

Extraction of rare earths from bauxite residue (red mud) by dry digestion followed by water leaching



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ABSTRACT

In this work, the extraction of selected rare earth elements from bauxite residue by dry digestion method followed by water leaching was investigated. Kinetic studies performed with HCl and H₂SO₄ demonstrated that, at ambient temperatures, silica dissolution increases with increasing acid concentration, which leads to the formation of silica gel. Dissolution of silica is limited to less than 5 wt% by applying a two-step process: dry digestion of bauxite residue with HCl or H₂SO₄, followed by water leaching. The extraction of aluminium was low because of the low solubility of aluminosilicate compounds. The extraction of iron and titanium increased with increasing acid concentrations. High extraction of the rare-earth elements (REEs) were achieved with the HCl-based dry digestion method, but the concentration in the leachate was limited to approximately 6–8 mg L⁻¹. About 40 wt% of scandium was recovered with a high co-dissolution of iron, due to the occurrence of scandium (III) ions in the lattice matrix of iron(III) oxide. Dry digestion method with multi-stage circulation of the acid leaching solution significantly increased the REEs concentration up to 20 mg L⁻¹, while achieving an acid consumption of 788 g of HCl per kilogram of bauxite residue, and a significant reduction of water consumption (60%) relative to the single-stage acidic leaching method. The low water consumption allows to increase the filtration efficiency of the leach liquor due to the avoidance of silica gel formation.

1. Introduction

Bauxite residue (BR, also called red mud) is the waste product generated during alumina production from bauxite by the Bayer process (Patterson et al., 1986). It is composed essentially of compounds that are insoluble in concentrated sodium hydroxide solutions: iron and titanium minerals, undigested alumina minerals, sodium aluminium hydrosilicates and calcium compounds. It has been estimated that the annual global production of bauxite residue exceeds 150 million tonnes (Deady et al., 2016; Evans, 2016) and, according to numbers from the year 2007, about 2.7×10^9 tonnes have been already accumulated in tailing ponds, dry stacking and other dry disposal methods (Klauber et al., 2011). It is believed that today, this amount has increased to approximately 4×10^9 tonnes (Aluminium and the European Aluminium Association, 2015).

Bauxite residue represents an interesting source for major elements such as aluminium, iron and titanium, but also for rare-earth elements (REEs) (Binnemans et al., 2015). The chemical composition of bauxite residue shows a very wide variability, as it depends on the origin of the

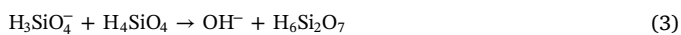
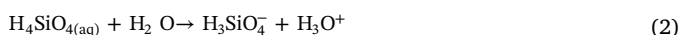
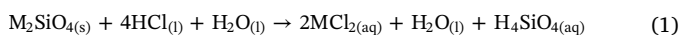
bauxite ore and the operational conditions during the Bayer process. A range on composition of minerals typically found on bauxite residue has been reported by Evans (Evans, 2016). REEs are normally associated to phosphate (e.g., monazite (REEPO₄)) and fluorocarbonate (e.g., bastnäsite (REECO₃F)) compounds (Mongelli, 1997). Bastnäsite is the most common host for rare-earth oxides in karst bauxites (Maksimovic and Panto, 1991; Mongelli, 1997). The enrichment factor of the rare earths in bauxite residue compared to bauxite is about a factor of two (Ochsenkuhn-Petropulu et al., 1994). The concentration of rare earths in bauxite residue may vary between 500 and 1700 mg kg⁻¹ (Akçil et al., 2017).

Scandium represents 95% of the economic value of the REEs present in bauxite residue (Borra et al., 2015b). Ores with a scandium content range between 20 and 50 mg kg⁻¹ are considered as resources and are worthy of exploitation (Shaoquan and Suqing, 1996). The highest concentration of scandium is found in Jamaica bauxite residue, with concentration as high as 260 mg kg⁻¹ (Borra et al., 2016a). This concentration is ten times higher than the average concentration of scandium in the Earth's crust. Several methods based on direct leaching by

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acids have been reported for recovering valuable metals from bauxite residue (Borra et al., 2016a; Liu and Li, 2015; Wang et al., 2011; Zhang et al., 2016a). The extraction efficiencies depend on the acid concentration with more extraction achieved at higher acid concentrations, but the amount of iron dissolution increases with acid concentration as well and this limits the REE concentration in the leachate (Borra et al., 2015b; Ochsenkuhn-Petropulu et al., 1994; Ochsenkuhn-Petropulu et al., 1996; Rivera et al., 2017). Although conventional direct acidic leaching of bauxite residue allows a high extraction of REEs with a low iron dissolution (Rivera et al., 2017), the concentration of REEs in the leachate (5–9 mg L⁻¹) is still about one hundred times lower than the iron concentration (about 900 mg L⁻¹), which hampers the extraction of REEs in further processing, for instance in the solvent extraction step (Onghena et al., 2017). However, the concentration of REEs in the leachate may be increased by a multi-stage treatment. The method has demonstrated promising results in terms of acid consumption reduction and enhancement of leaching efficiency, by which the concentration of metals in the leach liquor is increased (Onghena et al., 2017; Xia et al., 2015; Zhu et al., 2012). The application of the multi-stage leaching method to bauxite residue may increase the REE concentration in the leachate, although a high silica dissolution may also be expected, as well as an accumulation of major metals in the final leachate. A high silica dissolution leads to a greater silicon supersaturation index (SSI), which represents the ratio of dissolved silica with respect to the maximum silica solubility (Kokhanenko et al., 2016). The increase of SSI is considered to be the driving force for silica polymerization (Hamouda and Amiri, 2014; Tobler et al., 2009). In HCl or H₂SO₄ media, at relatively low pH values, i.e. below the isoelectric point for silica in the solution (pH_{iso} between 1.7 and 2.2) (Wilhelm and Kind, 2015), the hydrolysis of silica occurs very fast to produce H₄SiO₄ and H₃SiO₄⁻ (Eqs. (1) and (2)), which are the precursors for silica gel polymerization (Hamouda and Amiri, 2014; Zerda et al., 1986). Initially, silica monomers (e.g., H₄SiO₄, H₃SiO₄⁻) polymerize via dimers, trimers, etc. to cyclic oligomers (Si_{n+1}O_{m+2}OH), according to Eqs. (3) and (4). These oligomers continue to react until a gel network is formed via Ostwald ripening, i.e. dissolution of smaller particles and precipitation on larger particles, which finally results in the formation of an acidic silica gel (Tobler et al., 2009)



Among others, quartz, sodalite and cancrinite are the most abundant silica bearing minerals in bauxite residue, although silica gel is produced by the acidification of amorphous silicate minerals. Such compounds have a higher solubility in comparison to quartz, which makes these minerals of special interest for further research (Friedrich et al., 2016).

Silica gel formation represents a serious drawback in the extraction of metals from ores and process residues by hydrometallurgical methods because the gel solutions can no longer be filtered (Abkoshk et al., 2014; Queneau and Berthold, 1986; Shi et al., 2017; Zhang et al., 2016b). Additionally, this gelatinous precipitate may blind ore particles from further dissolution and reduce the leaching kinetics significantly. According to the literature, silica (and also iron) can remain undissolved when the bauxite residue is processed by the consecutive combination of sulfation, roasting and leaching processes, which also allows to achieve a high selectivity for REEs (Borra et al., 2016c; Onghena et al., 2017). However, this method is limited by the high energy consumption due to the decomposition of sulfates during roasting and evaporation of water during sulfation (Borra et al., 2016b). Another method, dry digestion, is an effective way to avoid the dissolution of amorphous silica from silicate minerals mainly because it

may take place at ambient conditions. The method consists in contacting silicate minerals with strong acids in a water-deficient system, i.e. a high solid concentration, by which silica is effectively rejected from the respective minerals (Dufresne, 1976). It is stated that in a water-deficient system, the interaction between the metal and the acid (i.e. formation of MSO₄ or MCl₂ with concentrated H₂SO₄ or HCl, respectively, where M represents the valuable metal) scavenges the available water of the system, so that no hydration of the silica is possible. This way, the silica polymerization is avoided, and the dehydrated silica (i.e. SiO₂) is readily filterable. The same principle applies in the so-called acid pugging and curing method, but the technique requires temperatures in the range of 100–200 °C (Amer et al., 2000). The dry digestion method is applied at ambient temperature, which represents its most remarkable advantage.

Although there exist no literature reports on the application of dry digestion to bauxite residue, researchers have reported promising results on the use of this technique for extraction of metals from eudialyte (Davris et al., 2017; Friedrich et al., 2017, 2016; Voßenkaul et al., 2017), but also from different silicate minerals for zinc and manganese extraction (Dufresne, 1976; Groot et al., 2013; Kazadi et al., 2016; Zhang et al., 2016b).

The objective of this paper is to evaluate the extraction of REEs from bauxite residue by dry digestion with concentrated mineral acids (i.e. HCl, H₂SO₄), followed by water leaching. Valuable metals can be effectively washed out by using this method since silica polymerization does not occur, which significantly can improve the filterability of the leach liquor. Direct leaching experiments of bauxite residue are performed with HCl and H₂SO₄ at different concentrations in order to study the behaviour of silicon during acid leaching over time. A multi-stage leaching was applied after dry digestion to increase the REEs concentration in the leachate. The process has been compared with the conventional direct acidic leaching method in terms of selected REEs and iron concentration, and acid consumption.

2. Material and methods

The bauxite residue studied in this paper was kindly provided by Aluminium of Greece (Agios Nikolaos, Greece). It originates from a mixture of karst and lateritic bauxites. It was received from the alumina refinery after dewatering by filter pressing and drying at room temperature. Upon arrival in the lab, the sample was further dried at 105 °C for 24 h. Chemical analysis of the major elements in bauxite residue was performed by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400). Chemical analysis of the minor elements was performed after complete dissolution of the bauxite residue by alkali fusion and acid digestion in 3 vol% HNO₃ solution, followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) analysis. The alkali fusion was carried out by mixing 0.5 g of bauxite residue with 1.5 g of sodium carbonate and 1.5 g of sodium tetraborate decahydrate, followed by heating the mixture in a platinum crucible at 1100 °C for 30 min. The mineralogy of the samples was studied by X-ray powder diffraction (XRD, Bruker D2 Phaser). The obtained data were evaluated with EVA V.3.1 (Bruker AXS) and quantified with Topas-Academic V.5, using the Rietveld method.

Leaching experiments of bauxite residue over time were performed in a 150 mL glass reactor with HCl (37 vol%, Fisher Scientific) and H₂SO₄ (95–97 vol%, Sigma-Aldrich) solutions of a fixed concentration (0.5, 1.0 and 1.5 N) at ambient conditions, i.e. 25 °C. The experimental set-up consists of a hot-plate magnetic-stirrer device, a pH-electrode (Hamilton, VWR) and a thermocouple (Pt100, VWR). Within the reactor solid particles were mixed with 100 mL of the corresponding solution at a liquid-to-solid ratio (L/S) of 5:1. The entire experiment lasted for 60 min, in which aliquots (about 2 mL) of slurry were extracted from the glass reactor at specific time intervals. The mixtures were continuously agitated during the whole experiment to ensure a homogenous suspension. Each aliquot was filtered using a syringe and a

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