

Recovering of REEs from unconventional resources – Bauxite Residue

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Bauxite Residue

‘*Bauxite Residue*’ (BR) refers to the insoluble solid material, generated during the extraction of alumina (Al₂O₃) from Bauxite ore using the Bayer process. When bauxite ore is treated with caustic soda, the aluminium hydroxides/oxides contained within, are solubilized, with approximately 50% of the bauxite mass being transferred to the liquid phase, while the remaining solid fraction constitutes the -bauxite- residue.

Active lime is usually added during digestion to control and reduce caustic soda and alumina losses from the formation of desilication products.. The solid-liquid separation after ore digestion takes place in thickeners and washers, resulting in the formation of a red-colored bauxite residue slurry (approx. 50% solids) which was previously termed ‘red mud’. Nowadays many plants use, as a final step of slurry treatment, high pressure filtration (the most efficient method of alkali recovery), in which the bauxite residue slurry is pressed to remove the maximum of remaining liquor and produce a compact filtercake with a relative humidity of 25-30%.

It is estimated that for each ton of alumina produced 1.0- 1.5 tons of solid residue (on a dry basis) is generated depending on the initial bauxite ore grade and alumina extraction efficiency (Evans 2016). Bauxite residue consists of various metal oxides of Fe, Al, Ti, Si, Ca, Na, V, Ga (depending on the initial chemical composition of the bauxite ore) along with inclusions of unwashed sodium aluminate solution.

As the global demand for primary aluminium metal increases so will the BR production, currently in excess of 150 million tons per year worldwide (Power et al. 2011). This is generated at more than 100 active alumina refining plants worldwide. In addition, there are at least another 50 closed legacy sites, so the combined stockpile of bauxite residue at active and legacy sites is estimated at three thousand million tons. (World Aluminium and the European Aluminium Association, 2015)

The primary aluminium industry has always focused on discovering potential applications for BR utilization. The vast amount of research and studies on BR utilisation is justified by more than 734 patents since 1964. Possible applications can broadly be broken down into various categories, such as cement and building materials production, iron production, trace element (Ga, REE, V,etc.) recovery, use as soil amelioration, landfill capping, acid mine drainage treatment and others (Evans 2016). The recent REE crisis fueled significant research effort in recovering the REE that are found in some BRs in concentrations between 1 - 2 kg of total REE / t of BR. Given the large quantity of the annual BR production, the total amount of contained REE becomes significant and could cover part of the global REE demand (Balomenos et al., 2017a). Furthermore, while the treatment of BR for the recovery of REEs does not solve the BR deposition

problem, as the volume of the waste remains practically unaffected, it does help in the economic viability of holistic processing flowsheet seeking to achieve near zero-waste through multiple processing steps (Balomenos et al., 2017b).

Rare Earths in Bauxite Residue

The bauxite ore is one of the factors that affect the concentration of REE in bauxite Residue. Bauxites are classified in three categories, lateritic bauxites (88%), karstic bauxites (11,5%) and Tikhvin type bauxites (0,5%) (Bardossy, 1982; Bárdossy and Aleva, 1990). Karstic bauxites are mainly found in Europe, Jamaica, Russia and China. The karstic bauxites contain higher concentrations of REE than the lateritic bauxites. REE are detected in bauxite ore as fluorcarbonate or phosphate minerals which are very similar to the main industrial minerals of REE (bastnaesite - monazite) (Li et al., 2013; Mouchos et al., 2017; Ochsenkühn-Petropulu 1995; Vind et al., 2018a). It has also been reported that in the Bayer process REE end up in the BR in 2:1 ratio, compared to the initial bauxite ore. (Derevyankin et al., 1981; Ochsenkühn-Petropulu et al., 1994; Wagh and Pinnock, 1987).

The worldwide typical concentration of REE in BR is 800-2500 mg/kg and is related to the initial bauxite ore and the operating conditions of the Bayer process (Deady et al., 2018). Recent research shows that REE in BR can be found in secondary mineral phases produced by the Bayer process, known as the desilication product (DSP). DSP is the result of the silicon removal from the aluminate solution during the leaching of the bauxite ore, as silicon is major pollutant for the final alumina product. Presence of REE in the DSP can be attributed to REE from the bauxite ore being dissolved in the Bayer process; these REE are incorporated into the newly formed DSP mineral matrix that contains a mixture of Fe, Ti, Si, Al Ca and Na ions (Vind et al., 2018a).

Scandium (Sc) often differs from the other REE behavior. Especially in lateritic bauxites and their corresponding BR, it is often correlated with iron and titanium and zircon minerals (Vind et al., 2018a) (Liu et al., 2018; Zhang et al., 2017), which for the most part are unaffected by the Bayer process. This is also confirmed by the laterite deposits in Australia and the Greek BR (Chassé et al., 2016) where the main mineral, with high concentration of Sc is goethite (Vind et al., 2018b). However, there are cases of BR ,where Sc is found to be related to larger extent to the soluble Al-bearing minerals, as is reported by Russian researchers (Suss et al., 2018).

Published chemical analysis and leaching studies of bauxite residue focus on the concentration of Sc, because Sc represents 95% of REE's financial values found in BR (case of Greek Bauxite, reported by Ochsenkühn-Petropoulou et al., 2002). Table 1 presents the Sc concentration in different Bauxite Residues worldwide as reported in literature.

Table 1 Concentration of Scandium in Different Bauxite Residues

| BAUXITE RESIDUE | SCANDIUM CONCENTRATION ppm | Reference |
|-----------------|----------------------------|--------------------------|
| Guangxi, China | 115 | (Gu et al., 2018) |
| Henan, China | 66 | (Gu et al., 2018) |
| Shandong, China | 54 | (Gu et al., 2018) |
| Shandong, China | 80 | (Liu et al., 2017) |
| Shandong, China | 76 | (Liu et al., 2018) |
| Chinalco, China | 158 | (Qu and Lian, 2013) |
| China | 41-93 | (Wang et al., 2011) |
| Australia | 54 | (Wang et al., 2013) |
| Australia | 68 | (Rayzman, 1998) |
| India | 50 | (Abhilash et al., 2014) |
| Jamaica | 130-254 | (Wagh and Pinnock, 1987) |
| Jamaica | 230 | (Rayzman, 1998) |
| Jamaica | 55 | (Narayanan et al., 2018) |

| BAUXITE RESIDUE | SCANDIUM CONCENTRATION ppm | Reference |
|-------------------------|----------------------------|---|
| Kazakhstan | 55 | (Rayzman, 1998) |
| Russia | 100-150 | (Yatsenko and Pyagai, 2010) |
| Russia | 110 | (Rayzman, 1998) |
| Russia | 240 | (Petrakova et al., 2016) |
| Ural, Russia | 90 | (Petrakova et al., 2016) |
| Nikolaev, Russia | 60 | (Smirnov and Molchanova, 1997) |
| Aghios Nikolaos, Greece | 100-135 | (Borra et al., 2015; Davris et al., 2016b; Ochsenkühn-F |
| Akja Hungary | 80 | (Ujaczki et al., 2017) |
| Hamburg Germany | 59 | (Hoffman et al, 2019) |
| Canada | 47 | (Reid et al., 2017) |

It has been estimated that 70% of the world's Sc resources might be found in bauxite minerals and bauxite residue (Petrakova et al., 2016). Scandium is a very rarely concentrated element, making commercially usable deposits of this critical material very rare. As a result it usually extracted as by- product from the metallurgical residues from primary extraction of TiO₂ from ilmenite and other ores, Nickel-Cobalt from laterites, U₃O₈ from various ores, Rare Earth oxides and others (Wang et al., 2011). For this reason scandium concentrations of 50-60 mg/kg are considered as exploitable (Wang et al., 2011). The main application of scandium is in the production of high strength aluminum alloys suitable for aerospace applications (Ahmad, 2003). Due to the potentially large Al alloy market, the production of scandium from bauxite residue is easily connected with the primary production of aluminum to produce Al-Sc alloy.

There have been many studies on the extraction of REEs, and particularly scandium, from bauxite residue. Several authors have reported different methods based mainly on hydro- or combined pyro- and hydro-metallurgical methods and these are reviewed in the paragraphs below.

Direct leaching with inorganic acids

REE are a small fraction of the BR. Direct leaching of BR with mineral acids, requires significant acid consumption, as BR is by nature highly alkaline, and results in leach solutions with low REE concentrations (<1000mg/l), while the major BR metals such as Fe, Al, Ti, Ca, Na and Si dissolve extensively and are thus found in concentrations of several g/l. This complicates the REE extraction and refining from such solutions, as established methods (solvent extraction – ion exchange) start with solutions of several g/l of REEs. Hence, most researchers focus on the selective solubilization of REE against major elements like Fe, looking to produce leach solutions that can be further processed economically.

Initially, selective solubilization of REE with weak acids was performed in BR from Jamaica (Fulford et al., 1991a). Sulfurous acid H₂SO₃, produced by SO₂ gas pumped through bauxite residue pulp, reduces gradually the pH of the pulp, allowing the selective leaching of REE against iron. The leaching takes place in 2-3 stages and the recoveries of REE reach 85% (expressed by the recovery of Y) while the recovery of Sc is not reported. The same team also separated the REE directly from the pregnant solution using DEHPA organic solvent (Fulford et al., 1991b). Selectivity achieved for pH values in the range of 1,5-3. In this range, Fe remains insoluble, while other metals such as Ca, Na are completely dissolved.

The use of inorganic acids (H₂SO₄, HCl, HNO₃), results in selective leaching of REEs from Greek Bauxite Residue, but the recovery levels are quite low (Borra et al., 2016a). For instance, Sc selective leaching ranges always between 30-50% even at 150°C (Sugita et al., 2016). It has been found that HCl addition in the Greek Bauxite Residue leads to a maximum Sc leaching of 50% against Fe (5%), while the increased recovery levels correspond to high Fe solubilization, indicating indirect correlation between Sc and mineral Fe phases (Borra et al., 2015). The same team reports that during solubilization the complete Ca, Na dissolution takes place, while Al, Ti, Si are recovered in the range of 30-40%. REE recoveries varied between 30-60% after 24 hours treatment in a 2% w/v pulp density with 0.5-1,5 mol/L HCl. Increasing the HCl concentration to 3-6 mol/L,

increases REE and Fe recovery above 70%. At the same time 30-50% of Al, Ti and Si is dissolved. Increasing the pulp density during leaching (at the same acid concentration) reduces the recovery of REE. Finally, the increase of temperature during the HCl leaching does not affect REE recoveries (Borra et al., 2015). The absence of significant effect of factors such as temperature and pressure during the leaching of Greek BR are also reported in previous studies (Ochsenkühn-Petropulu et al., 1996). On the other hand, there are studies that report opposite results (Sugita et al., 2016). This happens because the leaching stage takes place under different conditions and there is heterogeneity between bauxite residues from different plants (processing different bauxite ores). Heterogeneity also occurs even from the same bauxite residue supplier in samples taken at different times due to possible changes in Bayer process conditions or more importantly the bauxite ore (mixture) used in the plant. This fact does not always allow the direct comparison of results between different BR acids leaching.

Greek BR leached with nitric acid (HNO_3) results in selective recovery of Rare Earths against Fe (Ochsenkühn-Petropulu et al., 1996). The selectivity of Rare Earths from Bauxite Residue based on the consumed acid increases with the following order $\text{H}_2\text{SO}_4 < \text{HCl} < \text{HNO}_3$. During the HNO_3 leaching, Y recovery was about 90%, heavy lanthanides (Dy, Er, Yb) recovery was up to 70%, for the middle (Nd, Sm, Eu, Gd) up to 50% and for the light lanthanides (La, Ce, Pr) up to 30% (Ochsenkühn-Petropulu et al., 1996). Leaching with diluted HNO_3 was applied and optimized on a pilot scale (Ochsenkühn-Petropoulou et al., 2002), where scandium recovery reaches 70% after a 3 steps of consecutive HNO_3 leaching. Furthermore, pH must be kept between 0 and 0.2 for the highest Sc/Fe ratio in the pregnant solution. The final solution undergoes purification stages to recover REE using ion exchange resin Dowex 50 and then solvent extraction with DEHPA (Ochsenkühn-Petropoulou et al., 2002; Ochsenkühn-Petropulu et al., 1995). Finally, Sc extraction from the organic solvent is performed with NaOH, while REE are separated in a subsequent step with liquid chromatography (Tsakanika et al., 2004). The main drawback of this method is the large volume of liquid wastes containing nitrate anions when produced by the solid residue washing after leaching (Petrakova, 2014).

H_2SO_4 was selected as the most suitable extracting agent for the Australian BR leaching. Sc recovery is 47% against Fe 7%, while Y recovery is 5% at 10% w/v pulp, 1 mol/L H_2SO_4 at 50°C for 2 h (Wang et al., 2013). Recent leaching studies in Greek BR using H_2SO_4 didn't show significant improvement in REEs recovery. Nevertheless, efforts have been made to reduce acid consumption by neutralizing BR with CO_2 (Rivera et al., 2017) as well as attempting to avoid the formation of silica gel by the method of digestion with concentrated acids and final water dilution (Rivera et al., 2018). Scandium recoveries are between 30-40% with high Fe dissolution due to the use of concentrated HCl and H_2SO_4 . Furthermore, the avoidance of silica gel and Sc (68%), Ti (91%) recovery can, also, be achieved with 2,5M H_2O_2 solution in 2,5M H_2SO_4 but leaching is not selective (Alkan et al., 2018). The main scandium leaching mechanism from BR selectively using H_2SO_4 is described by the shrinking core model- thin film diffusion (Hatzilyberis et al., 2018), while the reaction rate is first class with the scandium recovery up to 50% selectively at 2% w/v pulp density, 1-3 mol/L for 1 h.

Correspondingly, in Canadian BRs, three different acids were examined. H_2SO_4 selected as the most appropriate, based on the leaching efficiency, cost and practical part (Reid et al., 2017). In the kinetic model, the process of BR's REEs leaching is described by the expansion of acid through the boundary layer at the boundary of grain. Pretreatment of BR in direct microwave exposure before leaching, nano-sized pores were grown on the surface of grains, allowing for an increase in REE leaching efficiency, which means 40,0-64,2% Sc and 54,3-78,7% Nd, no results on recoveries for other main metals are given (Reid et al., 2017).

The relatively moderate recoveries of REE and especially the Sc recovery, during the direct selective leaching, led many teams to use more concentrated acids in higher temperatures to achieve higher scandium recovery. The processing of BR with concentrated acids provides the extraction of critical and other metals with no selectivity. BR leaching with HCl in 6mol/L at 50°C for 1 h and 20% w/v pulp density can leach up to 80% Sc with 21,2 mol HCl consumption per kg of BR (Wang et al., 2010). In a bauxite residue digestion process with concentrated H_2SO_4 at high temperatures followed by leaching with water and addition of H_2SO_4 , the optimum conditions were determined as an average particle size of 65-80 μm , 90°C, 3h and solid to liquid ratio 3:1 recovering 85% of Sc (Xue et al., 2010). In a similar like process (Zhang et al., 2005), 6mol/L HCl,

solid to liquid ratio 4:1 are leached at 50 for 1 h recovering 80% of Sc and then the residue is treated with H_2SO_4 at 92%wt H_2SO_4 , with solid to liquid ratio 3:1, at 200, for 1.5 h to leach 97% of Ti. In these studies, the recoveries of other metals from BR as well as the subsequent recovery of Sc from the solutions produced are not reported. Nonselective leaching of Sc with concentrated sulfuric acid (3-4 mol/L) at 95 °C at 10-20% pulp densities has also been reported for the Greek BR, leading to 90% Sc and 95% Fe extraction. The produced PLS (Pregnant Liquid Solution) was reported having 7g/l Al, 5 g/L Ti, 42 g/L Fe and 15 mg/l of Sc (Davris et al. 2018c).

For the non-selective recovery of metals from BR, Orbite Technology Inc. (Boudreault et al., 2017) developed a hydrometallurgical process in which the BR is treated with concentrated HCl (18-33% wt.) solution in an autoclave at 140-170 °C. During the leaching, all metals (except Ti) are dissolved. Aluminum, iron and magnesium is recovered by treating the solution with HCl gas and subsequently removing steps (Figure 1). REE are separated from the pregnant solution using organic solvents. The use of corrosive HCl, which requires glass-lined reactors as well as valves and tubes of high chemical resistance polymers, results in high cost and maintenance demand. In addition, the handling and storage of the produced insoluble acidic solid is of high importance, rendering the process as less effective.

Hosted file

image1.emf available at <https://authorea.com/users/595209/articles/629392--recovering-of-rees-from-unconventional-resources-bauxite-residue>

Figure 1 Leaching process with concentrated HCl developed by Orbite Technology Inc. (Borra et al., 2016a)

Direct leaching with organic acids

BR leaching using organic acids has been studied in the same way as inorganic acids. Greek BR treatment with citric, methanesulfonic and acetic acids can correspond to inefficient rare earths leaching, resulting in lower recoveries compared to inorganic acids. Exceptionally, high REE recoveries, which are comparable to inorganic acids, can be achieved after citric acid treatment under rising temperature (Borra et al., 2015). In contrast to these results BR studies from Russia revealed that a mixture of formic -acetic acid at 80°C, pH 1-3,6 obtained 63-74% Sc recovery and similar Al recovery (yield), while the recoveries of other REE are not reported; further increase of pH during the leaching led to silica gel formation with filtration disorder (Bogomazov and Senyuta, 2017). Use organic acids for BR leaching results in more expensive process as the cost of the solvents is higher and additional recycling steps with distillation are needed to recover and reuse the organic solvents after the leaching stage.

Bioleaching process is based on a more indirect use of BR leaching with organic acids. During bioleaching, metals are extracted with microorganisms (bacteria or fungi) which produce organic acids. Fungi are mainly used for the BR leaching because they can survive at high pH and produce organic acids, amino acids and proteins in the presence of an organic agent forming complexes with metal ions. The produced organic acids are usually a mixture of citric, oxalic and gluconic acid. REE were leached from BR with the nematode fungi RM-10 in the presence of a sucrose agent (Qu and Lian, 2013). The authors found that leaching in two steps (pre fungi culture followed by leaching) was better than the one step leaching (culture in the presence of BR). Similarly, *Aspergillus niger* fungi was used (Qu et al., 2013) both in batch and continuous leaching. During the batch leaching at 2% w/v pulp density after 10 days recovery of Sc is 44%, while the increase of pulp density to 10% w/v reduce the Sc recovery at 30% under continuous operation.

Leaching with ionic liquids

Ionic liquids (IL's) are versatile solvents consisting solely of ions, having superior properties against classic organic solvents in terms of low vapor pressure and inflammability. Ionic liquids have been applied as lixivants to selectively dissolve rare earth elements (REE) from bauxite residue.

A new leaching process that developed is based on a hydrophobic ionic liquid betainium

bis(trifluoromethylsulfonyl)imide [Hbet][Tf2N] (Davris et al, 2016 and 2018). Leaching bauxite residue with HbetTf2N-water mixture (40%v/v water) at autoclave conditions of 150°C for 4h at 10% pulp density (w/v) can selectively dissolve REE (>70%) against Fe, Al, Ti and Si in the Greek BR. Scandium followed a different leaching behavior from the rest REE with maximum 45% recovery upon leaching, whereas Ca and Na content are totally dissolved. The metals ions present in HbetTf2N leachate obtained after filtration, are stripped with an aqueous acidic solution while hydrophobic HbetTf2N is regenerated for reuse. During stripping and upon pH adjustment a preconcentrated Sc solution with fewer impurities is generated. Where the concentration of the Sc in the organic phase before the stripping was 5-6 mg/l (directly comparable with the mineral acid selective leaching presented in section 1.1.2), in the aqueous strip solution concentrations of 100 mg/l Sc have been achieved. This significant increase in concentration along with the complete avoidance of silica gel formation are the most promising factors of this novel approach

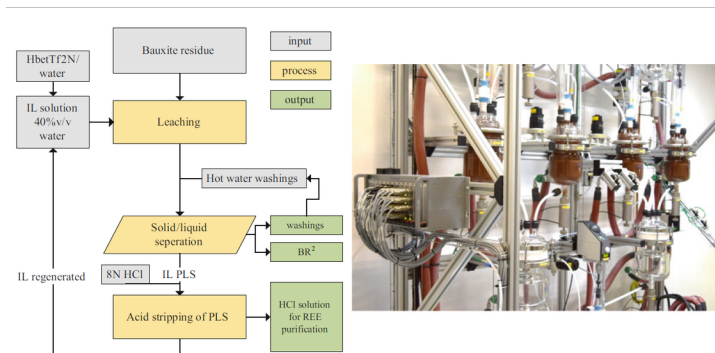


Fig. 7 BR flowsheet treatment with HbetTf2N to produce a final REE solution and regenerate the IL for reuse (left). Demonstration of the proposed flowsheet to a mini pilot plant built in Athens (right)

Table 6 Chemical analysis of the intermediate precipitate obtained during HCl solution neutralization and wise step precipitation using NaOH

| Element | Sc | Y | La | Ce | Nd | Al | Fe | Ca | Na |
|---------|----|---|----|----|----|----|----|----|----|
|---------|----|---|----|----|----|----|----|----|----|

Figure 2 BR leaching process in bench scale with Ionic liquid HbetTf2N [Davris et al, 2018]

The proposed IL process (Figure 2) provides selectivity, recyclability of the leaching agent and more efficient acid input in the process. Yet the high price of the ionic liquid in conjunction with the unavoidable IL losses in each contact with aqueous phases (in total 3-10% IL losses can be expected per cycle) makes this process financially unattractive. Future studies are focused on minimizing IL losses while maintaining the advantages of this newly developed process.

Leaching with NaHCO₃

Leaching BR studies at Russia indicated that selective Sc leaching can be achieved avoiding the acidification stage through alkaline leaching using NaHCO₃ as the leaching agent and utilizing CO₂ to regulate pH. It has been found that Sc has higher solubility in NaHCO₃ (16.7 g/L) than in Na₂CO₃ (0.43g/L) solutions, (Petrakova et al., 2016; Suss et al., 2018; Yatsenko and Pyagai, 2010). During alkaline leaching, part of NaHCO₃ is converted into Na₂CO₃, reducing Sc solubility. With the addition of CO₂ gas to the pulp, the NaHCO₃ content is increased allowing for higher Sc recovery. The flowsheet and the pilot plant developed by RUSAL are shown in Figure 3. During leaching, 26% of Sc is selectively recovered at 60 °C with pCO₂=6 atm and liquid to solid ratio 1:4 (Petrakova et al., 2016). About 30% Na, 68% Zr and 6% Ti are dissolved and extracted during the purification of the pregnant solution. Efforts to avoid Sc losses during the leaching are made by introducing resins directly into the pulp (Suss et al., 2018). At present, this process is the only Sc extraction application from BR at a semi- industrial scale, allowing Rusal to produce 3 tn of Sc₂O₃ per year.

The low recovery of Sc ~25% and the zero recovery of the other REE are the main drawbacks in this case. The advantage of this process is the production of Sc with no acid addition, while the final pH=8 of BR after

the process results in a less environmentally aggressive by-product to be handled. In addition, this method is one of the few that allows for actual CO₂ sequestration. It should be noted that this technology is effective when Sc is associated with Aluminium mineral phases. Tests in the Greek BR (where Sc is in the mineral phases of Fe) did not result in significant Sc dissolution (<3%).

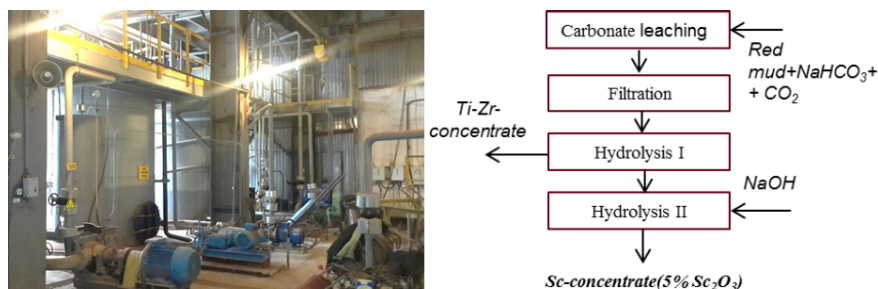


Figure 3 Sc pilot production at Rusal facilities (Petrakova et al., 2016)

Comparison of leaching methods

Table 2 presents a comparison study of direct BR leaching. In most REE studies it is reported that the direct BR leaching by inorganic acids (HCl, HNO₃ and H₂SO₄) is more advanced than the use of organic acids such as citric acid, acetic acid, etc. (Borra et al., 2015; Ujaczki et al., 2017; Yatsenko and Pyagai, 2010). However, the recovery of REE with some of the organic acids is comparable or even better to those of inorganic acids, especially under a high temperature leaching process. Nevertheless, the use of H₂SO₄ is considered to be most appropriate for BR leaching in terms of low cost and easy to handle process (Petrakova, 2014).

According to the chemical cost, it seems that citric acid leaching presents a double price compared to bio-leaching, while H₂SO₄ leaching is the most economically viable solution (Qu et al., 2015). The main disadvantages of acid extraction are the consumption of large acid quantities for the BR's neutralization, the waste manipulation and the acidic residue's reuse after leaching (Table 2) (Petrakova, 2014). In addition, acid leaching dissolves large amounts of Fe, Ti and Al by reducing selectivity (Wang and Cheng, 2011; Wang et al., 2011). The high concentration of these metals in the pregnant solution reduces the recovery efficiency during refining with ion-exchange resins, while increasing the acid consumption during the washing-regeneration phase of the resins. Unlike the acidic route, alkali extraction such as NaHCO₃ is advantageous due to the lack of neutralization and the production of less caustic BR, and while the scandium recovery in this process is quite low, it seems to be profitable as Sc₂O₃ can be produced at cost of well below US\$ 900 / kg. However, this process is only effective in certain BRs from Russia. The patent of Orbite Aluminae Inc. is also very promising, as it promotes metal recovery and acid reuse, resulting in the minimization of the waste production. However, the use of concentrated HCl requires corrosion resistant equipment, increasing the total investment and operational cost. The IL leaching process is also very promising in delivering a concentrated Sc solution with low Fe, Ti, Al impurities and overall low acid consumption, but it is uneconomic given the reported IL losses in each processing cycle and the current cost of the IL reagents.

Table 2 Comparison of direct BR leaching methods

| Leaching means | Main advantages | Main disadvantages |
|---|---|---|
| H ₂ SO ₄ , HCl, HNO ₃ | 20-80% REE extraction. Possibility to modify the recovery ratio of REE and Fe depending on acid concentration and leaching steps. By-products production (Orbite Patent, and HNO ₃ Pilot NTUA). | Low REE's recovery. Large amounts of effluents and acid wastes. As acid concentration increases, selectivity decreases. Special equipment for corrosion resistance is needed in case of HCl. Silica gel formation at low acid concentrations. |
| H ₂ SO ₃ | Digestion in 2-3 stages of selective dissolution of REE, up to 85% Y recovery (Patent Alcan). | No data available for the Sc extraction. |
| Carboxylic acids such as formic, citric, acetic, methanesulfonic acid, etc. | Selective REE's leaching (similar to mineral acids), Ca and Al versus Fe. Bio-leaching (Rusal Patent). | Difficulty in recycling organic acids by distillation, producing large amounts of calcium sulphate. In some cases, low REE extraction. More expensive solvents than inorganic acids. |
| CO ₂ , NaHCO ₃ | Selective metals recovery such as Sc, Ti and Zr producing carbonate complexes in the caustic solution. Large intake of CO ₂ in pulp (Rusal pilot plant for production of 2 tons per year Sc ₂ O ₃). | Low Sc recovery (<26%) No REE recovery. |
| Ionic Liquid (HBET-TF2N) | High selectivity of REE against Fe Si and Ti; Similar to mineral acid recoveries; low acid consumption (regeneration of IL), and purification and up concentration of REE solution. | High cost of IL (non commercial commodity-synthesized on demand), IL losses in aqueous phases. |

The case of low-level Sc leaching with mineral acid

A different approach to Sc leaching from BR was recently published under the SCALE project (Balomenos et al, 2021a). The leaching conditions were selected based on criteria of cost and effectiveness of the produced PLS in a subsequent ion-exchange process to extract Sc into a marketable concentrate. To achieve low cost in leaching, sulfuric acid was used at high pulp densities and to achieve effectiveness of the ion-exchange process iron and titanium in the PLS were kept below 200 mg/l and 50 mg/l respectively. The conditions meeting these demands were leaching the BR with 0.26 – 0.28 kg conc. sulfuric acid/kg BR at 85°C for 1 h with 40% solid to liquid ratio. At these conditions silica gel formation was avoided (Si concentration in PLS 120-150 mg/l). The process was demonstrated at pilot scale at MYTILINEOS in Greece, where on average from 1 t BR, 17,15g Sc were dissolved into PLS, consuming 0.27t of H₂SO₄ (21% Sc leaching yield, 12-14 mg/l of Sc in the PLS). With more than 10t of BR leached in this way, sufficient PLS was generated to process in ion-exchange pilot utilizing II-VI's SIR resin, resulting in a solid concentrate with 22% wt Sc (Balomenos et al, 2021b).

Sulfuric acid baking

The BR baking process with H_2SO_4 was developed, after extensive research, as a suitable method to increase the selective solubilization of REEs against major metals in BR, reducing the consumption of large quantities of chemical reagents (Borra et al., 2016c; Liu et al., 2017; Narayanan et al., 2018; Onghena et al., 2017). In this process, BR is digested at 100-120 ° C with concentrated H_2SO_4 to form Fe, Al, Ti and REE sulphates, and baking at 650-750 ° C to break down non-stable sulfates such as Fe, Al, Ti in the form of oxides. REE's sulfate salts remain in the form of sulfates even at 750 ° C allowing their selective solubilization in a subsequent step using water. The solid residue from the process contains mainly oxides Al, Ti, Fe, Si and CaSO_4 . This process results in the selective extraction of REEs with 60% Sc-90% REE recoveries (Borra et al., 2016c). In a similar study, 75% Sc-88% REE recoveries have been reported (Narayanan et al., 2018). The factors influencing the selective extraction are the amount of acid in the BR, the baking temperature and the baking time. A big advantage of the method is the reduction in acid consumption and the high selectivity of REE over Fe, Al, Si, Ti. The slow rate of REEs water leaching after the sulfate baking stage, which is reported between 2-7 days, and the SO_2 emissions are the main drawbacks of the process.

Combined pyro-hydrometallurgical leaching techniques

The pyrometallurgical recovery of Fe from BR is a stepping stone for the development of holistic exploitation, valorizing about half the amount of BR and adjusting the properties of the slag to be further processed for critical metals extraction or to be used as building material. Iron recovery through the pyro-metallurgical BR treatment can be achieved by reductive smelting or by reductive roasting and magnetic separation; REE oxides cannot be reduced by carbon and therefore will never follow the metal phase produced in such processes and will be found in enhanced concentrations in the produced slag or from the non-magnetic fraction respectively.

Reductive smelting processes can be applied by several technologies (Corex, Finex, Hismelt, Romelt, AusIron and Electric Arc Furnace EAF) to BR for the production of pig iron (Panov et al., 2012; Xenidis et al., 2016). So far, two methods have been applied on a large scale for the BR reductive smelting: the Romelt method (Mishra and Bagchi, 2002) and the electric arc furnace (EAF) (Balomenos et al., 2011; Grzymek et al., 1982; Guccione, 1971; Logomerac, 1979). The Moscow Institute for Steel and Alloys (MISA), with National Aluminium Company Limited (NALCO) and Romelt-SAIL (India) Ltd., studied the pyro metallurgical processing of BR using the Romelt method (Mishra and Bagchi, 2002). The advantage of this method is that it accepts feed materials with moisture levels of up to 10% wt. The main disadvantage is the high energy consumption and the production of poor quality of pig iron with a high concentration of S and P (Panov et al., 2012). In the EAF reductive smelting, a mixture of BR, carbon and fluxes, at 1500-1700 °C to form pig iron with > 95% iron recovery (Balomenos et al., 2014; Balomenos et al., 2011; Balomenos et al., 2016). Recovery of residual iron can be further improved by later magnetic separation of slag dust (Borra et al., 2016b; Ercas and Apak, 1997). Post-melting slag can be used to produce rockwool or building materials (Balomenos et al., 2016; Raspopov et al., 2013) and for the recovery of non-ferrous metals and REE (Alkan et al., 2017 Borra et al., 2016b; Udy, 1958). REE is extracted from the slag using strong inorganic acids (Sargic and Logomerac, 1974; Shaoquan and Suqing, 1996). In particular, slag extraction with 60% wt. H_2SO_4 dissolves virtually all of the Al and Ti contents residing predominantly in the silicon oxide (Udy, 1958), while extraction with inorganic acids HCl and HNO_3 results in high REE recovery yields (60-100%) in solids to liquid (1/50) at 90 ° C for 1 hour at 2-3 mol/L acid concentration (Borra et al., 2016b). The use of H_2SO_4 in the same conditions showed similar recovery for Sc but lower for the remaining rare earths probably due to the formation of calcium sulphate. It is clear that a high acid concentration is required to dissolve REE from the slag, however, the number of studies presented in the literature is limited in relation to the extraction of slag for Sc recovery using sulfuric acid as well as the description of extraction problems (Rivera et al., 2019). Interferences such as silicon gel formation, secondary CaSO_4 precipitation and secondary aluminium sulphate precipitation have been reported and should be taken into account during the processing of the slag (Davris et al., 2018b).

BR sintering with Na, Ca carbonates (soda roasting) leads to the destruction of the alumino-silicate matrixes and the recovery of alumina. In such process, BR is mixed with sodium carbonate (Na_2CO_3) and the mixture is heated to temperatures between 800 and 1200 °C by converting the alumina into soluble phases of sodium aluminate, followed by extraction with water or mild alkaline solutions. Many research groups have applied this method for the recovery of alumina and sodium by BR (Bruckard et al., 2010; Chun et al., 2014; Kaußen and Friedrich, 2016; Li et al., 2009; Liu et al. 2012; Zhu et al., 2012). The resulting residue can be used for iron reduction by reducing smelting, while the produced slag is enriched in REE and Ti where they can be extracted with strong inorganic acids (Borra et al., 2017). Additionally, the sequence of sintering and reductive smelting process implementation does not affect the REE extraction at the final stage. Alternatively, a combined cabothermic reduction and soda roasting can also be applied to produce a magnetic iron fraction, soluble alumina phases and a residue with upgraded REE content (Cardenia et al., 2018).

A process was investigated during the gradual extraction of Fe, Al, Ti and REE (Borra et al., 2017) where initially BR sintering takes place with Na_2CO_3 at 950 °C for 4 hours followed by water leaching at 80 °C to recover Al (75%) with further treatment of the insoluble residue by reductive smelting to recover Fe (98%) and extraction of the produced slag to recover Sc (80%) while recovery of the remaining REE is <5%. The produced slag is converted into amorphous oxides by fast cooling, while more than 80% of the Ti content, REE is recovered by leaching with 1M HCl at 25 °C and 2% w / v pulp density. However, the presence of silica gel during the leaching process results in problematic liquid-solid separation. According to the BR sintering process with Na_2CO_3 and lignite (Li et al., 2014) the reduction of the hematite content to magnetite is achieved and is removed after breakage and magnetic separation. The non-magnetic fraction is extracted in 2 steps (Deng et al., 2017), firstly with H_3PO_4 to recover SiO_2 and secondly with NaOH to recover Al, while the final insoluble solid is enriched in Sc and Ti obtaining the fourfold concentration compared to the original BR.

If CaO is added to the BR reductive smelting an alkaline slag can be formed suitable for leaching alumina in alkaline environments (variation of the Pedersen process). The residue of the alkaline leaching, can then be treated with acid leaching to recover REE as well as Ti (Alkan et al., 2017, Vafeias et al. 2018)

An indicative mapping of various processing options aiming at extracting Fe, Al, and REE is presented in Figure 4.

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image4.emf available at <https://authorea.com/users/595209/articles/629392--recovering-of-rees-from-unconventional-resources-bauxite-residue>

Figure 4 Main methods for major metals & REE extraction from BR by combining pyro- and hydro-metallurgical processes.

Such flowsheets result in more efficient leaching of the REE as the complex mineral matrix of the BR has been destroyed and significant amounts of base metals have been removed. At the same time such flowsheets allow for significant reduction of the final residue that needs to be disposed and may even achieve financially a near break-even status (Balomenos et al. 2016). On the other hand, the numerous processing steps and the back and forth between wet and dry materials make for a very energy and cost intensive processes. To achieve such processing in a sustainable (environmentally and financially) manner, a right balance between bulk applications with low value products (i.e. pig iron production) and low volume niche products (i.e. Scandium) needs to be found.

Conclusions

Bauxite Residue constitute a significant resource for REE and especially Scandium production. However, there is significant complexity in extracting these minor metal values form BR, as upon direct leaching with high Sc leaching yields, solutions dilute in REEs and rich in major metals (g/l) like Fe, Ca, Na, Al, etc are produced; effectively hampering downstream refining of the REE. To bypass such problems, processes

with low Sc leaching yields (<30%) have to be considered, such as the ones demonstrated by RUSAL and MYTILINEOS. Combined pyro- and hydro- routes that aim to recover major metals like Fe, Al and Ti and at the same time up concentrate the REEs in slags could be more attractive as they would produce richer and cleaner REE leach solutions (allowing for high Sc leaching yields), while at the same time valorizing significant volumes of the BR itself. The goal of a near zero-waste and near break-even flowsheet for BR processing would be ideal for both the alumina and the REE industries. The realization of such a flowsheet, however, requires a high degree of industrial symbiosis and favorable logistics between different industries.

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