

## Valorization of Canadian Bauxite Residue for the Recovery of Strategic Materials

John Anawati<sup>1</sup>, and Gisele Azimi<sup>2</sup>

1. PhD Candidate

2. Assistant Professor

University of Toronto, Toronto, Canada

Corresponding author: g.azimi@utoronto.ca

### Abstract



With the aim of moving toward a sustainable future and building the circular economy, waste valorization is highly motivated. 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 as well as aluminum and iron, some of which are considered critical materials and initiatives have begun to mine them from secondary sources, such as landfilled industrial process residues. In this study, a two-step process consisting of carbothermic smelting followed by acid baking-water leaching was developed. During carbothermic smelting, iron is separated in the metallic phase and other valuable metals are concentrated in the slag phase and they are leached in the acid baking-water leaching step. Design of experiments methodology was utilized to investigate the effect of the various operating parameters and optimize both processing steps. Furthermore, fundamental investigations were carried out to elucidate the physiochemical mechanisms governing both processing steps. The developed process proves to be a promising technique as the first step of a potential near-zero-waste integrated process for the sustainable valorization of bauxite residue to help build the circular economy.

**Keywords:** Bauxite residue, carbothermic smelting, acid baking-water leaching, rare earth elements, near-zero-waste.

### 1. Introduction

Bauxite residue (BR), the solid by-product of the Bayer process for alumina production, is increasingly viewed less as a problematic waste product, and more as a potential valuable resource for the sustainable recovery of critical materials such as scandium (Sc), rare earth elements (REEs), titanium (Ti), hafnium (Hf), aluminum (Al), iron (Fe), and others. Bauxite residue is an abundant, economical, and sustainable resource because it is produced globally (on all continents except Antarctica) at a rate of 150 million tonnes per year, with 3 billion tonnes stockpiled worldwide. [1–3] Several efforts have been made to develop a method to recover the valuable materials that become enriched in the residue during the Bayer process,[4–6] in particular Sc, which is extremely valuable (US \$4600/kg<sub>Sc2O3</sub>)[7] due to its low rates of worldwide production, and important applications for producing lightweight Al-Sc alloys and solid-oxide fuel cells. However, no valorization strategy has been adopted because the complex mineralogy of the residue makes efficient and economical extraction and purification of the target materials difficult. Furthermore, bauxite residues from different regions are different, depending on the characteristics of the starting bauxite ore, and the specific Bayer process parameters, meaning that no single solution is universally applicable.

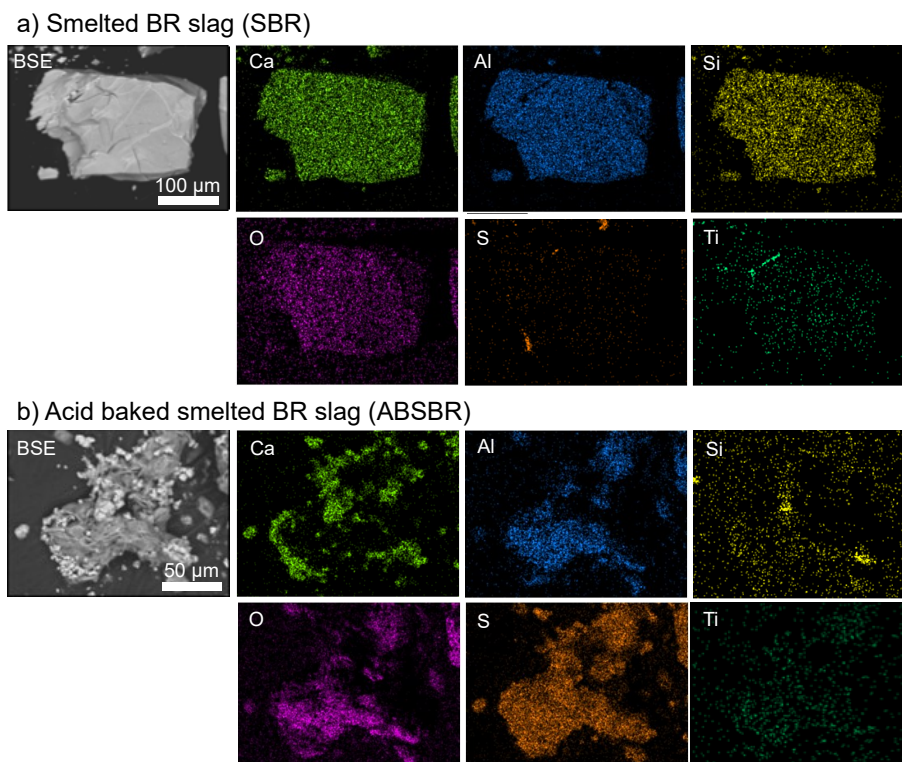
A common challenge for the separation and purification of valuable materials from bauxite residue leachates is the separation of scandium and iron, because of the close association between Sc and the Fe-bearing mineral phases. Generally, any direct leaching process that recovers Sc results in co-extraction of Fe.[8] As a result, Sc recovery processes generally require complex solvent extraction, selective precipitation, or ion-exchange approaches. One proposed alternative

route for the removal of iron from the system is a pyrometallurgical carbothermic smelting to reduce the Fe content (+3 oxidation number) in the BR to molten Fe (0 oxidation number), which is immiscible with the liquid slag phase formed by the remaining aluminum, calcium, silicon, and sodium oxides, and it can be recovered as a crude iron product. Most of the target valuable materials (scandium, REEs, titanium, hafnium) partition into the slag phase.

A summary of previous studies examining the application of smelting to the valorization of bauxite residue is given in Table . In most cases, bauxite residue was mixed with carbon and a fluxing agent (calcium/silicon oxides, or other industrial waste products), similar to the blast furnace process for producing metallic iron from iron ore. The carbon is used to reduce the iron, and the flux is used to reduce the temperature and viscosity of the melt, allowing for efficient phase separation. Because the reduced iron and the slag are immiscible both in the molten state and after solidification, the two phases can be readily separated, allowing the production of an iron-depleted slag that can be used for the recovery of the valuable materials via leaching processes.[9]

**Table 1. Previous studies on carbothermic reduction smelting for iron recovery from bauxite residue.**

Reference	BR Source	Smelting temperature (°C)	Smelting duration	Flux composition	Flux amount (wt%)	Carbon amount (wt%)	Additional Notes
Alkan (2017) [10]	Greece	1500-1550	1 h	CaO	10-50	1	Controlled cooling used
Alkan (2018) [11]	Greece	1500-1550	1 h	CaO	20	10	Dry acid digestion of slag (75 °C conc. H <sub>2</sub> SO <sub>4</sub> ), then water leach
Balomenos (2014) [12]	Greece	1580		0.9-1.1 (CaO + MgO): 1 SiO <sub>2</sub> (wt ratio)	33-35	13-20	
Borra (2016) [13]	Greece	1500-1600	1 h	CaSiO <sub>3</sub>	5-40	5	Slag leached with HCl, HNO <sub>3</sub> or H <sub>2</sub> SO <sub>4</sub> at 90 °C
He (2017) [14]	China	1600	35 min	N/A	3-9	25	BR mixed with laterite nickel ore as feedstock
Kaußen (2015) [9]	Germany	1600-1700	100 min	N/A	0	6.25	
Lucas (2018)	Greece	1500	1 h	CaO, MSWI bottom ash*	20	10	MSWI bottom ash



**Figure 5. EDS elemental mapping of the smelted BR slag (SBR) a) before and b) after acid baking (ABSBR: SBR + 1 mLH<sub>2</sub>SO<sub>4</sub>/gSBR + 200 °C (2 h)).**

The morphology and composition were characterized using SEM-EDS.

#### 4. Conclusions

In this study, it was demonstrated that carbothermic reduction smelting process can be utilized to separate Fe from the bulk bauxite residue and to concentrate Sc and other valuable elements in the slag phase. Acid baking-water leaching can then be utilized to extract the valuable materials from the slag phase. This study consisted of a preliminary investigation of the “smelting-ABWL process”, which demonstrated its feasibility for valorizing bauxite residue. Work is currently underway to study the specific effects of different smelting and ABWL process parameters, such as smelting temperature, flux and carbon composition, acid-SBR ratio, baking temperature, and water-ABSBR ratio, to gain a fundamental understanding of the underlying physicochemical mechanisms, and to achieve an economically and operationally optimal set of process parameters. The ultimate goal of this research is to develop a near-zero-waste bauxite residue valorization process to meet modern society’s demand for several critical materials, while reducing dependence on environmentally damaging primary extraction processes, exploiting an abundant and readily available resource, and reducing the accumulation of bauxite residue in landfills.

#### 5. References

1. K. Evans, The History, Challenges, and New Developments in the Management and Use of Bauxite Residue, *J. Sustain. Metall.* 2 (2016) 316–331. doi:10.1007/s40831-016-0060-x.
2. Y. Liu, R. Naidu, Hidden values in bauxite residue (red mud): Recovery of metals, *Waste Manag.* 34 (2014) 2662–2673. doi:10.1016/j.wasman.2014.09.003.
3. The International Aluminium Institute, PRIMARY ALUMINIUM PRODUCTION - Global Data for Jan 1973 to Jan 2018, 2018.

- <http://www.world-aluminium.org/statistics/#data>.
4. C.R. Borra, B. Blanpain, Y. Pontikes, K. Binnemans, T. Van Gerven, Recovery of Rare Earths and Other Valuable Metals From Bauxite Residue (Red Mud): A Review, *J. Sustain. Metall.* 2 (2016) 365–386. doi:10.1007/s40831-016-0068-2.
  5. N. Zhang, H.X. Li, X.M. Liu, Recovery of scandium from bauxite residue—red mud: a review, *Rare Met.* 35 (2016) 887–900. doi:10.1007/s12598-016-0805-5.
  6. A. Akcil, N. Akhmediyeva, R. Abdulvaliyev, A. Meshram, P. Meshram, Overview On Extraction and Separation of Rare Earth Elements from Red Mud : Focus on Scandium, *Miner. Process. Extr. Metall. Rev.* 00 (2017) 1–7. doi:10.1080/08827508.2017.1288116.
  7. U.S. Geological Survey, Mineral Commodity Summaries, 2019. doi:10.3133/70202434.
  8. C.R. Borra, Y. Pontikes, K. Binnemans, T. Van Gerven, Leaching of rare earths from bauxite residue (red mud), *Miner. Eng.* 76 (2015) 20–27. doi:10.1016/j.mineng.2015.01.005.
  9. F. Kaußen, B. Friedrich, Reductive Smelting of Red Mud for Iron Recovery, *Chemie-Ingenieur-Technik.* 87 (2015) 1535–1542. doi:10.1002/cite.201500067.
  10. G. Alkan, B. Xakalache, B. Yagmurlu, F. Kaussen, B. Friedrich, Conditioning of Red Mud for Subsequent Titanium and Scandium Recovery – A Conceptual Design Study, *World Metall. – ERZMETALL.* 70 (2017) 5–12.
  11. G. Alkan, B. Yagmurlu, Y. Ma, B. Xakalache, S. Stopic, C. Dittrich, B. Friedrich, Combining pyrometallurgical conditioning and dry acid digestion of red mud for selective Sc extraction and TiO<sub>2</sub> enrichment in mineral phase, in: Y. Pontikes (Ed.), *Proc. 2nd Int. Bauxite Residue Valor. Best Pract. Conf., Athens, 2018*: pp. 215–222.
  12. E. Balommenos, D. Kastritis, D. Panias, I. Paspaliaris, D. Boufounos, THE ENEXAL BAUXITE RESIDUE TREATMENT PROCESS: INDUSTRIAL SCALE PILOT PLANT RESULTS, *Light Met.* 2014. (2014) 143–147.
  13. C.R. Borra, B. Blanpain, Y. Pontikes, K. Binnemans, T. Van Gerven, Smelting of Bauxite Residue (Red Mud) in View of Iron and Selective Rare Earths Recovery, *J. Sustain. Metall.* 2 (2016) 28–37. doi:10.1007/s40831-015-0026-4.
  14. A. He, J. Zeng, Direct preparation of low Ni-Cr alloy cast iron from red mud and laterite nickel ore, *Mater. Des.* 115 (2017) 433–440. doi:10.1016/j.matdes.2016.11.068.
  15. H. Lucas, G. Alkan, B. Xakalache, B. Friedrich, Conditioning of bauxite residue with bottom ash in view of recovery of valuable metals: a sustainable approach, in: *Proc. 2nd Int. Bauxite Residue Valor. Best Pract. Conf., 2018*: pp. 263–270.
  16. R.M. Rivera, B. Xakalache, G. Ounoughene, K. Binnemans, B. Friedrich, T. Van Gerven, Hydrometallurgy Selective rare earth element extraction using high-pressure acid leaching of slags arising from the smelting of bauxite residue, *Hydrometallurgy.* 184 (2019) 162–174. doi:10.1016/j.hydromet.2019.01.005.
  17. B. Xakalache, B. Friedrich, Combined carbothermic reduction of bauxite residue and basic oxygen furnace slag for enhanced recovery of Fe and slag conditioning, in: *Proc. 2nd Int. Bauxite Residue Valor. Best Pract. Conf., 2018*: pp. 233–240.
  18. B. Yagmurlu, G. Alkan, B. Xakalache, B. Friedrich, S. Stopic, Combined SAF Smelting and Hydrometallurgical Treatment of Bauxite Residue for Enhanced Valuable Metal Recovery, 35th Int. ICSOBA Conf. Hamburg, Ger. 2 – 5 October, 2017. (2017) 587–594. doi:10.13140/RG.2.2.21659.36644.
  19. J. Zeng, J. Wang, A. He, Experimental Investigation on Reduction of Cast Iron from Bayer Red Mud and Laterite Nickel, in: *Light Met.* 2018, 2018: pp. 117–121. doi:10.1007/978-3-319-72284-9\_16.
  20. D. Zhang, W. Zhang, X. Hou, D. Liu, G. Liu, B. Wang, Alumina, iron and titanium extracting from bauxite residue with low lime sinter method, *Miner. Met. Mater. Ser. Part F4* (2018) 143–148. doi:10.1007/978-3-319-72284-9\_19.
  21. J. Anawati, G. Azimi, Recovery of scandium from Canadian bauxite residue utilizing acid baking followed by water leaching, *Waste Manag.* 95 (2019) 549–559. doi:10.1016/j.wasman.2019.06.044.

22. L. Brewer, J. Margrave, The vapor pressures of lithium and sodium oxides, *J. Phys. Chem.* 59 (1955) 421–425. doi:10.1021/j150527a010.
23. B. Yagmurlu, C. Dittrich, B. Friedrich, Effect of Aqueous Media on the Recovery of Scandium by Selective Precipitation, *Metals (Basel)*. 8 (2018) 1–13. doi:10.3390/met8050314.
24. B. Onghena, C.R. Borra, T. Van Gerven, K. Binnemans, Recovery of scandium from sulfation-roasted leachates of bauxite residue by solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, *Sep. Purif. Technol.* 176 (2017) 208–219. doi:10.1016/j.seppur.2016.12.009.
25. M. Ochsenkühn-Petropulu, T. Lyberopulu, G. Parissakis, Selective separation and determination of scandium from yttrium and lanthanides in red mud by a combined ion exchange/solvent extraction method, *Anal. Chim. Acta.* 315 (1995) 231–237. doi:10.1016/0003-2670(95)00309-N.