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Influence of the cooling conditions on the nature and the size of the mineral phases in a Basic Oxygen Furnace (BOF) slag

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ABSTRACT

This paper presents the influence of different cooling conditions on the nature and size of the major mineral phases present in a BOF slag. XRD, SEM and image analysis are used. The objective of this work is to optimise the industrial process in order to better recycle BOF slag.

INTRODUCTION

Europe has today a double challenge. First the pressure on natural resources must be reduced. Second, the emissions of greenhouse gases have to remain in the objectives set by the Kyoto protocol (down 8% over 4 years).

The slag is produced by the industrial processes of iron and steel. About 2/3 of the slag are reused after different cycles prior preparation. Blast furnace slag for example, after granulation and grinding, are for the most part reused in the cement manufacture and contribute to saving CO₂ emissions (representing 2 million of tons in France).

The quantities are extremely important because about 100 kg of BOF slag are produced per ton of steel. In France, this represents 1.2 million tons of slag produced each year. But depending on the type of slag, wide disparities in the recycled quantities exist. While the blast furnace slag has a recycling rate close to 100%, this rate is lower for BOF (basic oxygen furnace) slag.

The current valorization markets are primarily in aggregates for roads, embankments or harbour works. However, for road applications, the swelling due to hydration and carbonation of the free lime and free magnesia contained in the slag is highly problematic. The third of slag production is not recycled in France, representing 330 000 tonnes per year which are stored on site, or landfilled.

To a lesser extent the BOF slag are used in very small quantities for fertilizer and agricultural amendments or in the cement manufacture, as a raw material providing lime and iron oxide. Murphy *et al.* (1997) and Tsakiridis *et al.* (2008) notably characterised clinkers prepared with the using of a small fraction of BOF slag. To maximize the current recycling (especially limit the quantities of free lime and free magnesia) and

consider other valorizations, it is important to investigate BOF slag and in particular studying the influence of treatments performed on liquid slag and its cooling.

The aim of this study was to investigate the effect of different cooling conditions on the properties of the BOF slag. The work particularly focused on studying the thermochemical processing, the phase combinations, the mineralogical and microstructural changes that occur in the slag since the end of the conversion process (around 1600°C) until the cooling at room temperature.

MATERIALS AND METHODS

Materials

A BOF slag with an average chemical composition was selected among eight other representative samples from an industrial site (Table 1, details in Bodenan *et al.*, 2009).

Table 1 : Chemical composition of the studied slag measured by ICP-AES (oxide weight %)

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	P ₂ O ₅	LOI 1000°C
wt %	12.8	0.7	1.4	18.4	2.9	5.2	52.4	2.3	0.3

* All iron is expressed under FeO (Iron speciation : 1,3% Fe⁰, 12,7% Fe^{II} and 9,0% Fe^{III})

Three cooling treatments have been studied: first an industrial cooling which is the original slag from the industrial site, representing the industrial process (cooling time estimated between 24 and 48h, with an important skin effect). Then two coolings have been reproduced in the laboratory from 1600°C to ambient temperature (Figure 1): a very rapid cooling (quenching water) and a slow one of about 72 hours, which gets closer to the thermodynamic equilibrium. For both, the same procedure was followed. Approximately 15 grams of slag (size ≤ 4 mm) were introduced into platinum crucibles. After heating to 1600 ° C (ramp to 300 ° C/h) and a level of 5 hours at this temperature, cooling was conducted.

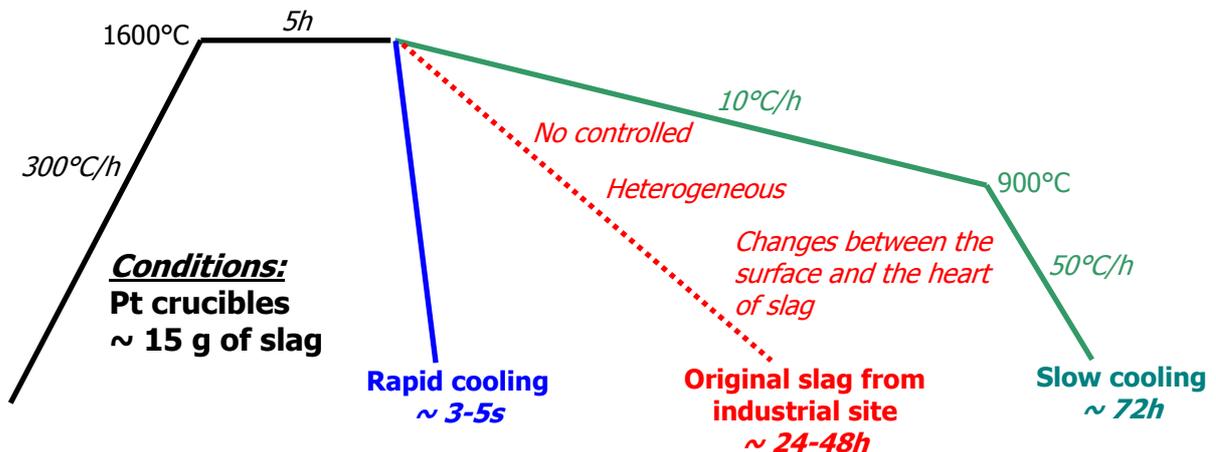


Figure 1 : Scheme of the protocol used for cooling.

Methods

Thermodynamic predictions were performed on FactSage. This software allows the study of materials composed by a mixture of pure components at the thermodynamic equilibrium. Solid, liquid and gas phases are estimated at the thermodynamic thanks to specific models.

As all results are expressed at the equilibrium, it should be noted that the calculation is obtained regardless of cooling rate because there is no consideration of the kinetics in these calculations. The modelling of transformations in slag allows the prediction of phases, the determination of solidus and liquidus compositions and the conditions for the crystallization of main components.

Different analytical techniques were used to characterize the samples. Results of XRD, SEM and optical microscopy are described in this paper.

RESULTS

Thermodynamic prevision

Starting from the composition of the slag (Table 1), the objective was to predict the evolution of the solid phases as a function of temperature. Phosphorus and sulfur were not taken into account. Calculated major phases are only shown on Figure 2.

The oxygen activity is difficult to determine precisely. Indeed, between the end of conversion of steel and the total cooling of the slag, several oxidation states are taken into account in the kinetics. In the converter slag is in equilibrium with iron metal ($p_{O_2} \sim 10^{-12} - 10^{-14}$ atm). At the end of cooling, the slag at the border of the casting is in contact with air and thus is oxidized ($p_{O_2} = 0.23$ atm). On the contrary conditions are less oxidised when approaching the center of the casting.

Extreme behaviours -low and more oxidising conditions- were calculated. In Figure 2 a schematic representation of the evolution of each phase with temperature is presenting for medium oxidising conditions.

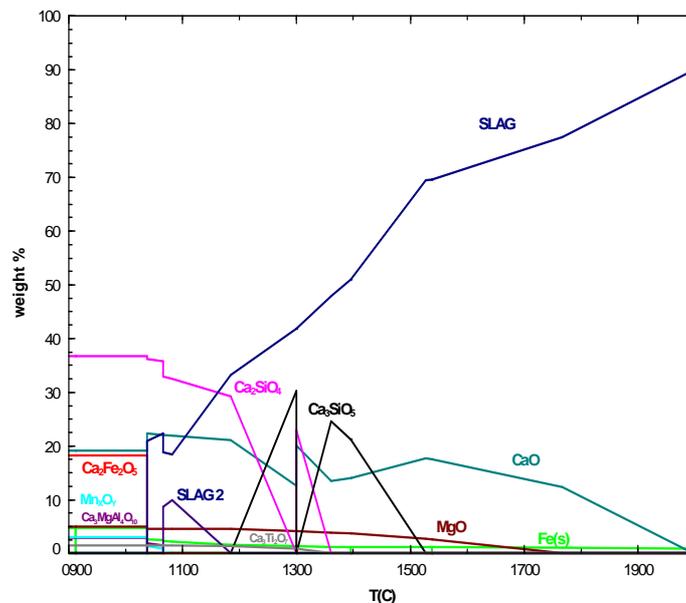


Figure 2 : Prediction of the behavior of the slag with temperature for medium oxidising conditions.

According to FactSage predictions, slag is mainly liquid when temperatures are close to the temperature of the end of steel conversion (1650°C). At 1650°C, between 10% and

20% of CaO is observed. Under reducing environments, it seems that MgO may also be observed around 1650°C. With cooling Ca_3SiO_5 is transformed into Ca_2SiO_4 and CaO around 1300°C in oxidizing environment and $\text{Ca}_2\text{Fe}_2\text{O}_5$ also appears at this temperature. Around this temperature the amount of slag decreases. Under reducing conditions the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ is delayed by an increasing amount of slag between 1300 and 1100°C. Also under reducing conditions, iron is liquid at high temperatures (above 1550°C) and solid iron could be observed between 1550 and 1350°C. Small amounts of magnesium and manganese oxides and to a lesser extent $\text{Ca}_3\text{Al}_2\text{O}_3$ and $\text{Ca}_3\text{Ti}_2\text{O}_7$ can be observed. However under reducing conditions the magnesium oxide crystallizes at higher temperatures.

Experimental results

XRD analysis

The XRD (Figure 3) allows the identification of phases present in each sample. The diffractograms show peaks characteristic of crystalline phases. The background of the diffractograms is relatively constant and no increase or presence of large diffusion bands is observed suggesting a very limited part of amorphous phase in all samples even in the quenched one.

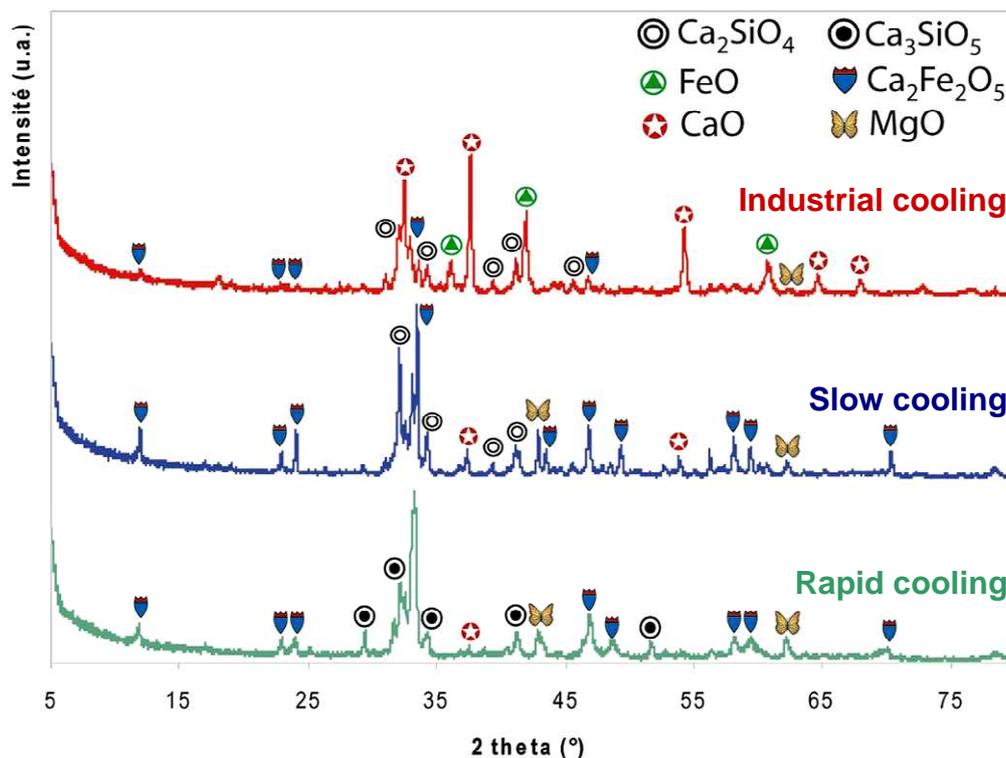


Figure 3 : X-ray diffraction of samples of BOF slag after industrial, slow and rapid coolings.

The industrial slag contains many phases: free lime (CaO), calcium silicates, wustite (FeO), calcium ferrites and periclase (MgO). Calcium silicates are mainly identified as Ca_2SiO_4 . Srebrodolskite ferrite formula is approximated by $\text{Ca}_2\text{Fe}_2\text{O}_5$ with possible substitutions of Fe by Al and Ti.

In the slowly cooled slag, the same phases are observed: calcium silicates, mainly as larnite (Ca_2SiO_4), calcium ferrites very close to the stoichiometry $\text{Ca}_2\text{Fe}_2\text{O}_5$, although some substitutions of Fe can be considered. Lime is observed but the quantities are weaker than previously in industrial cooling. Periclase and manganese oxides ($\text{Mn}_{2.03}\text{O}_4$) are also identified on the diffractogram.

Water quenching slag is composed of calcium silicates (Ca_3SiO_5 and Ca_2SiO_4), calcium ferrite with important substitutions, magnesium oxides and a small amount of CaO.

Identification of phases by SEM

Scanning electron microscope observations coupled with EDS spot analyses allow determine each phase accord to XRD results.

In industrial cooling (Figure 4), three major phases were detected. A first phase consists as crystals of various sizes and is mainly composed of calcium and silicon with very low amount of iron oxide. It can be identified as calcium silicates. Two different types of calcium silicates are highlighted (details of their formations are given in Bodenan *et al.*, 2009). A second group composed of several phases may be explained by the presence of both lime and calcium ferrite. In these phases, the presence of manganese and/or magnesium in small quantities is highlighted. According to SEM observations, the calcium ferrites correspond to the small white crystals, while the darker phase seems to correspond to free lime. A third phase, which appears clearer and seems to be the matrix, is mainly composed of iron and magnesium oxides, and also of manganese oxides in small quantities.

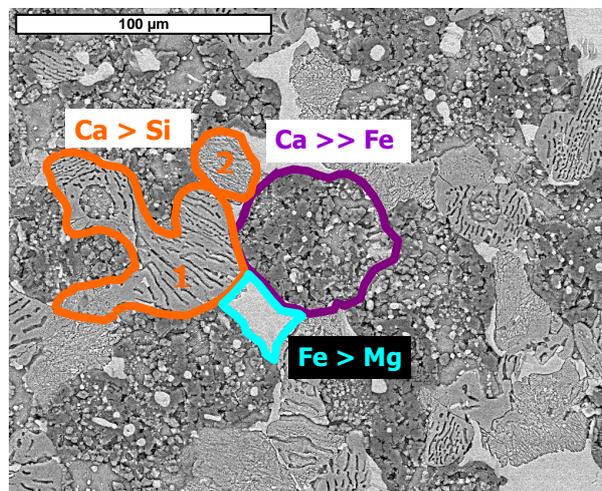


Figure 4 : SEM pictures of industrially cooled slag.

In studying the slowly cooled sample (Figure 5), the first conclusion from SEM observations concerns the size of the crystals: they are larger due to a better crystallization. Under these cooling conditions, the sample is closer to the equilibrium.

Again 3 types of phases are observed:

- A first phase consisting of very large homogeneous crystals, representative of calcium silicates.

- A second phase composed of very dark crystals, rather small in size and relatively pure, representative of well crystallized periclase.
 - A final phase consisting mainly of calcium and iron indicative srebrodolskite ferrite type, with small amounts of Al, Si and even Mg and Mn.
- It is important to note that unless the sample undergoes an industrial cooling; no presence of lime is underlined suggesting that all calcium is in the form of calcium silicates and calcium ferrite.

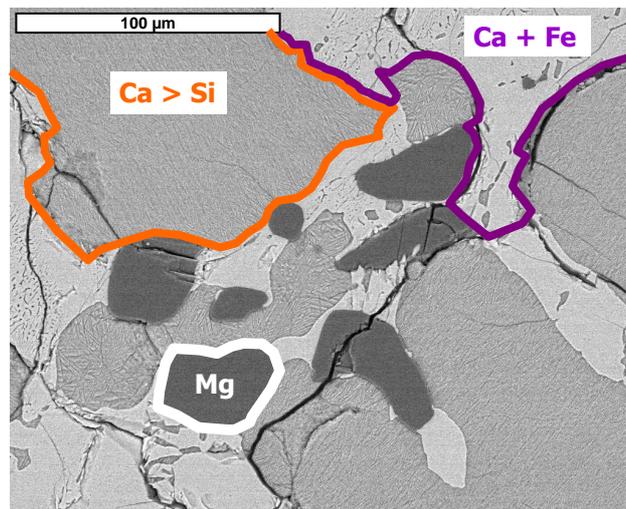


Figure 5 : SEM pictures of slowly cooled slag.

In the case of rapid cooling (Figure 6), slag samples look completely different. Quenching resulting in a rapid and low crystallization, only small crystals mainly in dendritic shapes are observed. In these conditions, it is difficult to clearly identify each phase. The analyses are more heterogeneous. However, it is revealed that the dark parts correspond mainly to calcium silicates that crystallized first with cooling. Analyses reveal the presence of a small amount of iron. The clearest parts are composed mainly of calcium and iron, and correspond to the calcium ferrite, possibly associated with lime. Magnesium, manganese and/or silicon may also be analyzed in significant quantities in this phase.

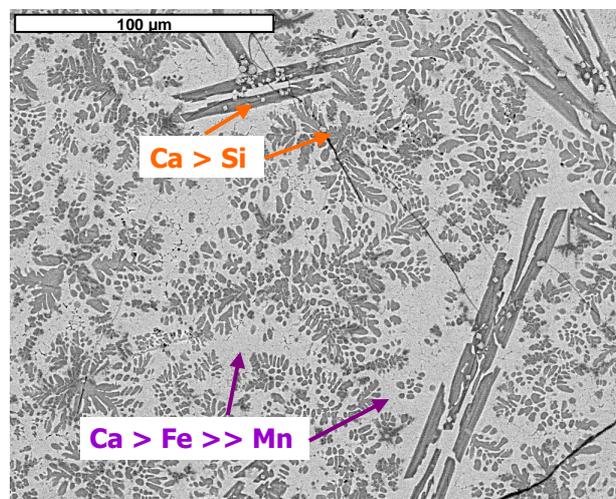
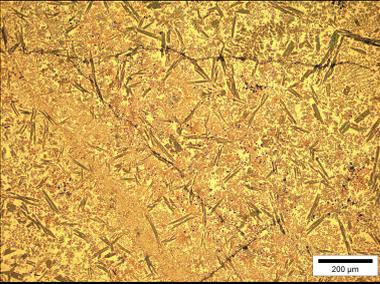
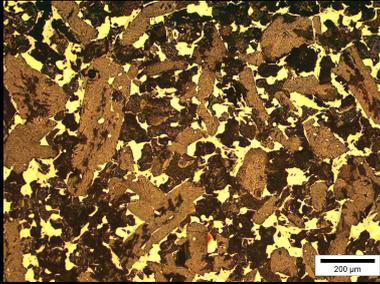
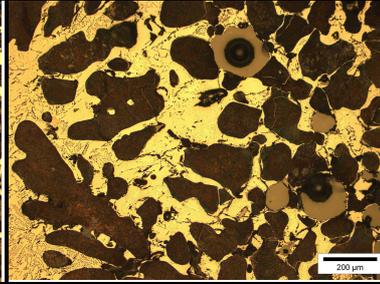


Figure 6 : SEM pictures of rapidly cooled slag.

Image analyses

From the pictures obtained by optical microscopy, some analyses were performed to determine the average size of crystals and the distribution of each phase. The results are summarized in Table 2.

Table 2 : Main results obtained from optical microscopy and image analyses.

Rapid cooling	Industrial cooling	Slow cooling
		
Small dendritic crystals (3-10 µm) and larger (20-80 µm length) [Ca _x SiO _y]	Heterogeneous crystals. Average size of silicates : 50-150 µm	Homogeneous crystals. Average size of silicates : 180-250 µm
Calcium silicates : 56% Calcium ferrites : 44%	Calcium silicates : 40% Calcium ferrites : 44% FeO/MgO : 16%	Calcium silicates : 62% Calcium ferrites : 30% MgO : 8%

The size of the crystals differs significantly depending on the speed of cooling. Rapid cooling shows some fine and elongated crystals of around 20 to 80 µm. The majority of the crystals observed are small dendrites from 3 to 10 µm. In industrial cooling, the crystal size is heterogeneous and around 50-150 µm for calcium silicates. In the case of slow cooling, these sizes are more homogeneous around 180 to 250 µm. The overall size of the crystals is more uniform and larger. The analyses of the distribution of phases highlight two major phases: calcium silicates and calcium ferrite. Close to thermodynamic equilibrium (slow cooling), the partition of each phase is improved.

CONCLUSION

The main identified phases are calcium silicate (with Ca₃SiO₅ and Ca₂SiO₄ theoretical formula), calcium ferrite (Ca₂Fe₂O₅ theoretical formula), free lime (CaO), wustite (FeO) and periclase (MgO). The cooling rate has a significant influence on the quantities of each phase observed. For example, the quantities of CaO and Ca₃SiO₅ in the slowly cooled slag are very low, while the proportion of Ca₂SiO₄ and crystallized MgO is higher in this case. With the optimization of the cooling, the quantities of free lime and free magnesia can be controlled in the slag to improve the stability of the product for applications as an aggregate. The quantities of glass are very low, even with the rapid cooling experiment.

It is observed that the size of crystals differs significantly depending on the cooling time. A slow cooling promotes the growth of crystals. The results are particularly significant with silicate phase. From sizes around 10-50 µm for rapid cooling, crystals can reach 300 µm in the case of slow cooling. The size of periclases is also changing.

All the results are well correlated to the FactSage calculated sequence of cooling:

- Slag is mainly liquid at 1650°C and CaO is the main solid phase.
- During the cooling, calcium silicates (Ca_3SiO_5 form) appear first.
- Around 1300°C Ca_3SiO_5 is transformed into Ca_2SiO_4 and lime (CaO).
- The last phase to crystallize in large quantities is the calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$).
- Calcium, magnesium and manganese oxides are also highlighted in concentrations below 10 wt%.
- In very low quantities, multiple oxides may also be highlighted ($\text{Ca}_3\text{MgAl}_4\text{O}_{10}$, $\text{Ca}_3\text{Ti}_2\text{O}_7$...).

Electron microprobe analyses and high temperatures measurements (thermic analysis, XRD) are underway to precise the composition of each phases and the phases transformations observed above 1100°C.

REFERENCES

Bodéan F., Gautier M., Rafai N., Poirier J., Piantone P., Franceschini G., Moulin I., Chaurand P., Rose J. (2009) Phosphorus speciation in dicalcium silicate polymorphs of basic oxygen furnace (BOF) slag – Preliminary results. *WASCON Proceedings, Lyon*.

Murphy J.N., Meadowcroft T.R. and Barr P.V. (1997) Enhancement of the cementitious properties of steelmaking slag. *Canadian Metallurgical Quarterly*, 36, 315-331.

Tsakiridis P.E., Papadimitriou G.D., Tsvilis S. and Koroneos C. (2008) Utilization of steel slag for Portland cement clinker production. *Journal of Hazardous Materials*, 152, 805-811.

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