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Review of Technologies in the Recovery of Iron, Aluminium, Titanium and Rare Earth Elements from Bauxite Residue (Red Mud)

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Abstract

Bauxite residue (BR), also known as red mud (RM), is the main waste product of the Bayer process in producing alumina from bauxite ores and is currently being managed via stockpiling, storage within settling pond and landfilling. However, these approaches are disadvantageous in terms of potential risk for the environment and the processing of RM as raw material brings about its own challenges. In recent years, research has been focused on the reuse of RM and the recovery of metals to transform the waste into a more viable secondary source of raw materials. This paper will further explore and thoroughly review technologies and processing techniques that have been previously available as well as ones that are currently being developed. The scope of this paper will be focused on iron, aluminium, titanium and rare earths.

Introduction

Bauxite residue (i.e. red mud, RM) is the main waste product of the Bayer process in producing alumina from bauxite ores. About 1 to 1.5 tonnes RM is generated per tonne of alumina[1]. Current global production rates are about 100 to 120 million tonnes per annum[2]. The management of RM involves stockpiling, storage within settling pond and landfilling[3]. However, these approaches are disadvantageous in terms of potential risk for the environment, such as an accidental dam failure in the case of the Ajka alumina sludge spill in Hungary[4] (2010) as well as the degradation of large areas used for storing huge amounts of RM.

The processing of RM as raw material has its challenges such as high economic costing for energy requirements in drying RM, acid-consuming nature of RM due to high alkalinity, interfering elements and complex structure of minerals that inhibit the metal extraction process, and restrictions in physical and chemical parameters of extractive agents[2,3,5,6]. Exergy analysis of Bayer process performed by Balomenos et al.[7] reported very low exergy efficiency value 2.94% indicating that the process is inefficient from exergetic point of view mainly due to high exergy content of the unexploitable by-products[2]. Within our research focusing on red mud reuse and metals recovery, there are various possibilities for the industries to improve the efficiency of the overall Bayer process[2,7].

The technospheric stocks of secondary resources have been receiving increased attention lately compared to the virgin resources from geological stocks. Technospheric mining has been defined as technospheric mineral stocks extraction that have been excluded from current anthropogenic material flows[8]. The development of recovery of metals from bauxite residue as our secondary resources can be investigated in various pathways of technospheric mining, as seen in Figure 1.

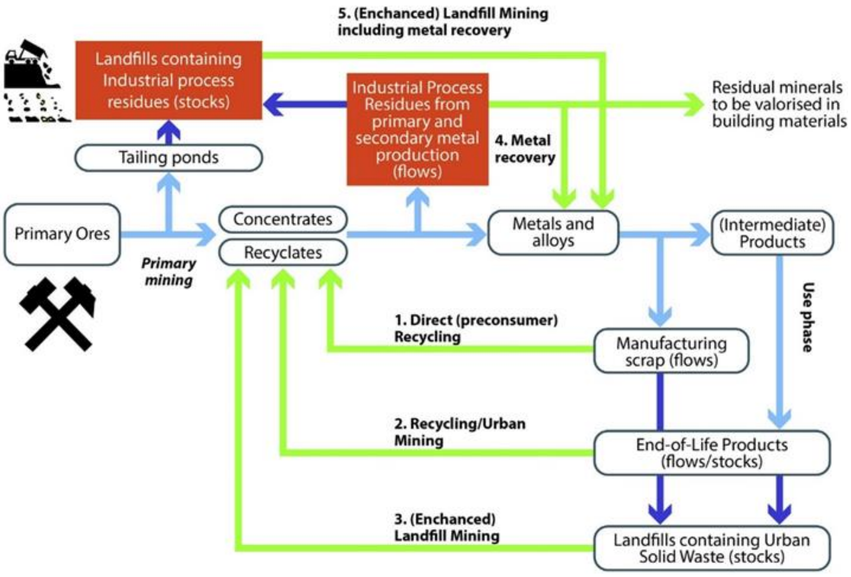

Figure 1: Metal recovery stocks and flows in primary and secondary metal production[9]

The various pathways of metal recovery development are (1) the direct recycling of pre-consumer manufacturing scrap/residues, (2) the urban mining of post-consumer End-of-Life products, (3) landfill mining of historic urban solid waste, (4) metal recovery from industrial streams from primary and secondary metal production and (5) metal recovery from stocks and landfilled industrial process residues[9]. By looking into different flows in the mining loop, full usage of resources were explored to find a feasible solution in reaching zero-waste valorisation[9]. This thus becomes the driving force of recovery and reuse of metals in secondary resources such as bauxite residue, encouraging economic growth and environmental acceptability[6].

Bauxite residue contains a significant portion of recoverable and economically valuable base metals and trace elements (e.g. Fe, Al, Ti and Rare Earth Elements (REEs)) in terms of volume of waste produced per annum[6]. BR usually consists of 14-45% iron[10] (Fe), 5-14% aluminium[10] (Al), 2-12% titanium[10] (Ti) and 0.1-1% REEs[11]. The range of metal composition in BR is dependent on the ore composition, residual alkalinity and other added materials during refining, and Bayer processing techniques[5,6,12]. This paper will review the processing techniques in the recovery of available metals (i.e. Fe, Al, Ti, REEs) in bauxite residue. Metals recovery methods will span from pyrometallurgy, hydrometallurgy and biohydrometallurgy routes, as well as the much more recent ionometallurgy and solvometallurgical alternatives.

Review of Technologies

Recovery of Iron in Bauxite Residue

This review will focus on several techniques involved in the recovery of Fe for BR. Iron is typically the major constituent in bauxite residue and is often present as oxide/oxyhydroxides[6].

Three different approaches are developed in literature to recover iron from BR: direct magnetic separation, pyrometallurgical processes and hydrometallurgical processes[6].Figure 2(I) shows the direct magnetic separation process. Stickney et al.[13] studied the direct application of high intensity magnetic separation process in Fe recovery from RM in a slurry form. Though the recovery of iron by Stickney et al.[13] was low, two products (magnetic and non-magnetic portions) were obtained. The resulting magnetic product can be used as an ingredient for ironmaking or as a pigment for pottery making. The non-magnetic portion can be applied in building materials or supplemented back into the Bayer process[14]. Thereafter Li[15] reported that the pulsating high-gradient magnetic dressing provided better results compared to common magnetic separation, especially for red mud .

One of the most effective way to separate the fine magnetic particles in liquid suspensions is through the high gradient superconducting magnetic separation (HGSMS) system, as it generates stronger magnetic field and is generally inexpensive compared to the ordinary ferromagnetic-core electromagnets[16]. Li et al.[16] developed a technique to separate the extremely fine red mud particles (<100 µm) into high iron content and low iron content parts with the HGSMS system. The results of this study indicated that, after the separation process, high iron content part of RM could be the source for iron-making furnace whereas RM with low iron content could be reused in sintering process of alumina production [16]. One of the few disadvantages of HGSMS iron recovery would be the inter-growth of Fe weak magnetic and non-metallic materials that would lead to the decrease of concentrate grade. Peng and Huang[17] investigated the Fe recovery with SLon® vertical ring and pulsating high gradient magnetic separators. Authors indicated that 53–58% iron grade was achieved for this case study but a low overall recovery rate (28–35%) was reported[17].

The direct magnetic separation approach is inefficient for Fe recovery from RM due to the lack of magnetic iron-bearing mineralogical phases. Therefore, the pyrometallurgical route was developed, involving a combination of reductive roasting of RM for production of iron bearing mineralogical phases with high magnetic susceptibility combined with magnetic separation (Figure 2(II)).

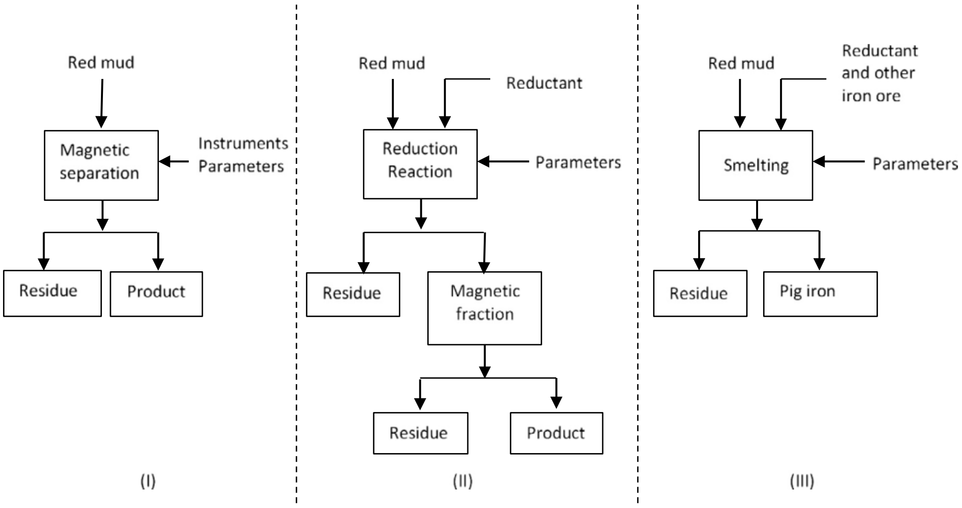

Figure 2: Simplified schemes illustrating iron recovery from red mud investigated by (I) direct magnetic separation; (II) pyrometallurgical recovery by reduction and separation and (III) red mud used directly in iron ore smelting[6]

The cost of the combined route reductive roasting/magnetic separation is elevated compared to direct magnetic separation because of reductant and additives requirements as well as higher energy consumption; many attempts have been made to find an economically feasible technology for practical industrial applications[18]. Different reductants in various studies have been investigated, including carbon powder[19-21], graphite[22], soft coal[23], coal char[24], and coke[25]. Liu and Mei[26] analysed the influence of the reactivity and ash content of coal used, on the extent and rate of metal reduction. The ideal quality of the coal used should have the following characteristics: low ash content, high reactivity, large ratio of $(F_c + V_m):(A + W)$ (where F_c is fixed carbon content, V_m is volatile content, A is the ash content, W is the other incombustible content) and high ash composition ratio (SiO_2 + TFe):(Al_2O_3 + other) and capable of forming moderate porosity[26].

Additives such as magnesium, calcium and/or sodium salts have been proved efficient in improving the reactivity of iron oxide during the reductive roasting of RM[21]. The presence of additives decreases the apparent activation energy of iron oxides reduction and increases thus the reduction rate[27]. Rao et al.[28] confirmed that the addition of sodium sulphate and sodium carbonate in the reduction roasting process have improved the metallisation degree of iron and the extent of magnetic concentrate recovery. At optimum conditions of experiments, iron recovery of 94.95% and a magnetic concentrate containing 90,12% Fe were obtained from a red mud containing 48,23% iron in the presence of 6% Na_2SO_4 and 6% Na_2CO_3[28].

Several parameters to optimise the roasting-magnetic process have been studied extensively; among those were the carbon source, carbon-to-bauxite residue ratio, roasting temperature, reduction time and magnetic conditions. Liu et al.[20] focused on carbon reductants influencing direct reduction roasting of bauxite residue. The optimum conditions were obtained when samples with red mud, carbon and additives were mixed (Carbon:Additives:RM ratio of 18:6:100) and roasted at 1300°C for 110 min. After smelting, the product was separated with a magnetic separator. The total content of iron in materials was found to be 88.77%, with a metallisation of 97.69% and a recovery of 81.40%[20]. Zhu et al.[24] added 1% binder and 8% sodium carbonate to the mixture of red mud and soft coal prior to direct reduction. A recovery of 95.7% of Fe was achieved after grinding, sintering and magnetic separation.

Through the simultaneous metals recovery route, Liu et al.[25] used a soda-lime reductive roasting process prior to leaching and magnetic separation of the fine red mud (< 75 µm). The additives promoted the formation of sodium aluminosilicate during the roasting process, which were leached and subsequently achieving 75.7% Al and 80.7% Na recoveries. Magnetic separation was applied on the leaching residue and 51.2% of Fe was recovered in a magnetic concentrate.

Li et al.[20] and Rao et al.[29] have conducted thermodynamic analysis to further investigate the simultaneous reduction process of red mud oxides using reductants. The experiment of Li et al.[20] involved reduction-sintering, leaching and magnetic beneficiation. Results suggested that, under the optimised sintering conditions, i.e. Reduction temperature range of 800-1075°C in a controlled atmosphere during the sintering process and a magnetic field intensity between 48 and 240 kA/m, the reduction to ferrite can be achieved with 61.78% Fe in magnetite concentrate.

Microwave radiation was also used as a source of heat in reductive roasting of RM. Microwave heating is unique and offers a number of advantages over conventional heating such as generating heat instantaneously inside moderately absorptive materials (dielectrics), rather than waiting for heat to conduct in from the outside surface[32]. Worth mentioning is the study of Samouhos et al.[33], where the authors used a process involving microwaves for the roasting step. This research work included the reduction of red mud using lignite (30.15 wt.% C_{Fix}), followed by wet magnetic separation (feed: 10 wt.% solids, intensity: 0.3 A) to produce a raw material which was suitable for sponge or cast iron production. Both the reductive agent content and microwave heating time controlled the reduction degree of iron. Iron reduction pathway was found to follow the sequence $Fe_2O_3/Fe_3O_4/FeO/Fe$. Under optimised conditions (Lignite-to-RM: 0.3, 800W of power supply), a magnetic concentrate of iron (35.2%) with a metallisation of 69.3% was obtained and a comparison was made between the conventional and the microwave reductive roasting techniques. They showed that the latter decreases the duration of roasting by approximately 40%, whereas the magnetic concentrate presented higher metallisation degree.

In addition to the reductive roasting, the reductive smelting is another pyrometallurgical approach that has been studied for iron recovery from RM. Guo et al.[30] obtained iron nuggets containing 96.52 wt.% Fe by directly reducing the carbon-bearing pellets of BR at 1400 °C for 30 min. The nuggets composed mainly of 96.52 wt.% Fe, 3.09 wt.% C, and traces of 0.051 wt.% Si, 0.013 wt.% Mn, 0.076 wt.% P and 0.091 wt.% S. However, iron losses were observed in the slag in the forms of reduced metallic Fe and Fayalite (Fe_2SiO_4).

Raspopov et al.[22] reported the results of experiments on the use of Russian red mud in traditional pyrometallurgical processes. Cast iron and slag phases generated after reduction and smelting of BR (1200–1500°C) with excess carbon, could easily be separated whereas the C content in the cast iron ranged from 2.0% to 2.3%. Jayasankar et al.[23] reduced red mud through the use of thermal plasma technology (arc thermal plasma reactor) to produce pig iron. BR was mixed with fluxes (10% dolomite and lime) as well as graphite as reductant and the mixture was smelted for 25 min at 1823-1923 K. This parameters allowed an optimal recovery of Fe around 71%.

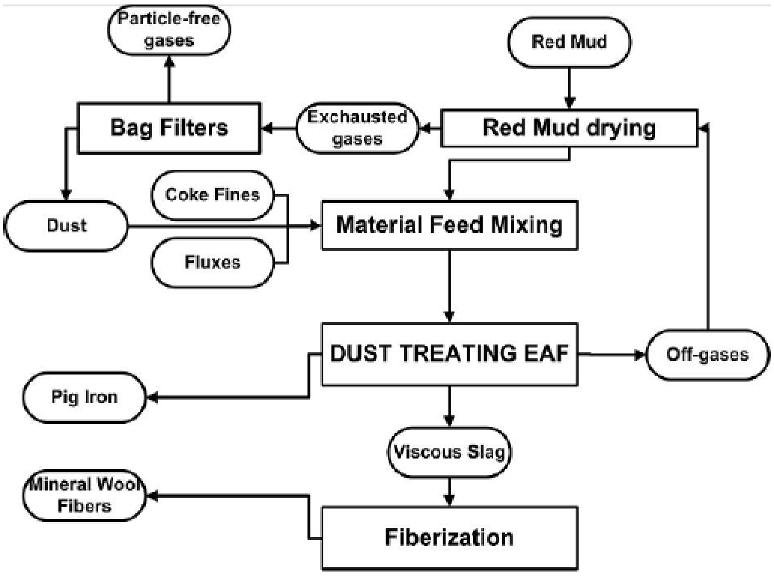

Figure 3: ENEXAL BR treatment flowsheet[2]

Within the ENEXAL project, Balomenos et al.[2] extensively studied reductive smelting of BR and coke as reducing agent in an electric arc furnace (EAF) via preliminary thermodynamic modelling, laboratory experiments that translated into a full-scale pilot plant operation. Fig 3 shows flow diagram of the BR treatment in industrial scale at 1 MVA EAF in the Aluminium of Greece. This “zero-waste” process is developed for the direct transformation of RM into valuable products: pig iron and mineral wool fibres[29]. Initial year pilot plant results obtained approximately 5 tonnes pig iron and 16 tonnes of slag to be fiberized. The final pig iron obtained presented an iron content of 95.47 wt.%[2]. This “zero waste” process has the potential to utilize BR completely, transforming the non-iron bearing slag by-product to a high value-added thermal insulation material thus offsetting the high operating cost of the pyrometallurgical treatment.

Hydrometallurgical processes have been also developed for extracting Fe from red mud. Debadatta and Pramanik[30] have investigated the dissolution of iron from red mud using sulphuric acid. Debadatta and Pramanik[30] achieved a low recovery of iron of 47% with leaching conditions of 100 ° C, 24 h, using 8 N sulphuric acid and as a solid-to-liquid ratio of 5:100. Oxalic acid can also be applied as a leachate to extract Fe from red mud[31]. The iron content of red mud was solubilised as Fe(III) oxalate and the extraction rate of iron was about 96% after leaching process, using 1 $mol \cdot L^{-1}$ oxalic acid at 75 °C for 2 h[31]. Subsequently, the solution was irradiated with UV light to reduce Fe(III) to Fe(II) and thus to accelerate its precipitation in the form of Fe(II) oxalate.

In the preceding years, bioleaching processes have been investigated extensively as ‘clean’ and economically viable alternatives to traditional metal recovery techniques[32]. As written in the article of Eisele and Gabby[33], these processes can be efficiently applied for iron recovery from refractory ores that cannot be beneficiated by the conventional ore dressing processes. Bioleaching processes have been studied and applied in various fields, such as the removal of iron from kaolin[34] and silica[35]. However, no such efforts have been made for the removal of iron from bauxite residue [36-39]. This is because of the high pH value of red mud that is not favourable for bacterial growth. Laguna et al.[32] have managed to investigate the dissolution of iron at pH>7 using mixed bacterial cultures. This study offers the possibility of using a multi-step procedure to recover iron, involving bioleaching process following by acid leaching and reduction of pH with other acidic wastes. There is potential for bioleaching technology to be a convenient and efficient way of recovery of Fe from red mud in the future.

Recovery of Aluminium in Bauxite Residue

In Bayer processing, bauxite ores of either lateritic or karstic origin are used to extract aluminium in the form of alumina (Al_2O_3) using caustic Bayer liquor. The extraction yield of alumina from the Bayer process is often limited due to the formation of undissolved sodium and calcium aluminium silicate compounds from silicates reaction with sodium hydroxide or calcium oxide, also referred to as desilication products (DSP)[40]. Exposure to the high caustic environment of Bayer process changes the mineral composition contained in the bauxite residue which more or less does not reflect the mineralogical composition of the initial bauxite ore[41]. The resulting aluminium-based components (i.e. DSP, gibbsite, boehmite and diaspore) in the bauxite residue is often regarded as alumina losses within the Bayer process.

Aluminium recovery from BR has always been attempted in conjunction with the recovery of other metals such as Fe, Ti and Na. Once more, pyro- and hydro-metallurgical processes have been developed in laboratory scale but none of them have been applied in industrial scale. The pyrometallurgical processes are divided in two groups: a) reductive or non-reductive roasting in the presence of soda ash and/or lime followed by magnetic separation for iron recovery and alkaline leaching for recovery of Al and Na[24,41], b) reductive or non-reductive smelting using calcite or dolomite as fluxes followed by leaching of slag for Al recovery[42,43].

Mishra et al.[41] used dried Jamaican BR that was sinter-roasted in the presence of Na_2CO_3 (T: 1005^{o}C, t_r: 4 hr). Al was transformed into a sodium aluminate product that was leached in 0.125 M NaOH. After washing of the leaching tailings and filtration, the Al recovery achieved was 83.1%. The tailings after drying were subjected to magnetic separation to recover iron. In another approach by Chun et al.[12], China BR was roasted with Na_2CO_3 followed with magnetic separation for iron recovery. The non-magnetic tailings were leached with an alkaline Na_2CO_3 solution under atmospheric conditions. Under optimum conditions (70^{o}C, 60 min, 20% Na_2CO_3, liquid-to-solid ratio of 15 mL/g and 400rpm), the Al recovery achieved was 80.3%. Reductive roasting in the presence of sodium salts[19,23,24] has been attempted in order to improve the iron recovery through magnetic separation. Al is recovered from the reductive roasting cinders with leaching in alkaline environment or water. The achieved Al recoveries are almost identical with the ones achieved after non-reductive roasting.

Bruckard et al.[43] investigated smelted slag and recycled liquor to improve the recovery of leaching process. Australian BR[43] was smelted (1390-1450°C, 0.5-3 h) with the addition of $CaCO_3$ as a flux in order to modify in the resulted slag the CaO/SiO_2 ratio to the value 2:1. The slag was then leached with water (25-95°C, 8 h, 20-50 wt.% Solids). The highest Al recovery achieved was 58.5% (4h, 60°C, 20 wt.% Solids, 500μm particle sizing). Reductive smelting is used in order to improve the Fe recovery and especially to separate Fe from the other useful metals such as Al and Ti thus simplifying their hydrometallurgical recovery. The approach of Erçağ and Apak[42] involved Turkish BR which was mixed with dolomite and coke and next pelletized, pre-heated and sintered (1100°C, 1h). The sintered product was smelted, (1550°C, 3h) in order to produce pig iron and slag. The slag was then leached with 30% H_2SO_4 (90°C, 1h). The leachate was diluted and dissolved iron was reduced with SO_2. Metals were finally extracted through solvent extraction in an organic solution of 5% D2EHPA in kerosene. Al recovery was reported to be 85%.

Several hydrometallurgical processes have been developed for Al recovery from BR. Mineral acids (H_2SO_4, HNO_3, HCl) have been tested for recovery of Fe, Al and Ti from dried Iranian BR[44] under atmospheric conditions (100°C, 6N, 2h). The highest recovery of aluminium (91.3%) was observed when the leaching was performed with a mixture of H_2SO_4 and HCl acids at 3:1 ratio respectively. Direct ultrasonic leaching of Korean BR in H_2SO_4 solution[54] was attempted by Lim and Shon[45] for the recovery of Fe, Al and Ti. The optimum result for recovery of Al (72.9%) was obtained during leaching with 6N H_2SO_4 solution at 70°C, solid-to-liquid ratio of 2%(w/v) and for 2h retention time under an ultrasonic field of 150W at 60Hz. Uzun and Gulfen[46] looked into sulphuric acid leaching for Al and Fe extraction, though not directly from Turkish BR but from the cinders of the calcination of BR under different temperatures. The optimum conditions for the metals recovery was at 600°C for 1h in preheated air for the calcination step and 6M H_2SO_4 solution at 105°C for 30min for the leaching step. The achieved Al recovery was 64.4%.

Vachon et al.[47] reported mixtures of organic acids being used for leaching of aluminium from Canadian BR. The highest Al solubilisation recovery (96%) was obtained during the BR leaching at 28°C with a mixture of citric and oxalic acids at 2:1 ratio using H_2SO_4 for lowering the pH to 1.5. The beneficial effect of organic acids on Al recovery due to their high complexing capacity led to the development of bioleaching processes which employed sewage sludge bacteria and pure strains of fungi for the insitu production of organic acids as products of their metabolism[47]. Optimum Al solubilisation of 75% was achieved by leaching BR with the organic acids produced from the strain

P.simplicissimum (sp.) at 10% v/v initial BR concentration (28°C, 200 rpm under aseptic conditions).

In addition to acid leaching, BR was also leached in alkaline environment. The main difference between acid and alkaline BR leaching for aluminium recovery is that the latter is performed under pressure in autoclaves while the former is always performed under atmospheric conditions. China BR was leached in an autoclave with a concentrated NaOH solution and the addition of milk of lime; Zhong et al.[48] reports. Under the optimum conditions (45% v/v NaOH solution, CaO-to-BR mass ratio of 0.25, Liquid-to-solid ratio of 0.9, 200°C, 3.5h, 8atm) the recovery of aluminium was 87.8%. In an alternative approach by Zhang et al.[1], dried and grinded China BR was leached at high temperature and pressure in a NaOH solution doped with sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) in order to bring the SiO_2 concentration in the alkaline solution at 150g/l and to synthesize sodalite right away upon dissolution of aluminium in it. Under the optimum conditions (200°C, 2h, 8 atm, SiO_2 concentration 150g/l), the achieved Al recovery was 76%.

Ionic liquid, also known as molten salts with an organic cation and organic or inorganic anion. This new field is called “ionometallurgy” and is an emergent technology. Ionic liquids can be used as metallurgical solvents for primary resources[49]. Poulimenou et al.[50,51] reported on dissolution of metallurgical and hydrated alumina and bauxites using 1-ethyl-3-methyl-imidazolium hydrogen sulphate ([Emim]HSO_4), recovering 87% of Al_2O_3 from gibbsitic bauxite[50,51]. Park et al.[49] mentioned the unique property ranges of ionic liquids useful as it is liquid at room temperature, and depending on its application, the ionic liquids can be used either as solvents or electrolytes. The potential future use of ionic liquids in metallurgical processes can be extended towards secondary resources like the bauxite residue.

Recovery of Titanium in Bauxite Residue

Titanium dioxide (TiO_2), better known as titania, is a popular photocatalyst and it is applied in the industry of white pigment[18]. In bauxite residue, it is present either in the form of rutile or anatase, or it can coexist with other minerals[6].There are different methods to recover titanium from red mud, pyrometallurgical and hydrometallurgical processes, or a combination of them. Pyrometallurgy is normally used as a pretreatment method for recovery of iron from BR. Reductive smelting of BR[2] either as it is or after pelletisation with a carbonaceous reducing agent is the prefered method. Molten iron and a slag that contains mainly titanium dioxide, alumina and silica are obtained. After separation of the molten pig iron, the slag is digested to recover aluminium and titanium from solution[6].

There are two main acidic treatments to recover titanium, by hydrochloric or sulphuric acid leaching. Agatzini-Leonardou et al.[52] suggested that through a 6N sulphuric acid leaching at 60°C with a solid-to-liquid ratio of 5%, titanium recovery can reach up to 64.5%. Kasliwal and Sai[53] carried out experiments which involved a leaching step of bauxite residue with hydrochloric acid. They found that the titanium dioxide content in the leaching tailings was enriched from 18% in the raw BR to 36% under the optimum leaching conditions (90^oC, acid to BR ratio 10.3, acid concentration 5.2M). In order to enrich more the tailings in $TiO_{2,}$ they added a second treatment step which was consisting of roasting the leaching tailings with sodium carbonate and subsequently leaching the resulted cinders with water. Under the optimum roasting conditions (1150^oC, Na_2O/Al_2O_3 molar ratio 2.8, retention time 115 min) and followed by water leaching, the resulted tailings had a TiO_2 content of 76%.

Ghorbani and Fakhariyan[44] made a comparison between a single acid leaching of red mud and a combination of two acids at different ratios. The highest extraction of titanium was 97.7% and it was obtained with a combination of concentrated sulphuric and hydrochloric acids with 3:1 ratio at 100^oC and 2h retention time. Additionally, the co-dissolutions of iron and aluminium were 92% and 91.3% respectively[44].

Recovery of Rare Earth Elements in Bauxite Residue

According to the IUPAC definition, Rare Earth Elements (REEs) are a family of 17 elements in the periodic table[54]. Fifteen of these elements belong to the group of lanthanides from lanthanum to lutetium, whereas the other two are yttrium (Y) and scandium (Sc) which have similar chemical and physical properties to lanthanides.

With the current expansion of the technology market, the demand of REEs is increasing as they are essential in electronics (i.e. smartphones, flat-panel televisions, hybrid cars, permanent magnets and others). As a result of long-term forecast (until 2020) on the demand growth per year, heavy REEs (yttrium, terbium-lutetium) have the strongest rates, exceeding 8% per year and light REEs (lanthanum-gadolinium) have about 6% per year[55]. In 2010, the European Commission, has drawn up a list of raw material defined as critical in terms of economic importance and supply risk (implemented in 2013): REEs (with the exception of scandium) are the most critical raw materials with the highest supply risk. REEs are not produced within the European Union and in 2009, China provided 97% of market worldwide[56].

Researchers have examined several metallurgical techniques for REEs recovery from bauxite residue. REEs in bauxite residue are often enriched by factor of two, in comparison with the original ore[57]. Different approaches can be employed for REEs recovery such as hydrometallurgical, electrometallurgical and pyrometallurgical processes[58], but the recovery of REEs from bauxite residue is mainly focused on hydrometallurgical techniques[6] or a combination of pyrometallurgical and hydrometallurgical processes. Most of them use the pyrometallurgical treatment to recover iron leaving behind rare earths which are leached by acid. After the leaching step, REEs can be recovered by solvent extraction or by selective precipitation as oxalate[59].

Ochsenkiihn-Petropulu et al.[60] recovered selectively and almost quantitatively up to 93% scandium from BR. They dissolved red mud in 1.5 M of HCl and the solution was then passed through a chromatographic column containing a cation resin. The metals Fe, Al, Ca, Si, Ti, Na Ni, Mn, Cr were eluted with 1.75 M HCl. REEs were eluted with 6M HCl. They extracted scandium with di(2-ethylhexyl)phosphoric acid (DEHPA) in hexane and Sc was back-stripped with 2M NaOH[60]. In a following work, the same team recovered lanthanides and yttrium from BR by selective leaching using diluted mineral acids and subsequent liquid-liquid extraction. Results showed that diluted HNO_3 could leach successfully heavy REEs (about 60-80%) but not iron at ambient temperature and pressure. Diluted HCl revealed similar results for the recovery of REEs, but it is not selective for iron. They have also studied different types of pre-treatment such as the oxidising roast, the magnetic separation and the size fractionation by sieving analysis. These treatments showed no significant enrichment of REEs in any fraction of red mud[11]. In a recent work, Borra et al.[61] compared six mineral and organic acids (HNO_3, HCl, H_2SO_4, citric acid, acetic acid, and methanesulphonic acid) to leach REEs from BR. They found that REEs dissolution increased with acid concentration. Extraction of REEs was the highest for HCl leaching (about 70-80%) followed unavoidably by high iron dissolution (about 60%)[61].

Abhilash et al.[62] investigated the recovery of lanthanum and cerium from Indian red mud by sulphuric acid leaching and subsequent liquid-liquid extraction. Maximum dissolution (99.9%) was achieved by leaching with 3M H_2SO_4 at ambient temperature for lanthanum and at 75°C for cerium. The liquid-liquid extraction from leaching liquor was found to be complete by Cyanex 301[62]. Qu and Lian[63] to recover REEs from red mud, used a bio-hydrometallurgical approach, carrying out bioleaching experiments with acid-producing fungi identified as *Penicillinium tricolor* RM-10 directly isolated from BR. They leached yttrium, heavy REEs and scandium with a higher efficiency than light REEs[63].

Davris et al.[64] studied the application of ionic liquids, specifically of protonated betaine bis(trifluoromethylsulfonyl)imide (HbetTf2N) on the direct leaching of bauxite residue. They recovered 48% of Y and 35% of Sc with a good selectivity for iron (Fe dissolution was significantly low, 2.7%). A previous study of the same team showed the use of imidazolium-based ionic liquid 1-ethyl-3-methylimidazolium hydrogen sulphate ($EmimHSO_4$) as leaching agent at high temperature. They recovered REEs such as yttrium, cerium, neodymium and scandium in a range of 60-70%. Lanthanum recovery was 100%. Iron and titanium were completely solubilised[64].

Conclusions

In this paper, several technologies that have been developed to recover valuable metals (i.e Fe, Al, Ti, REEs) from bauxite residue were reviewed. The developed technologies made use of several pyrometallurgical, hydrometallurgical, biohydrometallurgical and ionometallurgical tools that can stand by itself or in combinations.

With the global scarcity towards iron supply and the necessary issue of reutilising of red mud, recovering the iron portion within red mud is necessary in the long term basis. Increased demands and reduced supply of REEs as a critical raw material requires industries to participate in recovering REEs through alternative secondary resources such as the bauxite residue. The titanium recovery from BR has been scarcely researched and comprises an issue that necessitates more improvements and innovations in the coming future.

As the literature has shown, BR is a polymetallic resource that has to be treated metallurgically with such a way so that the majority of contained valuable metals to be selectively extracted and recovered sequentially. Finally, with the concern of recent days towards sustainable industry practices and for economical and environmentally-friendly approaches, zero-waste valorisation methods are encouraged to be realised applying either existing or novel technologies.

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