions are consistent with 3.1 (Fig.5(b)).

The results in Fig. 5(b) indicate that as the roasting temperature increased from 800 °C to 1100 °C, the iron grade of concentrate increased significantly from 45.60% to 68.26%, iron recovery also increased to

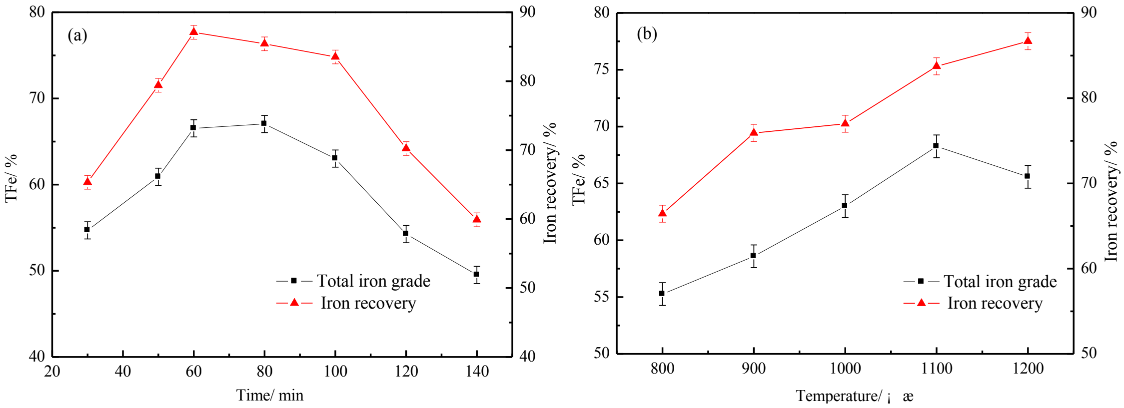

Fig. 5. Effect of roasting time (a) and roasting temperature (b) on extraction of iron

83.74%. Obviously, increasing the roasting temperature is beneficial to improve the iron separation index. This was due to the increase in temperature was beneficial for the formation of hydrogen chloride and at the same time increased the reaction rate, making the reaction more fully. From the temperature reached 1000 ℃, the recovery of iron is significantly improved. The reason for this is that the reduction reaction was the main reaction that occurred below 1000 ℃, and the in-situ reduction of iron oxide leads to lower iron extraction (Guo et al., 2018; Meng et al., 2018). When the temperature was higher than 1000 ℃, the iron oxide chlorination reaction was preferred and the ferric chloride diffused to the carbon surface and was reduced. When the temperature exceeds 1100 ℃, the iron recovery of a smaller increase in temperature may cause the energy costs to increase at the same time. Therefore, segregation roasting temperature of 1100 ℃ was the most appropriate.

3.6. Additive types

In other conditions unchanged, additive dosage is determined at 10 w.%, the effects of the type of additives on extraction of iron was carried out. As shown in Fig. 6(a), adding CaF_2, Na_2CO_3 and Na_2SO_4 can obviously improve the efficiency of segregation roasting-magnetic separation for iron extraction. On the one hand, the addition of sodium salt allows the alumina and silica preferentially react with additives to form nepheline and feldspar, thereby hindering the combination of alumina, silica and FeO, improving the reduction activity of FeO, and enhancing the reduction efficiency. Besides, the promotion effect of sodium salt is that it can destroy the structure of the ore, accelerate the formation of molten state, and promote the growth of iron particles. (Jiang et al., 2010; Bai et al., 2012).

In our previous study (Wei et al., 2019) it is proved that adding sodium sulfate during the segregation roasting process, it can make metallic iron and gangue minerals have clear boundaries, the liberation degree of metallic iron is enhanced and promote the chlorination reaction of iron oxide. The focus of CaF_2 optimization is to increase the aggregation of metallic iron particles, and it is easy to obtain high-quality iron concentrate. Considering these results, Na_2SO_4 was chosen as the additive.

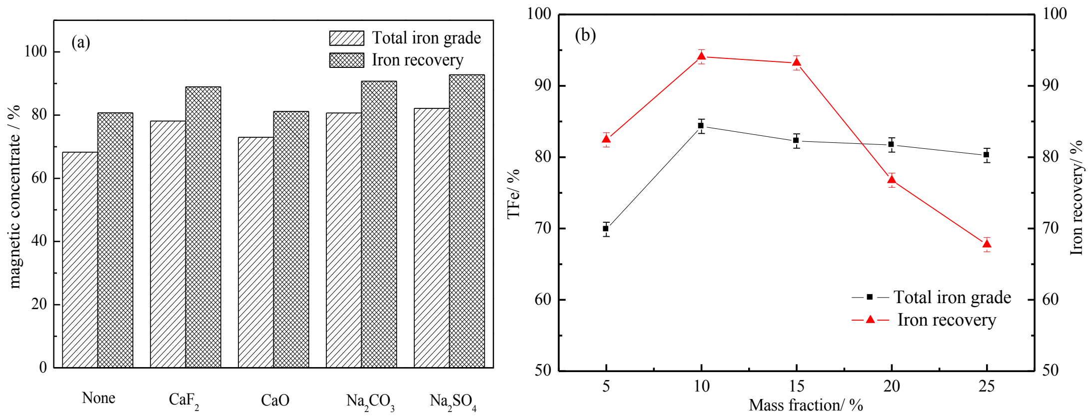

Fig. 6. Effects of the type of additive (a) and dosage of additive (b) on extraction of iron

3.7. Additive dosage

Influence of the mass fraction of the additive on extraction of iron was carried out. The type of additive is determined to be sodium sulfate, other parameters remain unchanged.

From Fig. 6(a), With sodium sulfate mass fraction increasing from 0 to 10 wt.%, iron grade of magnetic iron concentrate increases from 68.26% to 82.13%, and iron recovery rate increases from 83.74% to 92.78%. However, when the sodium sulfate mass fraction exceeds 10 wt.%, the iron grade and recovery in the iron concentrate gradually decreases. This was explained by sodium sulphate will produce sodium sulfide under abundant reducing atmosphere. Sodium sulfide is enriched on the surface of metal iron particles and reacts with metal iron to form troilite (FeS), which is a non-magnetic substance, thereby reducing iron recovery (Yu et al., 2016). In addition, excessive sodium sulfate leads to the formation of dense massive structure between the generated metallic iron and gangue minerals such as feldspar, which is harmful to the subsequent grinding-magnetic separation to extraction of iron. Taking into account iron extraction efficiency and production cost, sodium sulfate mass fraction of 10% was considered optimal. At this time, the grade and recovery of iron in the concentrate are 82.13% and 92.78%, respectively.

3.8. Repeated test of roasting–magnetic separation

To further investigate the process conditions for repeatability, the conditions for repeated test are as follows: raw material consisted of red mud, sodium chloride, coke and sodium sulfate at a ratio of 100: 15:15: 10, roasting temperature of 1100 ℃ for 60 min, magnetic separation feed size of -0.045 mm accounting for 90 wt.%, magnetic field intensity of 0.22 T.

The mass of the repeated test for each scale-up was 500 g, and the results are shown in Table 3. The results show that the repeated test index is consistent with the conditional test index. Most of the iron was extracted by magnetic separation.

Table 3. Repeated test results of iron extraction (wt.%)

Repeat	**Iron contents in the red mud**	**Iron contents in magnetic concentrate**	**Iron recovery**
1	19.6	79.9	91.8
2	19.9	79.6	92.7
3	19.7	78.9	92.1
4	20.1	79.7	93.3
5	19.7	78.9	92.2
6	19.8	79.7	91.9
Average	19.8	79.5	92.3
Range ($R = E_{max} - E_{min}$)		1.0	1.5
Arithmetic mean error $\left(\delta = \frac{\sum_{i=1}^{N} d_i}{N}\right)$		78.5	92.3
Sum square variation $SS = \sum_{i=1}^{N} d_i^2 = \sum_{i=1}^{N}(E_i - \bar{E})^2$		0.97	1.62
Average Deviation $MS = \frac{SS}{f}$		0.194	0.324
Standard deviation $S = \sqrt{\frac{\sum(E_i-\bar{E})^2}{N-1}} = \sqrt{MS}$		0.44	0.57

3.9. Discussion

3.9.1. Iron phase transformation mechanism in the roasting process

The course of segregation roasting involves the decomposition reaction of sodium chloride$_{(s)}$, the chlorination of iron oxides$_{(s)}$ and subsequently reducing of the ferric chloride$_{(g)}$. During the heating process, the chlorinating agent$_{(s)}$ reacts with water vapor$_{(g)}$ and silica$_{(s)}$ in the ore to generate hydrogen chloride$_{(g)}$, and the sodium sulfate$_{(s)}$ reacts with alumina$_{(s)}$ and silica$_{(s)}$ to form nepheline$_{(s)}$ and feldspar$_{(s)}$. Then, reaction of hydrogen chloride$_{(g)}$ with iron oxide$_{(s)}$ to generate theferric chloride$_{(g)}$. Finally, the ferric chloride$_{(g)}$ is reduced to metallic iron on the surface of coke(s) and the hydrogen chloride$_{(g)}$ is regenerated. The main chemical reactions that occur in the segregation roasting system are shown in Equations (1)-(11):

$$2NaCl_{(s)}+H_2O_{(g)}+XSiO_{2(s)} \rightarrow Na_2O{\cdot}xSiO_{2(s)}+2HCl_{(g)} \tag{1}$$

$$Fe_2O_{3(s)}+6HCl_{(g)} \rightarrow 2FeCl_{3(g)}+3H_2O_{(g)} \tag{2}$$

$$4FeCl_{3(g)}+3C_{(s)}+ 6H_2O_{(g)} \rightarrow 4Fe_{(s)}+12HCl_{(g)}+ 3CO_{2(g)} \tag{3}$$

$$Al_2O_{3(s)}+SiO_{2(s)}+Na_2SO_{4(s)} \rightarrow Na_2Al_2SiO_{4(s)}+SO_{3(g)} \tag{4}$$

$$2FeO_{\ (s)}+ SiO_{2\ (g)} \rightarrow Fe_2SiO4_{(s)} \tag{5}$$

$$Na_2SO_{4(s)}+CO_{(g)} \rightarrow Na_2O_{(s)}+SO_{2(g)}+CO_{2(g)} \tag{6}$$

$$Na_2O_{(s)}+2FeSiO_{4(s)} \rightarrow 4FeO_{(s)}+Na_2Si_2O_{5(s)} \tag{7}$$

However, some direct reduction of Fe_2O_3 by CO may also occur according to the reaction:

$$C_{(s)}+ H_2O_{(g)} \rightarrow CO_{(g)}+H_{2(g)} \tag{8}$$

$$3Fe_2O_{3(s)}+CO_{(g)} \rightarrow 2Fe_3O_{4(s)}+CO_{2\ (g)} \tag{9}$$

$$Fe_3O_{4(s)}+CO_{(g)} \rightarrow 3FeO_{\ (s)}+CO_{2\ (g)} \tag{10}$$

$$FeO_{(s)}+CO_{(g)} \rightarrow Fe_{\ (s)}+CO_{2\ (g)} \tag{11}$$

The thermodynamic calculation results for reactions (1)-(7) are shown in Fig. 7, reflecting the relationship between standard Gibbs free energy (ΔG^{θ}) and temperature (Dean, J. A. 1999; Jiang, et al., 2013).

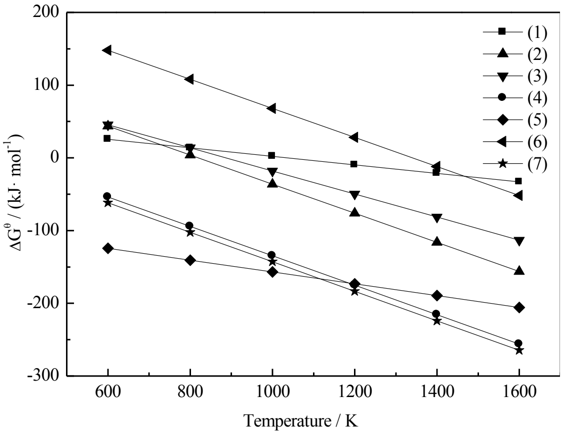

Fig. 7. Correlation of standard Gibbs free energy (ΔG^{θ}) with temperature for Reactions (1)–(7)

As shown in Fig. 7, with the temperature increases, the ΔG^{θ} value of Reactions (1)-(7) gradually approaches negative values. When the temperature reaches 1400K, ΔG^{θ} value of Reactions (1)-(7) are all negative, and these reactions can proceed spontaneously at this temperature. It is noteworthy that ΔG^{θ} value of Reactions (4) and (7) are much more negative than those of Reaction (5) at temperature of 1200–1600 K. So, During the segregation roasting process, Na_2SO_4 reacts with SiO_2 and Al_2O_3 to form sodium aluminosilicate via Reaction (4). By comparing Reaction (5) with Reaction (7), it can be seen that when Na_2SO_4 was added, Na_2O produced by Reaction (6) and it exchange with ferrous oxide in silicate minerals. Sodium sulfate plays a catalytic effect on the chlorination-reduction of red mud in the novel process.

3.9.2. Phase analysis

In order to reveal the variation regularity of iron phase during red mud segregation roasting, the magnetic separation, roasted ore and tailings was analyzed by XRD, SEM and EDS analysis. The results are shown in Table 4 and Fig. 8, 9.

Table 4. Chemical composition of magnetic concentrate (mass percent, %)

T_{Fe}	P	S	SiO_2	Al_2O_3	CaO	TiO_2	K_2O	MgO
82.13	0.11	0.26	4.70	4.37	2.06	1.62	0.65	0.47

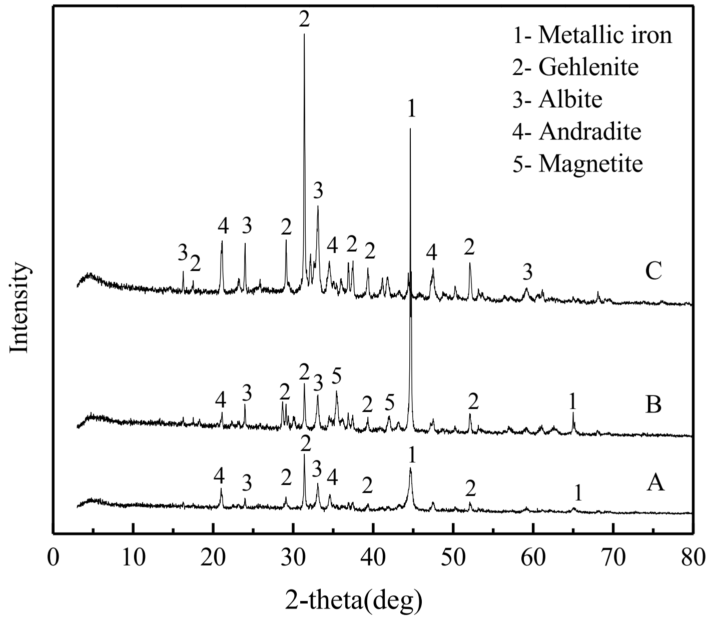

Fig. 8. XRD pattern of roasted ore (A), magnetic concentrate (B) and tailings (C)

According to the XRD patterns of red mud and roasted ore (Fig. 1, Fig. 8(A)), comparing with the iron phase of the red mud, which changed from hematite (Fe_2O_3) to a new iron phase dominated by metallic iron. Most of aluminum mineral and silica mineral reacted with sodium sulfate during the segregation roasting,and the minerals of gehlenite ($Ca_2Al_2SiO_7$), albite ($NaCaAlSiO_7$) and andradite ($Ca_3Al_2(SiO_4)_3$)were formed in roasted ore. The main composition is metallic iron, magnetite (Fe_3O_4) and a small amount of silicate minerals in final magnetic concentrate (Fig. 8(B)).

3.9.2. SEM-EDS analysis

The microstructure of the red mud, roasted ore, magnetic concentrate and the distribution of the main elements were analyzed by SEM coupled with EDS.

The SEM image of red mud in Fig. 9(a) clearly show red mud is composed of a large number of fine particles closely combined to form an accumulation body, and the whole is disordered shape. It can be seen from Fig. 9(b) that the particle size in the roasted ore is significantly increased, and the metallic iron particles are mixed with the silicate mineral. In the magnetic concentrate, metallic iron particles aggregate to form larger particles, and flaky metallic iron also exists (Fig. 9(c)). This is attribute to sodium oxide produced by sodium sulfate in a reducing atmosphere, and it could react with silicate minerals to form low melting point nepheline, the molten structure of the roasted ore accelerated the migration rate of metallic iron particles, which was promotes the growth of the metallic iron particles. The SEM-EDS of the magnetic concentrate further proves this view (Fig. 9(e)). Table 7 presents that the phase of iron in the magnetic concentrate obtained by segregation roasting-magnetic separation is mainly metallic iron, which has changed significantly compared with the red mud iron phase.

Table 5. Results of energy spectrum microanalysis of the magnetic concentrate (mass percent, %)

Number	O	Ca	Si	Fe	Al	Total
a	5.57	1.05	1.56	89.79	2.03	100.00
b	5.08	1.25	1.35	90.27	2.05	100.00
c	5.65	1.32	2.18	88.64	2.21	100.00
d	5.20	1.36	2.02	89.27	2.15	100.00
e	5.33	1.29	1.95	89.31	2.12	100.00
Average	5.34	1.25	1.81	89.47	2.12	100.00

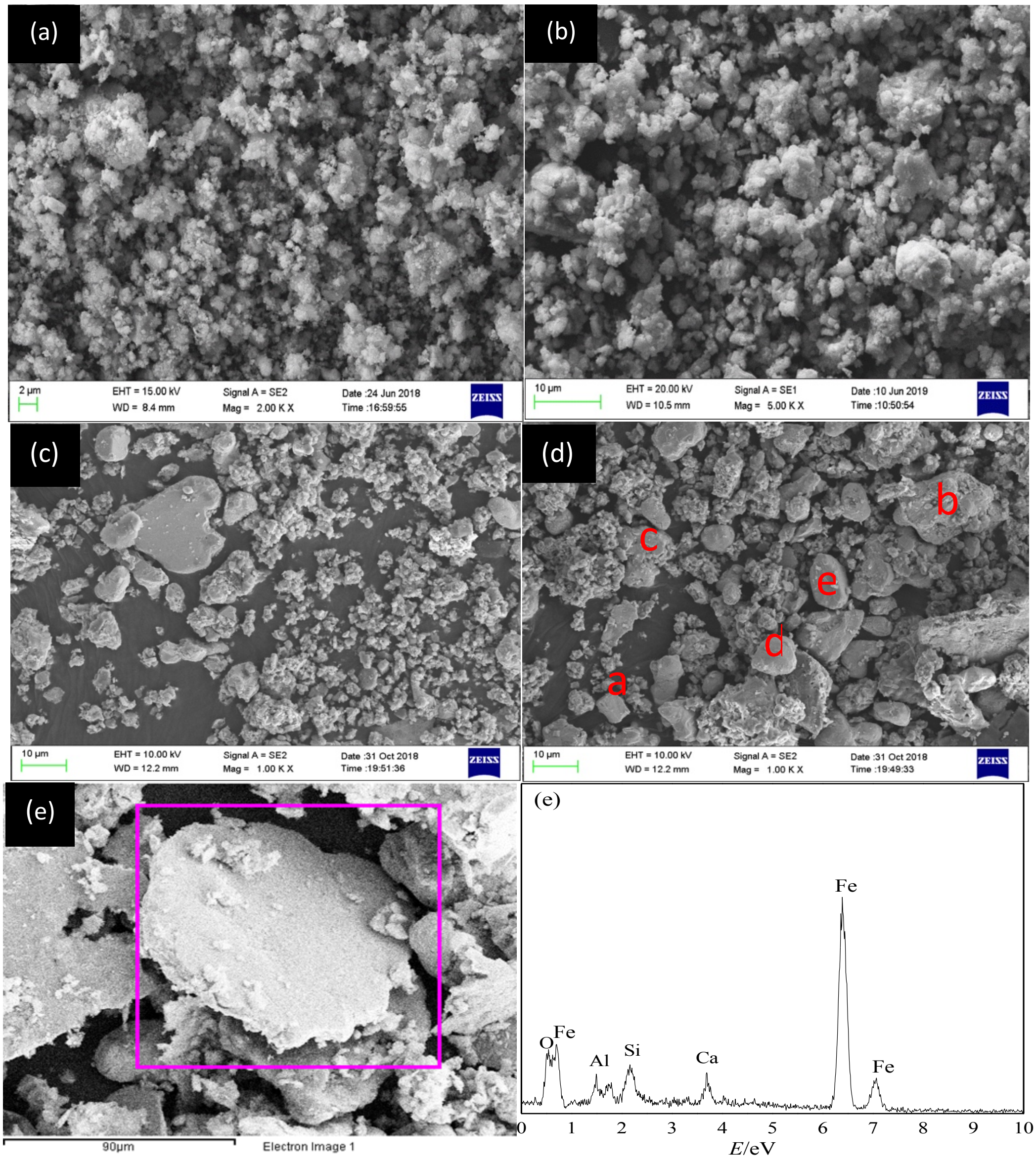

Fig. 9. The SEM images: red mud (a), roasted ore (b), magnetic concentrate (c), and SEM -EDS image of iron concentrate (d, e)

4. Conclusions

Based on the test results of extracting iron from the refractory red mud obtained in this study, we drew the main following conclusions:

(1) The segregation roasting-magnetic separation method can efficiently extract iron from red mud. The segregation roasting method is a one-step replacement for the reduction roasting method that simultaneously separates metallic iron from the red mud. The segregation roasting method is one of the effective methods to treat some refractory ores including red mud, nickeliferous laterite, and oolitic hematite.

(2) The red mud was investigated using segregation roasting–magnetic separation method to extraction of iron. The effects of various process parameters on the extraction of iron by segregation roasting-magnetic separation were studied, and the phase transformation behavior and microstructure of iron are explored. The final magnetic concentrate sorting index with T_{Fe} of 82.13% and overall iron recovery rate of 92.78%was obtained under the roasting temperature of 1100 °Cfor 60 min, mass ratio of red mud/sodium chloride/ coke/sodium sulfate of 100:15:15:10, and magnetic separation of the roasted ore by grinding up to 95% passing 0.045 mm at magnetic field intensity of 0.22 T. The presence of the additive sodium sulfate significantly enhances the effect of red mud separation roasting-magnetic

separation for iron extraction. XRD, SEM-EDS analysis of the roasted ore and magnetic concentrate presents that after the segregation roasting, the hematite was transformed into a new metal phase consisting of metallic iron and magnetite.

(3) High-grade iron concentrate can be used as the burden for steel making by electric arc furnace to replace some scrap steel. Compared with scrap steel, it has the advantages of low harmful impurities, quality stability and large resource. This increases the economic value of red mud, while also making it easier to handle and reducing the damage to the environment.

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