Electrochimica Acta 242 (2017) 300–306

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Removal of fluorine from red mud (bauxite residue) by electrokinetics

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ARTICLE INFO

Article history:
Received 10 December 2016
Received in revised form 27 February 2017
Accepted 7 May 2017
Available online 8 May 2017

Keywords:
Red mud
Fluorine
Electrokinetic
Electroosmosis
Electromigration

ABSTRACT

The feasibility of the electrokinetic treatment for the removal of fluorine from the red mud was evaluated. Three electrokinetic experiments were conducted in a self-made electrokinetic apparatus with deionized water as electrolyte, and the potential gradient was set at 0.5, 1.0 and 1.5 V/cm respectively. The effects of the potential gradient on the removal of fluorine and the chemicophysical properties of the red mud were investigated. The results revealed that the fluorine content in the red mud decreased gradually and the red mud properties such as pH and electrical conductivity (EC) were significantly redistributed from the cathode to the anode regions after the electrokinetic treatment. Among the given potential gradients the removal rate of fluorine increased with the potential gradient. 1.5 V/cm had the highest removal rate 63.2% and 1.0 V/cm had very significant and steady electroosmotic flow (EOF). This research shows that the electrokinetic treatment is a novel technique that has high efficiency and promising application for the removal of fluorine from the red mud.

1. Introduction

Red mud is a strong alkaline purplish-red powder-mud solid waste produced in the process of alumina extraction from bauxite. The production of 1 tonne of alumina generates about 1.5 tonnes of bauxite residue [1]. According to statistics, the alumina industry produces more than 1.2×10^8 tonnes of red mud each year and there is a total inventory of 3×10^9 tonnes all over the world [2]. China is the largest producer of both alumina and red mud in the world. In 2012, the red mud generation in China reached 4×10^7 tonnes and the total accumulative amount had been up to more than 2.5×10^8 tonnes [3]. Because there is about 0.01%$\sim$0.15% of fluorine in bauxite, a large number of fluorides exist in the red mud [4]. Literatures have suggested that the fluoride content in its soak solution is up to 11.5–26.7 mg/L [5]. Under the leaching action of rain water, the fluorides dissolve out from the red mud and enter into surface water and ground water, which leads to increasingly serious fluorine pollution, causes endemic fluorosis and does great harm to people's health [6]. According to the 2015 Chinese statistical bulletin of health and family planning career development China now has 1286 endemic fluorosis counties, 32.698 million dental fluorosis sufferers and 3.155 million skeletal fluorosis patients [7]. Therefore, the study on how to remove fluorine from the red mud is of great practical significance.

In the 1980s, researchers began to use electrokinetic technique (EK) to remove pollutants from contaminated soil [8]. At present, EK has shown good prospects for remediating the soils and sediments polluted by heavy metals and organic substances [9–14]. Some published literatures stated that this technique can also be used to remove fluorine from soil effectively [15,16]. Compared with other techniques for soil remediation, EK has demonstrated such advantages as removing various pollutants simultaneously, high removal rate, short remediation period, in-situ remediation, etc. especially in the treatment of the low permeability clay. Red mud, coincidentally, is fine-grained bauxite residue with lower hydraulic permeability and higher content of fluoride [1,5,17], which is similar to high-fluorine contaminated clay soil, so it is hard to remove fluorine from the red mud by conventional methods such as solvent washing [5,18]. Therefore, this research is trying to remove fluorine from the red mud by using electrokinetic treatment and to evaluate the feasibility of this technique. For this purpose, the red mud was loaded in a self-made electrolytic cell and DC electrical field was applied at both ends of the cell. The electric current through the cell and the potential distribution in the red mud were compared under different potential gradients. The changes of the electrolyte pH, conductivity and EOF during the treatment process were analyzed. The fluorine removal rate and the red mud chemicophysical properties after the treatment were also investigated. The results of this research would bring a novel

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http://dx.doi.org/10.1016/j.electacta.2017.05.040
0013-4686/

technique for removing fluorine from the red mud and provide technical support for further comprehensive utilization of the red mud.

2. Material and methods

2.1. Red mud

The red mud used in the experiments was collected from the tailing pond of Luoyang Xiangjiang Wanji aluminium Co., Ltd. The sintered lump red mud was air-dried, sieved through a 0.1 mm mesh screen and mixed thoroughly. The Chemical and physical characteristics of the red mud are shown in Table 1.

2.2. Experimental setup and methodology

The schematic of the experimental setup is shown in Fig. 1. The electrokinetic experiment device was composed of a rectangular Plexiglas box (22 cm × 8 cm × 6 cm) which was divided into three compartments. The central compartment was loaded with the red mud. The left and right parts served as cathode chamber and anode chamber respectively which were separated from the red mud by a 300 mesh number nylon mesh and a perforated plate. Each electrode chamber was connected by silicone tubes to an additional reservoir to store electrolyte. Two four-channel peristaltic pumps (BT100-1F + DG-4-B, Baoding Longer Precision Pump Co., Ltd. China) were utilized to circulate electrolyte and control the liquid level in the electrode chambers. High purity graphite sheets were used as electrodes, which were then connected to a DC power supply (GPC-6030D, Good Will Instrument Co., China) to provide constant voltage for the red mud column. A digital multimeter (F-15B, Fluke, USA) was utilized to measure the voltage distribution along the red mud specimen. The current values were monitored and recorded throughout the experiments by a DC transducer and a paperless recorder (MIK-DZI–500 + MIK-200D, Hangzhou Meacon Automation Technology Co., Ltd. China).

700.0 g red mud and 375.0 mL deionized water were mixed manually and put into the central part of the electrolytic cell, which was then tapped on wood floor to consolidate the red mud. On the cell there was a cover with 13 holes through which inert needle electrodes were inserted into the red mud to measure the electric potential between the cathode and each needle electrode at fixed time. The distances between the needle electrodes were 1.0 cm. After the red mud was equilibrated for 18 hours, peristaltic pumps were switched on to add deionized water. The running speed of the peristaltic pump which inflowed the electrode chambers was 30 rpm and the flow rate was 4.8 mL/min (Fig. 1, blue real line). In this way the solution could always be added into the electrode chambers in a small flow. The running speed of the peristaltic pump which outflowed the electrode chambers was 40 rpm and the flow rate was 6.4 mL/min (Fig. 1, black broken line). Silicone tube heads were fixed on the solution surface in the electrode chambers, so excessive solution could be drawn out in time. Thereby, the solution levels in the electrode chambers as well as in the red mud compartment were controlled accurately throughout the tests in order to maintain a constant hydraulic gradient through the specimen. The solution in the electrode chambers was stirred with the other four channels of the peristaltic pumps.

The catholyte and anolyte were refreshed and collected on a daily basis during the experiments for the further measurement of the volume, fluorine content, pH and EC. After 168 hours of energization, the DC power supply was turned off. The red mud in the cell was sliced into ten pieces, each 1.4 cm in thickness. After the red mud slices were dried and grounded, the fluorine content, pH and EC of each slice were measured.

Three groups of tests were carried out under potential gradient of 0.5, 1.0 and 1.5 V/cm respectively, and deionized water (initial pH 6.98) was used as electrolyte. The initial fluorine content, pH and EC of the red mud were 3000.3 mg/kg, 10.51 and 3450 μS/cm before the experiment.

2.3. Analytical methods

The fluorine content in the red mud was measured by way of acid digestion in conjunction with a fluorine ion selective electrode and that in the electrolyte by fluorine ion selective electrode method (pF-1-01 fluorine ion selective electrode and a 232-01 reference electrode, Shanghai INESA Scientific Instrument Co., Ltd. China) [19,20]. Before measuring F^-, 10.0 ml total ionic strength adjusting buffer (85.0 g $NaNO_3$ and 58.8 g $C_6H_5Na_3O_7 \cdot 2H_2O$ in 1 L) was added into the supernatant to liberate fluorine ion and to adjust the solution pH to about 5.5. The detection limit of the fluorine ion selective electrode was 6.5×10^{-7} mol/L.

The pH of the red mud (1:2.5 red mud/water suspension) and the electrolyte were determined with pH meter (pHSJ-3F), and the EC of them with a conductometer (DDSJ-308A, Shanghai Precision and Scientific Instrument Co., Ltd. China).

3. Results and discussion

3.1. Electric current

During the electrokinetic process, the electric current was the response of the ions to the charge transportation from one electrode to the other in the red mud. Meanwhile, the current through the cell was also an important factor affecting the fluorine removal rate and power consumption [9]. The variation of electric current during the experiments is shown in Fig. 2. As shown, the current exhibited different tendency in the three tests. When the potential gradient was 0.5 V/cm, the initial current was 22.6 mA, then, it progressively decreased to a stable range of 10–12 mA. The current for 1.0 V/cm potential gradient reached its maximum (108.9 mA) after experimenting for 2 hours, then decreased gradually. For 1.5 V/cm potential gradient, the current significantly increased at the initial stage of energization and reached a maximum value (216.8 mA) after 1 hour, then dropped down dramatically to 75 mA within 10 hours and decreased further thereafter. After 72 hours, the current in the three tests stabilized and remained nearly constant (10 mA).

Similar findings have been reported on the extraction of pollutants from soil by electrokinetics [10,11]. During the process of removing fluorine from the red mud by electrokinetics, the current passing through the cell was dependent on the

Table 1
Chemical and physical characteristics of red mud.

Al_2O_3 (%)	CaO (%)	SiO_2 (%)	Fe_2O_3 (%)	MgO (%)	TiO_2 (%)	Na_2O (%)	K_2O (%)	Specific surface area (m^2/g)	Pore volume ($\times 10^{-3} cm^3/g$)	Average pore size (nm)	Fluorine content (mg/kg)	F^- content (mg/kg)
7.48	40.88	25.36	11.29	2.12	1.72	3.19	1.04	10.74	10.96	3.78	3000.3	425.1

Fluorine content means the content of all forms of fluorine in the red mud. F^- content means the content of the water soluble fluorine in the red mud.