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Study on the roasting and leaching behavior of high-sulfur bauxite using ammonium bisulfate

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ABSTRACT

High sulfur content is one of the many challenges in processing the refractory bauxites of China. A new method to prepare Al_2O_3 from high-sulfur bauxite with the NH_4HSO_4 roasting process was studied. The paper offers a possible alternative method for desulfurization of bauxite that may improve overall process economics and environmental impact. The roasting mechanism and various parameters including the amount of the ammonium bisulfate addition, roasting temperature and roasting time were investigated. The results showed that the control step of the roasting process was chemical control and the apparent activation energy was 65.74 kJ/mol over the reaction temperature range from 623 to 648 K. The leaching kinetics of the sintered clinker by water was investigated, which was affected by temperature, mass ratio of liquid to solid and time. Analysis of the kinetic data indicates that the dissolution of bauxite ore was controlled by the shrinking core with surface reaction model. The apparent activation energy of the leaching process was found to be 37.94 kJ/mol from 323 to 363 K. The maximum aluminum dissolution ratio reaches about 93% under the optimal condition. This paper aims at giving some revelation and instruction for the further research and practice on high sulfur bauxites development and application.

1. Introduction

China is in a stage of rapid development of industrialization and urbanization, so the demand for aluminum resources is increasing. Bauxite ores can be used for the production of aluminum, which has a broad application in the preparation of abrasive, high alumina cement, refractories, ceramics, chemical and pharmaceutical fields. In China, the reserve of high-sulfur diasporic bauxite has been estimated at 1.5 billion ton (He and Luo, 1996). These ores are mainly composed of aluminum of middle-high proportion, silicon of middle-low proportion, sulfur of high proportion (sulfur content is greater than 0.7%) and middle-high Al/Si ratio (A/S) ores (Hu et al., 2011), but they can't be used for alumina production because of the harmfulness of sulfur, such as the loss of Na_2O, the corrosion of steel material, the rise of the iron concentration in the solution and even the decrease digestibility of the alumina (Bi, 2006). In order to improve the utilization of bauxite resources and to promote the development of alumina industry in China, the application of high-sulfur bauxite has become an important research field.

High sulfur content is one of the many challenges in processing the refractory bauxites of China. For a long time, attention is turning to the removal of sulfur from high-sulfur bauxite, but because of the low removal efficiency, high production cost, and complex desulfurization process, most of these methods have met with marginal success (Fan, 2013; Hu et al., 2010a, 2010b; Lan et al., 2008; Ma et al., 2014; Li et al., 2011; Liang et al., 2011; Lv et al., 2008; Niu et al., 2007; Wang et al., 2009, 2010, 2011), which greatly limits the effective use. The present paper deals with a new method for preparing Al_2O_3 from high-sulfur bauxite with the ammonium bisulfate roasting process without pre-desulfurization, which offers a possible alternative method for desulfurization of bauxite and may improve overall process of economics and environmental impact. The effects of roasting temperature, roasting time and molar ratio of Al_2O_3 in high-sulfur bauxite to NH_4HSO_4 on Al reaction ratio are examined. Moreover, the digestion temperature, the digestion time, stirring intensity and mass ratio of liquid to solid (L/S) are discussed in detail. On the basis of these data, the kinetics of the roasting and leaching processes has been explored.

2. Materials and methods

2.1. Materials

High-sulfur bauxite from Guizhou province was used for roasting and leaching experiments. It was ground using a vibrating grinding mill and screened to under 80 μm. The sieved sample was dried in an electric oven at about 105 °C, cooled to room temperature and stored in closed desiccators. All the chemicals used were of analytical grade.

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Tables 1
Chemical analysis of high-sulfur bauxite.

Al_2O_3%	SiO_2%	Fe_2O_3%	TiO_2%	S%	K% LOI%
63.83	9.78	4.74	4.74	3.11	1.77 11.23

The main chemical compositions of the bauxite are shown in Table 1, which were analyzed by chemical method. It belongs to the middle-grade bauxite (alumina/silica ratio, A/S = 6.5). The XRD pattern of high-sulfur bauxite is shown in Fig. 1(a).The XRD studies of the ore indicate diaspore as the major mineral phase and quartz, pyrite, and rutile as minor phases. It can be seen from Table 1 that the sulfur content is relatively high, and the sulfur in the bauxite mainly exists in the form of pyrite from XRD. SEM micrograph in Fig. 1(b) shows that the high-sulfur bauxite particles are agglomerate.

2.2. Characterization

Morphological features of high-sulfur bauxite have been studied using a scanning electron microscope (SEM) (Model: SSX-550). Powder X-ray diffraction (XRD) pattern, in the 2θ range of 5–90°, recorded at a scan rate of 12°/min using a Bruker diffractometer (Model: D/max 2500PC) with CuKα radiation has been used for phase identification.

2.3. Roasting and leaching experiments

The roasting experiments have been carried out in a high temperature sintering furnace VF-1200D8, with a temperature control accuracy of ±1 °C. After a known amount of powder-like high-sulfur bauxite was well mixed with a specific amount of the ammonium bisulfate in a crucible, it was quickly put into a furnace. When the furnace reached the specified temperature and maintained a period of time, the crucible was quickly taken out, cooled down and carried out the digestion experiment. For roasting kinetic studying, when the furnace temperature reached the set temperature, the samples were taken out at intervals, and immediately placed in an ice bath to stop the reaction.

The leaching experiments have been carried out at a certain ratio of liquid to solid. The vessel was immersed in a constant temperature bath with a temperature accuracy of ±1 °C, and continuously stirred. Once the predetermined temperature was reached and stabilized, the clinker of bauxite were transferred to the vessel and kept stirring for a period of time. At the end of leaching, the slurry was separated by filtration before analysis. For leaching kinetic studying, 2 ml aliquots were collected at appropriate time intervals from the liquor, filtered and analyzed for Al content using standard EDTA method.

3. Results and discussion

3.1. Roasting chemical reactions

Possible chemical reactions during roasting of high-sulfur bauxite with the ammonium bisulfate are:

$$Al_2O_3 + 4NH_4HSO_4 \rightarrow 2NH_4Al(SO_4)_2 + 2NH_3\uparrow + 3H_2O\uparrow \quad (1)$$

$$Fe_2O_3 + 4NH_4HSO_4 \rightarrow 2NH_4Fe(SO_4)_2 + 2NH_3\uparrow + 3H_2O\uparrow \quad (2)$$

$$NH_4HSO_4 \rightarrow NH_3\uparrow + H_2O\uparrow + SO_3\uparrow \quad (3)$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2\uparrow \quad (4)$$

$$4FeS_2 + 6H_2SO_4 + 11O_2 \rightarrow 2Fe_2(SO_4)_3 + 8SO_2\uparrow + 6H_2O\uparrow \quad (5)$$

NH_4HSO_4 occurs decomposition reaction at 450 °C releasing NH_3, SO_3 and H_2O (Li et al., 1992), which is unfavorable to the roasting process, so the roasting temperature was under 450 °C. According to Eq. (1), the molar ratio of Al_2O_3 in the bauxite to NH_4HSO_4 is 1:4. To ensure that the reaction is complete, NH_4HSO_4 should be excess. The effect of NH_4HSO_4 addition on the Al reaction ratio is discussed.

3.2. High-sulfur bauxite roasting mechanism

3.2.1. Effect of ammonium bisulfate addition

As shown in Fig. 2(a), the effect of different NH_4HSO_4 addition amount on the leaching ratio of Al at roasting temperature 350 °C and roasting time 180 min was studied. The results indicate that the dissolution ratio of Al increases with NH_4HSO_4 addition, which is an important effect. However, higher NH_4HSO_4 addition results in higher viscosity of the leaching slurry in the leaching process and difficult filtration (Shi et al., 2013). Based on the above, the mole ratio of NH_4HSO_4 to Al_2O_3 more reasonably was 7:1.

3.2.2. Effect of roasting temperature

The relationship between Al leaching ratio and roasting temperature from 250 °C to 450 °C under the conditions of roasting time 180 min and the mole ratio of NH_4HSO_4 to Al_2O_3 7:1 is presented in Fig. 2(b). It shows that increasing temperature can increase the equilibrium constant and accelerate the reaction rate under 350 °C, but because the boiling point of NH_4HSO_4 is 350 °C, increasing the temperature will speed up the evaporation, accelerate the decomposition and reduce the reaction efficiency. To ensure higher leaching ratio of Al, roasting temperature was chosen as 350 °C.

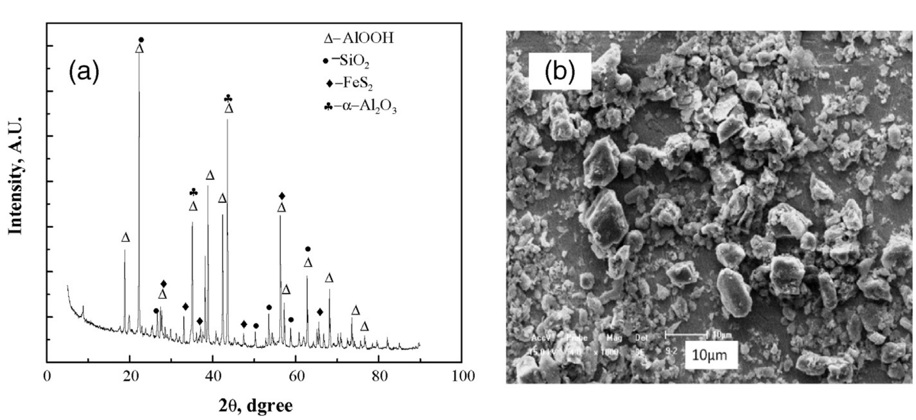

Fig. 1. (a) X-ray diffraction pattern of high-sulfur bauxite, (b) SEM micrograph of high-sulfur bauxite.

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