

Recovery of Selected Rare Earths from Bauxite Residue by Dry Digestion with Multi-stage Circulation of Leach liquor

Rodolfo Marin RIVERA¹, Ghania OUNOUGHENE¹, Koen BINNEMANS², Tom VAN GERVEN¹

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

² Department of Chemistry, KU Leuven, 3001 Heverlee, Belgium

rodolfoandres.marinrivera@kuleuven.be

Abstract

The combination of HCl-based dry digestion of bauxite residue and multi-stage circulation of the leach liquor was studied. The proposed processing technology allows to achieve a high selectivity for rare-earth elements with a limited co-dissolution of silica (< 5 wt%). The scandium concentration increased from 7 mg L⁻¹ in stage 1 to 19 mg L⁻¹ in stage 5, while the concentration of yttrium, lanthanum and neodymium increased from an average value of 7 mg L⁻¹ in stage 1 to an average of 18 mg L⁻¹ in stage 5, more than twice the concentration observed for single-stage leaching after dry digestion, and four times higher than the concentration achieved by a conventional direct acid leaching method. The water consumption was reduced by 60% in comparison to the conventional direct acid leaching method.

Introduction

Bauxite residue (BR) is an interesting source, not only for major elements such as aluminium, iron and titanium, but also for rare-earth elements (REEs).¹ Several methods based on direct leaching by acids have been reported for recovering valuable metals from bauxite residue.²⁻⁵ High extraction efficiencies of metals can be obtained with high acid concentration, but the amount of iron co-dissolved increases with acid concentration as well, and this limits the REE concentration in the leachate.⁶⁻⁹ The iron concentration in the leachate of Greek bauxite residue has been reported to be about 900 mg L⁻¹, while the concentration of REEs in the leachate has been reported to be about 5-9 mg L⁻¹. This is about two orders of magnitude lower than the iron concentration, which hampers the recovery of REEs in further processing, for instance in the solvent extraction step.¹⁰ The application of a multi-stage leaching method to bauxite residue may increase the REE concentration in the leachate, although a high silica dissolution may also be expected. A high silica dissolution can lead to silica gel formation, due to the polymerization of monomers formed during the decomposition of silicates minerals during acidic leaching.^{12,13} The polymerization of silica represents a serious drawback in the extraction of metals by hydrometallurgical methods, as the gel solution can no longer be filtered.

A dry digestion method 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, by which silica is effectively rejected from the respective minerals.¹⁴

The objective of this paper is to evaluate the recovery of REEs from bauxite residue by dry digestion with concentrated HCl, followed by water leaching. Kinetic studies are performed with HCl at different concentrations. 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.

Materials and Methods

The bauxite residue studied in this work was kindly provided by Aluminium of Greece (Agios Nikolaos, Greece). It originates from a mixture of karst and lateritic bauxites. 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 mineralogy of the samples was studied by X-ray powder diffraction (XRD, Bruker D2 Phaser).

Dry digestion experiments were initiated by mixing 2 g of sample with 2 mL of concentrated acid. The digestion time and the leaching time was evaluated during 24 h. After digestion, the paste was washed with Milli-Q water at a liquid-to-solid ratio, *L/S*, of 5:1. Milli-Q water was used in this investigation to make the interpretation of the scientific results more straightforward, as this solvent does not contain impurities. The experiments were performed at 25 °C in sealed polyethylene bottles with constant agitation (200 rpm) using a laboratory shaker (Gerhardt Laboshake). The pregnant leach solution (PLS) was filtered using a syringe filter (pore size of 0.45 µm) and diluted with 2 vol.% HNO₃ for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 8300) analysis for silicon and minor elements (Sc, Y, La, Nd).

Multi-stage leaching was performed by repeating the dry digestion process five times, each time on a fresh bauxite residue sample, but instead of leaching with water during the second and following cycles, the leachate of the previous cycle was used as the liquid phase. Since a small volume of the leachate was lost during filtration, extra water was added in each cycle to maintain a 5:1 *L/S* ratio. Aliquots of PLS (1 mL) were extracted at the end of each cycle, which were diluted with 2 vol.% HNO₃ for ICP-OES analysis. All other steps were performed in the same way as described above. All the experiments were carried out in triplicate to

ensure reproducibility of the results. The errors were determined as the standard deviations on the results.

Results and Discussion

Characterization of the bauxite residue

The chemical analysis of the major elements present in bauxite residue is shown in Table 1. Bauxite residue is rich in iron(III) oxide and alumina. REEs are also present in this bauxite residue. The concentration of scandium, yttrium, lanthanum, neodymium and cerium were 121 ± 10 , 76 ± 10 , 114 ± 15 , 99 ± 7 and 368 ± 68 mg kg⁻¹, respectively, which are among the highest for the REEs in this particular sample.⁶

Table 1. Major chemical components, expressed as oxide, in the bauxite residue.

Compound	Concentration, wt%
Fe ₂ O ₃	46.7
Al ₂ O ₃	18.1
CaO	8.5
SiO ₂	7.3
TiO ₂	5.8
Na ₂ O	2.8
Loss on ignition	8.5

Metal recovery with dry digestion method

Figure 1 shows the effect of acid concentration on the leaching of selected REEs. The extraction of REEs gradually increased, while the dissolution of silicon decreases, with increasing acid concentrations. Silicon dissolution was reduced from 6 wt% when the acid consumption was 400 g HCl/kg BR to about 2 wt% with an acid consumption of 1200 g HCl/kg BR. Scandium(III) ions are present in the iron(III) oxide lattice,¹⁵ which limits its complete dissolution (about 40 wt% of extraction efficiency). Furthermore, it has been reported that light REEs, with the exception of scandium, tend to be associated to perovskite phases, which makes the dissolution in acidic solutions very difficult.^{16,17} The extraction of neodymium and lanthanum was about 36 wt%.

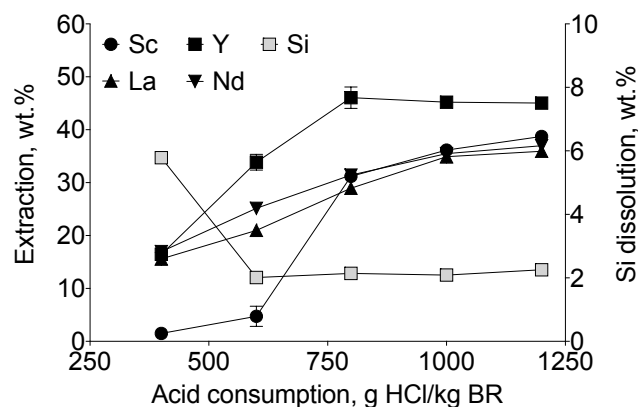


Figure 1. Effect of acid consumption on the extraction of selected REEs (Sc, Y, La, Nd) and Si after water leaching

Dry digestion method with multi-stage circulation of acid leaching solution

In the dry digestion method with multi-stage circulation of the acid leaching solution, the obtained leachate was filtered and repeatedly contacted again with dry-digested solid samples in multiple leaching stages, as described in Figure 2. Consequently, a more concentrated leachate was obtained and less water was consumed. The corresponding dry-digested samples were prepared in each stage by mixing the same amount of acid.

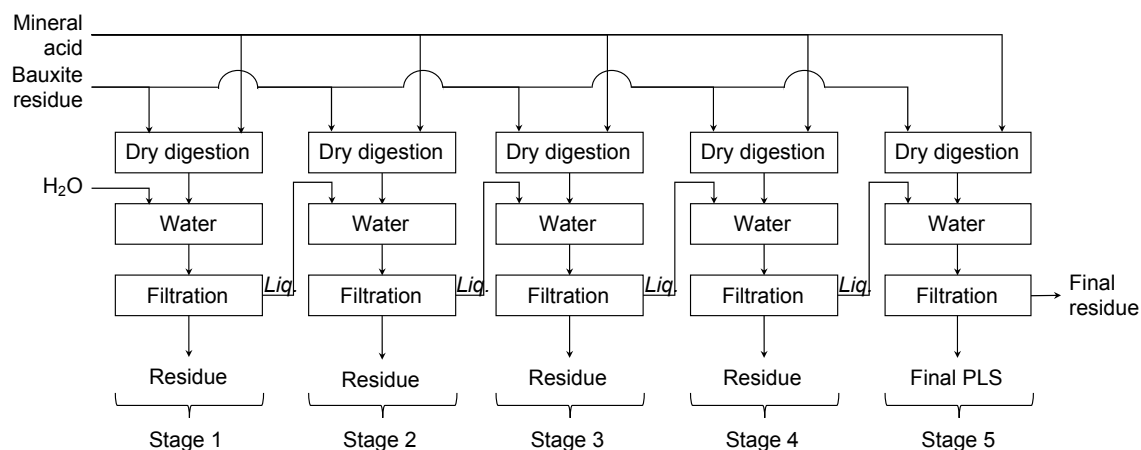


Figure 2. Conceptual process flow sheet for dry digestion of bauxite residue combined with multi-stage leaching

The lowest Al/Fe leaching ratio (i.e. 2:1) was obtained with 788 g HCl/kg BR. The same acid consumptions allowed a high REEs recovery. The water leaching step was always performed in a 5:1 L/S ratio.

The concentrations of the selected REEs and iron in the leachate after each stage are summarized in Figure 3. A single-stage dry digestion-water leaching limited the final concentration of REEs in the leachate to approximately 6 to 8 mg L⁻¹. However, the concentration of REEs increased during the following leaching stage. The scandium concentration increased from 7 mg L⁻¹ in stage 1 to 19 mg L⁻¹ in stage 5, while the concentration of yttrium, lanthanum and neodymium increased from an average value of 7 mg L⁻¹ in stage 1 to an average of 18 mg L⁻¹ in stage 5, more than twice the concentration observed by a single-stage method. Note that the concentration of silicon remained below 0.05 mg L⁻¹, so that no silica gel formation took place during the different stages. Therefore, the multi-stage leaching allows to successfully increase the concentration of REEs and of the major metals. The iron concentration reached a concentration of 7 g L⁻¹ in stage 5 (Figure 3). The concentration of aluminium was about 12 g L⁻¹ in stage 5, while the concentration of titanium was 0.5 g L⁻¹ in the last stage.

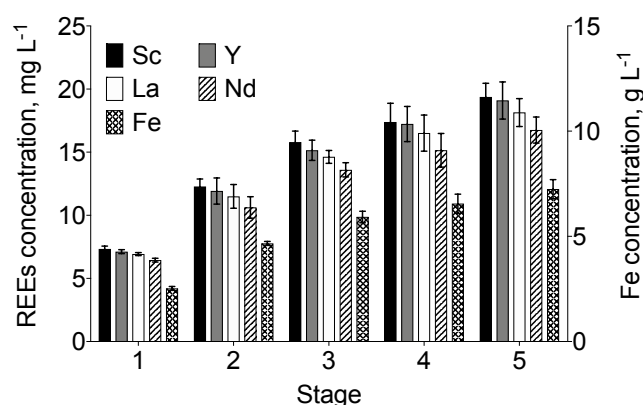


Figure 3. Concentration of selected REEs (expressed in mg L⁻¹) and iron (expressed in g L⁻¹) in the leachate after water leaching of each stage

The present method allows to process much more bauxite residue with a significant decrease in water consumption (Figure 4). The water consumption was reduced from 5.5 L H₂O/kg BR in stage 1 to about 2.3 L H₂O/kg BR in stage 5. This was caused by the treatment of fresh bauxite residue and the low amount of water added during the different stages.

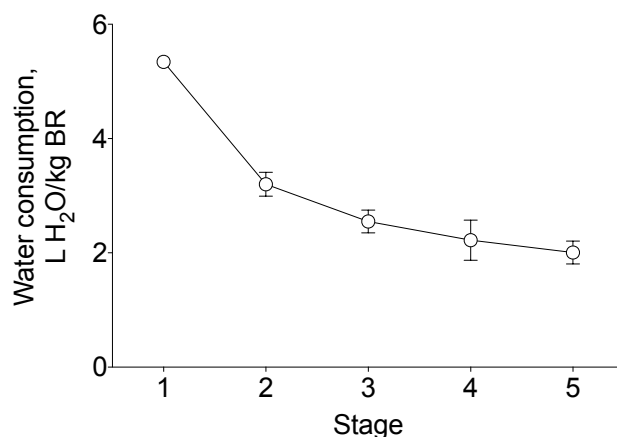


Figure 4. Water consumption in the different stages of multi-stage leaching

Conclusions

The two-step processing of bauxite residue by dry digestion and subsequent water leaching demonstrated a high recovery of REEs, while at the same time preventing silica polymerization. A single-stage dry digestion-water leaching process limits the final concentration of REEs in the leachate to approximately 6 to 8 mg L⁻¹, but it was significantly increased up to 20 mg L⁻¹, i.e. an enrichment by a factor of three to four times higher compared to a single-stage leaching method. The low water consumption results in a higher filtration efficiency of the leach liquor due to the avoidance of silica gel formation.

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