

Ionometallurgical Leaching Process of Bauxite Residue: a Comparison between Hydrophilic and Hydrophobic Ionic Liquids

Chiara Bonomi¹, Panagiotis Davris², Efthymios Balomenos³, Ioanna Giannopoulou⁴ and Dimitrios Panias⁵

1. PhD Candidate
2. PhD Candidate
3. Senior Researcher
4. Senior Researcher
5. Professor

National Technical University of Athens, School of Mining and Metallurgical Engineering, Athens, Greece

3. External Associate Residue Valorisation
Aluminium of Greece, St. Nicolas Plant, Viotia, Greece
Corresponding author: bonomich@metal.ntua.gr

Abstract



Bauxite residue (BR) is the solid waste generated from the Bayer process during alumina production from bauxite ore. It can be considered a secondary source of several base metals, but also critical metals such as rare earth elements (REEs). Hydrometallurgical methods have been mainly employed to extract REEs from BR. As an alternative to conventional mineral acid leaching, ionic liquids (ILs) could hold the key for developing an economical, sustainable and greener processing of low-grade REE resources. ILs are solvents consisting solely of ions and have been studied as leaching agents in metallurgical processes, hence the term ionometallurgy was coined. This paper aims to exploit two ionometallurgical approaches on treating BR, evaluating advantages and drawbacks of applying hydrophilic and hydrophobic ILs. The first leaching process involves a hydrophilic IL, [Emim][HSO₄], which can dissolve base metals and REEs at elevated temperatures resulting to high recovery yields of scandium (up to 75 %), iron (100 %) and titanium (90 %), whereas the hydrophobic IL leaching process using [Hbet][Tf₂N] is able to selectively dissolve REEs (up to 70 - 85 %) against iron (3 %). The findings of the studied processes provide great potential for exploiting ILs as lixivants on low-grade REE-containing metallurgical by-products.

Keywords: Bauxite residue, rare earth elements, scandium, ionometallurgy, ionic liquids.

1. Introduction

Bauxite residue (BR) is the major by-product of the alkali leaching of bauxite, through the Bayer process, for alumina production; for each tonne of alumina, 1 – 1.5 tonnes of BR is generated [1]. It is estimated that worldwide BR production is over 150 million tonnes per year [2]. Since it consists of base metals like iron (Fe), aluminium (Al), sodium (Na), silicon (Si), calcium (Ca) and titanium (Ti) but also critical metals such as REEs, BR can be considered a valuable secondary raw material resource.

During the Bayer process, REEs along with Fe, Ti and other undissolved material remain unchanged. As a result rare earths end up in BR with an enrichment factor of approximately 2 comparing to the initial ore [3]. Therefore, the aluminum industry through the Bayer process concentrates the critical metals found in bauxite into bauxite residue.

This fact has led to escalating research with regards to recover minor elements from metallurgical wastes. Rare earth elements have been highly rated in criticality lists [4] due to

their high economic value and supply risk. The main approaches on extracting REEs from BR are by hydrometallurgical or by combined pyro-hydrometallurgical processes [5]. Despite the many studies, patents and pilots scale implementations based on BR leaching for REE and particularly scandium [6], none of them yet has reach an industrial scale. Nowadays the impact of the zero-waste valorisation policy motivates the research community on finding innovative, greener and economical viable routes for metal extraction from complex polymetallic matrixes such as BR.

An innovative approach as alternative to conventional mineral acid leaching that can have significant impact to waste valorisation is ionometallurgical leaching. Ionometallurgy is the term that describes the use of ionic liquids as solvents in the field of metal processing. ILs, are room temperature molten salts, constituted by ions, generally an organic cation and an inorganic/organic anion. These solvents have superior properties against organic solvents such as negligible vapour pressure, low volatility, wide electrochemical window, non-flammability and high thermal stability. From the vast number of combinations of the cation and anion during synthesis, ILs properties can be tuned for the needs of the application rendering them as designer solvents. As such ILs have a wide range of application in extractive metallurgy since they can be used either as electrolytes for electrodeposition of reactive metals, as solvents for liquid-liquid metal extraction or separation as well as lixiviants. Several ILs have been studied as leaching agents in hydrometallurgical processes [7-9]. The driving force of applying ionometallurgical leaching on low grade secondary resources is the prospect of increasing selectivity, reduction of waste effluent and improved efficiency yields.

This work aims to compare two ionometallurgical approaches on recovering metals by directly leaching BR. By evaluating advantages and drawbacks of applying hydrophilic and hydrophobic ILs as leaching agents, different leaching strategies can be developed. The acidic ILs studied for direct leaching BR, are the water miscible ethyl-methyl-imidazolium hydrogen sulphate (EmimHSO_4), and the hydrophobic betainium bis(trifluoromethylsulfonyl)imide ($\text{Hbet}[\text{Tf}_2\text{N}]$). The results of this work indicate the different leaching behaviour of metals in Greek BR for each lixiviant tested, as well as the strategies on BR utilisation that each IL promotes with respect to base and critical metal recovery.

2. Materials and Methods

Bauxite residue samples were provided by Aluminium of Greece (AoG). Samples were characterised via fusion method (1000 °C for 1 hour with a mixture of $\text{Li}_2\text{B}_4\text{O}_7/\text{KNO}_3$ followed by direct dissolution in 6.5 % HNO_3 solution). Chemical analysis was performed by Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Mineralogical analysis was carried out by a Bruker D8 focus X-ray diffractometer and a quantitative analysis was performed using XDB software [10]. Particle size measurements were conducted with a Malvern Mastersizer TM laser particle size analyser. $[\text{Emim}][\text{HSO}_4]$ and $[\text{Hbet}][\text{Tf}_2\text{N}]$ ionic liquids were provided by Iolitec with > 97 % purity and further characterised. Viscosity measurements were performed with a Brookfield viscometer DV-I + LV supported by a Brookfield Thermosel accessory. Infrared measurements were carried out by a Perkin Elmer FTIR spectrum 100.

Leaching experiments were conducted in a Trallero and Schlee mini reactor combined with a mechanical stirrer and a temperature controller. After filtration, the leachates from $[\text{Emim}][\text{HSO}_4]$ were digested through acidic treatment (HNO_3 65 % and aqua regia) and then analysed by AAS, ICP-OES and ICP-MS. Leachates from the hydrophobic $[\text{Hbet}][\text{Tf}_2\text{N}]$ were stripped with HCl where, subsequently after phase separation, the collected acidic solution was analysed for its metal content by AAS and ICP-MS.

6. References

1. S. Kumar, R. Kumar, A. Bandopadhyay, Innovative methodologies for the utilisation of wastes from metallurgical and allied industries, *Resources, Conservation and Recycling* 48, (2006), 301-314.
2. Ken Evans, The History, Challenges, and New Developments in the Management and Use of Bauxite Residue, *Journal of Sustainable Metallurgy* 2, (2016), 316-331.
3. K. Binnemans, P.T. Jones, B. Blanpain, T.V. Gerven, Y. Pontikes, Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. *Journal of Cleaner Production* 99, (2015), 17-38.
4. EU, Report of the Ad hoc working group on defining critical raw materials, (2014).
5. Y. Liu, R. Naidu, Hidden values in bauxite residue (red mud): Recovery of metals, . *Waste Management* 34, (2014), 2662-2673.
6. C.R. Borra, B. Blanpain, Y. Pontikes, K. Binnemans, T.V. Gerven, Recovery of Rare Earths and Other Valuable Metals From Bauxite Residue (Red Mud): A Review, *Journal of Sustainable Metallurgy* 2, (2016), 365-386.
7. A.P. Abbott, G. Frisch, J. Hartley, K.S. Ryder, Processing of metals and metal oxides using ionic liquids, *Green Chemistry* 13, (2011), 471-481.
8. K. Binnemans, P.T. Jones, Solvometallurgy: An Emerging Branch of Extractive Metallurgy, *Journal of Sustainable Metallurgy*, Vol. 3, No. 3, (2017) 570–600.
9. G.-C. Tian, J. Li, Y.-X. Hua, Application of ionic liquids in hydrometallurgy of nonferrous metals, *Transactions of Nonferrous Metals Society of China* 20, (2010), 513-520.
10. I.E. Sajò, XDB powder diffraction phase analytical system, version 3.0, user's guide 2005.
11. P. Davris, E. Balomenos, D. Panias, I. Paspaliaris, Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid, *Hydrometallurgy* 164, (2016) 125-135.
12. Joseph Gambogi, U.S. Geological Survey, Mineral Commodity Summaries, (2015).
13. E. Balomenos, P. Davris, Y. Pontikes, D. Panias, Mud2Metal: Lessons Learned on the Path for Complete Utilization of Bauxite Residue Through Industrial Symbiosis, *Journal of Sustainable Metallurgy*, (2016).
14. Peter Smith, Reactions of lime under high temperature Bayer digestion conditions, *Hydrometallurgy* 170, (2017), 16-23.
15. M.S. Gruzdev, L.M. Ramenskaya, U.V. Kervonova, R.S. Kumeev, Preparation of 1-butyl-3-methylimidazolium salts and study of their phase behavior and intramolecular interactions, *Zhurnal Obshchi Khimii* 79, (2009), 1720-1727.
16. P. Nockemann, B. Thijs, T.N. Parac-Vogt, K. Van Hecke, L. Van Mervelt, B. Tinant, I. Hartenback, T. Schleid, V.T. Ngan, M.T. Nguyen, K. Binnemans Carboxyl-Functionalized Task-Specific Ionic Liquids for Solubilizing Metal Oxides, *Inorganic Chemistry* 47, (2008), 9987-9999.
17. P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Mervelt, B. Kirchner, K. Binnemans, Task-Specific Ionic Liquid for Solubilizing Metal Oxides, *The Journal of Physical Chemistry B* 110, (2006), 20978-20992.
18. J. Vind, P. Paiste, A. H. Tkaczyk, V. Vassiliadou, D. Panias, The behaviour of scandium in the Bayer process, *Proceedings of 2nd European Rare Earth Resources ERES Conference*, Santorini, 28-31/05/2017, 190-191.