

Alkaline Extraction of Alumina from Hydrogen Reduced Bauxite Residue Pellets

Georgia-Maria Tsaousi¹, Michail Vafeias², Adamantia Lazou³, Dimitrios Sparis⁴,
Dimitrios Kotsanis⁵, Efthymios Balomenos⁶ and Dimitrios Panias⁷

1. Senior Researcher

2. Supervising Researcher

3. Post-Doc Researcher

4. PhD Researcher

5. Materials Characterization specialist

6. Assistant Professor

7. Professor of Extractive Metallurgy, Head of Research Group

Technologies for Sustainable Metallurgy, Laboratory of Metallurgy, NTUA, Athens, Greece

Corresponding author: margitsaousi@metal.ntua.gr

<https://doi.org/10.71659/icsoba2024-br008>

Abstract

Several process alternatives are being investigated for the use of bauxite residue (BR) as a secondary metallurgical resource. These processes aim primarily at the extraction of the major metal values found in BR, i.e., Fe, Al and Na, and attempt to integrate novel metallurgical technologies to reduce the CO₂ footprint. One of these technologies is the reduction of BR with H₂ for the production of Fe, taking place in a temperature range below the melting point of Fe. In this process, the remaining unreduced oxides contain the Al content of BR in aluminate phases which need to be leached efficiently. In this paper, hydrogen reduced pellets of BR/CaO mixtures are being hydrometallurgically treated to leach the alumina content. The pellets are first chemically and physically characterized. The main challenges identified are (i) the entrapment of Fe in the oxide matrix and (ii) the formation of unleachable aluminate phases. Two approaches were tested in an attempt to assess the optimum way of separating the Fe content of the pellets and the efficient leaching of the aluminate phases: (a) an “alkaline leaching stage first/Fe separation second” approach, in which standard leaching tests are first performed with a Na₂CO₃ solution to separate the Fe from the leaching residue and (b) a “Fe separation first/alkaline leaching second” approach, where the pellets were smelted to separate pyrometallurgically the Fe content from the aluminate phases and then leaching was performed with a Na₂CO₃ solution. Results indicate that the second process route is more efficient for the separation of Fe.

Keywords: Hydrogen Reduction, Alumina leaching, Iron separation.

1. Introduction

Bauxite residue (BR) is an industrial by-product generated during the production of alumina from bauxite ores in the Bayer process. The current BR production level in the EU is 6.8 Mtpa (million tonnes per year); while the cumulative stockpiled level is a staggering > 250 Mt (dry matter). According to the International Aluminium Institute (IAI) Bauxite Residue (BR) production annually is approximately 170 Mt, while 8 Gt of bauxite residue will be stored globally by 2040, as the residue must be unavoidably landfilled [1].

BR is rich in metal oxides of e.g., Fe, Al, Ti, in addition, certain BR qualities contain reasonably high levels of rare-earth elements (REEs). BR is, therefore, an interesting potential resource for several metals, iron being the most attractive [2–4]. The processes explored for the extraction of Fe from BR typically involve reduction smelting in an EAF, with carbon being used as the reductant. Consequently, the reductive smelting of BR to produce pig-iron and slag is an energy-

intensive process that involves high-temperature melting (> 1300 °C) and is associated with a substantial environmental footprint [5, 6].

In this study, Fe separation from BR is proposed through a hydrogen-reduction process by an innovative metallurgical technology developed in the framework of the HARARE EU Horizon project [7]. The HARARE technology aims to validate the use of hydrogen as a reductant in the metallurgical sector as it has the biggest decarbonization potential and is therefore the most compatible option with the EU's climate neutrality goal and the decarbonization of Europe's economy [8]. The use of hydrogen in the production of Fe from its oxides allows, theoretically, for the reduction to take place in the solid state (below the melting point of the system), eliminating the need to melt the BR, and saving large amounts of energy. Moreover, using BR as a raw material decreases the raw material costs of the process.

The yield and recovery of Fe is dependent on the reduction conditions and the fluxing (chemistry) of the BR agglomerates, as well as the rate and extent of the reduction reactions and simultaneous sintering phenomena. The main challenge is to optimize the agglomeration and hydrogen reduction conditions to obtain high metal recovery in the separation, which is beneficial for the subsequent stage of alumina recovery. Thus, the second target of the process is the production of a non-metallic fraction which is predominantly of calcium aluminate composition. This easily leachable in Na_2CO_3 solutions alumina-containing fraction (slag) is a feedstock for alumina production [9]. For this reason, CaO is used as the main fluxing agent.

In this study, a sample of material produced after the laboratory hydrogen reduction of BR/CaO pellets (termed "H₂ reduced pellets") was characterized and tested for the leaching of Al. As the reduced pellets have not been subjected to any Fe separation process, a second goal of this work was to assess how the state of the Fe (particle size and morphology) might affect the hydrometallurgical process. Two approaches are presented: (a) an alkaline leaching stage first/Fe separation second approach, and (b) a Fe separation first/ alkaline leaching second approach. In the first approach, a standard leaching test is first performed on the reduced pellets with a Na_2CO_3 solution and then the separation of Fe from the leaching residue by magnetic separation is evaluated. In the second approach, the reduced pellets are smelted to pyrometallurgically separate the Fe content from the aluminate phases and then leaching is performed with a Na_2CO_3 solution.

2. Materials and Methods

2.1 Equipment and Instruments Used

The leaching tests were conducted inside a custom-made reactor. The body of the reactor (heating mantle, stirring unit and vessel) was built from parts of a Parr™ 4563 model. The vessel had a maximum volume of 0.6 L and was made from Inconel alloy. The reactor lid was replaced by a custom-made PTFE lid, suitable for leaching tests at atmospheric pressure. The lid was constructed with suitable sockets which allowed for: (a) attaching a vapor condenser, (b) the immersion of a thermocouple and a mechanical stirrer (c) the insertion of the solid sample. Heating and stirring were controlled by an external PLC unit.

Elemental chemical analysis of the aqueous samples was performed with a PerkinElmer™ PinAAcle 900 T Atomic Absorption Spectrometer (AAS) and a PerkinElmer™ Optima 800 Optical Emission Spectrometer (ICP-OES). Crystallographic analysis of the solid samples was performed in a Miniflex600 Rigaku diffractometer, with $\text{CuK}\alpha$ radiation ($V = 40$ kV and $I = 15$ mA). Phase identification was performed with Bruker™ Diffrac EVA software and use of ICDD™ Diffraction databases PDF-4+ 2023 and PDF-4 Minerals 2023 [10]. Particle size analysis was performed with a Horiba Partica LA-960 V2 laser scattering particle size distribution

- iii. Magnetic separation of the H₂ reduced pellets leaching residue was examined as an option for Fe removal, but this approach proved unsuccessful under the conditions used.
- The findings of the “Fe separation first/Leaching of slag second” approach were as follows:
 - i. Smelting of H₂ reduced pellets was tested as a second approach to separate pyrometallurgically the Fe content from the aluminate phases, producing a calcium aluminate slag and metallic Fe.
 - ii. After the successful Fe separation via smelting process, the slag (Fe-free) was used as raw material for standard leaching tests indicating low Al extraction efficiency despite Fe removal, due to the presence of C₃A in slag that is unleachable in Na₂CO₃ solutions.

This work showed that the smelting process proved to be a better route for the separation of Fe derived from H₂ reduction of BR. The reason for this is the extremely fine and dispersed particles of Fe that are locked into the oxide matrix and cannot be easily separated. The smelting conditions used are a key factor for the production of a slag with the appropriate mineralogical profile that can be effectively leached and optimized based on the already known experimental protocol.

5. Acknowledgements

This work was carried out in the framework of the H2020 HARARE project. The HARARE project receives funding from the European Community's Horizon 2020 Programme (H2020/20142020) under grant agreement n°958307 (cordis.europa.eu/project/id/958307).

6. References

1. International Aluminium Institute launches Bauxite Residue Roadmap, <https://international-aluminium.org/news-recycling/> (Accessed on 01/08/2024).
2. Ken Evans, The History, challenges, and new developments in the management and use of bauxite residue, *Journal of Sustainable Metallurgy*, Vol. 2 / Issue 4, (2016), 316–331
3. M. Archambo and Surendra Kawatra, Red Mud: Fundamental and New Avenues for utilization, *Mineral Processing and Extractive Metallurgy Review*, Vol. 42 / Issue 7, (2021), 427–450
4. M.A. Khairul, Jafar Zanganeh and Behdad Moghtaderi, The composition, recycling, and utilization of Bayer red mud, *Resources, Conservation and Recycling*, Vol. 141, (2019), 483–498
5. Craig Klauber, Markus Gräfe and Greg Power, Bauxite residue issues: II. options for residue utilization. *Hydrometallurgy*, Vol. 108 (2011), 11–32.
6. M. Archambo and Surendra Kawatra, Utilization of bauxite residue: recovering iron values using the iron nugget process, *Mineral Processing and Extractive Metallurgy Review*, Vol. 42 / Issue 4, (2021), 222–230
7. Hydrogen As the Reducing Agent in the Recovery of metals and minerals from metallurgical waste; <https://h2020harare.eu/> (Accessed on 01/08/2024).
8. RMIS – Raw Material Information System, <https://rmis.jrc.ec.europa.eu/?page=environmental-policies-and-regulation-f7695f>. (Accessed on 01/08/2024).
9. Michal Ksiazek et al., Iron removal from bauxite ores, *2nd International Bauxite Residue Valorisation and Best Practices Conference*, Athens, Greece, (2018), page 39. ISBN-number: 9789082825923
10. Stacy Gates-Rector and Thomas Blanton, The powder diffraction file: A quality materials characterization database. *Powder Diffraction*, (2019), Vol. 34 / No 4, 352–360.

11. Yuguan Zhang et al., Highly efficient separation of titanium minerals from a modified bauxite residue through direct reduction: A comparison study, *Journal of Materials Research and Technology*, 2023, 26, pp. 6331-6341, ISSN 2238-7854, doi.org/10.1016/j.jmrt.2023.09.017
12. Ganesh Pilla et al., Towards sustainable valorization of bauxite residue: Thermodynamic analysis, comprehensive characterization, and response surface methodology of H₂ reduced products for simultaneous metal recovery, *Journal of Cleaner Production*, 2024, 440, 140931, ISSN 0959-6526, doi.org/10.1016/j.jclepro.2024.140931
13. M.Z. Southard, R.L. Rowley, W.V. Wilding, Densities, D.W. Green, M.Z. Southard (Eds.), *Perry's Chemical Engineers' Handbook* (9th edition), McGraw-Hill Education, New York (2019)
14. Eirini Georgala et al., Aluminium extraction from a calcium aluminate slag using sodium carbonate based on the critical examination of the patented industrial Pedersen process, *Hydrometallurgy*, 2023, Vol. 222, 106188, ISSN 0304-386X, doi.org/10.1016/j.hydromet.2023.10618
15. C.W. Bale et al., FactSage thermochemical software and databases, 2010–2016, *Calphad*, 2016, Vol. 54, 35–53
16. Michalis Vafeias et al., Leaching of Ca-rich slags produced from reductive smelting of bauxite residue with Na₂CO₃ solutions for alumina extraction: Lab and pilot scale experiments, *Minerals*, 2021, Vol. 11, 896. <https://doi.org/10.3390/min11080896>
17. Adamantia Lazou, Liev Kolbeinsen and Jafar Safarian, Evaluation of calcium aluminate slags and pig irons produced from the smelting-reduction of diasporic bauxite, *Materials* 2021, Vol. 14, <https://doi.org/10.3390/ma14247740>.