Recovery of Rare Earth Elements and Refractory Metals from Bauxite Residue

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Abstract

To move towards a sustainable future and building a circular economy, there is a push towards waste valorization. Bauxite residue is the by-product of the Bayer process for alumina production. It contains considerable amounts of rare earth elements (REEs) and refractory metals, some of which are considered critical materials; to the point initiatives have begun to mine them from secondary sources, such as landfilled industrial process residues. Here, we develop a novel pyro-hydrometallurgical process called acid-baking water-leaching to extract REEs and refractory metals from bauxite residue. In this process, bauxite residue is mixed with concentrated sulfuric acid, baked at 200 – 400 °C, and leached in water at ambient conditions. Compared with conventional hydrometallurgical processes, the developed process offers the advantages of less acid consumption, less wastewater generation, and fast kinetics. This process is a promising technique as the first step of a potential near-zero-waste integrated process for the sustainable valorization of bauxite residue.

Keywords: Rare earth elements, refractory metals, acid baking water leaching, waste valorization

1. Introduction

In recent years, there has been an increasing push to minimize the environmental impact of industrial activities by the sustainable sourcing of raw materials, in particular by sourcing these materials from secondary or tertiary resources – in other words, from materials that are commonly considered to be waste, either industrial or post-consumer. One such secondary resource is bauxite residue, also referred-to as “Red Mud”, the solid side-product of Al_2O_3 production in the Bayer process.

Bauxite residue is produced worldwide at an estimated annual rate of 150 million tonnes. Considering the Bayer process has been employed industrially for over one hundred years, such an annual production rate results in a worldwide stockpile of approximately three billion tonnes [1 – 2]. Bauxite residue is a mineralogically complex product, containing iron (Fe) and aluminum (Al) oxides and hydroxides, and various calcium (Ca), titanium (Ti), and Al silicates [3] – the exact composition and production rate is a function of the characteristics of the starting bauxite ore, and the various Bayer process parameters [4].

Despite several initiatives to put this material to practical use, particularly as a component of cement in the construction industry, the global valorization rate of bauxite residue is low, approximately 3 % [1]. It has previously been shown that the Bayer process acts to concentrate various valuable minor elements found in the starting bauxite ore, in particular scandium, rare earth elements (REEs) [5] and refractory metals (such as titanium and niobium) [3], as such, bauxite residue represents a readily-available low-cost source of these materials.

Scandium (Sc) is a high-value ($ 4600/kg Sc_2O_3) metal, which is used to create high-strength lightweight aluminum and magnesium alloys, and is used in solid oxide fuel cells [6]. REEs, in particular yttrium (Y), cerium (Ce), lanthanum (La), samarium (Sm), and neodymium (Nd), are critical materials, which play crucial roles in several modern and green technologies, such as hybrid/electric vehicles, wind turbines, photonics equipment, and electronics [7 – 8]. Refractory metals, such as titanium (Ti), niobium (Nb), zirconium (Zr), and hafnium (Hf) are important for the aerospace, nuclear, and electronics industries because of their heat-, corrosion-, and wear-resistance properties [9 – 10] – the demand for Ti and Nb in particular is rapidly increasing worldwide.

Several efforts have been reported to extract valuable materials, mainly Sc and REEs, from bauxite residue via hydrometallurgical or pyrometallurgical methods. Direct acid leaching has traditionally dominated the literature on the subject; however, other methods have been reported, such as alkaline leaching, alkaline roasting, smelting, ionic liquid leaching, and bioleaching [11 – 14]. Despite its operational simplicity and the maturity of the technique, acid leaching possesses several limitations, such as moderate Sc extraction, elevated consumption of acids, water, and organic solvents, poor selectivity against Fe, the major leachate contaminant, the formation of silica gel, which interferes with downstream processing, and a high rate of hazardous waste production [15 – 16].

Recently, work has been carried-out to develop an alternative hybrid pyro-hydro-metallurgical extraction process based on Acid-Baking Water-Leaching (ABWL) or Acid-Roasting Water-Leaching (ARWL), sometimes referred-to as sulfation roasting. These techniques both involve mixing the bauxite residue with concentrated sulfuric acid to sulfate the component minerals, then heat-treating the acid-solids mixture to accelerate the reaction, before finally leaching the heat-treated material in water at ambient conditions. ABWL and ARWL differ primarily in the temperature used for the heat treatment step – ABWL involves treatment at low temperatures (200 – 400 °C), while ARWL uses higher temperatures (> 700 °C) [17 – 18]. In the past, this relatively uncommon technique has primarily been applied to REE ores, although some studies have been reported, which have applied ABWL to secondary/tertiary resources, such as end-of-life catalysts, NiMH batteries, and NdFeB magnets [19 – 22].

Previously, ARWL has been demonstrated as a promising technique for the recovery of Sc and REEs from bauxite residue, as the high-temperature roasting step can be used to selectively decompose the contaminant $Fe_2(SO_4)_3$ into water-insoluble Fe_2O_3, because it has a lower thermal stability than REE-sulfates, allowing for high REE recoveries with minimal co-extraction of undesirable matrix species, mainly Fe and Al; however, processes employing this technique have the disadvantages of requiring elevated processing temperatures (> 700 °C) and unfavorably slow leaching kinetics [23 – 24]. In contrast to ARWL, ABWL relies on considerably lower processing temperatures, thus reducing process complexity and energy costs, and allows for considerably faster leaching. This technique has not been extensively studied in the application of bauxite residue processing.

We have developed an ABWL process to extract REEs, Sc, and refractory metals from bauxite residue, in an effort to develop a larger near-zero-waste process to fully valorize bauxite residue, by using it as a feedstock for the recovery of various valuable materials.

2. Experimental Methods – The ABWL Process

ABWL is a hybrid pyro-hydro-metallurgical process, which involves three primary steps:

1. Feed preparation
2. Acid baking (dry digestion + heat treatment)
3. Water leaching

The schematic diagram of the process is presented in Figure 1. In the feed preparation step, wet bauxite residue was dried at 50 °C overnight (30 % ± 2 % mass loss), then coarsely crushed with a mortar and pestle. An important note with this step is that the dried bauxite residue required minimal force to crush into a fine powder; however, the powder tended to aggregate in small clumps. In the acid baking step, the dried and crushed powder was mixed with concentrated (95 wt %) sulfuric acid and mixed with a glass rod until homogenous (dry digestion). Care must be taken while handling this step as the mixing was highly exothermic. The dry-digested bauxite residue was then heat-treated in a muffle furnace between 200 and 400 °C. In the water leaching step, the acid-baked bauxite residue was leached with room-temperature deionized water. Sampling was performed at specified time points, and the leachate was filtered with 0.45 μm syringe filters prior to analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES).

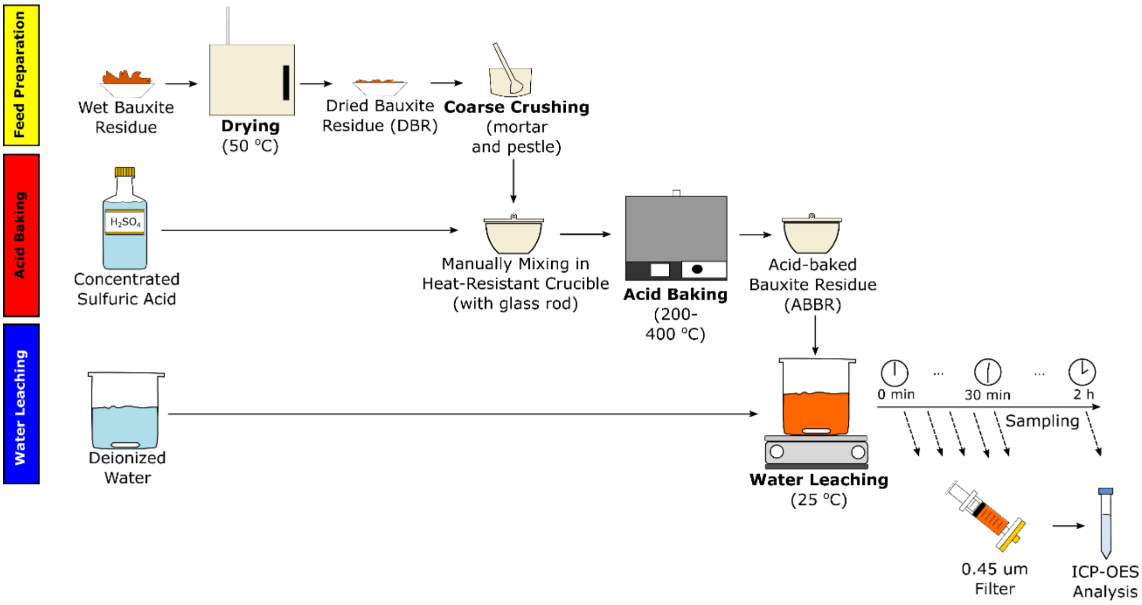

Figure 1. Schematic diagram of the ABWL process at the laboratory scale. Reprinted from Anawati [25].

3. Results and Discussion

3.1. Characterization of Feed Bauxite Residue

According to X-ray diffraction analysis, our feed bauxite residue had a complex mineralogical composition, containing the following phases: Fe_2O_3, $(Fe_{0.9}Al_{0.1})O(OH)$, $H(AlSi_2)O_6$, $Al(OH)_3$, $AlO(OH)$, $CaTiOSiO_4$, and $Na_6(Al_6(Si_{5.5}(H_4)_{0.5})O_{24}(NaCl)_{0.4}(NaOH)_{0.7}$. The elemental composition of the starting bauxite residue was determined by using alkali fusion – acid digestion to solubilize the residue, then the metals content was quantified by ICP-OES. The resulting composition is presented in Table 1.

Table 1. Elemental composition of dry bauxite residue. Data Source: Anawati & Azimi [3].

Minor Elements		Major Elements	
Element	**Composition (mg/kg$_{BR}$)**	**Element**	**Composition (wt%)**
Nd	39.9 ± 1.3	Fe	24.3 ± 1
Sm	10.0 ± 0.3	Al	11.8 ± 0.4
Ce	101.0 ± 8.3	Ca	2.3 ± 0.1
La	52.3 ± 0.4	Na	5.2 ± 0.2
Y	59.1 ± 2.5	Si	6.1 *(From XRF)
Sc	31.1 ± 0.9	Ti	3.8 ± 0.1
Nb	106.0 ± 8.7		
Hf	60.7 ± 4.5		
Zr	2171 ± 120		

**Si composition is taken from XRF numbers published in Reid et al [26].*

3.2. Effect of Acid Ratio, Solid/Liquid Ratio, and Baking Temperature.

Extraction trials, given a fixed baking duration and a fixed leaching duration, were carried to assess the effect of changing the acid to bauxite residue ratio in the acid baking step, the water to acid-baked bauxite residue ratio in the water leaching step, and the baking temperature in the acid baking step on the extraction of the REEs and refractory metals. The results are presented in Figure 2.

For Sc, at 200 °C, increasing both the acid ratio and the water ratio contribute to increasing the extraction efficiency, likely by increasing the acid digestion driving force (for the acid ratio) and the water dissolution driving force (for the water ratio). Increasing the baking temperature resulted in a decrease in extraction efficiency, which was primarily attributed to slower leaching kinetics at higher temperatures because of thermally-induced changes in the residue crystal structure [3]. Interestingly, for the high-temperature trials, changing the water-leaching ratio did not significantly affect the extraction efficiency. In contrast to Sc, for which the extraction mainly appeared to be driven by the acid ratio, the REE extraction efficiencies appeared to be primarily determined by the water leaching ratio, which had a major impact at both baking temperatures. It is known that in bauxite residue, Sc tends to incorporate into the crystal structure of Fe phases, requiring the breakdown of these Fe phases to access Sc [27], while REEs form their own distinct minor phases, adsorb on the surface of other minerals, or incorporate in other phases [4]. As such, these results may be explained by the acid preferentially attacking the REE-bearing phases over the Sc-bearing Fe phases – thus leading to a reduced dependence on the amount of acid required, relative to Sc. All the studied REEs generally behaved similarly, following similar trends. Overall, all REEs extracted less at higher baking temperature, except for Y, which saw enhanced extraction at higher temperatures.

The refractory metal extraction followed different trends. Ti extraction was mostly unaffected by the water leaching ratio but was strongly influenced by the acid ratio. The main effect of increasing baking temperature was to decrease the peak extractions observed at higher acid ratios. Zr extraction was enhanced by both acid and water ratios, although higher baking temperatures attenuated these effects. Nb and Hf both behaved similarly to Ti, which can be expected, as they have similar properties.

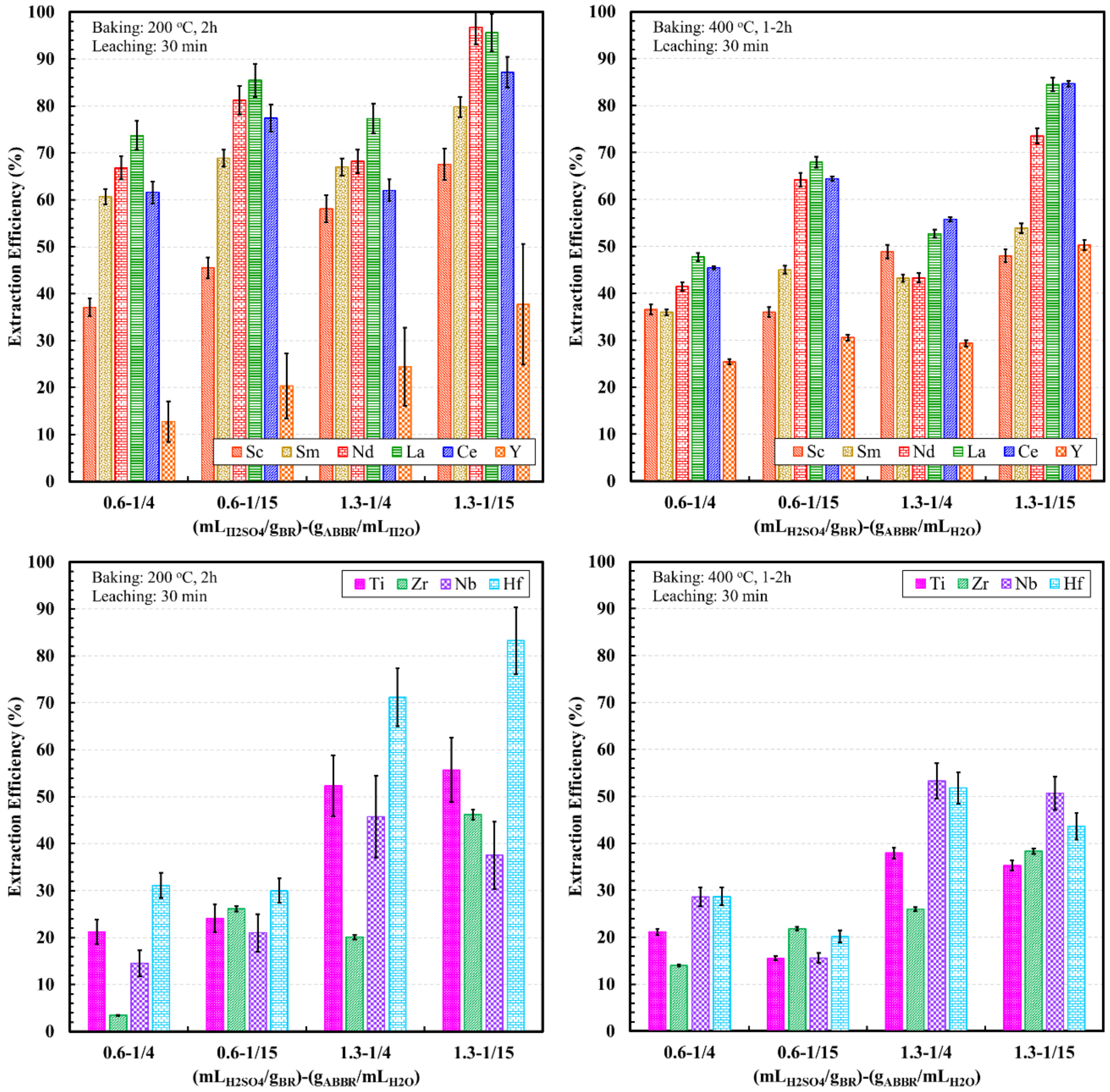

Figure 2. REE and refractory metal extraction results for ABWL trials. The trial groups are given as (acid to bauxite residue ratio for the acid baking step)-(acid-baked bauxite residue to water ratio for the water leaching step). The error bars represent the estimated standard deviation, based on repeated preliminary center-point trials. Data Source: Anawati & Azimi [3].

3.3. Effect of leaching time and baking temperature

To investigate the time dependence of the leaching process, and how it is affected by changing the baking temperature, kinetic leaching trials were performed, sampling the leachates at given time intervals, between one minute and two hours. For these trials, the baking time (2 h), acid ratio (0.95 mL H_2SO_4/g_{BR}), and the water ratio (9.5 mL H_2O/g_{ABBR}) were fixed. In addition to testing at 200 °C and 400 °C, extraction omitting the heat-treatment step, following the dry acid digestion step with a two-hour incubation at 25 °C was tested to assess the importance of the heat-treatment step. The results of these kinetic trials, for each of the studied elements, are presented in Figure 3.

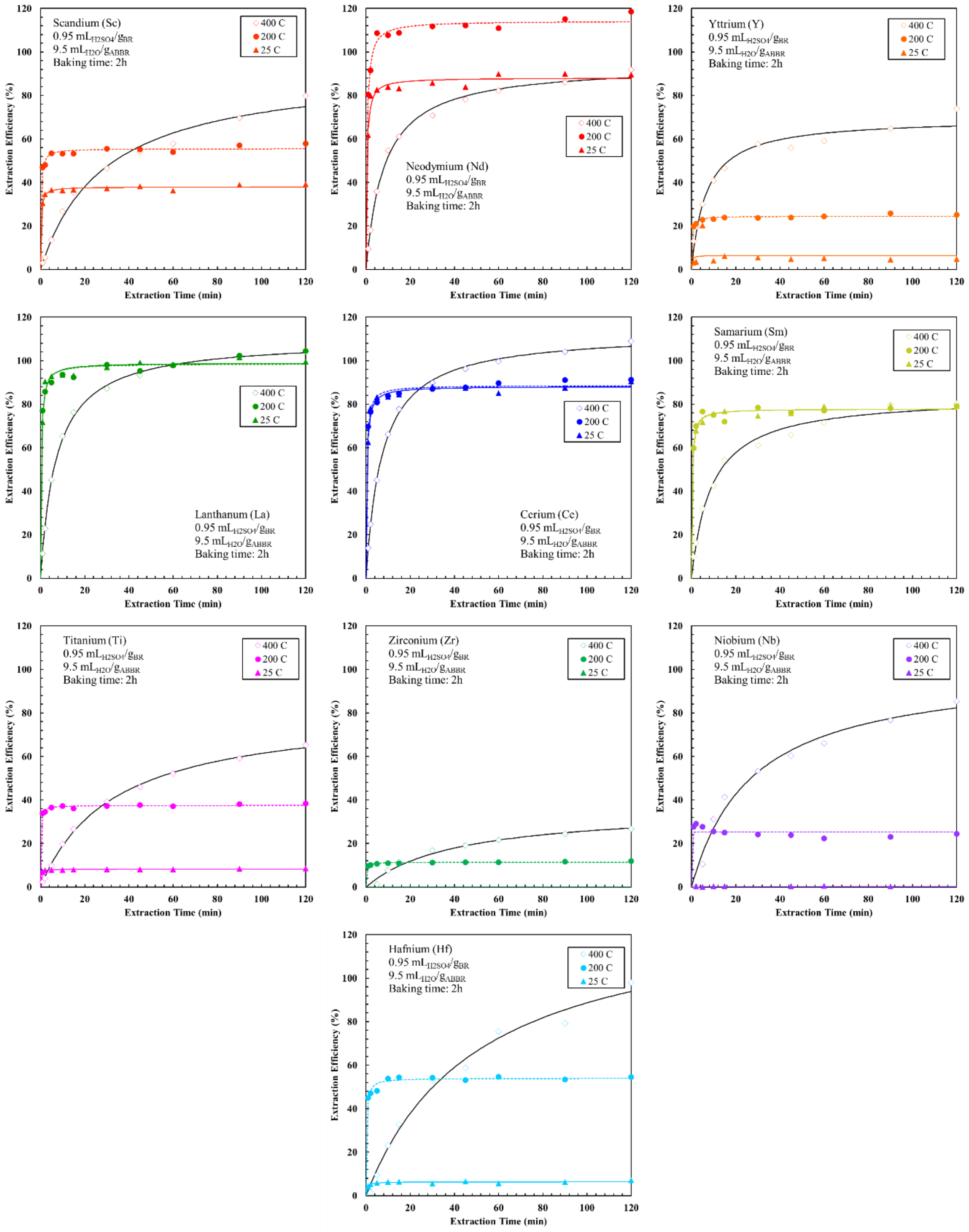

Figure 3. Kinetic leaching results for Sc, REEs, and refractory metals at baking temperatures of 25 °C, 200 °C, and 400 °C. The plotted curves represent the best fit second-order leaching model for each trial. Data source: Anawati & Azimi [3].

Scandium extraction efficiency was highly temperature dependent, with respect to both the saturation concentration and the leaching speed. The room-temperature incubation trial resulted in a relatively low saturation concentration, and extremely rapid leaching, reaching saturation within 5 min. By heat-treating at 200 °C for 2 h, the saturation concentration was increased considerably – remarkably, without affecting the extremely rapid leaching kinetics. Further increasing the baking temperature to 400 °C resulted in a further increase in saturation concentration; however, at this higher temperature, the leaching kinetics were slowed considerably, pushing saturation from 5 min to over 2 h.

We determined that this shift in leaching behavior in response to baking temperature was due to a temperature-dependent shift in crystal structure. At 200 °C, Fe and Al, the primary matrix constituents, adopt the $(H_3O)Fe(SO_4)_2$ and $(H_3O)Al(SO_4)_2$ oxonium double-sulfate crystal structures [3]. These structures are held together in planar layers by weak hydrogen bonding, and degrade rapidly in the presence of water [28], thus explaining the rapid leaching kinetics. In contrast, at 400 °C, Fe and Al form $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$, anhydrous sulfates, which do not possess the same level of instability in water, and thus leaching considerably more slowly.

Y and the refractory metals (Ti, Zr, Nb, Hf) all showed similar response to Sc with respect to the different baking temperatures; however, the effect in each case was considerably more extreme, with 25 °C incubation leading to near-zero extractions, which are increased to moderate levels with baking at 200 °C, and further increased by baking at 400 °C. In particular, the extraction of Y, Nb, and Hf benefit from the increased temperature.

In contrast, with the exception of Nd, the extraction of the studied lanthanides (Ce, La, Sm – all light rare earths) did not appear to benefit from baking at 200 °C, showing near identical response at both 25 °C and 200 °C. Increasing the baking temperature to 400 °C slowed leaching in all cases; although, not to the extent observed for Sc, Y, and the refractory metals. For Ce and La, the 400 °C baking temperature slightly increased extraction, while the effect was minimal for Nd and Sm.

In all the studied cases, the system response to the baking temperature was non-linear, and bi/trimodal, allowing the selection, via the use of the baking temperature as a switching signal, of different performance modes, depending on the design criteria of the process being developed – if rapid processing is required, and sub-optimal extraction yields can be tolerated, a lower baking temperature (200 °C) can be selected, while the higher temperature (400 °C) can be selected if a high extraction yield is desired, and longer processing times can be tolerated – effectively making the material extraction a tunable process.

4. Conclusions

We have developed an efficient, economical, and tunable process for the extraction of REEs, Sc, and refractory metals from bauxite residue, using acid-baking water-leaching. This process offers several advantages over conventional direct acid leaching for the processing of bauxite residue. This process will fit into a larger initiative to develop an integrated near-zero-waste process for the full valorization of bauxite residue. Future research will primarily focus on the development of a process to purify and recover the valuable materials from the leachate using novel and sustainable techniques, and the reuse/recycling of various waste streams coming off the process, such as the remainders of the acidic leachate after all the valuable contents are been removed.

5. References

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