

SELECTIVE LEACHING OF RARE EARTHS FROM BAUXITE RESIDUE AFTER SULPHATION ROASTING

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Abstract

During direct acid leaching of bauxite residue, high amounts of iron also dissolve at high REEs recovery. In this paper, a sulphation-roasting-leaching process was developed to selectively leach the REEs. The bauxite residue was mixed with water and concentrated H₂SO₄ followed by roasting and then leaching of the calcined product with water. Several parameters including roasting temperature, duration of roasting, amount of acid were studied under optimised conditions, about 60 wt% of scandium and more than 90 wt% of other REEs can be dissolved with very small amounts of iron (< 1 wt%) and other major elements reporting to the solution.

Introduction

Bauxite residue (red mud) that is generated from karst bauxite ores contain a significant amount of rare-earth elements (REEs). Practically all REEs end up in the bauxite residue during the processing of the bauxite in the Bayer process.¹ REEs can be recovered from the bauxite residue by direct acid leaching although their recoveries are relatively low. These recoveries can be improved by increasing the HCl acid concentrations but this also leads to more iron dissolution into the leach solution. Large amounts of iron in the leach solution generate problems in the subsequent downstream processes (e.g. solvent extraction) and require laborious purification steps. Therefore, a sulphation-roasting-leaching process was developed to selectively leach the REEs. This process was earlier developed for selective extraction of nickel and cobalt from lateritic ores.²⁻⁵ The flow sheet consists of three major steps: mixing the feed material with concentrated sulphuric acid, roasting and leaching with water (Figure 1). In this study, the bauxite residue was mixed with water and concentrated H₂SO₄ followed by roasting and then leaching of the roasted product with water. During acid mixing and the subsequent drying stages (e.g.

sulphation), most of the oxides convert to their respective sulphates. At roasting temperatures of 600–700 °C, sulphates with low thermal stability such as iron sulphates decompose to give their respective water-insoluble oxides (equation 1). The water-soluble rare-earth sulphates, on the other hand, are stable at such roasting temperature ranges⁶ and can dissolve during subsequent water leaching step leaving the iron oxides in the residue.

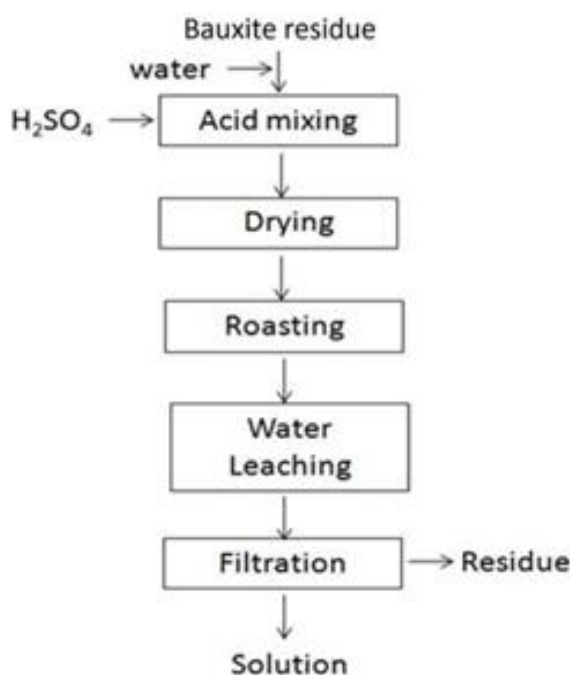


Figure 1: Flow sheet of the sulphation-roasting-leaching process

The main advantages of the sulphation-roasting-leaching process can be summarised as: (1) possibility of (consumed) acid regeneration; (2) high selectivity against iron, titanium and aluminium; (3) lower acid consumption and (4) small volumes of effluents generation compared to direct leaching. Additionally, the pH of the residue after water leaching is close to neutral (management and utilisation of this stream in other applications is easier). The main drawback of this process is its relatively high energy consumption during the roasting step when compared to direct acid leaching.

Sulphation–roasting–leaching of a Greek bauxite residue was investigated in the present work for the purpose of REEs extraction. This is the first of its kind study. The effect of different process parameters including the amount of sulphuric acid,

roasting temperature and roasting time on the leaching efficiencies of the different elements was studied.

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 in order to remove the entrapped moisture. The dried sample was then sieved with < 500 µm size mesh. The results for chemical and particle size analysis as well as TGA and XRD analysis have already been reported elsewhere.⁷

During the acid mixing step (e.g. sulphation), the dried sample was moistened with distilled water (40 wt%) in a porcelain crucible and then mixed with concentrated sulphuric acid (95-97 wt%, Sigma–Aldrich). The addition of water was to ensure homogenous mixing. After mixing, samples were dried at 120 °C for 12 h to ensure complete sulphation of the bauxite residue. After drying, the samples were subsequently roasted at a set temperature for a selected time in a muffle furnace. The roasted samples were leached at room temperature with distilled water in polyethylene bottles. After leaching, the solution was filtered with a syringe filter (pore size of 0.45 µm) and the obtained filtrate was diluted with acidified deionised water. The extraction percentage was calculated based on ICP-MS analysis on the clear leachate.

Results and Discussion

Effect of leaching duration

Leaching experiments were conducted without agitation at different time intervals for samples roasted at 650 °C for 1 h. The sulphuric acid to bauxite residue weight ratio was fixed at 1:1 (mass ratio). In Figure 2, REEs and major element dissolutions are given with respect to leaching time for non-agitated room temperature leaching. It can be seen that the leaching time has an important influence on the dissolution behavior of the REEs. Up to 85–95 wt% of the yttrium, lanthanum, cerium, neodymium and dysprosium could be extracted. After six days of leaching, a maximum was reached for all these REEs except scandium and their dissolution values remain constant. The effect of duration on the dissolution of scandium differs from that of the other REEs. It first increases rapidly during the first day, later on stagnates and remains around a maximum of about 64 wt%. The effect of leaching duration on the dissolution behavior of the major elements (sodium, aluminium, calcium, titanium and iron) is less significant. Already after one day of leaching, the

dissolution values of the major elements reached stationary levels. The dissolution of the major metals into the leachate is relatively high due to the large amount of sulphuric acid added (1:1 mass ratio) and the low roasting temperature (650 °C). Additional leaching experiments were conducted at higher temperature (80 °C) without agitation and at room temperature with agitation (160 rpm). Neither of these changes resulted in a remarkable improvement. Hence, further experiments were conducted at room temperature without agitation.

Effect of sulphuric acid amount

A series of experiments was carried out by varying the ratio of added amount of sulphuric acid to the amount of bauxite residue from 0.25 (1:4 mass ratio) to 1 (1:1 mass ratio). The samples were roasted for 1 h at the fixed temperature of 650 °C. After roasting, the samples were leached for seven days. The results are summarised in Figure 3 which depicts the extraction of the REEs and major elements in the leachate with increasing initial acid amount. As seen in Figure 3, the REE extraction is dramatically increasing with increasing acid to bauxite residue mass ratio up to 0.5. With further increase, this effect becomes less pronounced. Particularly, the recovery of scandium was 64 wt% at acid to bauxite residue mass ratio of 1. An additional experiment was conducted to evaluate whether recovery of scandium could be increased beyond this value with an acid to bauxite residue mass ratio of 2. However, even with this higher ratio the recovery of scandium remained unaffected. It was reported that the maximum iron conversion in sulphation-roasting as iron sulphate is around 60–70 wt%.⁸ That could be the reason for the poor scandium recovery since scandium(III) oxide is locked in the iron oxide lattice.⁹ Another reason for the poor scandium recovery might be due to the lower decomposition temperature of scandium (> 700 °C) compared to those for other REEs (~900 °C). The maximum extractions of the other REEs are between 85 wt% and 95 wt%. The increase in REE dissolution with increasing acid addition is due to the increasing reactivity at higher acid to bauxite residue ratios. Adding more sulphuric acid leads to an increased conversion of the oxides to sulphates which eventually increases the extraction. Both iron and aluminium extractions increase with increasing addition of acid. Titanium follows the same trend. This also is a consequence of the increasing sulphate formation when more acid is added. In this case, more iron and aluminium sulphates can be decomposed and hence more of these sulphates will remain after the roasting treatment. The remaining iron, aluminium and titanium sulphates are all dissolved in the leaching step since they are quite soluble in water. Sodium and calcium dissolution remains constant at 100 wt% and ~ 30 wt% extractions, respectively, in the examined range of acid addition. That is because of the fact that the added sulphuric acid is primarily consumed by sodium- and calcium-containing phases. Even at 0.25 acid to bauxite residue ratio, both types of phases already transformed to their respective sulphates. Primary consumption of acid for

neutralisation of alkali compounds in a bauxite residue was reported earlier by Borra et al.⁷ Although calcium-containing phases transform to their sulphate form easily, calcium dissolution is low due to the fact that calcium sulphates have very low solubility in water.¹⁰

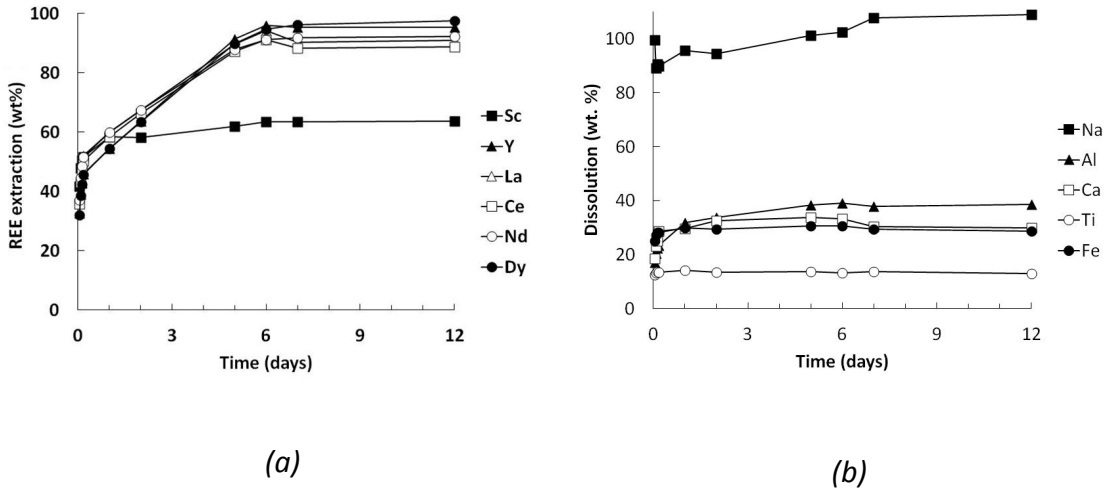


Figure 2: Effect of leaching duration on leaching of (a) REEs (b) major elements (roasting temperature: 650 °C, roasting duration: 1 h, acid to bauxite residue: 1, L/S ratio: 50)

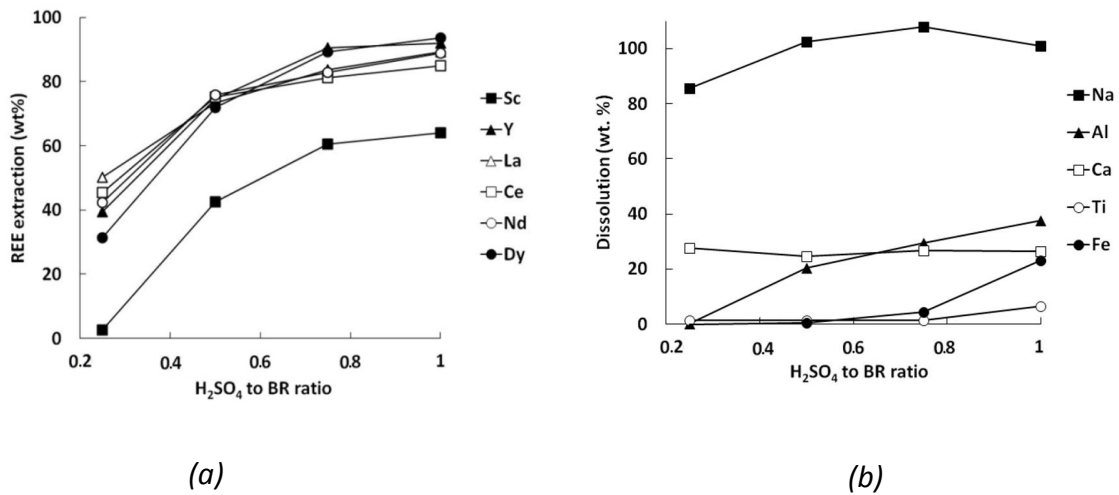


Figure 3: Effect of the acid amount on leaching of (a) REEs (b) major elements (roasting temperature: 650 °C, roasting time: 1 h, leaching time: 7 days, L/S ratio: 50)

Effect of roasting temperature

Iron(III) sulphate generally decomposes at temperatures around 600 to 700 °C.¹ Previous results show that some iron sulphate remains in the calcine after roasting at 650 °C. Therefore, experiments were conducted at 675 and 700 °C and compared with the results of 650 °C to understand the effect of temperature on the extraction behaviors of iron and other elements. Prepared samples were roasted for 1 h and then leached in water without agitation for 7 days. Since higher roasting temperatures will improve the decomposition kinetics of metal sulphates, one could expect lower extraction values. Figure 4 shows the effect of roasting temperature on extractions of REEs and major elements for an acid to bauxite residue mass ratio of 1. The recovery of all REEs slightly decrease with increasing roasting temperature. Also, the dissolution of aluminium, iron and titanium decreases with increasing roasting temperature. These results are in agreement with the expectations. On the other hand, sodium and calcium dissolutions remain practically constant because their sulphates decompose only at very high temperatures. Iron and aluminium extractions are lower when roasting is done at 700 °C compared to extractions after roasting at 650 °C. By increasing the temperature from 650 °C to 700 °C, it is possible to decrease the iron and aluminium extractions to about < 1 wt% and 20 wt%, respectively.

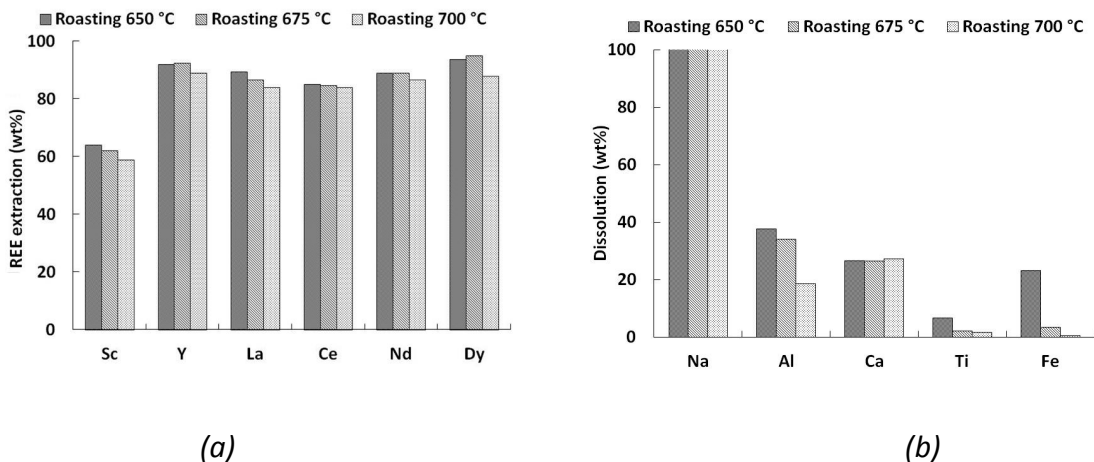


Figure 4: Effect of roasting temperature on leaching of (a) REEs (b) major elements (acid to bauxite residue ratio: 1, roasting time: 1 h, leaching time: 7 days, L/S ratio: 50)

Conclusions

A sulphation-roasting-leaching process was developed to selectively leach REEs from bauxite residue. At a roasting temperature around 700 °C for a roasting duration of 1

h and with an acid to bauxite residue mass ratio of 1:1 ca. 60 wt% of scandium and > 80 wt% of other REEs can be extracted after leaching for 7 days at room temperature without a need for agitation. The dissolution of some of the major elements was found to be very low compared to the direct acid leaching method. The dissolutions were < 1 wt% for iron, < 1 wt% for titanium and < 20 wt% for aluminium. Sodium was completely soluble and calcium was soluble up to the solubility limit of its sulphate in water.

Acknowledgements

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