



## Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching



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### ABSTRACT

Bauxite residue (red mud) that is generated from karst bauxite ores is rich in rare-earth elements (REEs). The REEs can be recovered from bauxite residue by direct acid leaching but the extraction yields are generally low. The extraction yields can be increased by increasing the acid concentration but this will increase the dissolution of iron as well. Large amounts of iron in the leach solution create problems in the further recovery processes. Therefore, a combined sulfation–roasting–leaching process was developed to selectively leach the REEs while leaving iron undissolved in the residue. In this process bauxite residue was mixed with water and concentrated H<sub>2</sub>SO<sub>4</sub> followed by drying, roasting and then leaching of the roasted product with water. Most of the oxides were converted to their respective sulfates during the sulfation process. During subsequent roasting, unstable sulfates (mainly iron(III) sulfate) decompose to their respective oxides. Rare-earth sulfates, on the other hand, are stable during roasting and dissolve during water leaching, leaving the iron oxides in the residue. The effect of the roasting temperature, roasting time and amount of acid on leaching of the different elements was studied. Decreasing the roasting temperature increased the dissolution of the REEs, but also that of iron and aluminum. Increasing the amount of acid led to higher REEs extraction. Acid to bauxite residue mass ratio beyond 0.75 at 650 °C increases the iron and aluminum dissolution due to increase in the iron(III) and aluminum sulfate amounts. The extraction of REEs slightly increased (<5%) with roasting time up to 2 h at 675 °C, but a further increase of the roasting time has a negative effect on the REEs extraction as the low amount of iron sulfate in the roasted mass increases the pH of the leach solution. About 60% of scandium and more than 90% of the other REEs can be dissolved at optimum conditions, while only a very small amount of iron (<1% of total iron) is solubilized. The residue after leaching was rich in Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CaSO<sub>4</sub>·0.5H<sub>2</sub>O.

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### 1. Introduction

Bauxite residue (red mud) is a waste generated during the Bayer process for alumina production. The annual global production of bauxite residue is about 140 million tons (Evans, 2015), while 2.7 billion tons of it is already stockpiled (Klauber et al., 2011). Storage of this material can pose an environmental challenge and space-consuming. However, bauxite residue that is generated from karst bauxite ores contains a significant amount of rare-earth elements (REEs). Practically all REEs end up in the bauxite residue during the Bayer process (Binnemans et al., 2015). Many researchers have

studied the direct acid leaching of bauxite residue for recovering REEs (Fulford et al., 1991; Ochsenkühn-Petropulu et al., 1996; Qu and Lian, 2013; Smirnov and Molchanova, 1997; Yatsenko and Pyagai, 2010), but the extraction yields are relatively low for the light REEs. These extraction yields can be improved by increasing the acid concentration, but an increase in acid concentration also leads to more iron dissolution into the leach solution (Borra et al., 2015). Large amounts of iron in the leach solution generate problems in the subsequent downstream processes, e.g. solvent extraction (Fulford et al., 1991). Therefore, iron removal from bauxite residue by smelting reduction prior to leaching could be an option for selective leaching of REEs (Binnemans et al., 2015; Borra et al., 2016; Logomerac, 1979; Sargic and Logomerac, 1974). However, high acid consumption, high temperature

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requirement during leaching, still considerable amount of iron dissolution are the major concerns in this route (Borra et al., 2016). Furthermore, large amounts of other impurities are also dissolved into the leach solution during direct and slag leaching, which generates large volume of effluents. Hence, a sulfation–roasting–leaching process was developed to selectively leach the REEs. This process was earlier developed for selective extraction of nickel and cobalt from iron rich lateritic ores (Guo et al., 2009; Kar and Swamy, 2000; Nicolas et al., 1968; Swamy et al., 2003) and recently applied for selective extraction of neodymium from neodymium–iron–boron (NdFeB) magnets (Önal et al., 2015).

Sulfation–roasting–leaching of a Greek bauxite residue was investigated in the present work for the purpose of REEs extraction. This is the first study for extraction of REEs from bauxite residue by this type of process. The effect of different process parameters including the amount of sulfuric acid, the roasting temperature, roasting time and different leaching parameters on the leaching efficiencies of the different elements were studied.

### 1.1. Sulfation–roasting–leaching

The flow sheet of the sulfation–roasting–leaching process consists of three major steps: (1) mixing the moistened feed material with concentrated sulfuric acid; (2) roasting and (3) leaching with water (Fig. 1). During acid mixing and the subsequent drying stages (e.g. sulfation), most of the oxides convert to their respective sulfates. As an example, at roasting temperatures of 600–700 °C, sulfates with low thermal stability such as iron(III) sulfate decompose to give their respective water-insoluble oxides (Eq. (1)).



The water-soluble rare-earth sulfates, on the other hand, are stable at such roasting temperature ranges (Bergmann, 1981) and they dissolve easily during the subsequent water leaching step leaving the iron oxides in the residue.

The main advantages of the sulfation–roasting–leaching process can be summarized as follows: (1) limited leaching of iron, titanium and aluminum; (2) no or very limited silica leaching, so that filtration problems can be avoided; (3) the possibility of (consumed) acid regeneration and therefore low acid consumption and (4) small volumes of waste water generation compared to direct leaching. Additionally, the pH of the residue after water

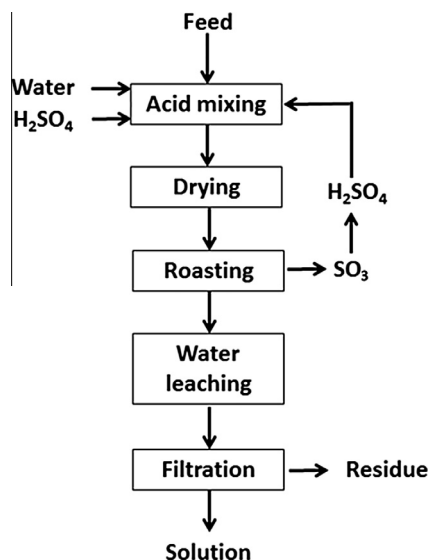


Fig. 1. Flow sheet of the sulfation–roasting–leaching process.

leaching is close to neutral and very low in sodium content (management and utilization of this stream in other applications is easier). The main drawback of this process is that it needs an extra processing (roasting) step.

## 2. Experimental

The bauxite residue used in this study was provided by Aluminium of Greece. The residue was first dried at 105 °C for 12 h. The dried sample was passed through 500 µm size sieve. Chemical analysis of the major elements was performed with wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400) whereas that of the minor elements was performed by complete dissolution of the bauxite residue by alkali fusion and acid digestion in a 1:1 (v/v) HCl solution, followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) analysis. Thermo-gravimetric analysis (TGA, Netzsch STA 409) experiments were carried out in nitrogen atmosphere from room temperature to 1000 °C at a heating rate of 10 °C min<sup>-1</sup>. The mineralogy of the samples was studied by X-ray diffraction technique (XRD, Philips PW1830). The powder morphology was investigated by scanning electron microscopy (SEM, Philips XL30). The particle size of the samples was measured by laser particle size analysis (Malvern Mastersizer 3000). The results for particle size, SEM, TGA and XRD analysis of bauxite residue have already been reported elsewhere (Borra et al., 2015).

Analytical reagent grade sulfuric acid (95–97%) (Sigma–Aldrich) was used in the present study. During the acid mixing step (i.e. sulfation), the dried sample was moistened with deionized water (bauxite residue to water mass ratio is 1:0.4, unless specified) in a porcelain crucible and then mixed with concentrated sulfuric acid based on the experimental conditions. The addition of water was to ensure homogenous mixing. After mixing, samples were heated at 120 °C for 12 h to ensure complete sulfation of the bauxite residue. After drying, the samples were subsequently roasted at a set temperature for a selected time in a muffle furnace. Non-agitated leaching experiments were conducted at room temperature with deionized water in polyethylene bottles. Agitation leaching experiments were carried out in sealed polyethylene bottles by using a laboratory shaker (Gerhardt Laboshake) at 160 rpm and 25 °C. High-temperature leaching experiments were carried out in a 500 ml glass reactor fitted with a reflux condenser and placed on a temperature-controlled ceramic hot plate with a magnetic stirring system. After leaching, the solution was filtered with a syringe filter (pore size of 0.45 µm) and the obtained filtrate was diluted with acidified deionized water (Milli-Q, resistance 18.2 MΩ cm). The percentage extraction was calculated based on ICP-MS analysis of the clear leachate.

## 3. Results and discussion

### 3.1. Bauxite residue characterization

The chemical analysis of the bauxite residue used in this study is shown in Tables 1 and 2. Table 1 shows that the bauxite residue

Table 1  
Major chemical components in the bauxite residue sample (Borra et al., 2015).

	wt%
Fe <sub>2</sub> O <sub>3</sub>	44.6
Al <sub>2</sub> O <sub>3</sub>	23.6
CaO	11.2
SiO <sub>2</sub>	10.2
TiO <sub>2</sub>	5.7
Na <sub>2</sub> O	2.5

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