Novel applications of microwaves in the metallurgical processing of a nickel-ferrous laterite ore and an aluminum industry waste

M Samouhos¹, M Taxiarchou¹ and E Kouvelos²
¹Laboratory of Metallurgy, School of Mining and Metallurgical Engineering, National Technical University of Athens, Zografou Campus, Athens, Greece
²Demokritos National Center of scientific research, Agia Paraskevi, Attiki, Athens, Greece

Email: msamouhos@metal.ntua.gr

Abstract. Microwave radiation is a relatively new source of energy in the pyrometallurgical process. In this study, the application of microwaves in the carbothermic reductive roasting of a nickeliferous hematitic laterite ore and a red mud are investigated. The effective microwave heating (at temperatures above 900 oC) of the aforementioned materials is attainable due to the relatively high values of their imaginary permittivity ($\varepsilon''$). In both two cases, the reduction of the included hematite was attempted, and the reduction degree was calculated as a function of: (a) the heating time and (b) the supplied microwave power. The mechanism of Fe+3 to Fe0 conversion was investigated using Mössbauer spectroscopy revealing the formation of magnetite, fayalite and nano-structured metallic iron. Finally, it should be noted that that the gaseous products of the microwave pyrometallurgical process were analyzed using a mass spectroscopic technique, which is an important novelty.

1. Introduction

Microwaves are electromagnetic radiation covering the frequency range between 300 MHz and 300 GHz. Microwave radiation interacts with microwave absorptive materials (dielectrics), generating heat instantaneously in their core. It is converted to heat via two main mechanisms; (a) hindered permanent dipole rotation and (b) electron/ion resistivity. The interaction between the microwave radiation and a non magnetic media is determined by the temperature-depended complex permittivity of the concrete media [1]:

$$\varepsilon^*(T) = i \cdot \varepsilon'_r(T) - j \cdot \varepsilon''_r(T)$$  \hspace{1cm} (1)

Where, $\varepsilon^*(T)$, is the complex relative permittivity, $\varepsilon'_r(T)$ is the real relative permittivity, and $\varepsilon''_r(T)$ is the imaginary relative permittivity. The real part represents the degree of the microwave absorbance, while the imaginary part represents the degree of the microwave power conversion to heat. The average power (PL) absorbed per unit volume is estimated by [1]:

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
\[ P_L = \frac{1}{2} \omega \varepsilon_r \varepsilon_0 \left( T \right) |E_{int}|^2 \text{ (watts/cubic metre)} \]  

(2)

Where: \( \omega \) is the angular frequency \((2\pi f, \text{ in radians } \text{s}^{-1})\), \( E_{int} \) is the internal electric field in the sample \((\text{Vm}^{-1})\) and \( \varepsilon_0 \) is the permittivity of free space.

This study discusses a novel reductive roasting processing of a laterite ore and a red mud under microwave heating. Both materials are of great industrial significance; laterite is the main nickel source, while the processing of red mud, which is the major waste of the aluminum industry, presents worldwide growing interest due to its high environmental impact [2, 3].

2. Experimental setup

Bulk chemical analysis of the rough and the reduced samples was performed using a Xepos Spectro Bench XRF spectrometer while their mineralogical characterization was carried out using a Bruker D8 Focus analyzer. The determination of the iron phases that appeared in the reduced laterite samples was realized by Mössbauer spectroscopy. The reduction degree of laterite was calculated following the E 1071-85 ASTM method. The metallic iron (Fe\text{m}) content of the reduced red mud samples was determined following the method of Zhiyong Xu et al. [4].

The reductive roasting experiments of the laterite ore and the red mud residue were performed using an appropriately modified Ceralink ThermWave 1.3 microwave oven working at 2.45 GHz (Figure 1a). A second microwave oven setup was designed for the chemical analysis of the off gases that were produced during the reduction of the laterite ore (Figure 1b). The sample of laterite-lignite mixture was placed into an airtight cylindrical fused silica sample holder. An air mixture of O\text{2}-He\text{2} (21:79 % w/w) was channeled by an aperture in the top of the sample holder, while the off gases were issued, and guided to a Pfeiffer (OmniStarTM) spectrometer, by a second lateral aperture. The total O\text{2}-He\text{2} flow rate was 160 mL/min.

![Figure 1](image_url)

Figure 1. (a) Schematic diagram of the microwave oven used in the microwave reduction of the ores

(1) power controller, (2) optical pyrometer, (3) 2.45 GHz chock tube, (4) alumina crucible,

(5) alumina latforn, (6) waveguide position, (7) water cooling system [5],

(b) Positioning of the sample holder for the chemical analysis of the laterite reduction off gases

The hematitic nickel-ferrous laterite ore that was used in the current study originates from the main open pit mine of the Greek FeNi producer LARCO in Lokrida, Greece, while the respective red mud sample was provided by the Greek aluminum industry “Aluminum of Greece S.A”. The bulk XRF chemical analyses of the laterite and the red mud samples are presented in Table 1. X-ray diffractometry showed that the iron content in both materials is almost exclusively contained in
hematite phase (Fe$^{+3}$). The reducing agent used at the reduction experiments was lignite (30.15% Cfix).

**Table 1.** Bulk XRF chemical analyses of the laterite ore and the red mud residue

| Species (w/w %) | Fe$_2$O$_3$ | SiO$_2$ | Al$_2$O$_3$ | MgO | CaO | TiO$_2$ | Cr$_2$O$_3$ | NiO | K$_2$O | Na$_2$O | ZrO | L.O.I |
|----------------|-------------|---------|-------------|-----|-----|---------|-------------|-----|-------|--------|------|------|
| Laterite       | 40.7        | 30.55   | 4.80        | 4.52| 3.20| -       | 4.00        | 1.33| 0.75  | -      | -    | 8.0  |
| RM             | 43.19       | 7.37    | 14.63       | 0.31| 12.03| 6.05    | 0.28        | -   | 0.07  | 2.14   | 1.12 | 12.19|

3. **Results and discussion**

The heating behavior of the laterite-lignite mixture powder under the microwave irradiation is presented in Figure 2, where the top-surface temperature of the sample is displayed as a function of the heating time, the power supply and the amount of carbon content.

It is evident that the mixture is susceptible in microwave absorption and can be rapidly heated over 900°C with an average heating rate of about 6.4°C/s at 800 W. Figure 3 presents the Mössbauer spectra of four reduced laterite samples received after their reduction for; (a) 2, (b) 4, (c) 6 and (d) 8 min. The conditions used were 800 W of output power supply and a twice stoichiometric carbon addition. “stoichiometric”, is defined as the required carbon amount for the complete reduction of the initial contained hematite to metallic iron according to the following reaction:

$$\text{Fe}_2\text{O}_3 + 1.5 \text{ C} \rightarrow 2 \text{ Fe} + 1.5 \text{ CO}_2 \quad \Delta H = 232 \text{ kJ/mol} \quad (3)$$

The relative amounts of the iron-containing phases are directly calculated from their corresponding sub-structural areas. Results show the gradual decreasing of the initial Fe$^{+3}$ content and its conversion to Fe$^{+3}$/Fe$^{+2}$ (magnetite), Fe$^{+2}$ (fayalite, ferrosillite) and Fe$^0$ (metallic iron) phases. The Fe$^{+2}$ content (initially zero in the rough laterite) is already high (42%) after 2 min of roasting while the metallic iron [under bcc Fe(Ni) form] content is 11%. A significant part of the formed iron-nickel alloy is present in a non-magnetic nanoscale phase. The reduction degree of the laterite ore was parametrically examined as a function of (a) the roasting time, and (b) the output power.
Figure 3. The Mössbauer spectra of reduced laterite samples after 2 (a), 4 (b), 6 (c) and 8 (d) min of roasting and their respective phase contents (wt.%) [5]

| Phases        | samples |
|---------------|---------|
| Fe\(^{2+}\)   | a: 31, b: 8, c: 2, d: 13 |
| Fe\(^{3+}\)   | a: 42, b: 72, c: 69, d: 29 |
| Fe\(^{2+}/Fe^{3+}\) | a: 16, b: 5, c: 2, d: 7 |
| α-Fe(Ni)      | a: 7, b: 4, c: 6, d: 18 |
| α-Fe(Ni)      | a: 4, b: 10, c: 19, d: 34 |

Figure 4. (a) Reduction degree of laterite as a function of roasting time and output power supply [5], (b) comparative reduction degree rates of microwave and conventionally heated laterite-lignite mixtures [6]

Figures 4(a) present the reduction degree of the laterite ore at three output power levels using a twice stoichiometric carbon addition. It is clear that the reduction reaction progress is significantly affected by the output microwave power. A rough comparison of the reduction degree rates between a conventionally and a microwave heated hematitic laterite (both from Lokrida open pit mines) is attempted in Figure 4(b). The conventionally roasting experiments were performed using a tube furnace [6]. Despite the differentiation of the experimental conditions (the conventional reductions were done under isothermal conditions, while the microwave reductions under non isothermal conditions), the results indicate the increase of the reduction reaction rate in case of the microwave heated laterite ore. The mass spectra of the off gases emitted by the laterite reduction in relation to the heating time are presented in Figure 5.
The results indicate the emission of H$_2$ (m/z=2), CO (m/z=28 and m/z=12) and CO$_2$ (m/z=44) after 2 min of microwave heating. The production of CO can be attributed to the Boudouard reaction while H$_2$ is produced via the following reaction after 700°C [7, 8]:

$$\text{C(s) + H}_2\text{O(g) } \rightarrow \text{ H}_2\text{(g) + CO(g) \quad \Delta H = 131.3 \text{ KJ/mol}}$$

(4)

It should be noted that the sample’s temperature at this moment exceeds 800 oC. Comparing the progress of the laterite ore’s reduction degree (Figure 9) with the evolution of the off gases emissions, it can be concluded that initially (up to 2 min) the reduction follows a solid-solid reaction mechanism while after 2 min the reducing agents H$_2$ and CO accelerates the reduction process.

Red mud residue presents a similar to laterite microwave heating behavior. As it can be seen in Figure 6, the heating of a red mud-lignite mixture is sufficient at 800 W, while the addition of 1wt.% (per total mixture’s mass) graphite, increases the heating rate and the maximum developed temperature.

The reducibility of the red mud was examined as a function of; (a) the roasting time, and (b) the amount of microwave power. Figure 7(a) shows the effect of roasting time on the metallization degree of a 22 g red mud sample using 600 W of power supply and a 0.3 (w/w) ratio of lignite/red mud. The effect of microwave power supply on the metallization degree is shown in Figure 7(b).
Roasting time was 12 min while a 2.5 times stoichiometric addition of carbon was used. The roasted concentrates were milled at the granulometry of -200 Mesh and subsequently they were magnetically separated into a Carpcoc (model MWL 3465) separator applying a 0.3 A current intensity. The magnetic product that was taken is enriched 10% in metallic iron [Figure 7(b)]. Although the high metallization degree (69%) of the magnetic concentrate, its content in total iron is relatively low.

![Figure 7](image)

**Figure 7.** (a) Metallization degree of red mud heated at 600 W as a function of time, (b) Metallization degree for roasted red mud samples (roasted con.) and its respective magnetic fractions (magnetic con.), Fetot in the magnetic and non magnetic fractions as function of power supply [9]

### 4. Conclusions and future work

Laterite-lignite and red mud-lignite mixtures are susceptible to microwave heating presenting an initial heating rate $> 6^\circ$/s and a temperature stabilization over 900$^\circ$C. The maximum achieved reduction degree of the laterite ore was 69% after 8 min of heating at 800 W. Similar results were achieved in the case of red mud reduction (metallization degree: 59% after 12 min at 1000 W). Mössbauer spectroscopy showed the formation of metallic iron, magnetite and iron-silicate (fayalite) phases during laterite reduction. Mass spectroscopic analysis of the off gases that were produced during laterite’s reductive roasting, showed the formation of CO and H$_2$.

Although reductive roasting of red mud proceeds rapidly and a high metallization degree is achieved, the magnetic separation of the roasted concentrate is ineffective due to the enclosing of Fe particles into an Al-Si-Ca amorphous matrix. As a future research goal, the reductive roasting of the red mud under gentle heating conditions, to Tmax=700$^\circ$C, is proposed. Under these conditions: (a) the vitrification will be avoided, while (b) hematite (Fe$^{3+}$) will be reduced to magnetite (Fe$^{3+}$, Fe$^{2+}$). The last phase disposes a high magnetic susceptibility ($\chi$) and will be effectively separated in a magnetic fraction.

### References

[1] Metaxas C A, Meredith JMR 1983 *Industrial Microwave Heating* (London: Peter Peregrinus)

[2] [http://redmud.org/home.html](http://redmud.org/home.html)

[3] Hind A R, Bhargava S K, Grocott S C 1999 *Physicochemical Engineering Aspects* 146 359

[4] Zhiyong X, Hwang J, Greenlund R, Huang X, Luo J, Anschuetz S 2003 *Journal of Minerals and Materials Characterization and Engineering* 2 65

[5] Samouhos M, Taxiarchou M, Hutcheon E, Devlin E 2012 *Minerals Engineering* 34 19

[6] Zevgolis E, Zografidis C, Halikia I 2010 *Mineral Processing and Extractive Metallurgy* 1 9

[7] Li Y L, Guo L J, Zhang X M, Jin H, Lu Y J 2010 *International Journal of Hydrogen Energy* 35 751

[8] Zhang R, Jiiang W, Cheng L, Sun B, Bi J 2010 *International Journal of Hydrogen Energy*, 35 11810

[9] Samouhos M, Taxiarchou M, Tsakiridis E, Potiriadis K 2013 *Journal of Hazardous Materials* 254-255 193