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Evaluation of arsenic immobilization in red mud by CO_2 or waste acid acidification combined ferrous (Fe^{2+}) treatment

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ABSTRACT

Arsenic was detected in a red mud (RM) produced during alumina production from bauxite known as the Bayer process. The transporting RM was a mixture of RM solid phase (RMsf) and RM liquid phase (RMlf). The mass content of RMsf in RM is about 30–40%. The alkalinities concentrations in the RMlf were in a range of 37.2×10^3 mg/l to 51.5×10^3 mg/l. Acidification by CO_2 or waste acid (WA) combined with ferrous (Fe^{2+}) treatment was evaluated for arsenic immobilization in the RM. The aqueous arsenic concentration in the RMlf decreased from 6.1 mg/l to 0.5 mg/l and 0.06 mg/l with the addition of CO_2 and WA, respectively. Ferrous was then added to decrease the aqueous arsenic concentration to be lower than 0.05 mg/l. The cost-effective dosages of CO_2 or WA were 80.1 g/l or 26.7 g/l, and the corresponding dosages of ferrous were both 6 g/l. A 2^3 full factorial design was employed to evaluate the importance of chemical components of the RM in the cost of arsenic immobilization. High concentrations of arsenic and alkalinities in the RM will increase the cost while the effects of alumina contents varied during the different acidifications. Dissolvable arsenic in the RMsf was 8.2% and 9.5% after the CO_2 and WA combined ferrous treatments, respectively.

1. Introduction

Each year, about 120 million tons of alumina are produced all over the world [1]. Generally, 1–1.5 tons of red mud (RM) will be produced with each ton of alumina produced. RM has accumulated over the years and caused serious environmental problem because of its high alkalinity and large amount [2]. Although researches have focused on the reutilization of RM [3–5], large amounts of RM are still disposed during alumina production.

RM is usually transported to the RM disposal area in the form of a mixture of solid phase (RMsf) and liquid phase (RMlf). The transporting RM has a solid content of 30–40%. The RMsf is disposed in the RM disposal area and the RMlf is recycled or discharged after treatment. The chemical compositions of the RM were affected by bauxites and additives in alumina production. Arsenic was detected as a harmful component in the RM, which is a neurotoxic material which poses great threat to human health. It was reported that arsenic was contained in the RM (110 mg/kg dry mass) and unleashed by the spill during Hungarian reservoir wall cracks in 2010 [6]. Mobilized arsenic in the RM posed a risk for environment and human health.

Therefore, arsenic immobilization is significant in the RM disposal. There were numerous studies that focused on aqueous arsenic removal or immobilization [7–9]. Up to now, many approaches such as coagulation/precipitation, adsorption, membrane treatment and biological methods were increasingly being used for aqueous arsenic removal or immobilization. Coagulation/precipitation was widely used for its simplicity and low-cost nature, especially in developing countries [10].

It was reported that a high concentration of carbonate inhibited aqueous arsenic removal by coagulation/precipitation [11,12]. The complex chemical composition of the RM, especially the high concentration of alkalinities, could affect the arsenic immobilization efficiency. Therefore, a cost effective technology with high arsenic immobilization efficiency is significant for the RM treatment.

Aqueous arsenic immobilization in the RM has not been reported previously. The main objective of this work was to investigate a cost effective technology for arsenic immobilization in the RM. Carbon dioxide (CO_2) is produced from sintering process for alumina production in the No. 1 factory of Shandong Branch, Aluminum Corporation of China. Industrial waste acid (WA) is a low-cost byproduct. Therefore, CO_2 and WA were used as the cost-effective acidifier in this work. The arsenic contained RM samples were collected from the No. 2 factory of Shandong Branch, Aluminum Corporation of China. The effects and costs of arsenic immobilization technologies in treating RM were evaluated.

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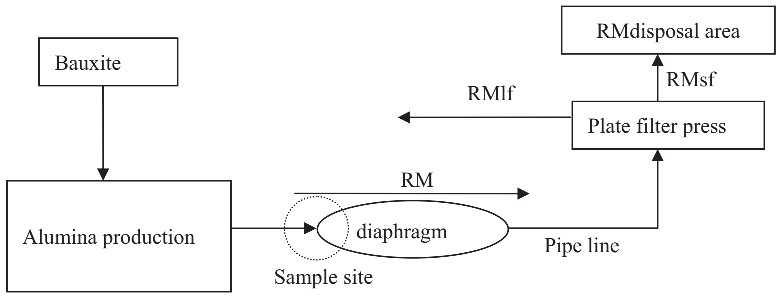

Fig. 1. Schematic explanation of the fate of RM slurry after alumina production.

2. Materials and methods

2.1. RM samples

The RM samples were provided by the No. 2 factory of Shandong Branch, Aluminum Corporation of China. Two samples were collected at the sample site (before diaphragm) in February and October 2010, as shown in Fig. 1

The RMsf contents in these two samples were about 30–40% (w/w). The chemical compositions of RMsf and RMlf were evaluated after solid–liquid separation. The RM was centrifuged at 8000 rpm for 20 min; after that, RMlf and RMsf were collected. The RMlf were filtered through 0.45 μm PVDF membrane filters, and the chemical compositions were evaluated. The RMsf were washed with deionized water three times and then dried at 75°C. An X-ray diffractometer (ShimadzuXRD-6000) operated at 40 kV and 30 mA. Cu Kα (l = 0.15418 nm) radiation over the range of 2 from 10 to 80° was used to identify the crystal structure and crystallinity. The main mineral phases of the RM were hematite, anatase, quartz, $CaCO_3$ and α-$Al(OH)_3$.

2.2. WA pre-acidification

Industrial waste acid (WA, mainly hydrochloric acid) was provided by Zibo City Economic and Trade Co., Ltd. The free H^+ concentration in WA was 5.9 M. WA was quantitatively added to a 1000 ml RM, which was placed in a plastic jar. The mixture was mixed with a stirrer at 300 rpm for 20 min and the pH was measured. A 20 ml volume of RM was collected after WA pre-acidification. The collected RM was centrifuged at 8000 rpm for 20 min. The RMlf were filtered through a Type HA filter (0.45 μm, Millipore) and the chemical compositions of elements were measured. The RMsf were 24 h continuous freeze drying to preserve the original structure of the mineral phase.

2.3. CO_2 pre-acidification

A schematic diagram of the aeration equipment is shown in Fig. 2. Carbon dioxide was provided by a high-pressure gas cylinder and the aeration rate of 100 ml/min was controlled by a rotameter. The aeration time and flow rate were used to calculate the amount of carbon dioxide. 1000 ml of the RM was placed in the plastic beaker, which was mixed with carbon dioxide by a stirrer at 500 rpm. A plastic cover was placed on top of the jar to improve the gas utilization efficiency. The pH detector was placed in the jar, and the results were measured during CO_2 added. Meanwhile, a 20 ml volume of RM was collected. The collected samples were centrifuged at 8000 rpm for 5 min. The supernatant was filtered through a Type HA filter (0.45 μm, Millipore) and the chemical compositions of elements were measured. The residue was freeze dried for 24 h to preserve the original structures of the RMsf.

2.4. Iron precipitation

Ferrous stock solution was prepared by quantitatively dissolving $FeSO_4·6H_2O$ (analytical grade) in deionized water. Ferrous was added in the RM followed by 300 rpm mixing for 30 min using a multiple stirrer apparatus. Collected samples were treated by the method previously described. Supernatants and residues were separated by a centrifuge (LD5-2A, Beijing Lab Centrifuge Co., Ltd.). A leachability test was conducted to evaluate the mobility of arsenic in the RMsf.

2.5. Cost evaluation

The cost for arsenic immobilization in the RM was evaluated. Total cost consisted of acidification and ferrous treatment. The costs for RM transportation, gas purging, and mixing are only a small proportion in the total cost. CO_2 is produced and emitted directly in No. 1 factory of Shandong Branch, Aluminum Corporation of China, and the cost was not considered in the evaluation. Ferrous and WA were about 23.3 US dollar/t and 6.2 US dollar/t, respectively. The exchange rate of the RMB against the US dollar was about 1–6.5 in 2010. Furthermore, a 2^3 full factorial design was employed to evaluate the importance of chemicals content in the RM on the cost of arsenic immobilization. The different alumina, arsenic and alkalinity concentrations were artificially prepared with analytical-grade chemicals added to the RM samples.

2.6. Leachability test of arsenic in the RMsf by water elution

Because of the base condition and buffer ability of RM, the leachability test did not follow the standard TCLP test. A four-stage water elution test [13] was carried out to determine the arsenic retention in the RMsf. Briefly, after freeze-drying, 1 g of

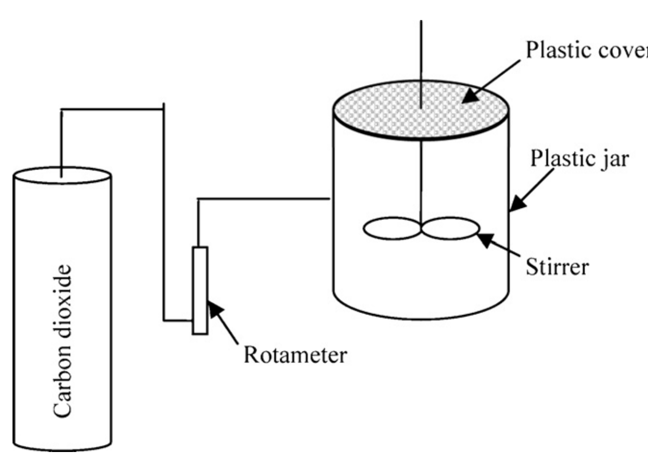

Fig. 2. Schematic explanation of carbon dioxide aeration system.