Optimization of Microwave Reductive Roasting Process of Bauxite Residue

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Abstract: In this study, microwave-assisted heating is presented as a suitable method to transform the hematite and goethite contained in bauxite residue into magnetite, wüstite, and metallic iron, with a short processing time. The final target was the production of a sinter with strong magnetic properties, allowing the magnetic separation of Fe from the residue. The influence of microwave energy on the sample, the effect of irradiation time, and the carbon/bauxite residue mass ratio (C/BR) were the parameters that have been analyzed to optimize the process. Their optimized combination allowed transforming 79% of the iron present in the sinter into metallic iron. However, hercynite was also formed, and the presence of this mineralogical phase could be considered a possible drawback for its magnetic properties.

Keywords: bauxite residue; red mud; microwave roasting process; iron recovery

1. Introduction

Bauxite residue (BR), also known as red mud, is the reddish solid waste generated during the production of alumina from bauxite ores. In particular, the production of 1 metric ton of alumina normally creates between 0.8 and 1.5 metric tons of residue, although the range can be somewhat broader, depending on the composition of initial bauxite ore and the processing conditions [1,2].

Due to its high alkalinity, with a pH range between 10 and 13 [3–5], the handling of this waste is a challenge for the alumina industry. In addition, the massive volume of BR produced, which exceeds 160 million metric tons per year worldwide [2], is causing a drastic scarcity of available storage areas [2,6]. In the last decades, much research has been concentrated to find environmentally friendly and cost-effective methods to dispose of or utilize the bauxite residue [7].

In a multitude of scientific research papers, different processes to recover elements from BR instead of storing it have been extensively investigated, as it was thoroughly discussed in a previous work [8]. The alumina by-product can be considered as a secondary raw material resource for the presence of valuable elements such us iron (Fe), titanium (Ti), aluminum (Al), and rare earth elements (REEs) [9–11].

In particular, a major driver for the continuous research was the recovery of REEs and the focus was addressed to scandium (Sc), due to its high concentration in BR [12], which is much higher than in the Earth’s crust [13]. Consequently, Sc recovery from BR represents a high economic interest, since it has also been listed as a critical raw material by the European Commission due to its high economic importance and supply risk [14].
In the last decades, an increasing demand for sustainable industrial processing and the depletion of available ores have supported technology development based on secondary raw materials with almost zero-waste production [12].

For this reason, Fe recovery from BR has attracted major attention [7,15–17], as the iron recovered can be used as feedstock in the iron industry [18], although iron content in bauxite residue (14–45 wt.%) is not as high as in average iron ores (60 wt.%) used in the iron industry [10].

Iron removal studies from bauxite residue are mainly based on pyrometallurgical processes. In particular, these works can be grouped into two methods for producing either high-grade magnetite ($Fe_3O_4$) or metallic Fe: the solid-state reductive roasting followed by magnetic separation [18–21] and the reductive smelting process by employing different furnaces (blast furnace, electric arc furnace (EAF), and other types) [7,17,22–25]. Although these two processes are the most promising to extract iron from BR, some drawbacks related for example to capital and operational expenditures as well as to several environmental issues [23] have led the research to find an alternative method to recover iron from alumina production waste.

An emerging technology of mineral processing is the microwave treatment, which has the advantage of significantly faster reaction times. Thus, it has potentially lower energy requirements in comparison to conventional heat treatment methods [26]. These advantages depend on the molecular interactions with the electromagnetic field generated during the process. Based on dielectric properties, materials can be classified into absorbers (materials that absorb microwave energy and easily heat), insulators (which are transparent to microwave energy), and conductors (which reflect the energy) [27–29]. Compared to the conventional heating method, the microwave instantaneously generates heat inside the absorber material, rather than heating the outside surface and slowly conducting it inside [30].

Thank to these advantages, microwave has found applications in pyrometallurgical processes, such as metal recovery [26,28,31–33].

In this framework, the aim of this study was to develop a reductive roasting process by using a microwave furnace, to transform hematite ($Fe_2O_3$) and goethite ($Fe_2O_3 \cdot H_2O$) present in BR into magnetite ($Fe_3O_4$), wüstite ($FeO$), and metallic iron ($Fe^0$) according with the iron reduction pathway $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$.

Due to the fact that hematite and goethite are not good microwave receptors [31], a carbon (C) source (metallurgical coke) was added to BR as a reducing agent as well as a microwave energy absorber. Different parameters have been studied (irradiation time, carbon/bauxite residue ratio, and the influence of microwave energy on the sample) to optimize the process. The aim was to liberate the iron-based components from the sinter-produced matrix and concentrate them into the magnetic product by using a wet high-intensity magnetic separator.

2. Materials and Methods

Experiments were carried out with a 2-kW microwave furnace (Fricke und Mallah Microwave Technology GmbH, Peine, Germany), and a schematic diagram of the equipment is shown in Figure 1. The above-mentioned furnace comprised a power supply, a 2.45 GHz air-cooled magnetron, a circulator connected with a multimeter through a detector, a rectangular aluminium wave guide with a 3-stub tuner, and a water-cooled cylindrical aluminium cavity (diameter 150 mm and height 165 mm).

The magnetron converts electrical energy into high-frequency microwaves and the power capacity can be set from 0 kW (0%) to 2 kW (100%) through a potentiometer located on the switch-mode power supply. The microwave energy runs via the rectangular waveguide to the cylindrical cavity, where the sample is placed.

The 3-stubs tuner present in the waveguide allowed modifying microwave energy to accomplish the highest sample absorption for the entire experimental period. The reaction occurred in accordance with the materials’ ability to absorb the microwave energy.
The BR used in the microwave experiment as the main raw material was provided by the Aluminium of Greece plant, Metallurgy Business Unit, Mytilineos S.A. (AoG) (Agios Nikolaos, Greece). The sample was firstly homogenized by using laboratory sampling procedures (riffling method); then, a representative sample was dried in a static furnace at 105 °C for 24 h. Subsequently, the material was milled using a vibratory disc mill (Alfa Test, Bedfordshire, UK), and the sample was fully characterized.

Chemical analyses of major and minor elements were executed via the fusion method (1000 °C for 1 h with a mixture of Li$_2$B$_4$O$_7$/KNO$_3$ followed by direct dissolution in 10% HNO$_3$ solution) through a Perkin Elmer 2100 Atomic Absorption Spectrometer (AAS) (Perkin Elme, Waltham, MA, USA), a Spector Xepos Energy-Dispersive X-ray Fluorescence Spectroscope (ED-XRF) (SPECTRO, Kleve, Germany), a Thermo Fisher Scientific X-series 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Thermo Fisher Scientific, Waltham, MA, USA), and a Perkin Elmer Optima 8000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Perkin Elmer, Waltham, MA, USA), whereas the loss of ignition (LOI) of the sample was provided by differential thermal analysis (DTA), using a SETARAM TG Labys-DS-C (SETARAM, Caluire, France) system in the temperature range of 25–1000 °C with a 10 °C/min heating rate in air atmosphere.

Mineralogical phases were detected by X-ray diffraction analysis (XRD) using a Bruker D8 Focus powder diffractometer (Bruker, Billerica, MA, USA) with nickel-filtered CuK$_\alpha$ radiation ($\lambda = 1.5405$ Å) coupled with the XDB Powder Diffraction Phase Analytical System version 3.107 (Aluterv-FKI, Budapest, Hungary), which evaluated the quantification of mineral phases via profile fitting specifically for bauxite ore and bauxite residue [34,35].

The chemical distribution and microstructural composition of the samples were examined through a scanning electron microscope JEOL 6380LV (SEM) (JEOL, Tokyo, Japan) combined with an Oxford INCA energy-dispersive spectrometer (EDS) (Oxford Instruments, Bristol, UK). The particle size analysis was investigated by using a Malvern Mastersizer TM Laser particle size analyzer (Malvern Instruments, Malvern, UK).

The sample was composed by mixing BR and metallurgical coke as the carbon source. The powder was transformed in tablets with dimensions of 2 cm × 2 cm × 3 mm and approximate weights of 10 g by using a manual hydraulic press.

To ensure the interaction between the modified BR and MW wavelength, the samples were settled in the furnace on the top of a tower constituted by alumina crucibles and quartz glasses with 7 cm height and 3 cm length, which were located at the center of the cylindrical cavity. A borosilicate glass dome (Pyrex) was positioned in order to cover the sample and protect the cavity from the possible plasma formation during the experiment.

The optical pyrometer, IMPAC Pyrometer IGA 6/23 Advanced with a RS 485 converter LumaSense Technology (LumaSense Technology, Frankfurt, Germany), was located on the top of the chamber lid to record the temperature variation during the whole reaction period. Nitrogen flow of 1 L/min was
maintained throughout the experiments in order to ensure inert atmosphere during the reduction of Fe$^{3+}$ oxide into Fe$^{2+}$ oxide and metallic iron.

To determine the content of metallic iron in the samples the Zhiyong Xu method with a tolerable error ranged below 1 wt.% [36] was used; the analysis was conducted with AAS.

3. Results

3.1. Characterization of Bauxite Residue and Metallurgical Coke

The chemical analysis results of the BR are shown in Figure 2. Iron oxide content (Fe$_2$O$_3$) is 42.34 wt.%, and it can be considered the major component followed by aluminium oxide (16.25 wt.%), calcium oxide (11.64 wt.%), silicon oxide (6.97 wt.%), titanium oxide (4.27 wt.%), and sodium oxide (3.83 wt.%), while the rare earth elements (REEs) content, as oxides, is 0.19 wt.%.

![Figure 2. Bauxite residue chemical analysis.](image)

In addition, the LOI (12.66 wt.%) value is constituted by dehydration and the decarbonation of mineral phases existing in the residue.

The particle size distribution of the dried sample showed that the median particle size ($D_{50}$) of the ground material was 1.87 $\mu$m, while 90% of the particles ($D_{90}$) were below 42.87 $\mu$m.

The mineralogical phases of BR are presented in Table 1 and according with the quantification analysis carried out with the XDB software, hematite is the main mineral in BR with 30 wt.%. The other iron mineralogical phases were calcium aluminium iron silicate hydroxide, goethite, and chamosite with 17 wt.%, 9 wt.%, and 4 wt.% respectively.

| Minerals      | Formula           | wt.% |
|---------------|-------------------|------|
| Hematite      | $\alpha$-Fe$_2$O$_3$ | 30   |
| Goethite      | Fe$_2$O$_3$·H$_2$O | 9    |
| Boehmite      | $\gamma$-AlOOH    | 3    |
| Diaspore      | $\alpha$-AlOOH    | 9    |
| Gibbsite      | Al$_2$O$_3$·3H$_2$O| 2    |
| Calcite       | CaCO$_3$          | 4    |
| Anatase       | TiO$_2$           | 0.5  |

Table 1. Bauxite residue mineralogical phases.
Table 1. Cont.

| Minerals                        | Formula                                      | wt.% |
|---------------------------------|----------------------------------------------|------|
| Rutile                          | TiO$_2$                                      | 0.5  |
| Perovskite                      | CaTiO$_3$                                    | 4.5  |
| Cancrinite                      | Na$_6$Ca$_2$(AlSiO$_4$)$_6$(CO$_3$)$_2$       | 15   |
| Calcium aluminum iron silicate hydroxide | Ca$_3$AlFe(SiO$_4$)(OH)$_8$                  | 17   |
| Chamosite                       | (Fe$_{2+}$,$Mg$)$_5$Al(AlSiO$_4$)$_2$(OH)$_8$ | 4    |
| Sum                             |                                              | 98.5 |

The chemical analysis results of metallurgical coke presented in Table 2 proved carbon as the main component of the sample with 80.31 wt.%. Thanks to its high fixed carbon (Fixed C) content, metallurgical coke was used as the reductant in all the experiments carried out in this work.

Table 2. Metallurgical coke chemical analysis. Fixed C: fixed carbon, LOI: loss of ignition.

| Composition | Fe$_2$O$_3$ | SiO$_2$ | CaO | MgO | Al$_2$O$_3$ | TiO$_2$ | Na$_2$O | Fixed C | S | P | H$_2$O moist | LOI | OTHERS |
|-------------|-------------|---------|-----|-----|-------------|---------|---------|---------|---|---|--------------|-----|--------|
| wt.%        | 0.83        | 3.42    | 1.26| 0.14| 1.91        | 0.10    | 0.16    | 80.31   | 0.77 | 0.03 | 3.31         | 7.38 | 0.39   |

3.2. Microwave Roasting Process Optimization

The influence of microwave energy on the sample, the effect of irradiation time, and the addition of carbon source to BR (C/BR ratio) were the parameters investigated to find the optimized combination to convert iron oxides into metallic iron, according to the sequence of Fe$_2$O$_3$→Fe$_3$O$_4$→FeO→Fe [31,37,38].

3.2.1. Influence of Microwave Energy

A possible approach to determine the microwave’s influence on the given material is the quantification of the absorbed power from the sample, with a laboratory-scale microwave system [39].

The power absorbed by a sample per unit volume at a specific area in the material $P_v(z)$ is given by the Equation (1) [39–41]:

$$P_v(z) = 2\pi f \varepsilon_0 \varepsilon'' \left| E(z) \right|^2$$

where $f$ is the frequency of microwaves, $\varepsilon_0$ is the permittivity of free space, and $\varepsilon''$ is the relative dielectric loss, which accounts for the conversion of microwave (MW) energy into heat. $E(z)$ is the root mean square of the electric field strength. As defined by the equation above, $P_v(z)$ directly depends on the dielectric properties of the sample and the electric field strength.

One of the aims of this study was to understand the behavior of BR on power conversion during the roasting process. In this perspective, the whole range of power capacity was investigated (0–2 kW) by doing experiments at 0.6 kW (30%), 1.2 kW (60%), and 1.8 kW (90%).

BR was mixed with metallurgical coke (C/BR mass ratio 0.180) and transformed into tablets. The C to BR ratio was chosen according to the optimized results obtained from a previous work [19], which featured a BR roasting process in a conventional tube furnace. The reaction time was set to 5 min, and the nitrogen flow (N$_2$) of 1 L/min was maintained constant for the entire experimental period.

In order to analyze the effect of power capacity on BR, the experiments were carried out by measuring the microwave absorption of the empty cavity and subsequently in the presence of the sample. The absorbed energy from the samples was evaluated by collecting the values through the multimeter and combining the two series of experiments with the same power capacity (Figure 3). The percentage of absorbed energy from the sample at a specific time $A\% (t)$ is given in Equation (2):

$$A\% (t) = \left[ 100 - \left( \frac{A_s(t) \cdot 100}{A_v(t)} \right) \right]$$
where \( A_s(t) \) is the absorbance value of the sample collected with a multimeter, and \( A_e(t) \) is the absorbance value of the empty chamber collected with a multimeter.

![Figure 3. Percentage of the absorbed microwave power from bauxite residue (BR), mixed with metallurgical coke (C/BR 0.180), by choosing three different power capacities, 0.6 kW, 1.2 kW and 1.8 kW at a 1 L/min \( \text{N}_2 \) flow constant for 5 min.](image)

During the experiment, at 0.6 kW (blue line) at the above-mentioned conditions, the modified BR absorbed 100% microwave energy in 10 s. As it possible to observe in Figure 3, after 10 s, the absorption decreased due to the reduction of the samples and the liberation of the off-gases. To achieve the highest sample absorption, the 3-stubs tuner present in the waveguide was employed and the absorption was maintained constant around 94% for 0.6 kW.

When the power capacity was set at 1.2 kW (red line) and successively at 1.8 kW (green line), a rapid absorption of microwave energy (5 s for 1.2 kW and less than 1 s for 1.8 kW) from the BR was observed. Increasing the power capacity, the electromagnetic field increased \((E(z) \text{ Equation (1)})\), and the consequence is an extremely fast microwave absorption.

On the other hand, the absorption was retained at above 85% for the experiment at 1.2 kW and 80% with 1.8 kW power capacity.

This behavior is attributed to the reduction of \( \text{Fe}^{3+} \) oxides into \( \text{Fe}^{2+} \) oxides and into metallic iron, as it is confirmed in the XRD profile (Figure 4). As the reaction proceeds, the matrix of material is continuously changing as well as its dielectric properties affecting the microwave energy absorption \([42]\). Then, the energy absorption from the sample is controlled by using the 3-stub system of the furnace.
The presence of metal in the sample caused a reflection of microwave energy, due to the high material conductivity [27,32,40] that reduced the 3-stub tuner effect.

As a consequence of the energy absorbed from the given material, the sample temperature increased, and this behavior is explained by Equation (3):

$$P_v = \rho C_p \frac{\Delta T}{\Delta t}$$

where $\rho$ is the density of the material, $C_p$ is the specific heat of the material, $\Delta T$ is the temperature variation, and $\Delta t$ is the time variation [43,44].

Since the effectiveness of the microwave energy absorption by the sample is reflected on the instantaneous heating of the material, the temperature has been recorded during the whole duration of the test by using an optical pyrometer, which was pointed at the sample surface (Figure 5).
Figure 5. Heating rates of BR mixed with metallurgical coke (C/BR 0.180), by choosing three different power capacities, 0.6 kW, 1.2 kW and 1.8 kW at 1 L/min N₂ flow constant for 5 min.

During the experiment at 0.6 kW, the sample has reacted at 998 °C in 10 s, absorbing the maximum of energy. The use of a 3-stub tuner allowed achieving a value above 950 °C.

In the case of 1.2 kW, a temperature of 1015 °C has been attained after 5 s, and then, the temperature was kept constant around 860 °C.

For the experiment at 1.8 kW, the temperature exponentially rose within a second to 1020 °C. However, it is possible to observe a considerable temperature decrease (at around 800 °C) due to the presence of conductive material, which defeats the effect of the 3-stub tuner.

The results obtained from the experiments have shown the behavior of BR by using different power capacities. When the power capacity was set at 0.6 kW, the iron phases present in the initial sample were converted into magnetite (Fe₃O₄), wüstite (FeO), metallic iron (Fe₀), and hercynite (FeAl₂O₄) with an absorbed microwave power of 95% and a maximum temperature of 998 °C.

3.2.2. Irradiation Time

To analyze the behavior of the sample by changing the irradiation time, different sets of experiments have been performed at 180 s, 300 s, and 600 s, while keeping constant all the other parameters at 0.6 kW, C/BR 0.180, and 1 L/min nitrogen flow.

From the comparison of the XRD spectra of BR and the sample after microwave heating treatments (Figure 6), it is possible to conclude that the complete transformation of iron-containing phases (hematite, goethite, and calcium aluminum iron silicate hydroxide) present in BR into metallic iron, wüstite, hercynite, magnetite, and maghemite is favored by increasing the irradiation time. The other elements (Ca, Si, Al, Ti and Na) are present mainly in sodium and calcium aluminosilicate phases as well as perovskite and calcium silicate.
Figure 6. XRD of sinters (C/BR 0.180, 0.6 kW, and 1 L/min N₂ flow) by changing the irradiation time at 180 s, 300 s, and 600 s compared with XRD of bauxite residue.

At 180 s, a peak of hematite is still observed. This is because the reaction was not complete, as the sample was exposed to the microwave radiation for a short period. As it can be seen in Figure 7, the tablet showed a black, partially molten state in the center, while the outer rim of the disk remained reddish, comparable to its initial state.

Figure 7. Tablet after 180 s irradiation time at 0.6 kW, C/BR 0.180, and 1 L/min nitrogen flow.

At 300 s and 600 s, the hematite and maghemite peaks disappeared, while magnetite, hercynite, wüstite, and metallic iron were the main iron mineralogical phases among the other constituents.
The above observations explain well the microwave heating behavior. The microwave radiation went through the sample, the heat was generated inside the tablet, and then it was transferred to the surface of the material [39]. Therefore, at 300 s, the tablet was completely roasted (Figure 8), promoting the reduction of trivalent iron oxide into bivalent ones and metallic iron.

![Figure 8](image-url)  
Figure 8. Tablet after 300 s irradiation time at 0.6 kW, C/BR 0.180, and 1 L/min nitrogen flow.

However, increasing the irradiation time, the presence of conductive material (such as metallic iron) caused a reflection of microwave energy. Indeed, after 300 s, the percentage of microwave absorption fluctuated, although the 3-stub tuner were employed for the entire experimental period (Figure 9).

![Figure 9](image-url)  
Figure 9. Percentage of the absorbed power from BR, mixed with metallurgical coke (C/BR 0.180) at 0.6 kW, 1 L/min N₂ flow constant for 600 s.

The result of the irradiation time optimization is the production of sinter containing Fe₃O₄, FeO, Fe⁰, and FeAl₂O₄ among the other constituents at 300 s.
3.2.3. Carbon Source Addition to BR

To clarify the role of C during the microwave roasting process and the heating behavior of BR, experiments were carried out by analyzing a BR tablet without the carbon source addition. The other parameters that were examined span the whole power capacity range (0–2 kW) and irradiation time between 300 and 900 s. The nitrogen flow remained constant at 1 L/min.

Figure 10a shows the percentage of absorbed microwave power by BR without the addition of C at 0.6 kW, 300 s, and 1 L/min nitrogen flow. Under these conditions, it is observed that the absorbed power was negligible because the sample can be considered as a poor receptor to microwave energy. This behavior was also confirmed during the experiments at a higher power capacity and irradiation time.

The above observation proved that the carbon source addition is required to facilitate the microwave absorption by the sample; in fact, carbon is a good receptor of microwave energy [31]. Therefore, the heat is transferred through the BR material, promoting the hematite and goethite reduction, as it was shown in the previous study [19].
To investigate the effect of C/BR ratio on microwave reductive roasting, several sets of experiments were performed at 0.6 kW, irradiation for 300 s, with a constant 1 L/min N₂ flow. The following C/BR ratios were studied: 0.122, 0.135, 0.158, 0.180, and 0.225.

As it is shown in Figure 10b, during the microwave absorption of the sample irradiated for 300 s at 0.6 kW with a C/BR of 0.122, a two-step absorption sequence was observed. Up to 30 s of irradiation time, no absorption was registered; while after that time, the absorption rose to 75% and remained constant by using the 3-stub tuner. At these conditions, the highest T recorded was at about 780 °C. Similar behavior with 0.135 C/BR was noted with 80% microwave energy absorption and a maximum temperature of 830 °C (Figure 10c). On the other hand, the absorption of microwave power is favored when increasing the carbon/bauxite residue ratio. As it is observed for 0.158 C/BR (Figure 10d), the energy absorption is kept almost constant at 90% with a temperature (T) value around 950 °C, while for 0.180 C/BR, the energy absorption is kept almost constant at 95% with a maximum T of 998 °C (Figure 10e). Regarding C/BR 0.225 (Figure 10f), an immediate absorption is noted, and by employing the 3-stub tuner, the energy absorption was controlled at 98% with a detected temperature of 1100 °C.

The mineralogical characterization of the treated and milled disks is present in Figure 11 and revealed the complete transformation of BR iron phases Fe₂O₃ and Fe₂O₃·H₂O into Fe₃O₄, γ-Fe₂O₃, FeO, Fe⁰, and FeAl₂O₄ already at 0.112 C/BR after 300 s and 0.6 kW. At the same time, under those conditions, all of the phases containing aluminium hydroxides or oxy-hydroxides BR (gibbsite, boehmite, diaspore, cancrinite, and calcium aluminates) have been transformed to corundum and also into nepheline, jendeide, and gehlenite, which are sodium aluminosilicate and calcium aluminosilicate phases that did not initially exist in BR. Regarding the titanium phases, these have been converted into perovskite, while the calcite peak disappeared due to its thermal decomposition [45].

Figure 11. XRD of sinters (300 s, 0.6 kW and 1 L/min N₂ flow) by changing the C/BR ratio between 0.122 and 0.225 compared to XRD of bauxite residue.
When increasing the C/BR ratio, an intensification of reduction conditions that foster the formation of metallic iron was observed. The Fe⁰ content in the samples was determined through the Zhiyong Xu method [36], and the results are shown in Table 3, confirming the XRD profiles.

**Table 3.** Percentage of metallic iron/total iron content of BR and 4 different C/BR ratio sinters determined with the Zhiyong Xu method [36].

| Sample | % Fe⁰/Fe₉₀₀ |
|--------|-------------|
| BR     | 0           |
| 0.122 C/BR | 20         |
| 0.135 C/BR | 29         |
| 0.158 C/BR | 35         |
| 0.180 C/BR | 57         |
| 0.225 C/BR | 79         |

By increasing the C/BR ratio from 0.122 to 0.225 C/BR, the metallic iron content also increased from 20% (0.122 C/BR) to 79% w/w (0.225 C/BR), respectively. This is attributable to the high temperatures generated during the experiments, facilitating the conversion of trivalent iron phases, which are present in BR, into Fe⁰.

Although 0.225 C/BR at 0.6 kW with a 1 L/min N₂ flow constant for 300 s can be considered the optimum conditions to obtain the best results (almost the 79% of total Fe content present in BR, converted to Fe⁰), hercynite (FeAl₂O₄) is still observed as the XRD analysis has shown. The backscattering electron (BES) image taken with SEM-EDS analyses confirmed the presence of FeAl₂O₄ (Figure 12c) with the metallic iron which is concentrated in almost spherical particles in the matrix of material (Figure 12b). In addition, the iron phases (FeAl₂O₄ and Fe⁰) are entrapped in the matrix, which is mainly composed of all of the other constituents (Figure 12a).

As Lu et al. [38] explained in their work, the hercynite is an unavoidable product. During the roasting process, the hematite can be reduced to magnetite [19] by the carbon source, but in the presence of alumina, it can be transformed also into hercynite.

Hercynite is a normal spinel structure, where one-eighth of the tetrahedral sites are occupied by Fe²⁺ cations and one-half of the octahedral sites are occupied by Al³⁺ cations [46]. This spinel exhibits a magnetization and can be considered as a magnetic material [46]. The presence of FeAl₂O₄ in the optimized sinter represents a drawback for the magnetic separation process, since the magnetic fraction would be composed by oxides that reduce its purity.

To avoid the presence of hercynite in the sinter, a possible scenario is to decrease the Al content in BR. In fact, by adding sodium carbonate as flux, all the alumina phases of BR are transformed into soluble sodium aluminates, which can be afterwards subjected to alkali leaching to recover alumina [21,47,48]. After this treatment, Fe³⁺ could be transformed into Fe²⁺ and Fe⁰ by using the microwave roasting process and the produced sinter treated with the magnetic separation process to recover iron from the other elements.
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Hercynite is a normal spinel structure, where one-eighth of the tetrahedral sites are occupied by Fe$^{2+}$ cations and one-half of the octahedral sites are occupied by Al$^{3+}$ cations [46]. This spinel exhibits a magnetization and can be considered as a magnetic material [46]. The presence of FeAl$^{2+}$O$_4$ in the optimized sinter represents a drawback for the magnetic separation process, since the magnetic fraction would be composed by oxides that reduce its purity.

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4. Conclusions

In this study, it was demonstrated that microwave-assisted heating is a suitable method to transform the Fe$^{3+}$ oxide contained in bauxite residue (hematite and goethite) into Fe$^{2+}$ oxide (magnetite, hercynite and wüstite) and metallic iron, within a short processing time.

Experiments have been carried out in a 2-kW microwave furnace with a 3-stub tuner present in the waveguide that allowed the modification of the microwave energy to accomplish the highest sample absorption for the entire experimental period. The quantification of the absorbed power by the sample as a possible approach to determine the microwave’s influence on the given material, the effect of irradiation time, and the addition of carbon source to BR (C/BR mass ratio) were the parameters investigated to optimize the carbothermic roasting process. At 0.6 kW and 0.225 C/BR with a 1 L/min N$_2$ flow constant for 300 s, the reduction of Fe$^{3+}$ oxides into Fe$^{2+}$ oxides and metallic iron was facilitated by the high temperature reached during the experiment (1100 °C). In particular, the result was the production of sinter with 79% of metallic iron, while the rest of the iron mineralogical phases were attributed to Fe$_3$O$_4$, FeO, and FeAl$_2$O$_4$.

The formation of hercynite was unavoidable during the microwave roasting process [38] and the presence of this iron aluminum oxide mineralogical phase is considered as a drawback for magnetic separation process due to its paramagnetic properties.

Figure 12. Backscattering electron (BES) image taken with SEM-EDS (energy-dispersive spectrometer) analysis of 0.225 C/BR sinter, (a) BES image of matrix composition, (b) BES image of metallic iron, (c) BES image of hercynite.
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