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Chapter 16

Recovery of Rare Earths from Bauxite Residue (Red Mud)

Chenna Rao Borra^{*,§,¶}, Bart Blanpain[†], Yiannis Pontikes[†], Koen Binnemans[‡],
and Tom Van Gerven[§]

** Department of Material Science and Engineering, TU Delft,
Delft, The Netherlands*

† Department of Materials Engineering, KU Leuven, Leuven, Belgium

‡ Department of Chemistry, KU Leuven, Leuven, Belgium

§ Department of Chemical Engineering, KU Leuven, Leuven, Belgium

¶ c.r.borra@tudelft.nl

The management of bauxite residue (BR) is a major issue for the aluminum industry because of its high alkalinity and the large volumes generated. Therefore, the recovery of rare earth elements (REEs) with or without other metals from BR and utilization of the generated residue can contribute to a solution on the management problem of BR and it can be one of the options to meet the demand of REEs. In view of the above, the selective recovery of REEs over major elements such as iron by direct acid leaching was studied initially. From the leaching results, either the recovery of REEs was low or the dissolution of iron was high. To address that, iron was removed from BR by smelting. The slag generated after smelting was leached with mineral acids. The selectivity of REEs over iron was greatly improved. However, the high level of alumina presence in BR required a large amount of fluxes thereby increasing the energy consumption in smelting. Hence, the removal (and recovery) of alumina from BR by sodium carbonate roasting was carried out. The sample, after alumina removal, was smelted and the REEs were successfully recovered from slag by leaching with mineral acids. An alternative process, called sulfation–roasting–leaching, was also developed by which the REEs can be selectively leached. The scandium recovery, however, was low. Preliminary energy and economic analysis showed that alkali roasting–smelting–leaching and sulfation–roasting–leaching were the most promising processes for the treatment of BR.

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16.1 Introduction

Bauxite residue (BR, also known as “red mud” in the slurry state) is a waste product generated during the Bayer process of alumina production from bauxite.^{1–4} About 140 million tonnes of BR are generated annually and almost 4×10^9 tonnes are already stockpiled. Long-term storage of such waste not only occupies valuable land resources but it is also potentially harmful to the environment, which in turn incurs major liabilities and costs to the alumina industry. The utilization of BR in other applications could be a sustainable solution for the BR problem. However, only 2–3% of this material is currently being used in cement and ceramic applications. The high residual sodium content and the presence of other alkaline solids in BR restricts its use in other applications.

The major elements that are present in BR are iron, aluminum, silicon, titanium and occasionally calcium. It also contains some valuable but minor elements such as gallium and rare-earth elements (REEs). Therefore, BR can be viewed as a potential polymetallic secondary raw material. Despite this potential, metal extraction has not been practiced so far, due to the fact that the concentration of many elements is too low to make recovery economically feasible. If it is not financially viable to recover all the metals, it might still be reasonable to recover at least the valuable metals, after which the remaining solid residue could be used for other applications like building materials or cementitious binders.

REEs are critical metals with high supply risks and their demand is increasing annually. The main applications of REEs are in green technologies⁵: the production of permanent magnets, lamp phosphors, rechargeable NiMH batteries, catalysts, alloys and other applications.⁶ Scandium is the most valuable element among the REEs in BR (>95% of the economic value of REEs in BR).² The price of scandium oxide (99.95%) was 4200 US\$/kg.⁷ Secondary sources like BR can potentially be considered as one of the options to meet the REEs demand. REEs present in the bauxite ore end up in BR during the Bayer process.² BR generated from karst bauxite ores are more rich in REEs compared to that generated from lateritic ores.⁸ Karst bauxite ores are mainly found in Europe, Jamaica, Russia and China. Only 13% of total bauxite reserves are rich in REEs. The recovery of scandium together with other REEs and perhaps additional metals combined with the utilization of the remaining residue can partly solve both the supply problem of REEs and the storage problem of BR.

There is literature available on the recovery of REEs from BR via direct hydrometallurgical processes, while very few studies involve combined pyro- and hydrometallurgical methods to recover REEs together with other metals.³ In the direct leaching studies, the majority of the literature focuses on scandium and very few on the other REEs.⁹ Furthermore, the dissolution of major elements was not studied in detail during leaching. There exist few studies on the removal of iron via a pyrometallurgical process, followed by a hydrometallurgical process to recover the REEs. However, large volumes of flux were used in these studies and there are no detailed data available on leaching of the REEs. Conceptual flow sheets for the recovery of iron, aluminum, titanium and REEs from BR have been reported in the literature.³ However, most of these studies have not yet been tested experimentally. There exists no complete study available on the combined recovery of iron, aluminum, titanium and REEs yet. Furthermore, most of the flow sheets contain a magnetic separation step after alumina removal, which does not allow complete iron recovery.

Greek BR was used in the present study as it is rich in REEs. In this work, we present different routes with a focus on recovering REEs to develop an economically viable, near-to-zero waste process. The different routes explained in this chapter to recover REEs from BR are shown in the form of a combined flow sheet (Fig. 16.1). In the first route, direct acid leaching of BR was studied to evaluate the yields and selectivity for the recovery of REEs. In the second route, iron was removed by smelting, followed by REEs and titanium leaching from the slag. In the third route, alumina in the

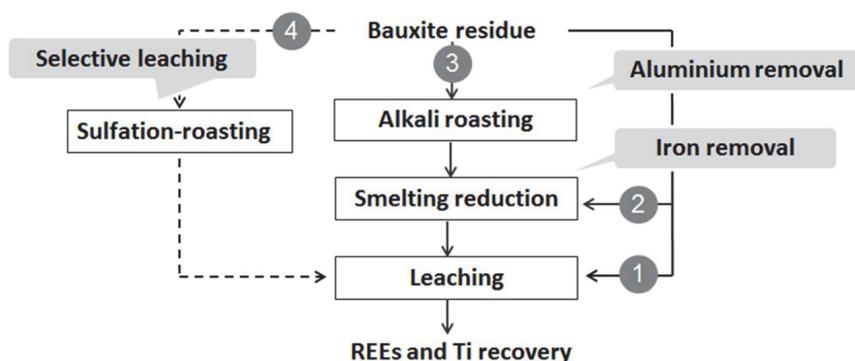


Fig. 16.1. Conceptual flow sheet for the processing of BR, with an indication of the four alternative processes.

BR was removed by alkali roasting prior to smelting and subsequently the residue from the alumina removal process was smelted without any additional flux. The slag generated after smelting was leached for recovery of REEs and titanium. A fourth route (called sulfation–roasting–leaching) was developed to selectively leach the REEs from BR. This process can selectively leach the REEs with very low amounts of major elements co-dissolved. The different routes will be described in the following sections, but more details can be found in the individual journal papers from which this chapter was derived.^{9–12}

16.2 Materials and Methods

The BR studied in this work was provided by Aluminum of Greece, Greece. Analytical grade chemicals were used in the present study. Chemical analysis of major elements in BR was performed using wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400). Chemical analysis of minor elements was performed after complete dissolution of BR 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.

The room temperature leaching was carried out in sealed polyethylene bottles by constant agitation 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. The leach solution sample was filtered using a syringe filter (pore size of 0.45 μm) and diluted with deionized water for ICP analysis.

Alkali roasting experiments were carried out in a muffle furnace at 950°C. After roasting, water leaching experiments were carried at 80°C for 60 min for alumina removal. Smelting studies were carried out in a high-temperature vertical alumina tube furnace (Gero HTRV 100–250/18). Sulfation–roasting experiments were carried out in a muffle furnace. Full experimental details of the processes developed in this study can be found elsewhere.^{9–12}

16.3 Results and Discussion

The chemical analysis of the BR sample used in this study is shown in Tables 16.1 and 16.2. BR contains high concentrations of iron oxide and alumina (Table 16.1). The total REE concentration in the BR is about

Table 16.1: Major Chemical Components in the Bauxite Residue Sample (Excluding LOI).⁹

	Concentration (wt%)
Fe ₂ O ₃	44.6
Al ₂ O ₃	23.6
CaO	11.2
SiO ₂	10.2
TiO ₂	5.7
Na ₂ O	2.5

Table 16.2: REEs Composition of the Bauxite Residue Sample.⁹

	Concentration (ppm)
Sc	121
Y	76
La	114
Ce	368
Pr	28
Nd	99
Sm	21
Eu	5
Gd	22
Tb	3
Dy	17
Ho	4
Er	13
Tm	2
Yb	14
Lu	2

0.1% (Table 16.2). XRD analysis showed that it contains different phases like hematite, goethite, gibbsite, diaspore, calcite and cancrinite.⁹

Route 1: Direct acid leaching⁹

Selective recovery of REEs compared to iron was studied in the case of direct acid leaching with mineral acids (HCl, HNO₃, and H₂SO₄). It was found that acid leaching at low acid concentrations (<1 N) yields low recovery of REEs (scandium and LREEs <50%, HREEs <70%). The recoveries were similar for all the mineral acids at low acid concentrations (<1 N). The yields could be improved (HREEs ~80%, scandium and LREEs > 70%) by increasing the acid concentrations (6 N), especially for HCl (Fig. 16.2), but the dissolution of iron (~60%) also became high. It was also found that

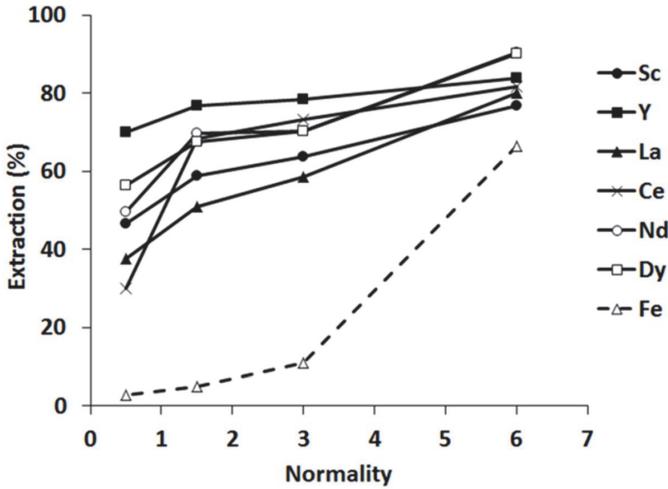


Fig. 16.2. Effect of HCl concentration on leaching of REEs from BR (T: 25°C, L/S: 50, t: 24 h).⁹

scandium is associated with the iron oxide phases in the residue, which makes it difficult to dissolve unless the iron is dissolved. Moreover, a large part of the major elements (Fe, Al, Ca, Si, Ti and Na) was also dissolving during direct leaching, which can generate large amounts of effluents. The large amount of iron going into solution during leaching poses problems in the downstream processes because of the similar behavior of iron and scandium in solvent extraction or ion exchange processes. Therefore, the removal of iron from BR by smelting reduction was studied prior to acid leaching.

Route 2: Smelting-leaching¹⁰

Smelting experiments of BR were carried out with the addition of wollastonite (CaSiO_3) as flux and graphite as reductant. Addition of wollastonite decreased the slag melting temperature and the viscosity, enhancing slag-metal separation. Graphite contents were higher than the optimum level reduced part of the silica and titania, which hindered the slag-metal separation. Iron was separated from the slag in the form of a nugget (Fig. 16.3). The optimum conditions were 1500°C, 20 wt% of wollastonite and 5 wt% of graphite. More than 95% of the iron was separated from the slag. The slag obtained after iron removal was treated with different mineral acids to extract REEs. The recovery yields for REEs were low (<70%) when the

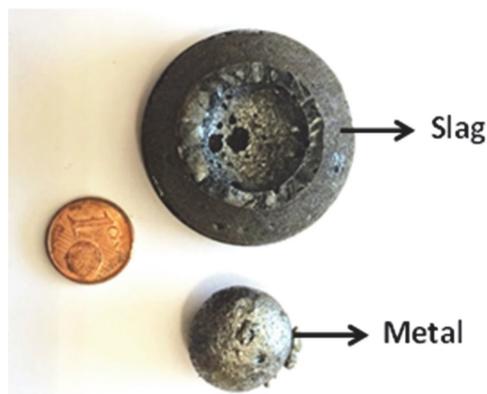


Fig. 16.3. Smelted sample (20% wollastonite, 5% graphite, 1500°C), with the iron nugget separated from the slag.¹⁰

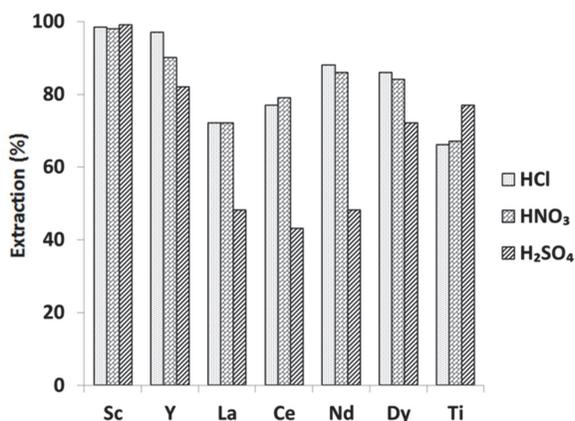


Fig. 16.4. Effect of acid concentration on leaching of REEs and titanium from slag (acid conc.: 3N, T: 90°C, t: 1 h, L/S: 50).¹⁰

leaching was done at room temperature. Hence, high-temperature leaching (90°C) experiments were also carried out. The selectivity of REEs over iron during slag leaching was improved compared to in direct leaching as >95% of iron was removed during smelting. All of the scandium, most of the other REEs and about 70% of the titanium could be leached using different mineral acids at 3 N acid concentration, a L/S ratio of 50:1, a temperature of 90°C and a reaction time of 1 h (Fig. 16.4). The REEs recovery was lower in H₂SO₄ solution and the effect is higher with increasing ionic radius, which is due to the formation of a solid product layer (CaSO₄).

Direct smelting of BR rich in alumina requires a large amount of fluxes and large energy consumption during smelting, and subsequently, large acid consumption during slag leaching. As a result, the cost of the overall process increases and make the sustainability of the process questionable. Therefore, the removal (and recovery) of alumina from BR by Na_2CO_3 roasting prior to smelting was carried out.

*Route 3: Alkali roasting-smelting-leaching*¹¹

BR was roasted with sodium carbonate at 950°C with a BR to alkali ratio of 1:0.5. The roasted mass was leached with water at 60°C to dissolve aluminum in the solution. The residue after alumina removal was smelted at 1500°C without any added flux and it was possible to obtain a clear slag-metal separation (Fig. 16.5). The slag after grinding was leached with different mineral acids at 90°C . However, the recoveries of the REEs, with the exception of scandium, were drastically lowered ($<50\%$) in the alumina-poor slags, compared to the direct smelting slags. This is due to the formation of a perovskite (CaTiO_3) phase, which strongly binds REEs (except scandium). Perovskite is a stable phase, does not dissolve in acids under normal conditions and ends up in leach residue. Therefore, the slag was cooled by water quenching. Leaching after quenching can dissolve REEs successfully from alumina-poor slags, even at room temperature. Most of REEs and about 90% of titanium could be leached from the quenched slag using mineral acids at a L/S ratio of 50:1, a temperature of 25°C

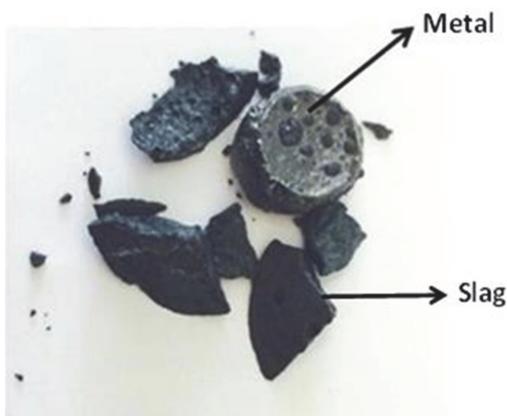


Fig. 16.5. Smelted sample (stoichiometric carbon, 1500°C). Reproduced from Borra et al.¹¹

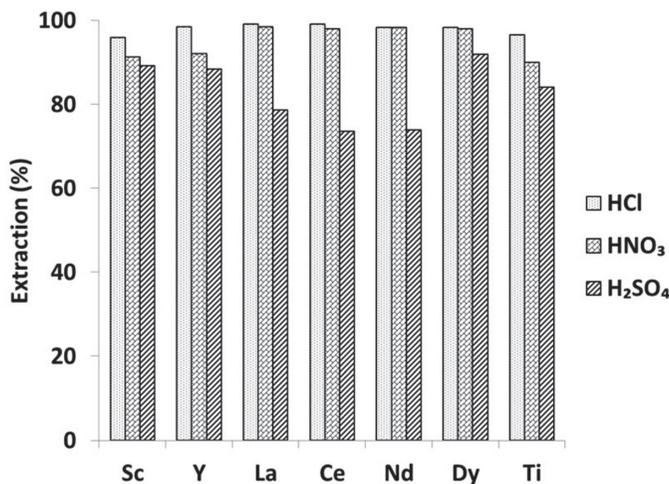


Fig. 16.6. Effect of type of acid on the leaching of REEs and titanium from a quenched slag. (acid conc.: 1 N, T: 25°C, t: 24 h, L/S: 50). Reproduced from Borra *et al.*¹¹

and a reaction time of 24 h (Fig. 16.6). The alkali-roasting temperature can be decreased to <500°C by using sodium hydroxide instead of sodium carbonate.

Route 4: Sulfation-roasting-leaching¹²

An alternative process, called sulfation–roasting–leaching, was also developed to selectively leach the REEs from BR, while leaving iron, titanium, aluminum and calcium undissolved in the residue. In this process, BR was mixed with water and concentrated H₂SO₄, followed by sulfation, roasting and finally water leaching of the roasted product in water. It was found that most of the oxides were converted to their respective sulfates during the sulfation process. In the subsequent roasting stage, unstable sulfates (mainly Fe₂(SO₄)₃) decomposed to their respective oxides. Rare-earth sulfates, on the other hand, were stable during roasting and dissolved in water leaving the iron oxides in the residue.

Figure 16.7 shows the effect of roasting temperature on the extraction of REEs and major elements. The extraction yields of all REEs slightly decrease with increasing the roasting temperature. The dissolution of aluminum, iron, and titanium also decreases with increasing roasting temperature. However, the dissolution of sodium and calcium did not change as their sulfates decompose only at very high temperatures. About 60% of

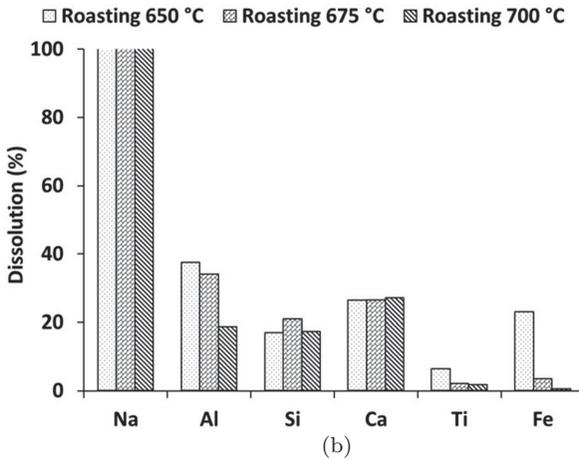
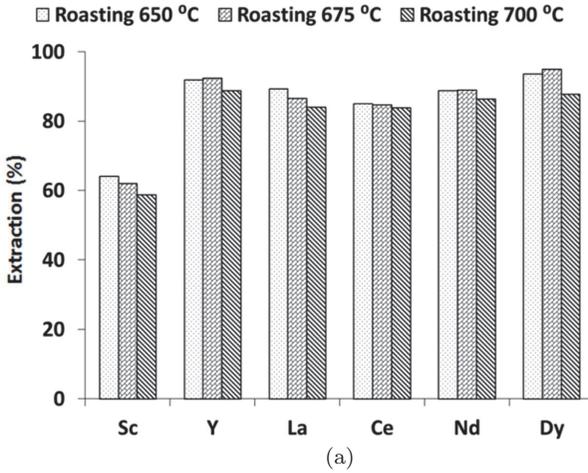


Fig. 16.7. Effect of roasting temperature on leaching of (a) REEs (b) major elements (acid to BR ratio: 1:1, roasting duration: 1 h, non-agitated leaching duration: 7 days, L/S ratio: 50). Reproduced from Borra *et al.*¹²

scandium and more than 90% of the other REEs could be dissolved at optimum conditions (roasting temperature: 700°C, roasting duration: 1 h, acid to BR ratio: 1, non-agitated leaching duration: 7 days, L/S ratio: 5), while only a very small amount of iron (<1% of total iron) was solubilized. The residue after leaching was found to be rich in Fe-, Al-, Si- phases and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and it is suggested that this residue can be used for instance in iron-rich cementitious binders.

Recovery of REEs and valuable metals from leach solutions

The recovery of REEs and other metals from the leach solutions can be performed by solvent extraction, ion exchange, precipitation, neutralization, hydrolysis etc. In solvent extraction and ionic exchange processes, conventional or new reagents can be investigated for selective scandium and other REEs recovery.^{13,14} Titanium can be precipitated from the leach solutions as TiOSO_4 at a temperature of ca. 140°C . Then TiO_2 can be recovered from TiOSO_4 by hydrolysis.¹⁵

Comparative analysis of the different processes¹⁶

A preliminary cost analysis of the developed processes is shown in Fig. 16.8 with two options, i.e. with current scandium price (4200 US\$/kg)⁷ and at 50% of the current price. This analysis includes only the costs of consumed reagents and energy and values of the generated products and does not include the capital and operating costs (CAPEX and OPEX) and metal recovery cost from solutions. This cost analysis shows that alkali roasting–smelting–quenching–leaching is the most promising process for treatment of BR and it is justified to further study this process at a pilot-scale to develop detailed techno-economics. MYTILINEOS S.A. (formerly Aluminum of Greece) and its project partners are going to study a process similar to alkali roasting–smelting–leaching process in a pilot scale project (RemovAL). The sulfation–roasting–leaching process could also be an economic process if the

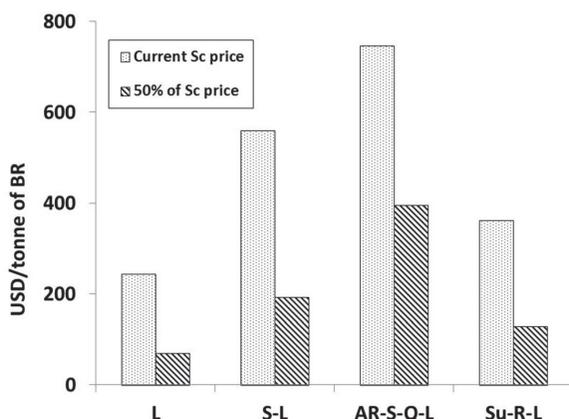


Fig. 16.8. Operational margins for different processing routes (L: leaching, S: smelting, AR: alkali roasting, q: quenching, Su: sulfation, R: roasting).¹⁶

scandium recovery was higher. In a recent study, Narayanan *et al.* were able to increase the recovery of scandium to about 90%.¹⁷

16.4 Conclusions

It is our hope that the study of the proposed processes (which are relevant for BR generated from karst bauxite ores) can contribute to the development of a near-zero-waste flow sheet for the processing of BR, including the recovery of major (Al, Fe and Ti) metals, the utilization of the residue in building applications and simultaneously the production of valuable REEs, thus partially decreasing the supply risk of these elements.

Several processing routes have been developed to recover REEs and valorize BR: 1) direct leaching; 2) smelting-leaching; 3) alkali roasting-smelting-leaching; 4) sulfation-roasting-leaching.

REEs recovery was low during direct acid leaching at low acid concentrations (1 N). High acid concentration can improve the recovery, especially for HCl, but the dissolution of iron (~60%) was also high. Direct smelting can allow recovery of more than 95% of the iron from BR and slag leaching can recover most of the REEs and titanium. Roasting in the presence of Na₂CO₃ at 950°C can remove > 75% of alumina. Smelting of the alumina removed sample, without any added flux, can remove > 95% of iron from slag. Most of REEs and about 90% of titanium could be leached from the quenched slag using mineral acids. In sulfation-roasting-water leaching about 60% of scandium and more than 90% of the other REEs can be dissolved at optimum conditions. Alkali roasting-smelting-leaching and sulfation-roasting-leaching processes should be studied at a pilot scale for detailed techno-economic analysis. We expect that these two processes can solve the BR problem and produce valuable REEs.

Acknowledgements

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