Combined SAF Smelting and Hydrometallurgical Treatment of Bauxite Residue for Enhanced Valuable Metal Recovery

Bengi Yagmurlu¹, Gözde Alkan², Buhle Xakalashe², Bernd Friedrich³, Srecko Stopic⁴ and Carsten Dittrich⁵

1. PhD candidate

RWTH Aachen University, IME Institute of Process Metallurgy and Metal Recycling, Aachen,

Germany

MEAB Chemie Technik GmbH, Aachen, Germany

2. PhD candidate

3. Professor

4. Dr.-Ing.

RWTH Aachen University, IME Institute of Process Metallurgy and Metal Recycling, Aachen,

Germany

5. General Manager, MEAB Chemie Technik GmbH, Aachen, Germany

Corresponding author: BXakalashe@metallurgie.rwth-aachen.de

Abstract



Reductive smelting trials were undertaken on a bauxite residue (red mud) sample via SAF (submerged arc furnace) treatment to produce pig iron (achieved Fe recovery > 95 %) and a critical metal enriched slag. Lignite coke was the selected reductant and CaO was used for fluxing achieving low operating temperatures (1500 - 1550 °C) and good slag-metal separation. The slag and the original bauxite residue as reference were subjected to leaching using 2.5 M H₂SO₄ and a 2.5 M H₂SO₄: 2.5 M H₂O₂ acid mixture with a liquid-to-solid ratio of 10 at 100 °C for 30 minutes. Decomposition of H₂O₂ at higher temperatures and formation of oxygen bubbles in the system introduce mechanical intensification of the leaching process. Leaching efficiencies for Ti and Sc were evaluated in a comparative manner between bauxite residue and slag. Selective precipitation process, Fe was removed by the addition of ammonia in the pH range between 3.3-3.8 with a dual stage step. Subsequent to removal of 95 % of the Fe in the solution, Sc was selectively precipitated as ScPO₄ with the introduction of a dibasic phosphate solution.

Keywords: Bauxite residue, pig iron, reductive smelting, titanium, scandium.

1. Introduction

During the production of alumina from bauxite via the Bayer process, a by-product is inevitably produced, namely bauxite residue. A wide range of components are contained in bauxite residue, the major components generally include Fe, Al, Ca, Si, Ti and Na [1]. The contained elements are usually present in lower concentrations compared to primary raw materials, however, bauxite residue offers a possibility for recovery of numerous product streams [2 - 3].

Iron is the most predominant element in this bauxite residue. Albeit found in high quantities, literature reports that iron recovery on its own is not economically viable [4]. The bauxite residue contains high value Ti and Sc which are attractive for recovery. An iron deficient feed material is beneficial for hydrometallurgical processing aiming for Ti and Sc due to minimising of waste (precipitation sludge) and therefore justifies upstream removal of iron. This is attributed to poor selectivity of Ti over the major constituents of bauxite residue during acidic leaching as reported in literature [5]. Methods that are explored widely in literature for Sc recovery from bauxite residue include solvent extraction and ion exchange. The presence of ions

such as Fe and Al in the leachate is unfavourable for Sc extraction. Hence, intensive purification steps are necessary for Sc recovery from bauxite residue leach solutions [6 - 7].

The innovation of the present study is on a combined pyrometallurgical and hydrometallurgical processing of bauxite residue concentrate production through carbothermic reduction of bauxite residue to produce a slag concentrate and to apply leaching and precipitation conditions to the produced slag concentrate for recovery of Ti and Sc [8]. Similar leaching and precipitation conditions were applied directly to bauxite residue in order to compare recovery efficiencies of Ti and Sc.

2. Experimental Procedure

The bauxite residue of interest was sourced from Aluminium of Greece. Sample preparation entailed drying of the bauxite residue over a period of 24 hours at 105 °C. The dried lumpy sample was subsequently mixed with lignite coke and lime containing 87 % fixed carbon and 95 % CaO respectively. The additions of lignite coke to bauxite residue and lime to bauxite residue were 1:10 and 1:5 respectively. Batch masses of 1.5 kg of the aforementioned recipes were fed into a 100 KVA DC electric arc furnace. The material was contained in a graphite crucible, and the smelting was undertaken at temperatures in the range between 1500 – 1550 °C for one hour. At the conclusion of the experiment the molten material was poured into a refractory lined mould where the material cooled down and the metal settled at the bottom of the mould. The cooled material was separated into slag and metal and then weighed. The slag was prepared for leaching where it was crushed and milled to obtain a slag fraction of -90 μ m. The original bauxite residue and slag sample were analysed by X-ray diffraction (XRD). Furthermore the dried bauxite residue and the milled slag were analysed via X-ray fluorescence (XRF) for the bulk chemical analysis and by inductively coupled plasma optical emission spectrometry (ICP-OES) for the trace elements as shown in Table 1.

Components (wt. %)	Fe ₂ O ₃	Al ₂ O ₃	CaO	SiO ₂	TiO ₂	LOI	Sc (mg/kg)	Y (mg/kg)	Nd (mg/kg)
Bauxite residue	43.5	24	10.2	5.5	5.6	10.1	130	90	110
Slag concentrate	1.8	38.3	43.2	7.6	7.6	-1.0	200	167	181

Table 1. Chemical analysis of the dried bauxite residue and the produced slag concentrate.

All leaching tests were carried out with the following: a glass beaker, heating plate and magnetic stirrer for controlling the reaction temperature and stirring speed. The bauxite residue and slag were each ground into fine particles and poured into pre-heated (70 °C) acid solution to start the leaching process. The experiments were carried out over a fixed leaching time of 120 minutes at a set temperature of 70 °C, 360 rpm with a solid: liquid ratio of 1:10. For both starting materials, two acid concentrations were utilised; 2.5 M sulfuric acid (H₂SO₄) and 2.5 M sulfuric acid (H₂SO₄): 2.5 M hydrogen peroxide (H₂O₂) mixture; which were based on preliminary studies about red mud leaching optimised for Ti and Sc recovery.

Dibasic phosphates were preferred since the pH effect on precipitation could be also investigated. 1 M dibasic phosphate ($(NH_4)_2HPO_4$) solution was chosen as phosphate donor and added until the target pH was reached. All precipitation stages were performed under mild stirring at room temperature. The resulting suspension for each case was then stabilised and homogenised at a given pH and temperature for 2 hours and subsequently filtered through fine filter paper via suction filtration. The separated solid residue was washed with distilled water and dried at 110 °C for 24 hours. Both filtered solutions and the solid residues as well as the concentrations of constituent ions in the liquid samples were assayed byICP-OES. The complete process flowsheet including smelting, leaching and precipitation is shown in Figure 1.

completely. The concentrate formed via precipitation was enriched in terms of Sc and Ti, the precipitate from sulfuric acid PLS contained 1 % and 52 % Sc and Ti respectively in its composition. The concentrate from the other PLS contained 1.8 % and 83 % Sc and Ti respectively. It is known that the solubility of titanium phosphate is very limited in highly acidic solutions. Both concentrates can be further upgraded by re-dissolving it in an acidic solution and removing titanium phosphate which can result in 10 % Sc content.

4. Conclusion

The recovery of iron from bauxite residue through carbothermic reduction in an electric arc furnace followed by hydrometallurgical processing for Ti and Sc recovery from the produced slag concentrate has been successfully undertaken and compared with direct recovery of Ti and Sc from bauxite residue by hydrometallurgical means. High iron recovery in excess of 95% to the pig iron was achieved resulting in a slag concentrate with low residual iron. The fluxing agent and additions were such that slag with a low melting point and a low silica content would be achieved. The Ti in the slag was found to be contained in a perovskite phase. The gangue components were concentrated in the slag and included the high value Sc.

The leaching efficiencies for Sc were higher for the slag in comparison to leaching of bauxite residue for both 2.5 M H_2SO_4 and a 2.5 M H_2SO_4 : 2.5 M H_2O_2 acid mixture; on the other hand, lower leaching efficiencies for Ti were achieved for the slag under the investigated leaching conditions. The lower leaching efficiencies for the slag could be attributed to the crystalline perovskite phase found in the slag. Modification of the slag with regards to crystallinity will be investigated further with the aim to improve Ti recovery during slag leaching. The utilisation of hydrogen peroxide in combination with sulfuric acid for slag leaching decreases the Si leaching rates considerably and therefore minimises the gelation problems.

Selective precipitation route followed after leaching to recover Ti and Sc from the leachate. In this precipitation process, Fe was removed by the addition of ammonia in the pH range between 3.3-3.8 with a dual stage step. Subsequent to removal of 95 % of the Fe in solution, Sc was selectively precipitated as ScPO₄ with the introduction of a dibasic phosphate solution.

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6. References

- 1. Ken Evans, Successes and challenges in the management and use of bauxite residue, *Bauxite Residue Valorisation and Best Practices*, Leuven, Belgium, October 2015, 113–127.
 - 2. Efthymios Balomenos et al., Enexal: Novel technologies for enhanced energy and exergy efficiencies in primary aluminium production industry, *Metallurgical & Materials Engineering*, Vol. 15, No. 4, (2009), 203–217.
 - 3. Frank Kaußen and Bernd Friedrich, Methods of Alkaline Recovery of Aluminium from bauxite residue, *Journal of Sustainable metallurgy* Vol. 2, No. 4, (2016), 353–364.
- 4. Yanju Liu and Ravi Naidu, Hidden values in bauxite residue (red mud): recovery of metals, *Journal of Waste Management* Vol. 34, No. 12, (2014), 2662–2673.

- 5. A Ghorbani, A Fakhariyan, Recovery of Al₂O₃, Fe₂O₃ and TiO₂ from bauxite processing waste (red mud) by using combination of different acids, *Journal of Basic and applied scientific research*. Vol. 3 (2013), 187–191.
- 6. M. Ochsenkühn-Petropoulou, T. Lyberopoulou, G. Parissakis, Selective separation and determination of scandium from yttrium and lanthanides in red mud by a combined ion exchange/solvent extraction method, *Analytica Chimica Acta*. Vol. (315), No. 1, (1995), 231–237.
- 7. Weiwei Wang, Chu Yong Cheng, Separation and purification of scandium by solvent extraction and related technologies: a review, *Journal of Chemical Technology and Biotechnology*. Vol. 86, No. 10, (2011), 1237–1246.
- 8. G. Alkan et al., Conditioning of red mud for subsequent titanium and scandium recovery a conceptual design study, *World of Metallurgy ERZMETALL*, Vol. 70, No. 2, (2017), 5–12.
- 9. Chenna Rao Borra et al., Leaching of rare earths from bauxite residue (red mud), *Journal of Minerals Engineering*. Vol. 76, (2015), 20–27.
- 10. B. Yagmurlu, C. Dittrich, B. Friedrich, Precipitation trends of scandium in synthetic red mud solutions with different precipitation agents, *Journal of Sustainable Metallurgy*. Vol. 3, No. 1, (2017), 90–98.