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Hydrogen in treatment of the bauxite residues (BR)

Srecko Stopic[1]*, Duško Kostić[1], Vladimir Damjanović[2], Radislav Filipovic[2], Nenad Nikolić[3], Mitar Perušić[4], Bernd Friedrich[1]

[1] *IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany*
[2] *Alumina Ltd. Zvornik, Bosnia and Hercegovina*
[3] *Institute for Multidisciplinary Research, Bosnia and Hercegovina*
[4] *Faculty of Technology Zvornik, University of East Sarajevo, Bosnia and Hercegovina*

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A B S T R A C T

Bauxite residue (red mud) is both an environmental liability and a potential secondary resource, particularly for iron and titanium. This study investigates an integrated, low-carbon flowsheet that combines hydrogen-based reduction with downstream hydrometallurgical upgrading. Bauxite residue from an alumina refinery was reduced in a rotary kiln under H_2/N_2 to generate a magnetically responsive product; physical separation yielded an iron-rich fraction, while the non-magnetic fraction was processed by high-pressure sulfuric-acid leaching in an autoclave under oxygen. Phase analysis of the reduced solid confirmed the formation of metallic iron and the transformation of aluminosilicate/calcium phases consistent with effective deoxygenation under hydrogen. The autoclave step achieved titanium dissolution with an efficiency of ≈99%, producing solutions suitable for $TiOSO_4$ preparation and a sulfate–silica residue. These results indicate that hydrogen reduction can decarbonize iron removal from red mud while enabling high-yield titanium recovery through selective leaching. We conclude that an H_2-reduction → magnetic separation → autoclave-leach sequence is a promising pathway for the valorization of bauxite residue; ongoing work will quantify iron recovery and enrichment, close element mass balances, and optimize separation, reagent consumption, and energy use to support scale-up and comparative techno-economic assessment.

Keywords: reduction, hydrogen, bauxite residue, decarbonizing.

1. Introduction

Hydrogen is the most abundant element in the universe (75 % by mass) and the lightest element (density of 0.00082 g/cm3). Hydrogen reduction of hazardous bauxite residue for green steel and sustainable alumina production with comparative study of hydrogen reduction of bauxite residue-calcium sintered and self-hardened pellets followed by magnetic separation for iron recovery found high potential for successful iron removal from bauxite residue (Kar et al., 2023, 2025). Thermodynamic analysis, comprehensive characterization, and response surface methodology of H_2-reduced products for simultaneous metal recovery confirmed high iron recovery efficiency (Pilla et al., 2022, 2024). Additionally, Studying the sintering behavior of H_2-reduced bauxite residue pellets using high-temperature thermal analysis was predicted optimal parameters for reduction (Hariswijaya and Safarian, 2025) Because of its presence in many different forms such as gaseous hydrogen, its plasma species, water, acid, alkaline, ammonia and hydrocarbons, has high application in different metallurgical unit operations (Stopic and Friedrich, 2023). The Bayer Process is the traditional industrial method to produce alumina from bauxite ore (Damjanovic et al. 2023). The chemical quality of precipitated aluminum hydroxide, and consequently the final alumina product in the Bayer process directly depends on the level of impurities in a refinery's Bayer liquor. In Europe, alumina refineries operate in Bosnia and Herzegovina (Alumina Ltd., Zvornik), France, Hungary, Germany, Greece, Ireland (AAL), Romania (ALUM), Spain and Ukraine, while significant bauxite residue deposits from refineries that have stopped their operations (legacy sites) exist in former Yugoslavia (Podgorica, Kidricevo, Mostar, Obrovac), Italy, France (RT), Germany, Hungary and other countries. Because of am environmental protection, development and progress on hydrogen metallurgy was considered in details (Tang et al., 2023)

* Corresponding author.
E-mail address: sstopic@ime-aachen.de (Srecko Stopic).

A study of the reduction of iron oxides from BR with hydrogen in the temperature range of 700–1000 °C in a tubular furnace in static conditions mentioned that an increase of temperature from 700 °C to 1000 °C leads to reduction of Fe2O3 to Fe, but also partial transformation to Fe3O4 that is more stable at lower reduction temperatures (Stopic et al. 2024). The most striking feature inferred from XRD is a progressive increase in metallic iron content accompanied by a decrease in magnetite content with an increase in reduction temperature whereas metallic iron is only identified iron phase at 1000 °C (Pilla et al., 2024). Similarly, the decrease in residual cancrinite content accompanied by the increase in nepheline content with the increase of reduction temperature is another observed trend in silicate mineralogy.

Now strategy was proposed for how this red mud can be turned into valuable and sustainable feed-stock for ironmaking using a fossil-free hydrogen-plasma-based reduction at higher temperatures in an electric arc furnace (more than 1600°C), thus mitigating a part of the steel-related carbon dioxide emissions by making it available for the production of several hundred million tonnes of green steel (Jovičević-Klug et al. 2024). The process proceeds through rapid liquid-state reduction, chemical partitioning, as well as density-driven and viscosity-driven separation between metal and oxides.

This paper will study the reduction of BR using a rotary kiln and the subsequent leaching of solid residues using high-pressure leaching with sulfuric acid in an autoclave using an oxygen atmosphere. The proposed flowchart is shown at Figure 1.

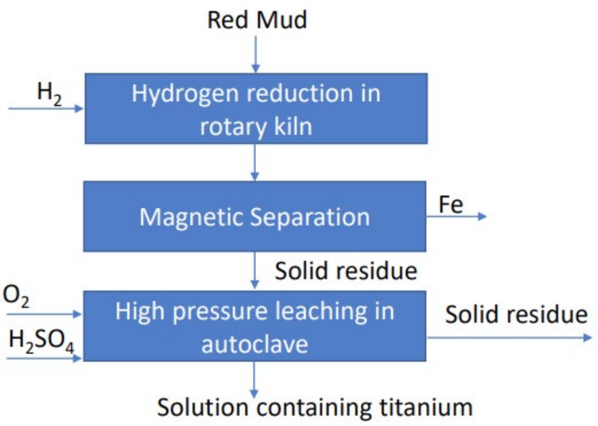

Fig. 1. The proposed combined research strategy for treatment of red mud

2. Materials and methods

The bauxite residue from Alumina Ltd., Zvornik was filtrated, washed and dried at 105 °C for 24 h. The main components in red mud (%): 49.3 Fe_2O_3; 12.0 Al_2O_3, 10.5 SiO_2; 8.2 CaO; 4.6 TiO_2, 2.5 Na_2O, 0.9 P_2O_5, 0.6 MgO and 0.2 % Ga_2O_3. XRD-analysis of red mud after finding the following phases: hematite, perovskite, cancrinite, ilmenite, calcite, diaspore, gibbsite and hydrogarnet. Iron is present in hematite and ilmenite structure. Titanium is present in perovskite and ilmenite structures, while aluminum is present in the structure of cancrinite, diaspore, boehmite, gibbsite and hydrogarnet, as shown in Figure 2.

The XRD-analysis in Figure 2 has confirmed the presence of hematite and other very stable oxides for hydrogen reduction. Particle size distribution analysis of BR found very fine particles with the following values ($x_{50,3}$= 4.70 µm and $x_{90,3}$= 5.98 µm).

Hydrogen reduction of BR, Zvornik was performed using rotary kiln Carbolite, Germany, as shown in Figure 3. The used parameters for hydrogen reduction: Initial mass of sample: 200 g, temperature: 920°C, atmosphere: hydrogen and nitrogen; flow rate: 1-2 L/min. Before the hydrogen reduction, nitrogen gas was used to evacuate oxygen from a cylindrical quartz tube situated in a rotary kiln, checking for leakage in system. Bubblers with demineralized water are used to check the continuous flow of gas in the system. Nitrogen is continuously supplied during heating. After successful BR reduction, the magnetic phase was separated from solid residues. Hydrogen reduction was performed below the iron melting point. Physical separation was employed to isolate magnetic from non-magnetic phases.

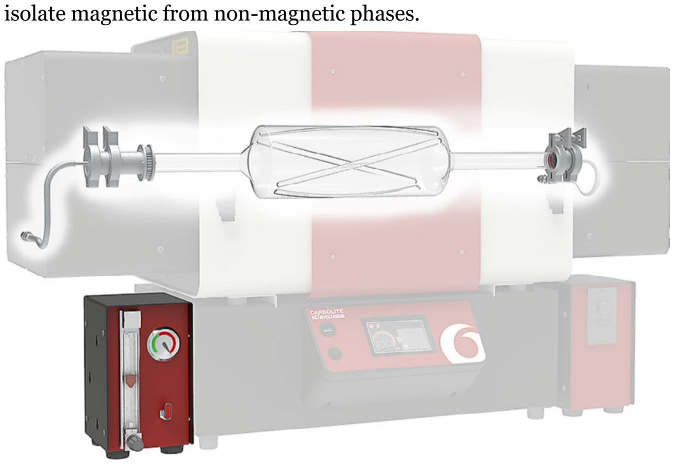

Fig. 3. Rotary kiln for hydrogen reduction

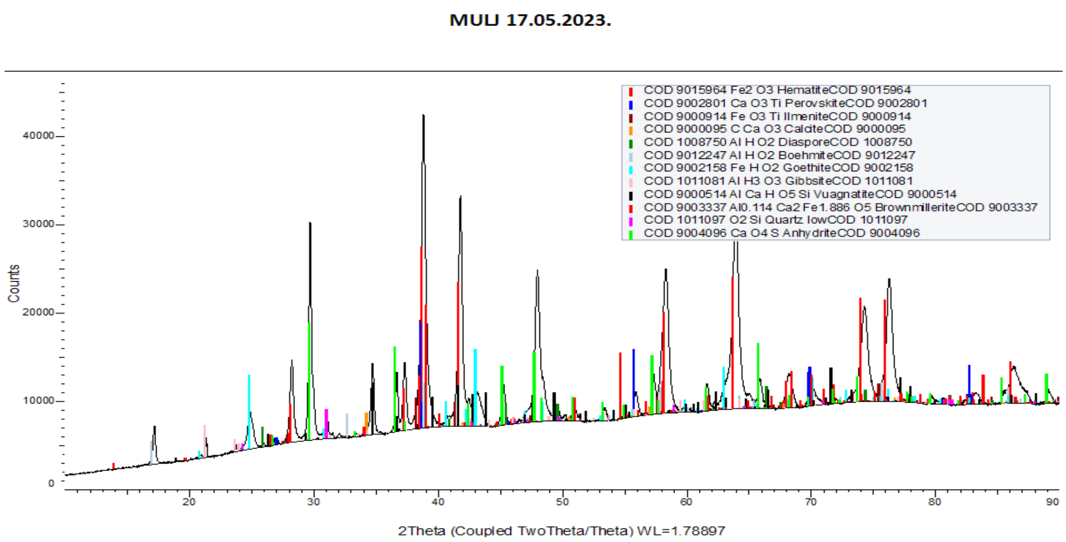

Fig. 2. XRD Analysis of BR, Zvornik

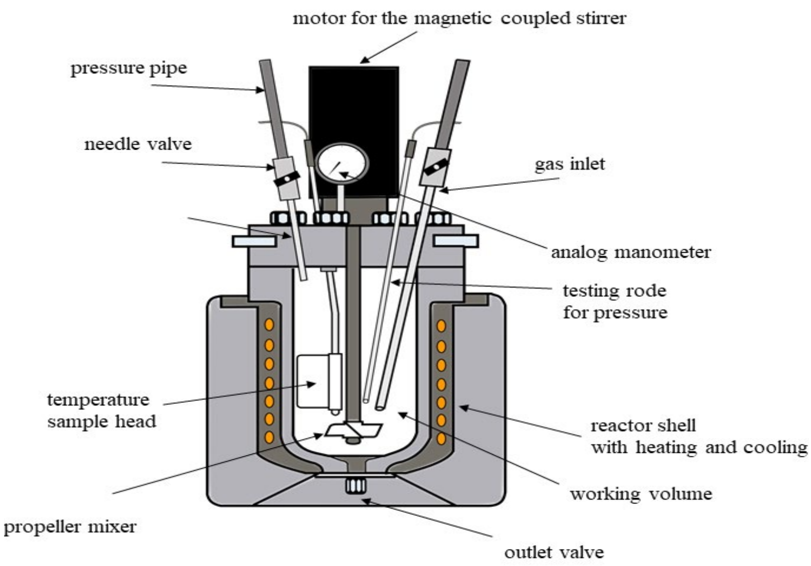

Fig. 4. Illustration of the high-pressure autoclave

This study investigates the extraction of valuable metals from reduced slag using sulfuric acid treatment. Key leaching parameters, including the solid-to-liquid ratio, pressure, and acid concentration, were maintained constant throughout the experiments. Variables such as temperature, reaction time, stirring speed, and particle size were optimized based on insights from prior experimental work. A 5 M sulfuric acid solution was prepared in a 1-liter flask and introduced into a Buchi autoclave (as shown in Figure 4), containing solid residue derived from the hydrogen reduction from the rotary kiln.

The system was pressurized to 9 bars with oxygen, the temperature was set to the desired level, and the magnetic stirrer was operated at a speed of 500 rpm. The leaching process was conducted for up to 120 minutes. The leaching process was performed in a Buchi autoclave, Switzerland, a specialized reactor from Hastelloy designed for high acid leaching with a capacity of 1.53 L, corrosion stable, a maximum pressure of 200 bars, and a maximum temperature of 270 °C, and 2000 rpm (Stopic et al. 2024).

The autoclave is equipped with a heat exchanger controlled by a thermostat, a mixer, pressure adjustment probes, and the capability for sample extraction during operation. The system is fully integrated with computer software, enabling precise control and real-time monitoring of operational parameters, with all data recorded for detailed post-experiment analysis. The pressure within the system was monitored using both a manometer and digital sensors, with the total pressure comprising oxygen (9-12 bars) and water vapour (12–15 bars). Cooling was achieved using a dedicated cooling system, and the heating rate was controlled at 10 °C/min. Prior to each run, the autoclave was manually sealed with screws and subjected to a pressure integrity test to ensure safe and reliable operation. After the leaching process was completed, the autoclave was cooled to room temperature, and the system pressure was carefully released. The leachate solution was then subjected to filtration and neutralization with distilled water. Filtration was conducted using a vacuum-assisted filtration system integrated into the setup, ensuring effective separation of solid and liquid phases.

3. Results and discussion

At 920°C, hydrogen is introduced at 1 L/min for 10 minutes, followed by 10 minutes of minimal hydrogen flow leads to the reduction of bauxite residue producing magnetic solid residue, as shown in Figure 5.

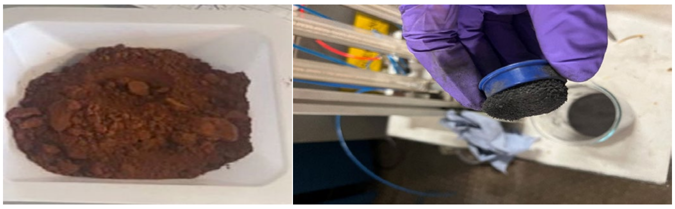

Fig. 5. a) BR, Zvornik and b) Solid residue after hydrogen reduction in rotary kiln

XRD analysis of solid residue after hydrogen reduction at 920°C is shown in Figure 6.

Identified Phases: Fe, Perovskite, and Gehlenite confirmed that Hematite (main phase in BR) was successfully reduced with hydrogen. The formation of perovskite and gehlenite confirms structural modifications. This experiment demonstrates the potential of hydrogen reduction in altering BR composition.

The obtained BR was leached in an autoclave at 200°C using 5mol/L sulfuric acid for 4 hours in an oxygen atmosphere (12 bar O_2). The obtained solution contains the following concentration of elements (g/L): 24.4 Fe; 2.29 Ti, 3.66 Al; 0.06 Si. The calculated leaching efficiency of titanium amounted 99%. This process avoids silica gel formation which is typical behavior during leaching at an atmospheric pressure. The obtained XRD-analysis of solid residue shown at Figure 7 confirms the presence of calcium sulfate and silica, what is expected according to our previous experiments.

4. Conclusion

This study demonstrates that bauxite residue from Alumina Ltd. Zvornik can be effectively treated by a hydrogen-based route coupled with high-pressure leaching. Rotary-kiln reduction at 920 °C under H_2/N_2 produced a solid product with pronounced magnetic properties and XRD evidence of metallic Fe together with phase evolution to perovskite and gehlenite, confirming the conversion of hematite under the selected conditions. While magnetic separation of the reduced product was feasible, practical difficulties indicate that separation performance will benefit from further optimization of reduction parameters and post-reduction handling (e.g., residence time, gas flow, cooling, and particle size/liberation).

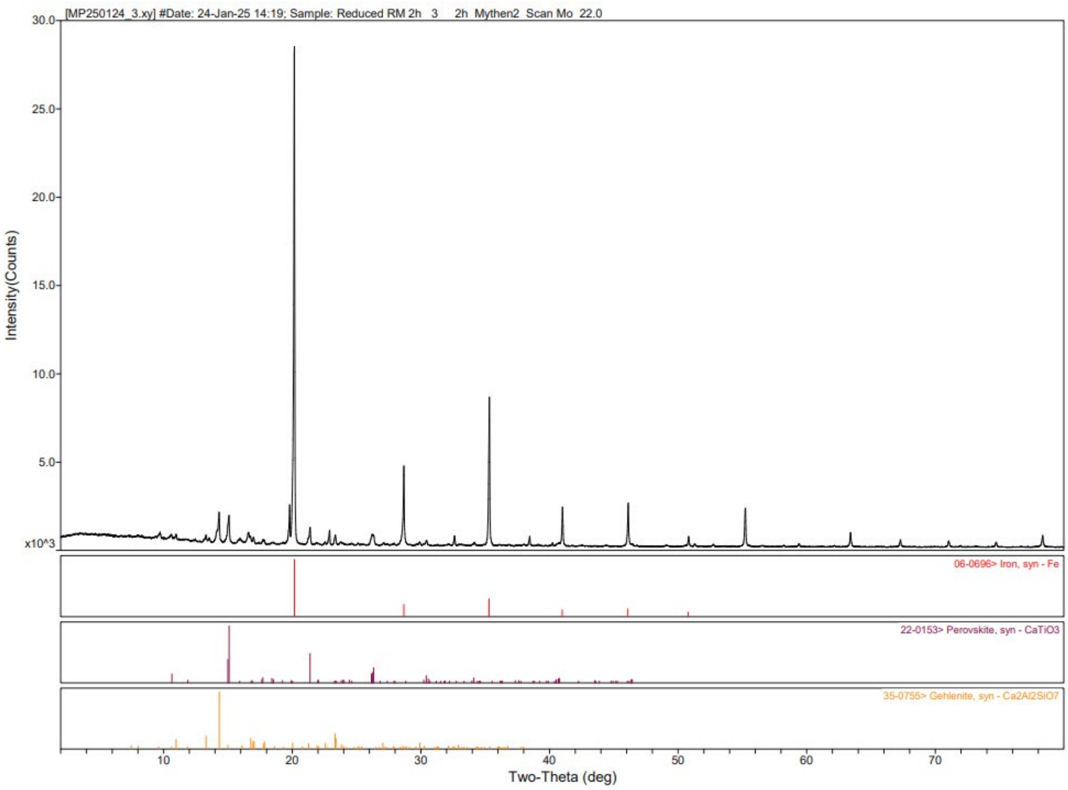

Fig. 6. XRD analysis of solid residue after hydrogen reduction in rotary kiln at 920°C

Downstream processing of the non-metallic fraction by autoclave leaching in 5 mol L^{-1} H_2SO_4 at 200 °C for 4 h under 12 bar O_2 achieved high titanium dissolution (≈99 %), yielding a solution suitable for $TiOSO_4$ formation—the required precursor for ultrasonic spray-pyrolysis production of TiO_2—and a residue primarily comprising $CaSO_4$ and SiO_2. Taken together, the results support an integrated flowsheet in which hydrogen reduction liberates an iron-rich magnetic phase for recovery while high-pressure acid leaching upgrades the remaining solid for titanium valorization. Future work should quantify iron recovery and enrichment factors across reduction–separation, close element mass balances (Fe, Ti, Al, Na), and refine operating windows in the rotary kiln and autoclave to improve separation efficiency, reagent economy, and overall process energy performance, thereby enabling a robust assessment of scale-up potential and decarbonization benefits relative to carbon-based routes.

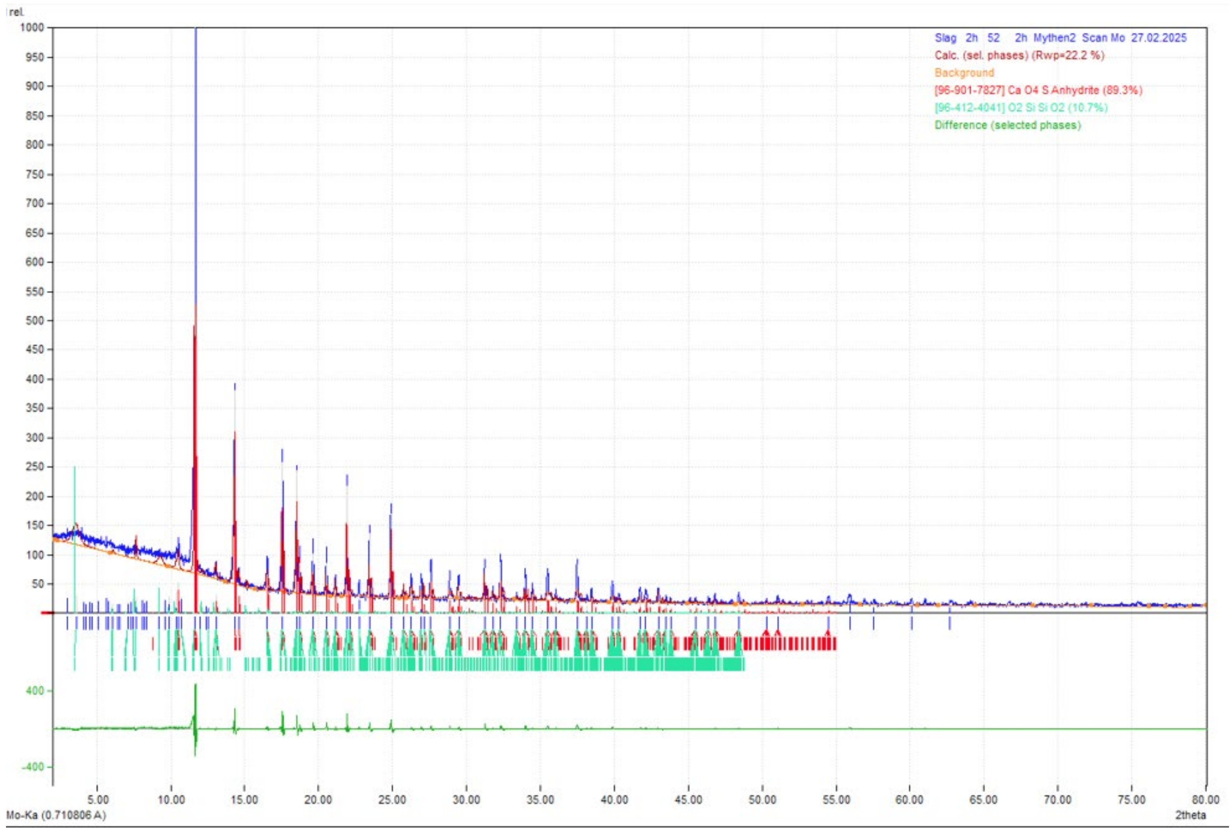

Fig. 7. XRD Analysis of solid residue obtained under high pressure leaching at 150°C in an autoclave

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