Hydrometallurgy 151 (2015) 98–106

Contents lists available at ScienceDirect

Hydrometallurgy

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

Reduction of alkalinity in bauxite residue during Bayer digestion in high-ferrite diasporic bauxite

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ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 25 November 2014
Accepted 27 November 2014
Available online 2 December 2014

Keywords:
Bayer process
Digestion
Hydrogarnet
Alkalinity
Bauxite residue

ABSTRACT

Bauxite residue is a hazardous solid waste generated during the Bayer process of extracting alumina from bauxite ore, the high alkalinity of which limits its large-scale industrial applications. In order to reduce the alkalinity of bauxite residue, rich lime additions from 0 to 30 wt.% and high digestion temperatures from 250 °C to 300 °C were performed on a high-ferrite diasporic bauxite during the Bayer digestion. The alumina extraction efficiency from bauxite and the Na_2O to SiO_2 weight ratio of the bauxite residue were systemically investigated. The alkalinity in the bauxite residue decreases considerably with the increasing lime addition, digestion temperature and duration. The bauxite residues after digestion are mainly comprised of hematite, zeolite, grossular hydrogarnet, andradite–grossular hydrogarnet and perovskite, but their proportions vary greatly. A new method to accurately calculate the mineralogical compositions is proposed according to both the chemical compositions and XRD analyses of the bauxite residues. The mechanisms of alkalinity reduction in the bauxite residue and performance change in bauxite digestion are discussed.

1. Introduction

Bauxite residue, also known as Bayer red mud, a hazardous solid waste generated during the Bayer process of extracting alumina from bauxite ore, has been attracting more and more attention due to the environmental damage caused by it (Power et al., 2011; Liu et al., 2009; Samal et al., 2013). The global inventory of stored bauxite residue is currently estimated to be over 2.7 billion tonnes, with an annual growth rate of approximately 120 million tonnes. As a huge industrial waste, a variety of technologies have been proposed to utilize the bauxite residue (Klauber et al., 2011), though little evidence exists of any significant utilization due to the great barriers of volume, performance, cost and risk. However, high alkalinity is the primary reason for the lack of large-scale industrial applications (Gräfe et al., 2011).

The pH in bauxite residue slurry (washer overflow) ranges 9.2–12.8 with an average value of 11.3 ± 1.0. The alkaline solids formed by the reaction of caustic soda with bauxite in the Bayer process are mainly comprised of various hydroxides, carbonates, aluminates and aluminosilicates. The usual chemical compositions of bauxite residue are Al_2O_3 18–25 wt.%, Na_2O 6–12 wt.%, SiO_2 15–20 wt.%, and TiO_2 2–5 wt.% (Palmer et al., 2009). Fe_2O_3 and CaO are also present, but their proportions vary greatly depending on the bauxite type and the leaching conditions (Cao et al., 2013). A large amount of alumina and alkali is lost during the Bayer digestion process when they combine with the silica in bauxite to form desilication products (DSPs), an insoluble solid and the primary existing form of alkali in the bauxite residue.

The mineralogy of DSPs formed during the conventional Bayer process is sodium aluminosilicate hydrate, which has several structures such as zeolite, sodalite and cancrinite (Barnes et al., 1999; Zheng et al., 1998). The general stoichiometry of sodium aluminosilicate hydrate is $Na_6[Al_6Si_6O_{24}]\cdot Na_2X\cdot nH_2O$, where X represents a variety of inorganic anions, such as CO_3^{2-}, SO_4^{2-}, $2Cl^-$, $2OH^-$ or $2NO_3^-$ (Whittington et al., 1998; Radomirovic et al., 2013). The DSPs formed during the non-conventional Bayer process with lime addition are mainly comprised of Ca-cancrinite and hydrogarnet (Xu et al., 2010; Whittington and Fallows, 1997). Ca-cancrinite, formed due to the existence of carbonate, has the stoichiometry of $Na_6[Al_6Si_6O_{24}]\cdot CaCO_3\cdot nH_2O$. Hydrogarnet, with the stoichiometry of $X_3Y_2(SiO_4)_n(OH)_{(12-4n)}$ where X and Y are cations, has a complex formation process. The crystal structure of hydrogarnet has the space group Ia3d and all cation positions are fixed by symmetry (Hawthorne, 1981). X, Y and Si denote dodecahedral, octahedral and tetrahedral coordination relative to O respectively (Ballaran and Woodland, 2006). These site occupancies involve Ca, Mg and Na in X-site, and Al, Fe and Ti in Y-site (Locock, 2008). Obviously, of all the DSPs, hydrogarnet is the ideal phase in terms of reduction of alkalinity in the bauxite residue.

The recovery of valuable metals from bauxite residue has been studied by many researchers (Zhong et al., 2009; Liu et al., 2012). These metals are mainly iron, aluminum, calcium, sodium and titanium as well as some minor or trace components of gallium and scandium. Among all the major metals, the recovery of iron is the most attractive. The reason is that iron oxides usually accounts for half of the bauxite

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http://dx.doi.org/10.1016/j.hydromet.2014.11.015

residue, even as high as over 60 wt.%. The composition of iron oxides in bauxite ore can reach 20–40 wt.% in the forms of hematite, goethite and magnetite. These bauxite ores are generally called high-ferrite bauxite or Al–Fe associated ore. If both Al and Fe can be extracted, there is a considerable economic advantage. A new and clean technology to process the high-ferrite diasporic bauxite with zero waste has been proposed by the authors, and the processing schematic is shown in Fig. 1 (China Patent, 2012). The basic technical route is to: firstly extract alumina by the Bayer process, then produce iron from the bauxite residue with low alkalinity by smelting reduction based on using coal, and extract alumina from the iron smelting slag by the sinter process (Smith, 2009). The leached smelting slag after alumina extraction is mainly comprised of calcite and dicalcium silicate, which can be used to produce cement.

However, the most difficult stage is to reduce the alkalinity of the bauxite residue in order to produce iron. The usual lime addition to the Bayer digestion process of diasporic bauxite is about 5–9 wt.% of the bauxite, and the corresponding DSPs formed during the high temperature digestion usually contain sodium aluminosilicate hydrate, Ca-cancrinite and hydrogarnet. Therefore, the alkali content in the bauxite residue is always over 6 wt.%. Since the addition of lime can promote the conversion of sodalite and cancrinite to hydrogarnet, the aim of this paper is to reduce the alkali content of bauxite residue to below 1 wt.% by adding excess lime and raising the digestion temperature. The corresponding reaction mechanisms are also discussed.

2. Materials and procedures

2.1. Materials

The high-ferrite diasporic bauxite was ground to particle size less than 0.28 mm. Lime with 93.12 wt.% reactive CaO was produced by calcination of industrial limestone at 1050 °C for 3 h. Sodium aluminate liquor for the digestion experiments was prepared by dissolving industrial sodium hydroxide and aluminum hydroxide into industrial Bayer liquor. The concentrations of industrial Bayer liquor are as follows: caustic alkali 244.2 g/L (in the form of Na_2O), total alkali 259.2 g/L (in the form of Na_2O), alumina 140.5 g/L, silica 0.5 g/L, organic carbon 5.8 g/L, chloride 6.4 g/L, and sulfate 0.9 g/L. The initial concentrations of caustic Na_2O and Al_2O_3 in the adjusted sodium aluminate liquor for all the digestion tests were 240.0 g/L and 136.1 g/L respectively.

2.2. Experimental procedures

The digestion experiments were carried out in a 150 mL bomb reactor. The reactor was heated by molten salt with a temperature control accuracy of ±1 °C and the bomb was rotated at 48 rpm. The slurry (28.57 g bauxite in 100 mL liquor) with different lime dosages was put into the bombs, sealed and rotated. The digestion experiments were performed at 250–300 °C for different durations. All the digestion experiments were repeated 2 or 3 times. The slurry was then cooled and separated by centrifuging. The solids were washed and dried. The alumina extraction efficiency from bauxite was calculated using the following formula:

$$\eta_{Al_2O_3} = \frac{(A/S)_{ore} - (A/S)_{residue}}{(A/S)_{ore}} \times 100\% \qquad (1)$$

$(A/S)_{ore}$ and $(A/S)_{residue}$ denote the weight ratios of Al_2O_3 to SiO_2 in the bauxite ore and bauxite residue respectively.

2.3. Solid analyses

The chemical compositions of the bauxite and bauxite residues were analyzed using an X-ray fluorescence spectrometer (XRF, ZSX100e). In order to identify the phase compositions of the bauxite and bauxite residues after digestion experiments, X-ray diffraction measurements (XRD, PANalytical PW3040/60) were performed using Cu-Kα X-radiation (all samples were ground to less than 45 μm in particle size). The scan rate was 3° 2θ/min. A semi-quantitative analysis using 10% crystalline MgO as an internal standard was performed to calculate the mineralogical composition of bauxite. Scanning electron microscopy

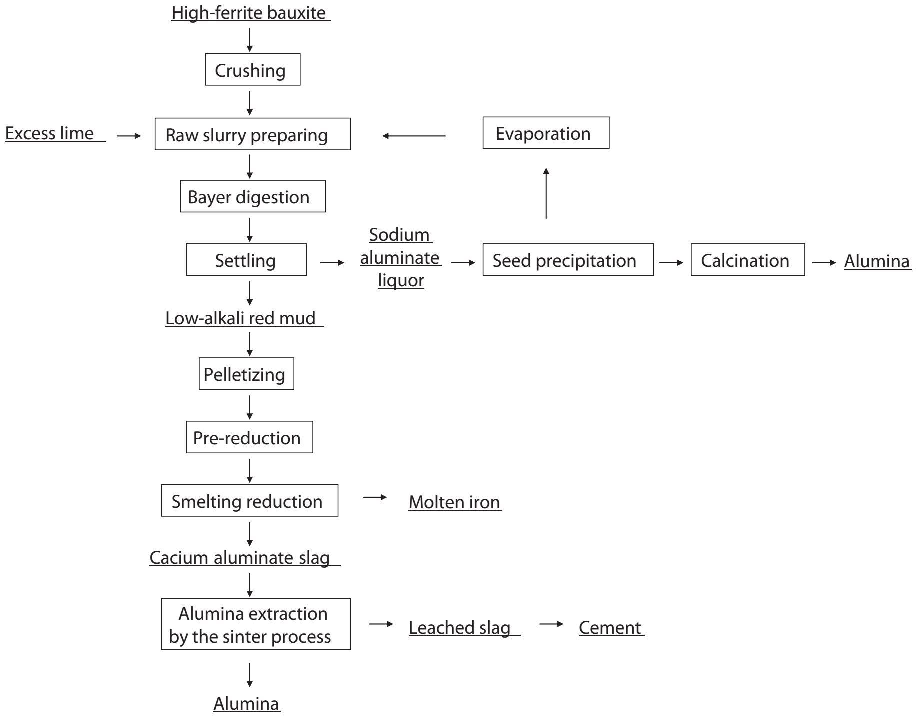

Fig. 1. Processing schematic of high-ferrite diasporic bauxite to extract alumina and iron.