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Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 26(2016) 1714–1720

# Effects of electrolyte recycling on desulfurization from bauxite water slurry electrolysis



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Received 29 July 2015; accepted 11 January 2016

Abstract: To lower the cost of bauxite electrolysis desulfurization using NaOH solution as the supporting electrolyte, effects of electrolyte recycling on bauxite electrolysis desulfurization were investigated. The results indicate that electrode corrosion, cell voltage, the desulfurization rate and the pH value of the electrolyte have no obvious changes with the increase of cycle times. Additionally, there were some transitive valence S-containing ions in electrolyte after the electrolysis, such as  $SO_3^{2-}$ ,  $S_2O_3^{2-}$ . However, most of the sulfur in bauxite was eventually oxidized into  $SO_4^{2-}$  into the electrolyte, and these S-containing ions did not affect the recycling utilization for electrolyte.

Key words: high sulfur bauxite; electrolysis; desulfurization; electrolyte; recycling

### **1** Introduction

During alumina production process, S-containing phase is transformed into sulfates (Na<sub>2</sub>SO<sub>4</sub>) [1], resulting in many problems, such as the decline of dissolution rate of Al<sub>2</sub>O<sub>3</sub>, the corrosion of equipment, the reduction of alumina production yield and quality [2]. Once the Na<sub>2</sub>SO<sub>4</sub> scale is generated, the operation efficiency of the whole production system and heat transfer coefficient of the equipment will be lowered, and thus increasing the energy consumption [2]. At present, there are many bauxite desulfurization, methods for including calcination [3], flotation [3,4], wet desulfurization [5] and sintering desulfurization with adding reducing agent and so on [6]. But these methods have many limitations, such as low desulfurization rate, harsh reaction condition and complex process, especially for SO<sub>2</sub> emission due to the calcination.

Pyrite, the main S-containing phase in high sulfur bauxite [3], is the same as the S-containing phase in coal. The process of electrolysis desulfurization relies mainly on the electrochemical oxidation. Pyrite could be oxidized into sulfate by oxidant produced from water electrolysis on anode, achieving the desulfurization through solid–liquid separation. Electrolysis desulfurization has many advantages, including low temperature, normal pressure and high desulfurization ratio [7]. It is noted that electrolysis could also remove simultaneously both organic and inorganic sulfur in minerals, such as coal desulfurization [8]. Additionally, based on the previous results [9–12], the electrolysis desulfurization is more suitable to inorganic ore compared with coal water slurry (CWS) electrolysis [13–16], since anode is covered by organic products as organic ore is electrolyzed.

In our previous work, the feasibility of bauxite electrolysis desulfurization had been verified [17]. To lower the cost of bauxite electrolysis, electrolyte recycling was proposed in this work. However, the process of electrolysis desulfurization might be affected by electrolyte recycling. With the increase of the electrolyte cycle times, the S-containing anions in electrolyte are accumulated gradually. It might bring

Foundation item: Projects (51004090, 51474198) supported by the National Natural Science Foundation of China; Project (KF13-03) supported by State Key Laboratory of Advanced Metallurgy University of Science and Technology Beijing; Project (2015036) supported by Youth Innovation Promotion Association, Chinese Academy of Sciences

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about bad effects to the desulfurization reaction, and finally affecting the desulfurization efficiency. However, if there are no effects of electrolyte recycling on electrolysis desulfurization, electrolyte recycling could be applied to the desulfurization of bauxite electrolysis, which not only could lower the cost of production, but also could lower the environmental pollutant risk. Thus, it is very essential to study the effects of electrolyte recycling on bauxite electrolysis desulfurization.

In this work, the optimal experiment was not done for the ore sample, and thus the best experimental conditions were not obtained. However, this research was focused on the feasibility of electrolyte recycling. It did not affect the experimental results. Grinded bauxite was prepared into slurry with NaOH solution, and the effects of electrolyte recycling on desulfurization from bauxite electrolysis were studied through a variety of characterization methods. Meanwhile, the desulfurization mechanism of bauxite electrolysis in NaOH solution and the conversion of sulfur state in the filtrate were examined by the analysis of the bauxite and the filtrate before and after electrolysis.

#### 2 Experimental

#### 2.1 Samples

A type of high sulfur bauxite from Guizhou province of China was selected as sample. Bauxite composition was analyzed by X-ray fluorescence (XRF, AXIOS, Holland), as listed in Table 1, and ore phase was characterized by X-ray diffraction (XRD, X' Pert PRO MPD, Holland), as shown in Fig. 1. Figure 2 shows the particle distribution of bauxite. As can be seen from

Table 1 Composition of bauxite sample (mass fraction, %)



Fig. 1 XRD pattern of bauxite



Fig. 2 Particle size distribution of bauxite

the data, the aluminum in bauxite mainly exists as the form of diaspore, and the sulfur mainly exists as the form of pyrite. Additionally, there are also potassium manganate and other impurities. The total sulfur content in bauxite is 3.95%.

All chemical compounds used in this work were listed as follows: NaOH solution (1.0 mol/L), dilute hydrochloric acid solution (1.0 mol/L, 3 mol/L), BaCl<sub>2</sub> solution (10%), Pb(Ac)<sub>2</sub> solution (1 mol/L), HNO<sub>3</sub> solution (2 mol/L), AgNO<sub>3</sub> solution (0.5 mol/L), ethanol (95%), Na<sub>2</sub>CO<sub>3</sub> solution (100 g/L), ZnSO<sub>4</sub> solution ((ZnSO<sub>4</sub>·7H<sub>2</sub>O) 100 g/L), glacial acetic acid (1 + 10), iodine standard solution (0.1 mol/L), starch indicator (5 g/L) and deionized water.

#### 2.2 Experiment

The experimental apparatus is shown in Fig. 3, including DC-3006 circulating water bath and WYK-3030S DC power supply. The active area of the nickel electrode was 4 cm × 4 cm. Electrolysis conditions were as follows: the current of 2.4 A, the electrolysis temperature of 90 °C, the electrolyte volume of 400 mL, the slurry concentration of 25 g/L, the stirring speed of 500 r/min, the concentration of NaOH of 1.0 mol/L and the electrolysis time of 4 h. After electrolysis, the filtrate was retained by suction filtration. 1.0 mol/L NaOH was added to the filtrate in each experiment until 400 mL, and then it was reused as the electrolyte. The filter residue was washed repeatedly until there is no white precipitate generated by adding the BaCl<sub>2</sub> solution acidified with hydrochloric acid, and then it was dried. Changes of the electrolysis voltage under the cycle constant current and the pH of the electrolyte before and after the reaction were recorded. Bauxite phase before and after electrolysis was analyzed by XRD, and the sulfur contents in bauxite before and after electrolysis were analyzed by C-S analyzer (LECO CS-344, USA). The sulfur states in the filtrate were

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