Reductive Roasting Process for the Recovery of Iron Oxides from Bauxite Residue through Rotary Kiln Furnace and Magnetic Separation

Chiara Cardenia[1], Buhle Xakalashe [2], Efthymios Balomenos [3], Dimitrios Panias[4] and Bernd Friedrich[5]
1. PhD Candidate
3. Senior Researcher,
4. 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: cardeniach@metal.ntua.gr
2. PhD Candidate,
5. Professor,
RWTH Aachen, IME, Process Metallurgy and Metal Recycling, Aachen, Germany

Abstract

Bauxite residue (BR), the main by-product formed during the Bayer process for alumina production, is a secondary raw material source, containing usually iron (Fe), titanium (Ti), aluminium (Al) and in some cases rare earth elements (REEs) including Sc. This work addresses the high temperature carbothermic conversion of hematite and goethite in the BR to magnetic iron phases. The reductive process developed in a laboratory scale static tube furnace, was scaled up using a rotary kiln furnace. Experiments were carried out by mixing BR with a carbon source (C/BR=0.225) and an additive (Na_2CO_3/BR=0.25), at 1000 °C in the presence of N_2. The results show that hematite is almost fully (> 99 wt.%) converted to magnetic iron phases after 1 hour. Subsequently, this work was focused on the magnetic separation process through a wet high-intensity magnetic separator. Two current intensities (0.01 and 0.5 A) were employed to collect three fractions (Magnetic I, Magnetic II and Non Magnetic), 70 % of the total Fe content was concentrated in the first magnetic fraction, producing a secondary iron concentrate while the non-magnetic fraction is enriched in Ti and REEs.

Keywords: Rotary kiln, iron recovery, magnetic separation, bauxite residue.

1. Introduction

Bauxite residue (BR), also known as red mud, is the major by-product of the alumina industry. During the production of alumina from bauxite ores, about 0.9 to 1.5 tonnes of BR are generated per tonne of alumina produced, through the Bayer process [1] and this value exceeds 150 million tonnes per year worldwide [2]. Since bauxite residue contains valuable substances including iron (Fe), titanium (Ti), aluminium (Al) and rare earth elements (REEs), it can be considered as a secondary raw material [3 - 4]. For this reason, the utilization of this waste has been explored in the last decades aiming to reach zero-waste valorisation [5]. Fe is generally present in BR in a range of 14 – 45 wt.% depending on the initial bauxite ore used [4].

Karst bauxites are usually high in iron, so various techniques have been investigated for iron recovery from the respective BR [6]. In this framework, the following research has been developed with the purpose of quantitatively converting hematite and goethite in the BR to magnetic iron phases by a carbothermic reductive roasting process carried out through a rotary kiln furnace and a subsequent magnetic separation. This process will foster the production of an iron rich concentrate and a non-magnetic residue enriched in Ti and REEs.

2. Experimental

Bauxite residue, provided by Aluminium of Greece S.A., was homogenised, grinded and sieved obtaining a sample with a D_{50} = 1.87 µm (MastersizerTM Particle Size Analyzer). To understand the composition and the distribution of iron phases in BR, physical and chemical characterisation were carried out.

X-ray diffraction analysis (XRD) was conducted using a Bruker D8 Focus analyser. The differential thermal analysis (DTA) was performed using a SETARAM TG Labys-DS-C system in the temperature range of 25 – 1000 °C with a 10 °C/min-heating rate, in air atmosphere. To examine the chemical distribution and composition of the samples microstructure, scanning electron microscopy Jeol 6380LV (SEM) combined with an Oxford INCA Energy Dispersive Spectrometer (EDS) were used. Chemical analyses were executed via fusion method (1000 °C for 1 hour with a mixture of $Li_2B_4O_7/KNO_3$ followed by direct dissolution in 6.5 % HNO_3 solution) through Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Atomic Absorption Spectroscopy (AAS).

BR was mixed with lignite coke as the reductant (C_{fix} = 87.5 % and ash = 9.0 %) and Na_2CO_3 as the flux following the optimised ratio developed in a laboratory scale static tube furnace (1 g BR: 0.250 g Na_2CO_3: 0.225 g C). The mixed samples were converted into pellets by using water as binder with a pellet size between 6.35 mm and 12.7 mm, then dried at 105 °C for 24 hours. The roasting process was conducted at 1000 °C in the presence of N_2 for 4 hours, employing a rotary kiln furnace. The batch masses per experiment were fixed to 1.5 kg pellets, and samples were taken at the following intervals: 1 hour, 2 hours, 3 hours and 4 hours.

The collected cinder was milled (< 90 µm) and then leached with water (H_2O) at 80 °C for 4 hours with 1.5 % pulp density. Thereafter, the leaching residues were directly processed with a wet high intensity magnetic separator (CarpoTM). To improve the separation between the magnetic portion of the sample and the gangue, two current intensities were applied: 0.01 A at the first pass and 0.5 A at the second pass. Three fractions were collected (Magnetic I, Magnetic II and Non Magnetic) and characterised by XRD, SEM – EDS and chemical analysis.

The process flow diagram for the entire process is presented in Figure 1.

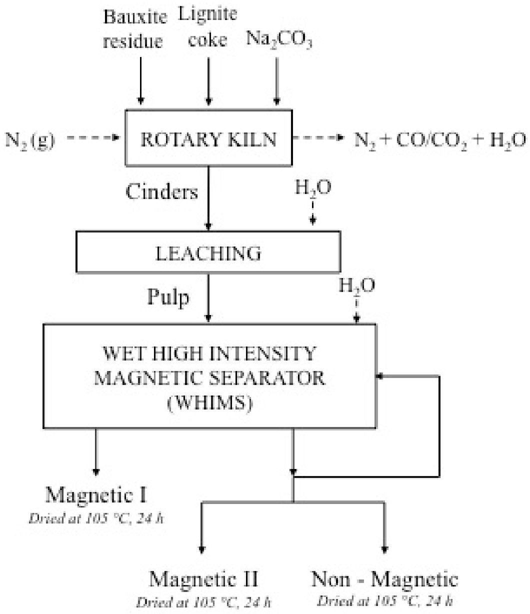


Figure 1. Process flowsheet of iron recovery from bauxite residue.

3. Results and Discussion

The total amount of iron (as Fe_2O_3) contained in BR is 42.34 wt.% and with this value, Fe is the main constituent of BR (Table 1).

Table 1. Chemical analysis of bauxite residue (via fusion method).

Component	wt.%
Fe_2O_3	42.34
Al_2O_3	16.25
SiO_2	6.97
TiO_2	4.27
CaO	11.64
Na_2O	3.83
Sc_2O_3	0.02
Nd_2O_3	0.01
La_2O_3	0.09
Y_2O_3	0.01
CeO_2	0.06

XRD analysis, combined to XDB database [7], which quantifies the amount of mineral phases via – profile fitting, have shown that iron containing mineralogical phases are hematite (α-Fe_2O_3), goethite ($Fe_2O_3{\cdot}H_2O$) and calcium aluminium iron silicate hydroxide $Ca_3AlFe(SiO_4)(OH)_8$ [8]. The Fe contribution in these mineralogical phases is distributed as following: 30 wt.% in α-Fe_2O_3, approximately 8 wt.% in $Fe_2O_3{\cdot}H_2O$ and 3 wt.% $Ca_3AlFe(SiO_4)(OH)_8$.

Roasting temperature, time, carbon:BR ratio (C/BR) under inert atmosphere were the parameters thoroughly examined with a thermochemical software (FactSage 6.4 ^{TM}) and studied in a laboratory scale static tube furnace. The optimum conditions from the lab scale experiments, were transferred to the rotary kiln furnace, where BR was mixed with a carbon source and an additive (1 kg BR: 250 g Na_2CO_3: 225 g C) and roasted at 1000 °C in the presence of N_2.

To investigate the kinetics of the reductive process of iron phases, four samples were collected at different times (at 1 hour, 2 hours, 3 hours and 4 hours). In Figure 2, XRD pattern of bauxite residue is compared with the first and the last samples of the experiment (1 hour and 4 hours). The results show that hematite is almost completely (> 99 wt.%) converted to magnetic phases such as metallic iron (Fe), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) after 1 hour.

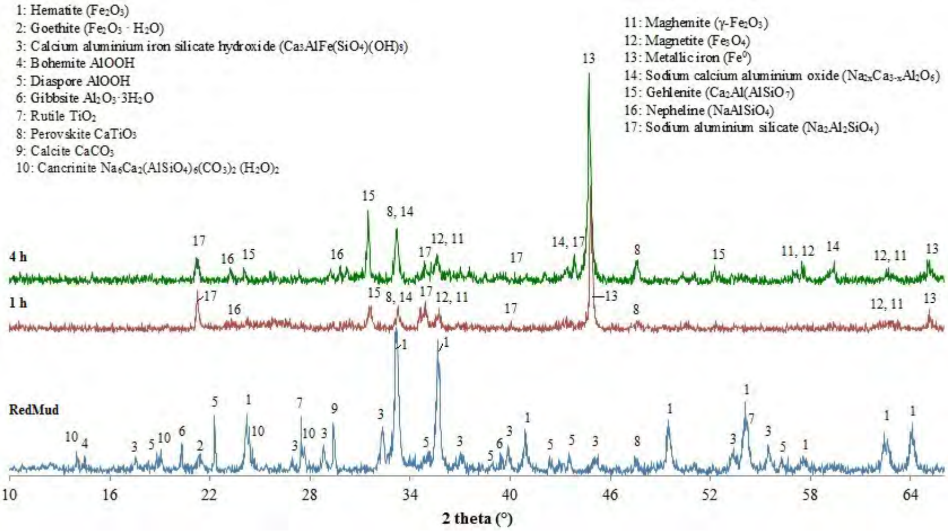
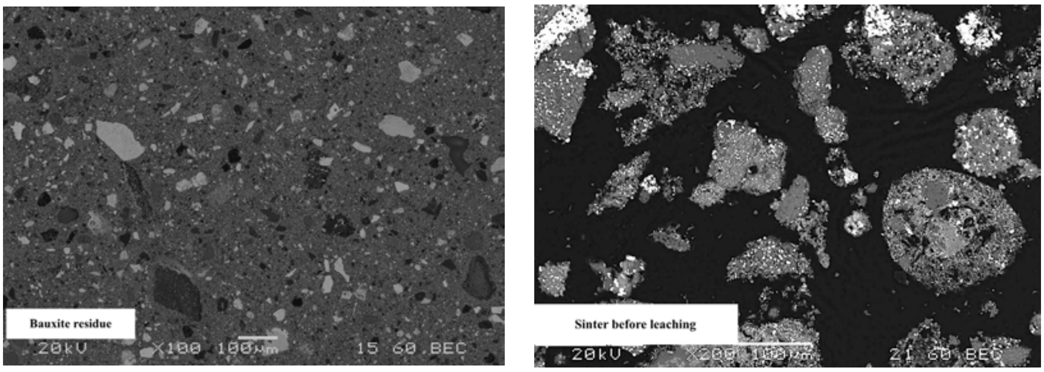


Figure 2. XRD profiles of mineralogical iron phases reduced from bauxite residue to 1h and 4h kinetic points.

SEM analysis confirmed the reduction of hematite to magnetic phases after 1 hour of roasting process. Analysing the distribution of the elements through EDS (Figure 3b), it is possible to observe that metallic iron (white particles) is concentrated in some grains of the material, although it is not fully liberated. On the other hand, SEM analyses of BR have shown Fe phases, hematite (α-Fe_2O_3), goethite ($Fe_2O_3 \cdot H_2O$) and calcium aluminium iron silicate hydroxide $Ca_3AlFe(SiO_4)(OH)_8$, mixed in the matrix and not located in specific areas (Figure 3a).



(a) **(b)**

Figure 3. SEM picture of bauxite residue compared with cinder after 1h of roasting process.

The addition of Na_2CO_3 during the roasting process promoted the formation of sodium aluminosilicate that can be easily dissolved during the H_2O leaching stage [9]. Consequently, part of Fe entrapped in alumina-silicate grains could be liberated. The chemical analysis of the leachate solution shows that 32 % of aluminium (Al) and 62 % of sodium (Na) are dissolved, as shown in Table 2, while iron (Fe), silicon (Si), calcium (Ca) and titanium (Ti) remain in the solid residue.

Table 2. Percentage amount of metals contained in BR that were dissolved during water leaching.

Element	%
Fe	10
Al	32
Si	7
Ti	13
Ca	6
Na	62

The leaching residue was passed through a wet high-intensity magnetic separator (WHIMS). Following the procedure already explained above, three fractions were produced (Magnetic I, Magnetic II and Non Magnetic). In Figure 4, the SEM picture of Magnetic I is presented; from this analysis it is possible to observe that Fe phases (white areas) are highly liberated in this fraction. In addition, Ca phases are present, since calcium titanate is also magnetic [10].

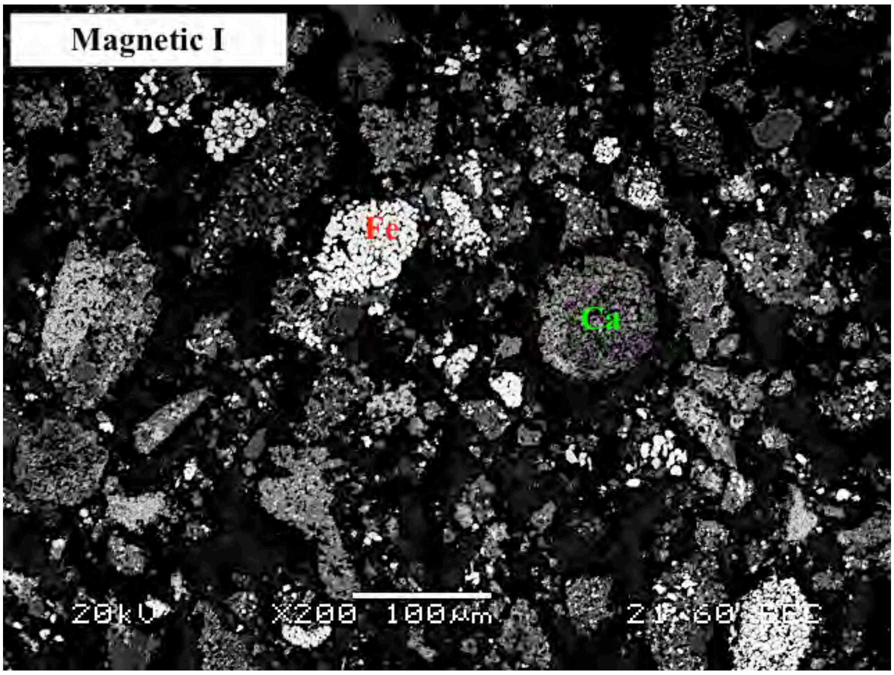


Figure 4. SEM picture of MAGNETIC I.

XRD analysis (Figure 5) has confirmed that the main mineralogical phases of the magnetic fraction (Magnetic I) are Fe and Ca containing phases.

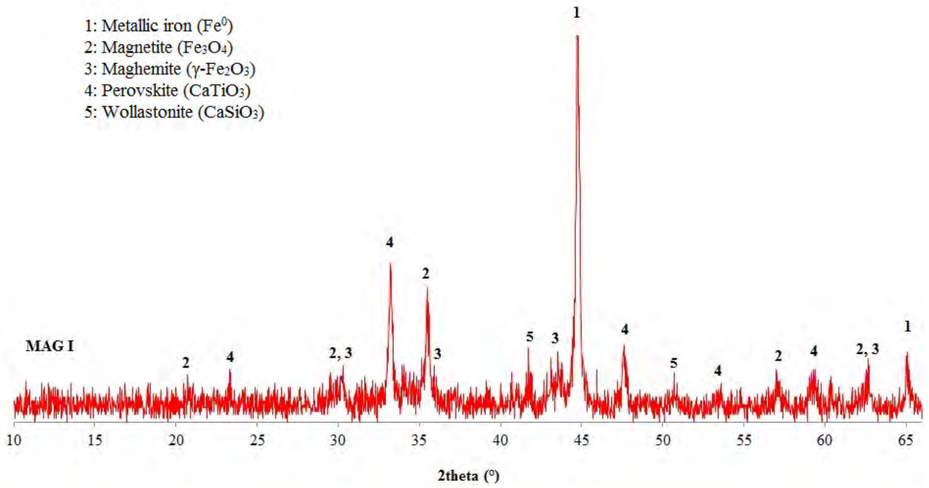


Figure 5. XRD analysis of Magnetic I.

The chemical composition of the Magnetic I fraction is shown in Table 3.

Table 3. Chemical composition of Magnetic I fraction.

Component	wt.%
Na_2O	0.52
MgO	0.49
Al_2O_3	4.24
SiO_2	10.14
CaO	13.72
TiO_2	12.81
V_2O_5	0.50
Cr_2O_3	0.44
Fe	22.00
Fe_2O_3	24.09
ZrO_2	1.37

The total content of Fe found in the first magnetic fraction represents 70 % of the whole amount of Fe in the initial BR. Using XDB software, it is found that metallic iron content is around 22 wt.% while γ-Fe_2O_3 and Fe_3O_4 are in total 16.86 wt.%. The MAG I fraction presents an attractive source of iron for blast furnaces. The Magnetic II and non-magnetic fractions are enriched principally in Ti and REEs, providing a resource for further treatments to recover these elements.

4. Conclusion

In this work a carbothermic reduction roasting of BR in a small rotary kiln furnace was presented to simulate actual industrial operation. To achieve the objective, BR was mixed with a carbon source and an additive (1 kg BR: 250 g Na_2CO_3: 225 g C) and roasted at 1000 °C for 4 hours in the presence of N_2. It was found that hematite was almost completely (> 99 wt.%) converted to magnetic phases such as metallic iron (Fe) maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) after 1 hour. In the second step, the collected cinder were leached with water at 80 °C for 4 hours allowing the dissolution of sodium aluminum-silicate phase and the liberation of Fe phases.

The leached products was passed through a wet high intensity magnetic separator, providing a high magnetic fraction that contains the 70 % of the total content of Fe and a non-magnetic residue that is enriched in Ti and REEs content. The magnetic separation process is still under development to increase the purity of the Magnetic I fraction.

5. Acknowledgments

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6. References

1. E. Balomenos, D. Panias, I. Paspaliaris, Energy and Exergy Analysis of the Primary Aluminium Production Processes – A Review on Current and Future Sustainability *Mineral Processing & Extractive Metall. Rev*. Vol. 32, (2011), 1 – 21.
2. Ken Evans, The history, challenges, and new developments in the management and used of bauxite residue, *Journal of Sustainable Metallurgy,* Vol. 2, No. 4, (2016), 316–331.
3. 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*, Vol. 3, No. 3, (2017) 551–560.
4. R.a.S. Kumar, J.P. Premchand, Utilization of iron values of red mud for metallurgical applications, *Environmental and Waste Management*, Publisher: National Metallurgical Laboratory, Jamshedpur, India, Editors: A. Bandopadhyay, N.G. Goswami, P.R. Rao, (1998), pp.108-119.
5. K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven & Y. Pontikes, Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review, *Journal of Cleaner Production*, Vol. 99, (2015) 17-38.
6. A. Xenidis, C. Zografidis, I. Kotsis and D. Boufounos, Reductive Roasting and Magnetic Separation of Greek Bauxite Residue for its Utilization in Iron Ore Industry, in Alumina Bauxite, *The Minerals, Metals & Materials Society*, (2009), 63 – 67
7. I.E. Sajó, XDB Powder Diffraction Phase Analytical System, Version 3.0, User's Guide, Budapest, 2005.
8. Peter Smith, Reaction of lime under high temperature Bayer digestion conditions, *Hydrometallurgy*, 170 (2017), 16 – 23.
9. W. Liu, S. Sun, L. Zhang, S. Jahanshahi, J. Yang, Experimental and simulative study on phase transformation in Bayer red mud soda-lime roasting system and recovery of Al, Na and Fe, *Minerals Engineering* 39, (2012) 213 – 218.
10. M. Johnsson and P. Lemmes, Crystallography and Chemistry of Perovskites *Handbook of Magnetism and Advanced Magnetic Materials* (2009).