Recovery of rare earths from bauxite residue slag by high-pressure acid leaching

Rodolfo Marin RIVERA[1], Buhle XAKALASHE[2], Ghania OUNOUGHENE[1], Koen BINNEMANS[3], Bernd FRIEDRICH[2], Tom VAN GERVEN[1]

[1] Department of Chemical Engineering, KU Leuven, 3001 Heverlee, Belgium

[2] Institute of Process Metallurgy and Metal Recycling, RWTH Aachen University, 52056 Aachen, Germany

[3] Department of Chemistry, KU Leuven, 3001 Heverlee, Belgium

rodolfoandres.marinrivera@kuleuven.be

Abstract

The recovery of rare-earth elements from an alumina and silica rich slag produced during the smelting reduction process of bauxite residue was studied. The slag was leached with sulfuric acid at different concentrations (1-3 N H_2SO_4) in a titanium autoclave at a liquid-to-solid ratio of 10:1 and different temperatures (100-180 °C). The dissolution of rare-earth elements increased with increasing acid concentration, but it decreased with increasing temperatures. About 95 wt% of the scandium could be extracted with 3 N H_2SO_4 at 100 °C, while about 87 wt% yttrium was extracted under the same conditions. Neodymium and lanthanum yields were about 45-60 wt%. Temperatures above 100 °C lead to a high selectivity of scandium over the other rare earths (i.e. yttrium, neodymium and lanthanum).

Introduction

Bauxite residue (BR, also called red mud) represents an interesting source for major elements such as aluminium, iron and titanium, but also for rare-earth elements (REEs).[1] Several methods based on direct acid leaching have been reported for recovering valuable metals from bauxite residue.[2-5] The extraction efficiencies depend on the acid concentration. Although higher acid concentrations lead to a more efficient extraction of major metals (e.g., iron, aluminium, titanium), the silica dissolution increases as well.[6,7] A high silica dissolution can lead to problems with silica gel formation and, consequently, the gel solutions can no longer be filtered.[9,10] However, kinetic studies have demonstrated that silica dissolution decreases when the temperature is increased and the acid concentration is reduced. This is due to an enhancement in the solubility of monomeric silicic acid formed during acid leaching.[11]

High-pressure acid leaching (HPAL) can limit the dissolution of not only silicon, but also of titanium, aluminium and iron, as hydrolysis of the ions of these elements takes place at high temperatures.[12] Therefore, the acid consumption can be

reduced. Since the REEs do not hydrolyze under these conditions, they can be selectively recovered from the solution. The HPAL process gave promising results for the recovery of scandium from nickel laterite ores,[13,14] but also in the recovery of other valuable metals from nickel converter and smelter slags.[12,15]

In this work, the bauxite residue sample was mixed with high purity graphite powder, CaO and SiO_2, and smelted in an electric arc furnace for iron separation, so that a slag with low iron content was generated. Subsequently, the leaching behaviour of selected REEs (Sc, Y, La, Nd) by high-pressure sulfuric acid leaching of the slag generated during reductive smelting is investigated. The effects of acid concentration and leaching temperature are evaluated.

Material and Methods

The bauxite residue used in this work was provided by Aluminum of Greece. It is generated predominantly from Greek (karst) bauxite ore. Chemical analysis of the major elements was performed using wavelength-dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400). Sample preparation was done by lithium metaborate ($LiBO_2$) fusion, followed by HNO_3 (3 vol%) digestion. The minor metal concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) analysis.

The bauxite residue sample was mixed with 10 wt% of local source of lignite coke (87 wt% of carbon, 10 wt% ash content), 8 wt% of CaO and 10 wt% of crystalline SiO_2 at a temperature of 1500 °C. The smelting reduction experiments were carried out in an electrical arc furnace (100 kVA DC). The mixture was heated at a heating rate of approximately 20 °C min^{-1} and kept at that pre-set temperature for 1 h. After heating, the sample was cooled to room temperature at a cooling rate of approximately 20 °C min^{-1}. The metal fraction produced in the smelting experiment was separated from the slag and kept for further analysis. The slag was crushed into small pieces (< 2 cm) with a hammer and was subsequently crushed in a laboratory jaw crusher (Retsch BB 51) to produce material finer than 1 mm. Later on, the material was ground in a ball mill to reduce the particle size to 100% < 90 µm. Small iron particles in the slag sample were removed by a magnet after grinding. The chemical analysis procedure for the slag is the same as the one described for the bauxite residue.

High-pressure acid leaching experiments were carried out in a titanium autoclave (Parr Company, series 4560) at different temperatures (100-180 °C). The experiments were performed at a liquid-to-solid ratio, *L/S*, of 10:1. Analytical reagent grade H_2SO_4 (95–97 vol%, Sigma–Aldrich) was used in the present study at

different concentrations (1-3 N). The slurries after leaching were filtered using filter paper (pore size 0.45 μm) and diluted with 2 vol.% HNO_3 (65 vol.%, Chem-lab) for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 8300) analysis.

Results and discussion

Characterization of the bauxite residue and slag

The composition of the major elements in the bauxite residue used in this study and in the slag generated after smelting reduction experiments is shown in Table 1. Iron oxide is the main constituent in the bauxite residue sample, but not in the slag. Iron was significantly reduced during the smelting experiment, so that its concentration in the slag is lower. The concentration of silica and lime in the slag was significantly higher in comparison to the concentration reported in the bauxite residue. This is due to the addition of an excess of silica and lime as fluxes during smelting.

Table 1. Major chemical components (in wt%), expressed as oxide, in the bauxite residue sample and in the slag generated after smelting experiments by XRF
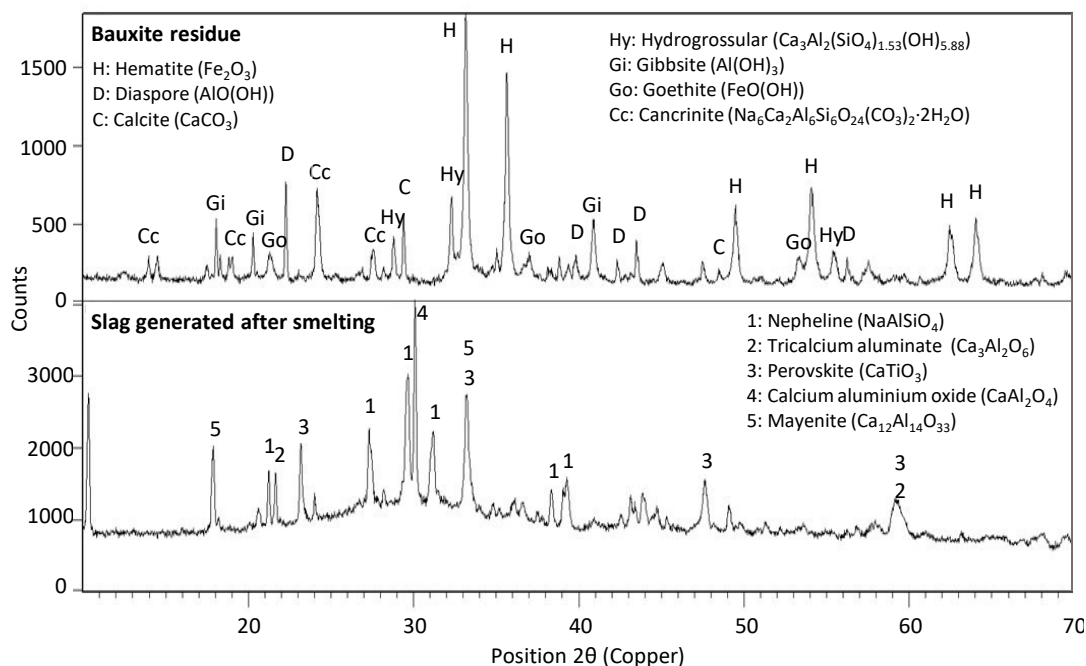
Element	Bauxite residue	Slag
Al_2O_3	18.1	36.0
CaO	8.5	22.8
SiO_2	7.3	21.7
TiO_2	5.8	8.7
Na_2O	2.8	3.1
Fe_2O_3	46.7	5.3

In Table 2, the concentrations of selected REEs are depicted. The concentrations of Sc, Y, La and Nd are shown because their concentrations in this bauxite residue are relatively high. The concentration of REEs in the slag sample was increased by a factor of about 1.4 compared to their concentration in the bauxite residue sample.

Table 2. Rare earth elements (in mg kg^{-1}) in the bauxite residue sample and in the slag generated after the smelting experiments by ICP-MS

Element	Bauxite residue			Slag		
Sc	97.8	±	1.7	124.0	±	1.6
Y	65.7	±	1.6	105.6	±	1.3
La	143.9	±	3.0	168.7	±	1.5
Nd	64.8	±	2.6	111.8	±	0.7

The following major minerals and compounds were identified by XRD in the bauxite residue sample: the iron minerals hematite and goethite; the aluminium minerals gibbsite and diaspore; the calcium mineral calcite and the sodium compound cancrinite, which also contains aluminium, silicon and calcium associated to CO_3 (Figure 1). The same analysis demonstrated that the slag generated after smelting, which was cooled down at ambient temperature, corresponds to a solid solution composed of nepheline, tricalcium aluminate, perovskite, calcium aluminium oxide and mayenite.


Figure 1. XRD patterns of the bauxite residue sample and the slag produced after the smelting experiments

High pressure acid leaching of the slag

The effect of the temperature on the extraction of the major elements (Al, Fe, Ti and Si) from smelt reduction slag of bauxite residue at two different acid concentrations is shown in Figure 2. The highest extraction of silicon was about 42 wt% when leaching was performed at 120 °C with 3 N H_2SO_4. Further increase in temperature led to a dramatic drop in silicon dissolution (< 0.5 wt%) with the same acid concentration. With such a low level of dissolution, the concentration of silicon in solution was lower than 0.5 g L^{-1} and, for instance, no silica gel formation was observed.[11] In addition, a low acid concentration led to a lower silicon extraction i.e. < 4 wt%. On the other hand, high acid concentrations led to high extraction levels of aluminium and iron. At 100 °C and 3 N, the highest extraction

of aluminium was 93 wt% (about 18 g L^{-1}), while the extraction of iron was 82 wt% (about 3 g L^{-1}). However, further increase in the leaching temperature led to a decrease of the corresponding extraction levels. Thus, aluminium extraction decreased to 47 wt% (about 9 g L^{-1}), while iron decreased to approximately 60 wt% (about 2 g L^{-1}) when leaching was performed at 180 °C. The titanium extraction was below 5 wt% in the whole range of temperatures and with both acid concentrations, presumably due to its chemical association to a perovskite phase (see Figure 1).
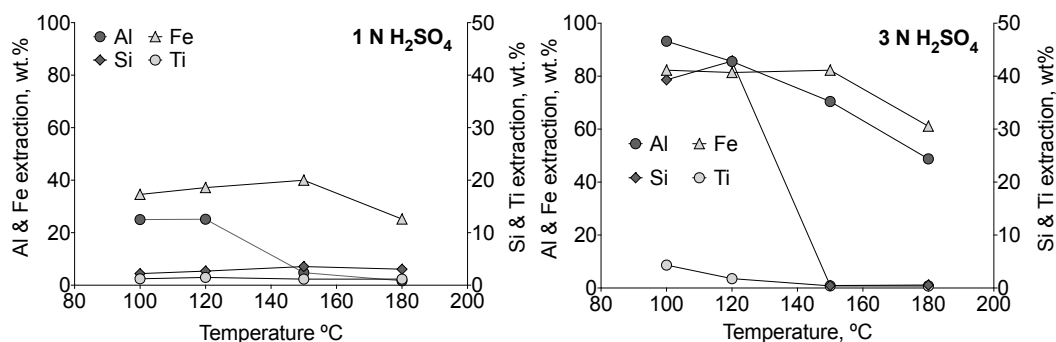
Figure 2. Effect of the temperature on the extraction of Al, Fe, Ti and Si from the slag at different acid concentrations (H_2SO_4, *L/S*: 10, t: 1 h)

In Figure 3, the effect of the temperature on the extraction of selected REEs (Sc, Y, La, Nd) from smelt reduction slag of bauxite residue at two different acid concentrations is shown. At 100 °C, the highest extraction of REEs was observed at the highest acid concentration. At 1 N, the extraction of REEs is very low due to the high pH of the solution (~ 2.5).[7] The scandium and yttrium extractions increased from about 34 wt% when the acid concentration was 1 N to approximately 95 and 87 wt%, respectively, when the acid concentration was increased to 3 N. The extraction of lanthanum and neodymium was also improved by increasing the acid concentration, i.e. from an extraction yield between 12-16 wt% when the acid concentration was 1 N to a value between 44-57 wt% when the acid concentration was increased to 3 N. However, the extraction of REEs, in particular that of yttrium, lanthanum and neodymium, decreases with increasing the temperatures. Thus, the lowest extraction level was observed at 180 °C. Therefore, the temperature effect was much more pronounced for yttrium, lanthanum and neodymium, than for scandium, because the former elements are presumably associated with the perovskite mineral phase.[2]
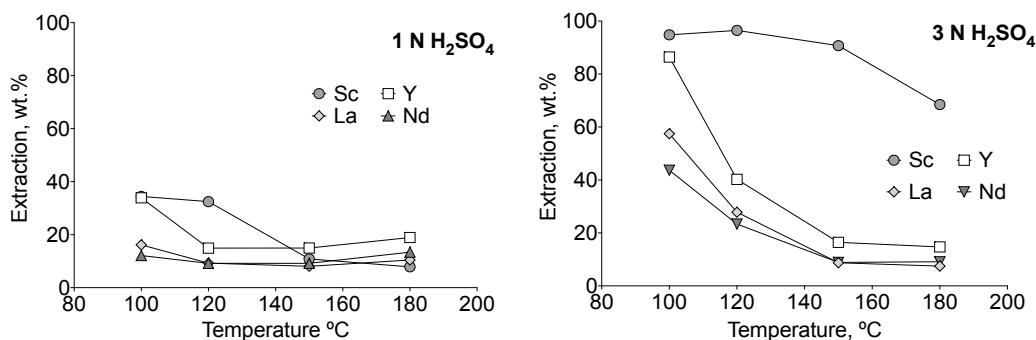
Figure 3. Effect of the temperature on the extraction of selected REEs (Sc, Y, La, Nd) from the slag at different acid concentrations (H_2SO_4, *L/S*: 10, t: 1 h).

Conclusions

More than 95 wt% of the iron could be extracted from bauxite residue by a smelting reduction process. High-pressure acid leaching of the slag sample gave high extraction yields of the REEs, particularly with high acid concentrations. Extraction yields of 95 wt% scandium and 87 wt% yttrium were achieved with 3 N H_2SO_4 at 100 °C. However, also a high dissolution of aluminium, iron and silicon was obtained. A high selectivity of scandium, over the other REEs, was found at temperatures above 100 °C.

Acknowledgements

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