

DETAILED MINERALOGY OF BLASTFURNACE SLAG SAMPLES FROM GALAȚI METALURGICAL PLANT, ROMANIA

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Abstract

In the southeastern part of Romania, near Galați, there is the largest slag waste dump in the country as a result of the metalurgical plant (now ArcelorMittal Galați) activity during the last decades. In order to assess the eventually re-use of the waste dump material, a detailed mineralogical study was carried out. Some 100 slag samples have been investigated and revealed a quite uniform composition. Their mineralogy is quite complex, from the point of view of mineral classes and comprises native elements, oxides, sulfides, phosphates and silicates. The main component is melilite, twinned and zoned, having with fine inclusions of native iron and oldhamite. Fayalite is rather frequent and zoned. Wüstite inclusions occur within the anorthite glass. Skeletal grains of merwinite have been observed, as well as perovskite associated with melilite. Hercynite and whitlockite occur as accessory components. The potential use of the slag material could be as construction material but also as a potential source of some rare elements.

Keywords: slag, melilite, fayalite, calcium disilicate, native iron, wüstite, magnetite, troilite, oldhamite.

1. INTRODUCTION

The Galați blastfurnace, the largest in Romania, was built in the 1960s. The plant, now ArcelorMittal Galați, a subsidiary of ArcelorMittal Steel Holdings AG, is located in southeastern part of Romania, at the Danube port of Galați, 80 km from the Black Sea. The steelmaking process starts with the processing of iron ore which is brought, from worldwide, as far as West Africa, North Canada, Brazil, Kazakhstan, etc. The samples studied here were collected from the furnace slag waste dumps.

A mineralogical investigation was carried out in order to reveal the mineral composition of the slag as a basis for eventual reprocessing. The mineralogy of Galați slag (GS) shows that it is predominantly silicate (melilite, wollastonite, dicalcium silicate, monticellite, anorthite and fayalite). In order of predominance, after the silicate class, follow the oxide class (wüstite, magnetite, hercynite, spinel, spinel-hercynite mixture) sulfides (oldhamite, troilite, pyrrhotite, Ni-sulfides) and native elements (native Fe). Rarely, some phosphates occur (whitlockite) as accessory minerals. This estimation is based upon careful microscopic investigation (in transmitted and reflected light) of over 100 slag samples covering almost the whole surface of the slag heaps.

2. MINERALOGY

2.1 Native elements

Native iron, Fe, cubic. It occurs typically in small blebs (Fig. 1). In polished sections it has a white colour, high reflectivity, and is isotropic. In the GS the native iron is associated with wüstite, troilite, magnetite and fayalite. The native iron is a very good indicator for highly reduced environments.

2.2. Oxides

Wüstite, FeO, cubic. In the GS wüstite occurs as massive or individual anhedral grains between other slag minerals like fayalite, or magnetite. In reflected light it has a light grey colour, with a faint greenish tint (Fig. 1). The wüstite from GS is formed at high temperatures and in a highly reducing environment, usually on fayalite.

Magnetite, $\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4$, cubic. It occurs rarely, as relic grains usually transformed in wüstite. In reflected light it is light grey with a brownish tint and has troilite inclusions (Fig. 1b).

Hercynite, FeAl_2O_4 , cubic. In transmitted light hercynite from GS has a red colour and is isotropic. It occurs in a very small quantity, being associated with fayalite (Fig. 2a).

Spinel, MgAl_2O_4 , no colour, isotrop. Spinel rarely occurs but in big grains.

Spinel-hercynite solid solution intermediate members, $(\text{Fe,Mg})\text{Al}_2\text{SiO}_4$, yellow colour, isotrop. All spinel terms occur in the Al rich areas, with some variations of Mg and Fe.

2.3. Sulphides

Oldhamite, (CaMg)S, cubic. It occurs as dendritic inclusions in melilite (Fig. 2b). In some melilite crystals there occur dendritic inclusions of oldhamite. Sometimes the oldhamite inclusions are very concentrated almost throughout the crystal giving it an opaque appearance. In some melilite samples, larger inclusions of oldhamite and stellate clusters (ca 0,4mm) occur. Oldhamite appears also as euhedral individual crystals.

Troilite, FeS, hexagonal. It is a rare sulphide mineral, being the end member of the pyrrhotite group. The pyrrhotite has the formula $\text{Fe}_{(1-x)}\text{S}$, with iron deficient. Troilite is enclosed in magnetite as small grains (Fig. 3a). In wüstite the troilite occurs as very fine filliform veins. In reflected light it has a light yellow colour and is anisotropic.

Pentlandite (?), (Ni,Fe)₉S₈, cubic, optically determined. It occurs rarely, as large grains. In reflected light it has a white colour, no cleavages, and it is isotropic. It is associated with magnetite (Fig. 3b). It will be correctly determined in our future researches by microprobe analyses.

2.4. Silicates.

The mineralogical constituents of GS silicates are in predominance order the following: melilite group, fayalite, dicalcium silicate and anorthite.

Melilite is the major crystalline phase in all samples and occurs as euhedral, prismatic forms with crystals sometimes twinned. It is a solid solution of akermanite ($2\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) and gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). The melilite occurs in clusters and as isolated crystals in concentric and sector type zones (Hîrtopanu et al, 2004). The microscopic features of melilite are very similar to those presented by Scott et al. (1986). The iron, oldhamite and troilite inclusions in melilite are common.

Fayalite, Fe₂SiO₄, orthorhombic. Fayalite is very rare in nature but is common in metallurgy, especially in iron slags. In the GS it presents a granular prismatic habit with moderate and imperfect cleavages. In transmitted light, the fayalite has a pale yellow to amber colour, with very faint pleochroism (Fig. 2a). Optically it is biaxial (-). It has inclusions of native iron and troilite, and is frequently substituted by wüstite (Fig. 4a).

Anorthite, CaO · Al₂O₃ · 2SiO₂, triclinic, occurs in the domain of low lime and high alumina contents, where the mineral may be formed. It is grey black, glassy and isotropic.

Dicalcium silicate, 2CaO · SiO₂, orthorhombic, may be formed in slag having a high lime content. It occurs as striated grains. The dicalcium silicate occurs in at least three different forms (Lee, 1974). The α -form occurs at temperatures above 1.420°C, when the slag is in a liquid state. When the temperature falls to about 675°C, the dicalcium silicate occurs in the β -form. So, the dominant form in the GS is β -form. When the dicalcium silicate changes from the β to the γ form, which it can be done at atmospheric temperatures, it increases in volume by about 10 % (Lee, 1974), and if the silicate is in sufficient quantity, the expansion will cause disintegration of the slag matrix, which has happened to the GS. Also, the oxidation of the reduced iron oxides from GS leads to expansion, which may cause disintegration of the GS.

2.5. Phosphates

Whitlockite, Ca₁₈(Fe,Mg)₂(H₂,Ca)(PO₄)₁₄, rhomboedral, anhydrous apatite, occurs rarely in GS, as accessory, in large grains (Hîrtopanu et al, 2004). The whitlockite, identical with the beta polymorph of $\text{Ca}_3(\text{PO}_4)_2$, first known from slag systems, was later found in nature. In transmitted light the whitlockite occurs as rhombohedral, colorless grains and has no cleavages. It is optically (-).

3. DISCUSSIONS

There is no silica present in the GS. It is probably all bound up in the melilite, fayalite, dicalcium silicate and anorthite. The anorthite is present as glass in which the iron reduced oxide, wüstite, and the silicates were dissolved. The small quantity of Al_2O_3 remaining after the forming of anorthite contributed to form the hercynite. The mineralogical composition of the GS in terms of hercynite, fayalite and wüstite assists in determining its melting temperature. If the mineralogical composition is inserted in the phase diagram in Fig. 5 for anorthite, silica and wüstite (Lee, 1974), the theoretical melting temperature can be read off. This can be seen to be about 1.100-1.200°C, which approximates the working temperature of the furnace.

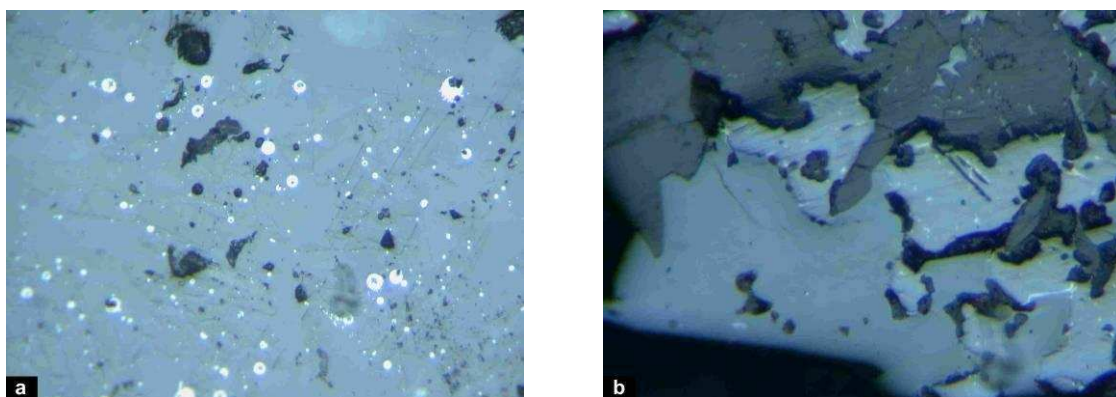


Figure 1. (a) Native iron (white, blebs) in wüstite (grey white); (b) wüstite (grey), magnetite with troilite inclusions (whitish grey) and fayalite (dark grey) with wüstite inclusions. Reflected light, x160, NII.

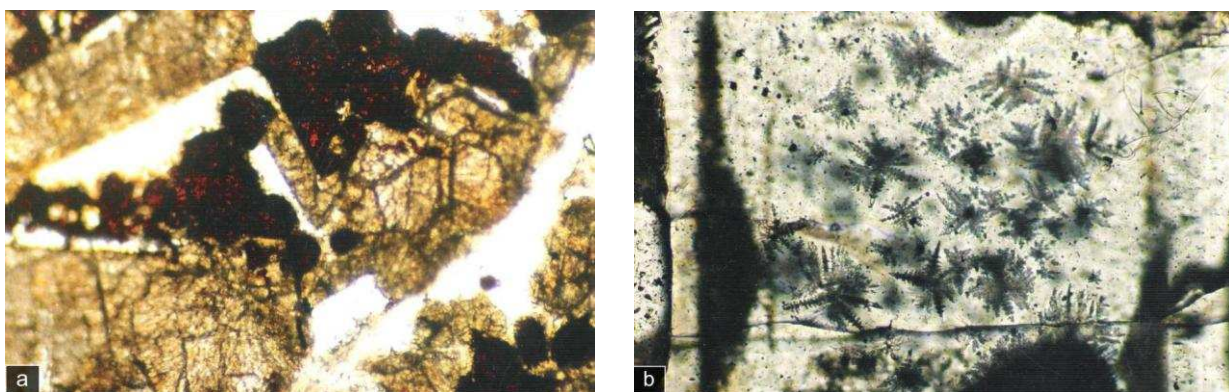


Figure 2. (a) Hercynite (red-brown), fayalite (yellow-brownish), x25, NII; (b) stellate oldhamite crystals and its dendritic growth within a melilite crystal (white grey). Transmitted light, x25, NII.

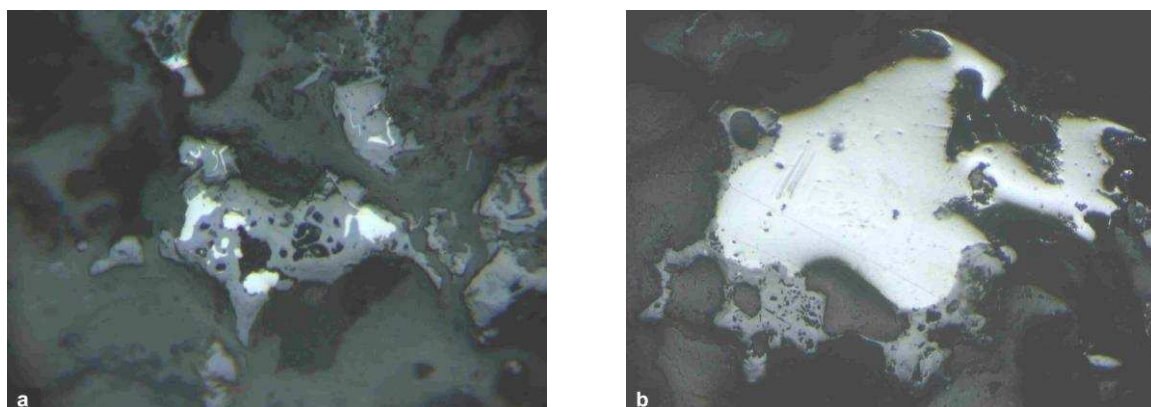


Figure 3. (a) Magnetite (grey) with troilite inclusions (white, anisotropic), x210, NII; (b) Ni-sulphides (pentlandite ?) (white, isotropic) and magnetite (grey, porous), x160, NII.

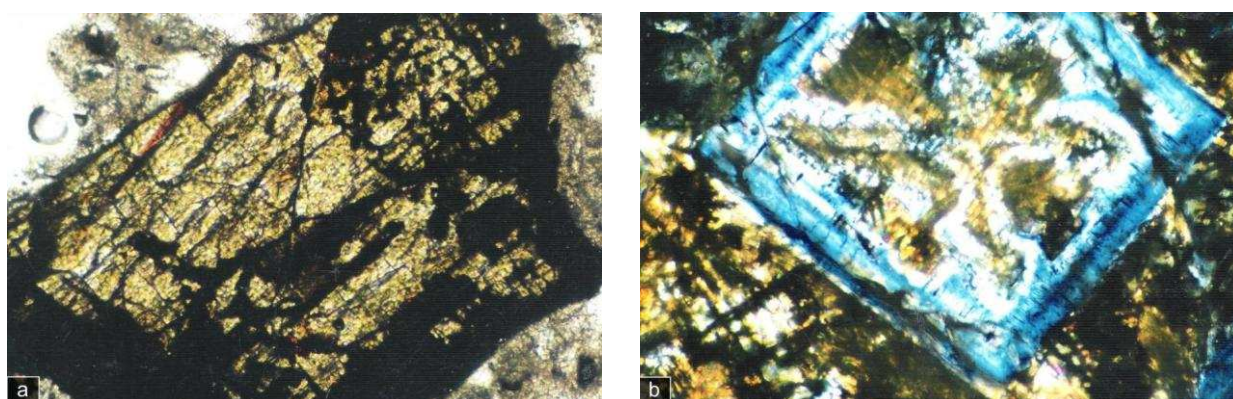


Figure 4. (a) Fayalite (brown-yellow) and wüstite (black), x20, NII; (b) zoned melilite crystal (bluish), x40, N+.

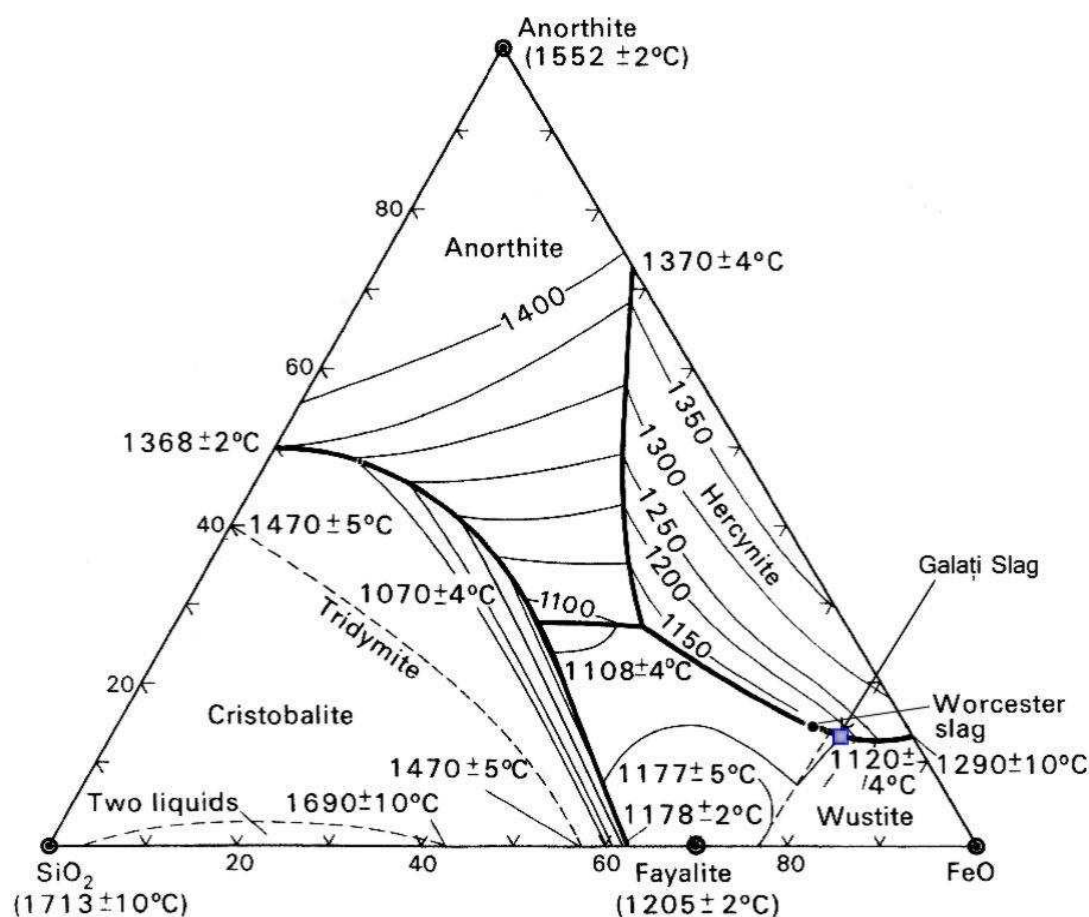


Figure 5. The system anorthite-wüstite-silica phase diagram; GS are situated within FeO right corner in the wüstite-fayalite-hercynite area (Lee, 1974).

4. CONCLUSIONS

In spite of common appearance (black to greyish colors) the microscopic analysis of GS revealed its diverse mineral composition. The determined minerals belong to 5 mineralogical classes: native elements, oxides, sulphides, silicates and phosphates. Most minerals are very rare, occurring in meteorites or on Mars and the Moon (troilite, oldhamite, native Fe). The most dominant mineral phases are those occurring at high temperature, resembling either the sideronitic textures or rapid quenching of high temperature assemblage (skeletal crystals, stellate crystals, e.g. oldhamite in melilite) etc. The mineralogy of GS could be more various and a complex study is in progress. Such a study is necessary to assess the potential for the re-use of GS as construction material. The GS could also be a source of some rare elements.

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