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Kinetics of titanium leaching with citric acid in sulfuric acid from red mud

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Abstract: The recovery of titanium with citric acid in sulfuric acid from red mud was put forward to strengthen acid leaching efficiency. The main factors on the recovery of titanium such as citric acid addition, sulfuric acid concentration, leaching temperature, time and liquid-to-solid ratio were studied. The kinetics analysis of titanium leaching from red mud was deeply investigated. The results show that the citric acid could increase the recovery of titanium and decrease the consumption of sulfuric acid. The recovery of titanium was increased from 65% to 82% and the consumption of sulfuric acid was decreased by about 30% with using 5% citric acid. The dissolution of perovskite, brookite, and hematite in red mud could easily be dissolved using citric acid. The acid leaching process was controlled by internal diffusion of shrinking core model (SCM) and the correlation coefficient was above 0.98. The apparent rate constant was increased from 0.0012 to 0.0019 with 5% citric acid at 90 °C. The apparent activation energy of titanium leaching decreased from 39.77 kJ/mol to 34.61 kJ/mol with 5% citric acid.
Key words: red mud; titanium; kinetics; citric acid; acid leaching

1 Introduction

Red mud is a kind of alkaline solid waste from the tailings during alumina production of bauxite [1−3]. About 0.8−1.5 t red muds are generated per ton of alumina and it is estimated that over 70 million tons of the waste are impounded annually in the world [4,5]. Meanwhile, the rising tendency of red mud output is increasing year by year. The disposal of damming up process on red mud is expensive and can cause environmental problems [6−8].

Red mud usually contains many kinds of metals such as Ti, Al, Ca, Na, V and Sc [9−11]. Titanium is a valuable metal which can be extracted from many kinds of minerals using direct acid leaching, alkaline leaching and activation roasting−acid leaching [12−14]. The recovery of titanium from Bayer process red mud was investigated with concentrated sulfuric acid [15]. The sulfuric acid concentration above 6 mol/L was needed and the recovery of titanium was lower than 70% [16]. For example, the extraction of titanium from red mud with sulfuric acid leaching under the condition of atmospheric pressure and without pretreatment was proposed by AGATZINILEONARDOU et al [17]. The recovery of titanium was 64.5% under the condition of sulfuric acid concentration of 6 mol/L, temperature of 60 °C and liquid-to-solid mass ratio of 20:1. Therefore, a lot of strong acid leaching solution was obtained due to the high sulfuric acid concentration and liquid-to-solid ratio [18,19]. However, there are few reports on the new effective agent and kinetics of titanium leaching from red mud.

In order to enhance leaching efficiency and decrease sulfuric acid consumption, the present research work was to investigate the recovery of titanium with citric acid from red mud. Furthermore, the process was scientifically explained using leaching kinetics to confirm titanium recovery from red mud.

2 Experimental

2.1 Materials

The red mud was collected from Henan Province, China. Its particle size distribution is shown in Fig. 1.

It is found that 50% of the red mud was smaller than 5 μm, whereas 100% of the sample was smaller than 33 μm. The sample was very fine and did not need to be

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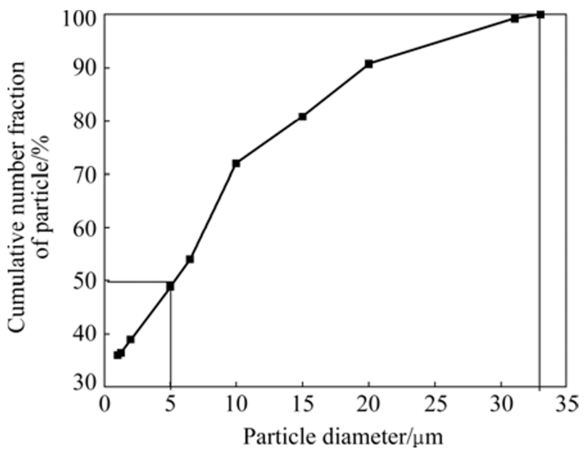

Fig. 1 Particle size distribution of red mud

crushed for acid leaching. The sample was assayed using inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the result is given in Table 1.

Table 1 Main chemical composition of red mud (mass fraction, %)

TiO_2	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	MgO	Sc_2O_3	V_2O_5
6.64	10.63	22.31	18.92	20.46	5.72	2.04	0.016	0.42

It is shown that the composition of this red mud complex contained many metallic oxides such titanium, aluminum, ferrum, calcium and vanadium oxides. The XRD pattern of the red mud sample is depicted in Fig. 2.

It is indicated that the main minerals in the red mud were perovskite, brookite, hematite, calcite, cancrinite, quartz and muscovite.

The analytical purity chemical reagent including citric acid and sulfuric acid from Dengke Chemical Reagent Technology Co., Ltd., was used. The water used in this work was distilled water.

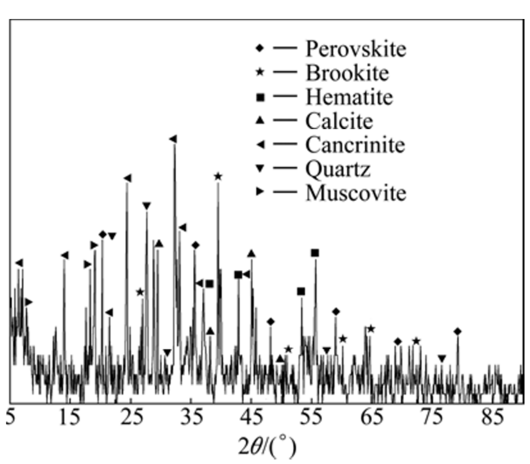

Fig. 2 XRD pattern of red mud sample

2.2 Methods

The sample was firstly dried at 95 °C for 12 h in a TE-DO130 drying oven (China), which was taken out of the drying oven and then cooled further to room temperature. Then 20 g dried sample was mixed citric acid with the sulfuric acid solution of different concentrations. Then, the ore slurry was stirred using a KX79-1 magnetic heating mixer (China) at the speed of 300 r/min under different conditions of time, temperature and liquid-to-solid ratio. The acid leaching solution was collected by filtration with a SHB-IIIA vacuum suction filter (China). The solid residue was dissolved in hydrofluoric acid solution and then the content of titanium was determined by ICP-AES. The recovery of titanium was calculated by the following equation.

$$\alpha = \frac{q - p}{q} \times 100\% \quad (1)$$

where α is the recovery of titanium, q is the titanium quantity of sample and p is the titanium quantity of final residue.

3 Results and discussion

3.1 Effect of citric acid

The effect of citric acid addition on the recovery of titanium is shown in Fig. 3 under the condition of sulfuric acid concentration of 5 mol/L, liquid-to-solid ratio of 5:1, temperature of 90 °C and reaction time of 60 min.

It can be observed that the recovery of titanium increased with increasing the citric acid addition. The increasing rate was sharp in low citric acid addition range, and became mild in citric acid addition ratio range. The recovery of titanium could reach 82% with adding 5% citric acid.

3.2 Effect of sulfuric acid concentration

The effects of sulfuric acid concentration without

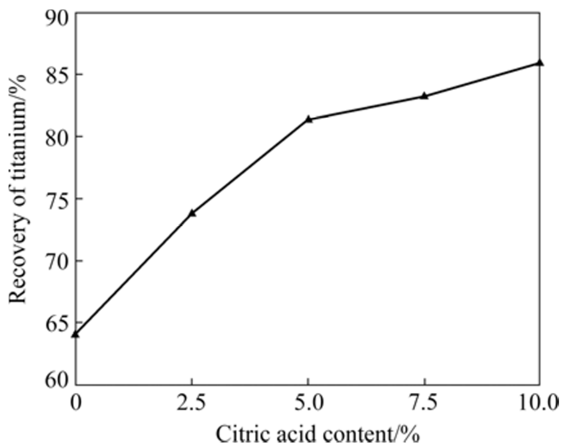

Fig. 3 Effect of citric acid addition on recovery of titanium