



Extraction of iron and aluminum from high-iron bauxite by ammonium sulfate roasting and water leaching

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Abstract

High iron content is one of the challenges in utilizing the refractory bauxites in China. An improved method for treating the high-iron bauxite by roasting with $(\text{NH}_4)_2\text{SO}_4$ was proposed, which offers a possible alternative method for utilizing the high-iron bauxite. The influences of the roasting time, roasting temperature, material ratio, and ore particle size on the extraction ratios of Fe and Al were studied, and the orthogonal test was used to optimize the reaction conditions. The optimized reaction conditions were proposed as follows: roasting temperature of 450 °C, roasting time of 120 min, material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore of 2.5:1.0, and ore particle size below 80 μm . The roasting mechanism and kinetic parameters including the apparent activation energy and reaction rate constant were investigated. The results showed that the control step of the roasting process was the internal diffusion on the product layer and the apparent activation energy was 19.22 kJ mol^{-1} in the reaction temperature range. The kinetic equation was obtained finally.

Keywords High-iron bauxite · Ammonium sulfate · Roasting · Reaction process · Kinetics

1 Introduction

Due to the rapid development of industrialization and urbanization, the demand for aluminum is growing exponentially [1]. As the main primary raw material, bauxite supplies more than 90% of material resources [2, 3]. China is the top producer and consumer of aluminum worldwide, and accounts for approximately 40% of the world's

aluminum production. However, the bauxite resources that can be utilized by the current industrial technology to produce Al_2O_3 are limited by its low commercial value [4–7]. The dependence on bauxite import is becoming more and more intensified.

Fortunately, the reserves of high-iron diasporic bauxite are abundant in China, such as in Guigang, Guangxi, China, where the high-iron bauxite is estimated to be more than 1.6 billion ton [8, 9]. The bauxite ores are mainly composed of aluminum with middle-high proportion, silicon with middle-low proportion and iron with high proportion [1, 5]. For a long time, attention is focused on the utilization of iron and aluminum from high-iron bauxite [2, 8]. However, there is no a technically feasible and economically reasonable countermeasure to deal with high-iron bauxite because of its complex structure and interwoven particles [10–13]. So far, most of high-iron bauxite ores have not been underutilized. Studies related to the effective, clean, and comprehensive utilization of high-iron bauxite ores are necessary and of great practical significance.

An improved process of roasting high-iron bauxite ore with ammonium sulfate was proposed for the effective utilization of high-iron bauxite ore. Iron and aluminum in

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ore were transformed into soluble sulfate and then separated from SiO_2 by leaching and filtration. The excessive $(\text{NH}_4)_2\text{SO}_4$ was recrystallized from SO_3 , NH_3 , and H_2O , and the additional NH_3 gas was absorbed by dilute H_2SO_4 to form $(\text{NH}_4)_2\text{SO}_4$, or absorbed by carbonic acid to form NH_4HCO_3 , which was used to precipitate Fe and Al. Iron and aluminum were selectively precipitated by adjusting the pH value of the solution based on the different chemical properties. Iron and aluminum were extracted and used, while ammonium sulfate was recycled.

As the significant step in effective utilization of high-iron bauxite ore, the roasting process is complex. Thus, in this work, the influences of material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore, roasting time, roasting temperature, and ore particle size on the extraction ratios of Fe and Al were investigated in details, and the roasting kinetics was discussed.

2 Experimental

2.1 Materials and characterization

The high-iron bauxite ore used in experiments was obtained from Guangxi, China. The chemical compositions of the bauxite ore were chemically analyzed. The mineral phases and micromorphology are shown in Fig. 1. The $(\text{NH}_4)_2\text{SO}_4$ from Sinapharm Chemical Reagent Co., Ltd. was of industrial grade, and the solvent was distilled water.

The main compositions in bauxite ore are Al_2O_3 , Fe_2O_3 , and SiO_2 , and the contents of Al_2O_3 , Fe_2O_3 , and SiO_2 are 28.96, 43.85, and 10.49%, respectively. The sum of those three components reached 83.3 mass%, which is dominated and of utilization values. The main mineral phases in high-iron bauxite are gibbsite, hematite, goethite, quartz, and aluminum hydroxide. That is, iron mainly exists in the form of hematite and goethite, and aluminum mainly in the form of gibbsite and aluminum hydroxide.

2.2 Procedure

Experiments were performed in a resistance wire heating furnace under air atmosphere. The ground high-iron bauxite ore and ammonium sulfate were homogeneously mixed in a medicine grinder, and then put into a corundum crucible. The corundum crucible was placed in the furnace and heated to the setting temperature and then held for a period of time. When the roasting ended, the sample was taken out and leached in 80 °C water for 60 min and filtered [8]. The contents of Fe and Al both in solution and filter residue were examined by titration method. It is noteworthy that the material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore was the mass ratio of $(\text{NH}_4)_2\text{SO}_4$ dosage to the stoichiometric

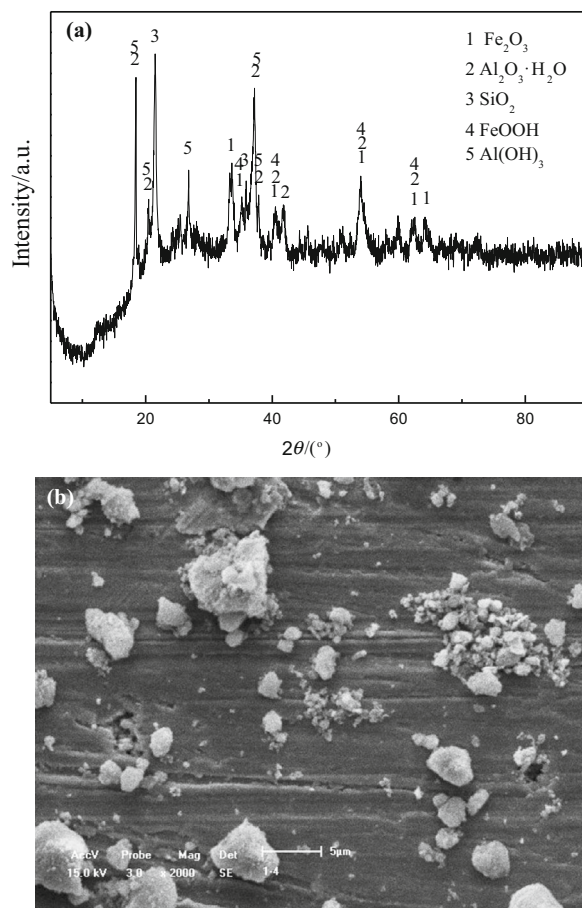


Fig. 1 XRD pattern (a) and scanning electron microscopy image (b) of high-iron gibbsitic bauxite

consumption of $(\text{NH}_4)_2\text{SO}_4$ that reacted with Al_2O_3 and Fe_2O_3 in bauxite ore.

At kinetics experiments, 25 g high-iron bauxite ore was used in each test. The mixed material was put into a series of corundum crucibles, which were placed in the roasting furnace and then heated. When the temperature reached the desired temperature, the time device was started. The crucibles were taken out one by one at specified time and cooled rapidly in order to reduce the measurement error. The roasted material was leached in 80 °C water for 60 min and filtered. The contents of Fe and Al both in solution and filter residue were examined by titration method.

The extraction ratio of Fe or Al was calculated using Eq. (1).

$$\eta = \frac{M c_1 v_1}{m_0 w_0} \quad (1)$$

where η is the extraction ratio of Fe or Al, %; M is the molecular mass of Fe or Al; c_1 is the concentration of Fe or Al, mol L^{-1} ; v_1 is the volume of Fe or Al, L; m_0 is the mass

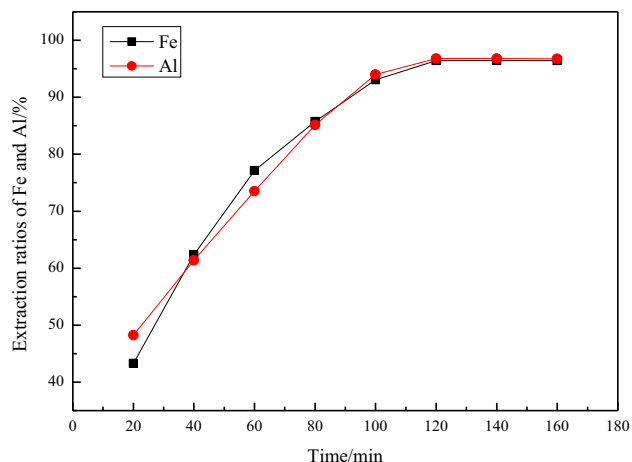


Fig. 2 Relationships between extraction ratios of Fe and Al and roasting time

of bauxite ore, g; and w_0 is the mass fraction of Fe or Al in bauxite ore, %.

3 Results and discussion

3.1 Effect of roasting time on extraction ratios of Fe and Al

The influence of roasting time on the extraction ratios of Fe and Al was investigated with ore particle size below 80 μm , roasting temperature of 450 $^{\circ}\text{C}$ and ammonium sulfate-to-ore ratio of 3.0:1.0, as shown in Fig. 2. The extraction ratios of Fe and Al increase rapidly when the roasting time varies from 20 to 120 min before reaching a plateau. That is, a thermostatic time of 120 min is sufficient for extracting Fe and Al. A longer roasting time will waste

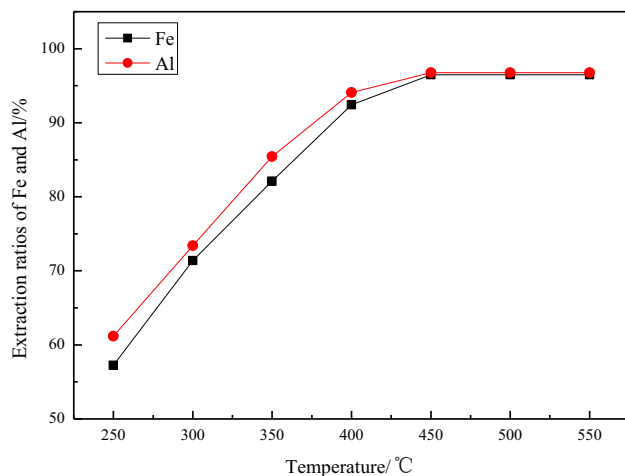


Fig. 3 Relationships between extraction ratios of Fe and Al and roasting temperature

not only time but also energy. 120 min is considered to be suitable.

3.2 Effect of roasting temperature on extraction ratios of Fe and Al

The influence of roasting temperature on the extraction ratios of Fe and Al was studied with ore particle size below 80 μm , roasting time of 120 min and ammonium sulfate-to-ore ratio of 3.0:1.0, as shown in Fig. 3.

The extraction ratios of Fe and Al increase gradually when the roasting temperature extends from 250 to 450 $^{\circ}\text{C}$ before reaching a plateau. From the kinetics point of view, high temperature can promote the movement of reaction molecules, thus facilitating the multi-phase reactions. When the high-iron bauxite ore reacted with ammonium sulfate or decomposed at 450 $^{\circ}\text{C}$ for 120 min, the extraction ratios of Fe and Al rose up to 98.5% and 98.8%, respectively. Thus, the roasting temperature of 450 $^{\circ}\text{C}$ was chosen in the following experiments.

3.3 Effect of material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore on extraction ratios of Fe and Al

The influence of material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore on the extraction ratios of Fe and Al was studied with ore particle size below 80 μm , roasting time of 120 min and roasting temperature 450 $^{\circ}\text{C}$. Figure 4 shows the relationships between extraction ratios of Fe and Al and material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore. The extraction ratios of Fe and Al increase gradually with the material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore varying from 1.0:1.0 to 2.5:1.0; then, the extraction ratios of Fe and Al are stabilized. When $(\text{NH}_4)_2\text{SO}_4$ is insufficient, the reaction between ore and $(\text{NH}_4)_2\text{SO}_4$ is inadequate. Increasing the dosage of $(\text{NH}_4)_2\text{SO}_4$ can

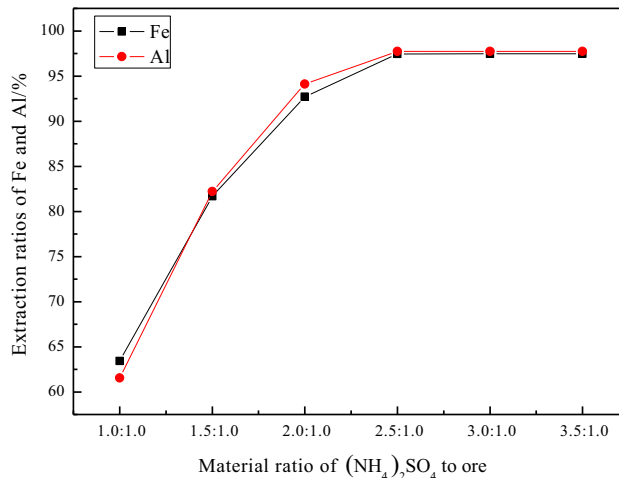


Fig. 4 Relationships between extraction ratios of Fe and Al and material ratio of ammonium sulfate to ore

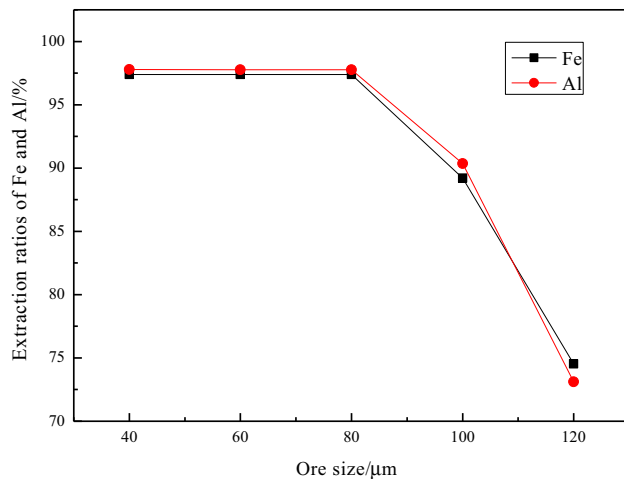


Fig. 5 Relationships between extraction ratios of Fe and Al and ore powder size

intensify the contact between $(\text{NH}_4)_2\text{SO}_4$ and its decomposition with bauxite ore, thereby promoting the reactions.

3.4 Effect of ore particle size on extraction ratios of Fe and Al

The influence of ore particle size on the extraction ratios of Fe and Al was studied at roasting time of 120 min, roasting temperature of 450 °C and material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore of 2.5:1.0. Figure 5 shows the relationships between extraction ratios of Fe and Al and ore particle size. The extraction ratios of Fe and Al increase rapidly with the ore particle size decreasing from 120 to 80 μm, and then, the extraction ratios of Fe and Al are stabilized. Additional energy consumption was needed if grinding the ore particles to smaller size.

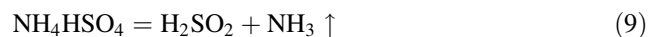
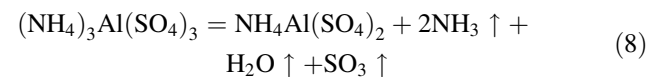
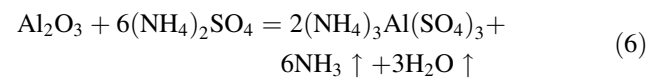
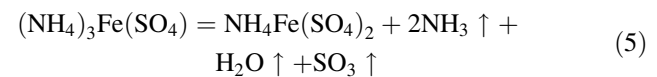
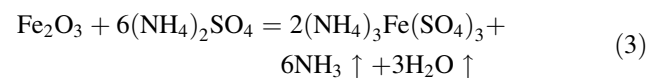
3.5 Orthogonal test

To optimize the reaction conditions of roasting high-iron bauxite ore using $(\text{NH}_4)_2\text{SO}_4$, the $\text{L}_9(3^4)$ tabulation including four factors and three levels was chosen based on the single factor experiments, as shown in Table 1. The results of the orthogonal test are listed in Table 2.

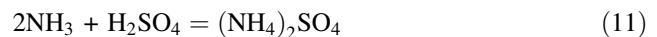
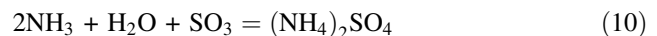
From Table 2, the order of those factors affecting the extraction ratios of Fe and Al was material ratio of $(\text{NH}_4)_2\text{SO}_4$

to ore, ore particle size, roasting temperature, and roasting time. The optimized reaction conditions were obtained as follows: roasting temperature of 450 °C, roasting time of 120 min, material ratio of $(\text{NH}_4)_2\text{SO}_4$ to ore of 2.5:1.0, and ore particle size below 80 μm. The extraction ratios of Fe and Al were both higher than 96% in the verification experiments under the optimized reaction conditions.

Scholars [14–17] suggest that the roasting process was complex, involving the decomposition of $(\text{NH}_4)_2\text{SO}_4$, the reactions between oxides of Fe and Al and $(\text{NH}_4)_2\text{SO}_4$ and its decomposition product, as well as the decompositions of sulfuric acid double salts. From the experimental results and the studies [14–17], the main chemical reactions were concluded as below:



The recrystallization of $(\text{NH}_4)_2\text{SO}_4$ and the additional NH_3 absorption reactions were:



4 Roasting kinetics analysis

As known, $(\text{NH}_4)_2\text{SO}_4$ can be decomposed as NH_3 and NH_4HSO_4 , and the NH_4HSO_4 will decompose into NH_3 and H_2SO_4 ; thus, the reaction process is a liquid–solid reaction.

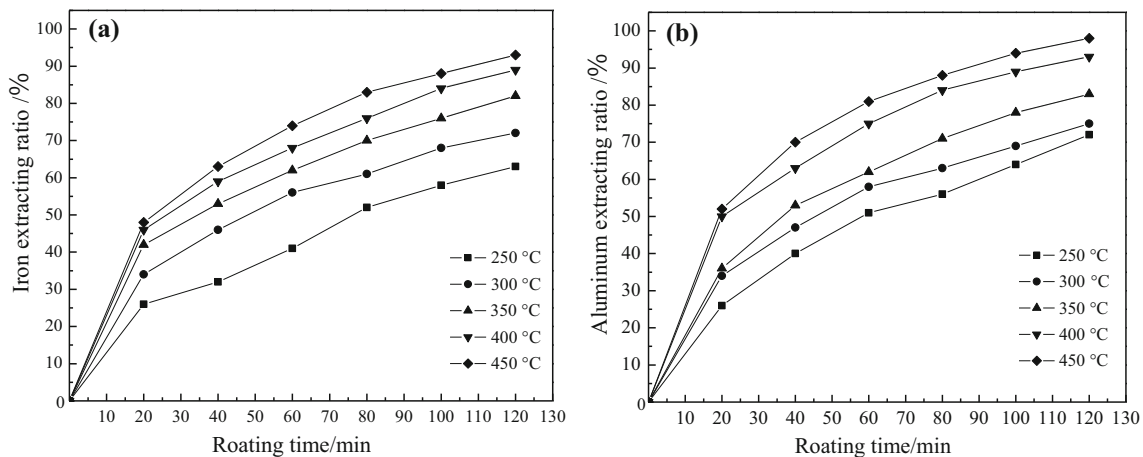
Table 1 Factors and levels of orthogonal test

Level	Factor			
	A Roasting temperature/°C	B Material ratio ($(\text{NH}_4)_2\text{SO}_4$ /ore)	C Roasting time/min	D Ore size/μm
1	350	1.5:1.0	80	< 120
2	400	2.0:1.0	100	< 100
3	450	2.5:1.0	120	< 80

Table 2 Results of orthogonal test

No.	A	B	C	D	Extraction ratio/%	
					Fe	Al
1	350	1.5:1.0	80	120	72.31	72.91
2	350	2.0:1.0	100	100	75.25	76.31
3	350	2.5:1.0	120	80	84.16	85.22
4	400	1.5:1.0	100	80	80.07	80.87
5	400	2.0:1.0	120	120	78.23	78.63
6	400	2.5:1.0	80	100	85.41	86.41
7	450	1.5:1.0	120	100	79.72	80.73
8	450	2.0:1.0	80	80	84.54	85.44
9	450	2.5:1.0	100	120	81.18	82.68
d_{1j}	77.24/78.14	76.03/76.83	77.42/78.25	77.23/78.07		
d_{2j}	78.57/79.30	77.73/78.12	77.50/78.62	78.79/79.81		
d_{3j}	79.81/80.95	82.25/83.44	80.70/81.53	79.59/80.81		
D	4.57/4.81	7.21/6.60	1.92/1.58	5.69/5.77		

d_{ij} ($i, j = 1, 2, 3$) denotes the average of each level for energy factor; D is the range

**Fig. 6** Relationships between extraction ratio and roasting time. **a** Iron; **b** aluminum

Therefore, the roasting process can be investigated by the shrinking unreacted model when the ore particles are regarded as sphere. The relationships of iron and aluminum extraction ratios to roasting temperature in the selected range are plotted in Fig. 6. The extraction ratios of Fe and Al increase with the roasting temperature increasing. And at a certain temperature, the extraction ratios of Fe and Al increase with prolonging the roasting time. When the mixed material was roasted at 450 °C for 120 min, the extraction ratios of Fe and Al rose to 90% and 93%, respectively.

Figure 6 was analyzed on the basis of the shrinking-core model. The experimental data were substituted into the Crank–Ginsting–Braunshtein’s kinetic equation [18–20]:

$$1 + 2(1 - \alpha) - 3(1 - \alpha)^{2/3} = kt \quad (12)$$

where α is the extraction ratio of iron or aluminum; k is the apparent rate constant; and t is the reaction time. The

corresponding relationships between the value of left side of Eq. (2) and the roasting time are plotted in Fig. 7. It was obvious that the value of $1 + 2(1 - \alpha) - 3(1 - \alpha)^{2/3}$ has significantly linear correlation with the roasting time, and the correlation coefficients R^2 were higher than 0.99. All of those indicated that the roasting process is fitted to the Crank–Ginsting–Braunshtein’s kinetic equation, which proves that the reaction rate is controlled by the internal diffusion on the solid product layer in the roasting process.

According to the Arrhenius expression,

$$\ln k = \ln A - E/(RT) \quad (13)$$

where A is the frequency factor; E is the apparent activation energy; R is the mole gas constant; and T is the absolute temperature. The relationships between $\ln k$ and $1/T$ are shown in Fig. 8. It can be seen that the approximation

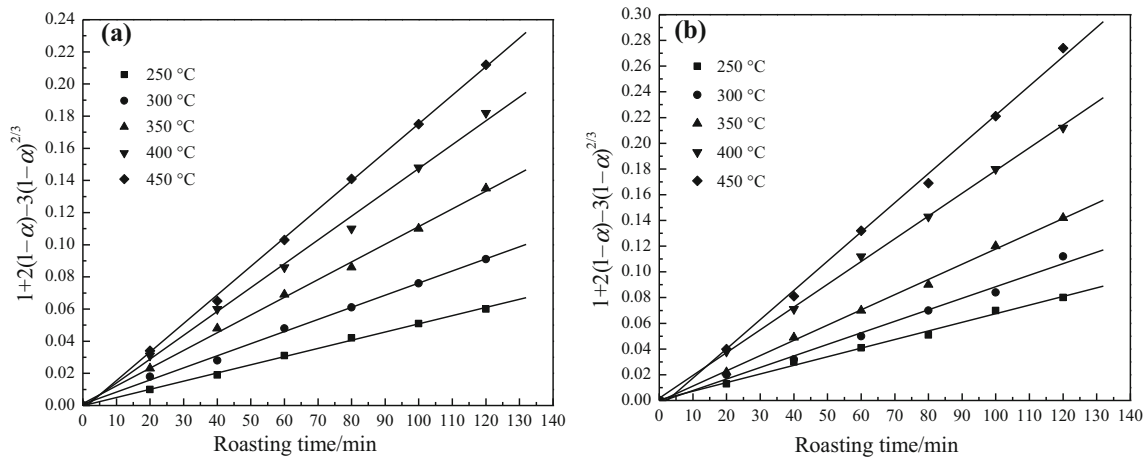


Fig. 7 Relationship between $1 + 2(1 - \alpha) - 3(1 - \alpha)^{2/3}$ and roasting time. **a** Iron; **b** aluminum

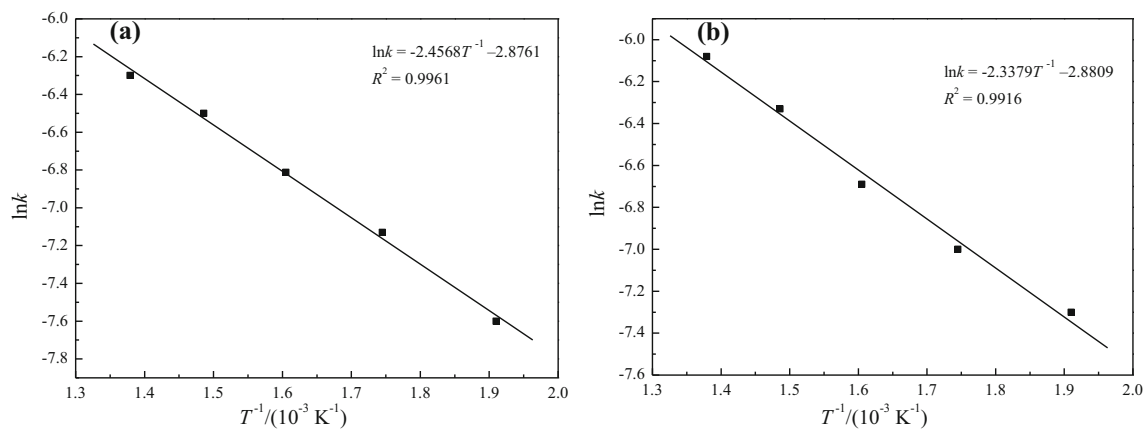


Fig. 8 Relationship between $\ln k$ and $1/T$. **a** Iron; **b** aluminum

of the apparent activation energy could be obtained by the slope of the straight line.

The apparent activation energy calculated from Fig. 8a, b was $20.43 \text{ kJ mol}^{-1}$ and $19.44 \text{ kJ mol}^{-1}$, respectively. Similarly, the k value obtained from Fig. 8 was 0.05635 and 0.05608 , respectively. The average E and k values were $19.94 \text{ kJ mol}^{-1}$ and 0.05622 , respectively. The results verified that the reaction rate was controlled by the internal diffusion.

Thus, in the experimental temperature range, the kinetic equation of roasting process could be described as follows:

$$1 + 2(1 - \alpha) - 3(1 - \alpha)^{2/3} = 0.05622 \exp[-19,220/(RT)]t \quad (14)$$

5 Conclusions

1. The optimized reaction conditions for roasting high-iron bauxite with $(\text{NH}_4)_2\text{SO}_4$ were obtained as roasting

temperature of $450 \text{ }^\circ\text{C}$, roasting time of 120 min, material ratio of $(\text{NH}_4)_2\text{SO}_4$ to bauxite of 2.5:1.0, and ore size of less than $80 \mu\text{m}$. Among them, the material ratio of $(\text{NH}_4)_2\text{SO}_4$ to bauxite was the most predominant factor.

2. The shrinking-core model was used to analyze the kinetics of roasting process. The control step of the roasting process was the internal diffusion on the solid product layer. The kinetic equation is obtained, and the apparent activation energy was $19.22 \text{ kJ mol}^{-1}$.

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