FOLLOW-UP AND MINERALOGICAL CHARACTERIZATION OF FREEZE LINING EVOLUTION: A RECORD OF FURNACE LIFE

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Abstract

Refractory linings of metallurgical furnaces have two main purposes: to control the heat flow, and to contain high temperature liquids (metal and slag). Through a proper management of heat flows, a layer of slag called freeze lining crystallizes on the internal walls of the furnace thereby protecting the bricks from the very corrosive high temperature liquid slag. The thickness, stability and properties of this frozen slag are key parameters for the performance of a safe and stable process. In situ observations of the crystallization process during furnace operations are very difficult. To overcome this difficulty, the present work proposes a combination of heat flow monitoring, numerical modeling of heat transfer and the mineralogical characterization of the residual freeze lining after the furnace operation. The combination of these tools helps with the management of the process and the understanding of how to preserve the thermal balance of the furnace and the stability of the refractory lining. Within a pilot furnace freeze lining, physical and chemical properties change depending on the operation parameters. The thickness of the free lining is one of the most important process variables to follow-up. An inverse heat transfer issue is solved using the software FLUENT in a simplified 2-D axisymmetric geometry of the furnace. After completion of the pilot, the freeze lining of the furnace is analyzed and characterized. All the significant evolutions in the operating parameters (temperature variations, slag chemistry changes) are recorded within the oxide layers of the skull. Additionally to characterization, the crystallization paths that occurred during the process can be calculated using thermodynamic equilibrium computations. This work provides a multi-disciplinary approach to understand usually unobservable phenomena within the furnace, allowing an estimation of the thickness, and physical and chemical properties of the freeze lining inside furnace.

Keywords: Metallurgy, freeze-lining, thermodynamic, characterization, Qemscan

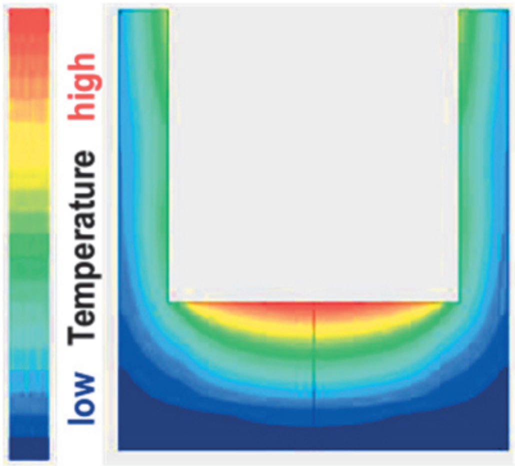
1. INTRODUCTION

In primary metallurgy, furnace sidewalls are subjected to highly variable thermal, mechanical and chemical conditions. When the sidewalls of a furnace are very conductive and high cooling rates are applied on the outer face, the hot slag solidifies onto the inner sidewall. Solidified slag creates a physical and thermal protection of the lining which plays a major role in a furnace lifetime, especially when the process generates important heat fluxes (>7 kW/m²). The stability of this frozen slag (called freeze lining) is therefore a key parameter to be carefully monitored and the usually performed by placing pairs of thermocouples inside the lining walls. These thermocouples allow the operator visualize hot spots on the lining or freeze lining loss. Heat fluxes through the sidewalls can also be evaluated.

2. SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

2.1. Pilot furnace and thermic measurements

Pilot campaigns are useful to test the impact of chemistry change in the feeding of the furnace, as well as to investigate process points and evaluate freeze lining stability. The size of a pilot furnace being quite small, the inertia of the process to a change of a process parameter is very short. At ERAMET, it is therefore a common procedure during process investigations accompanied by chemical analyses of the charge and the tapped liquids. Thermal measurements are regularly performed at each shift during a pilot campaign. The pilot furnace under consideration in this study is an electric device of 1.2 m in diameter and 4 m in height high which was divided in 6 sectors. During the pilot campaign, thermocouples were implanted inside the lining. Flow rate and temperature of the water used to cool down the sidewalls were also monitored in order to evaluate the heat balance at each sector. A numerical model was developed at ERAMET Research (using Fluent® and Scilab softwares) in order to use these data as input parameters to evaluate the freeze lining state all along the pilot campaign (**Fig. 1**). The numerical model aids to compare global heat balance performed with the water measurements to pseudo-1D heat flux calculations compiled with pairs of thermocouples thermic measurements with the purpose to estimate the overall heat flux through the entire height of the furnace for each sector (with 2D axisymmetric steady state hypothesis). Measurements and their interpretation allow on-line evaluation of growth and resorption of the oxide layer. Changes of process conditions (power load, excessive feeding…) could also be clearly traced during thermal measurements.



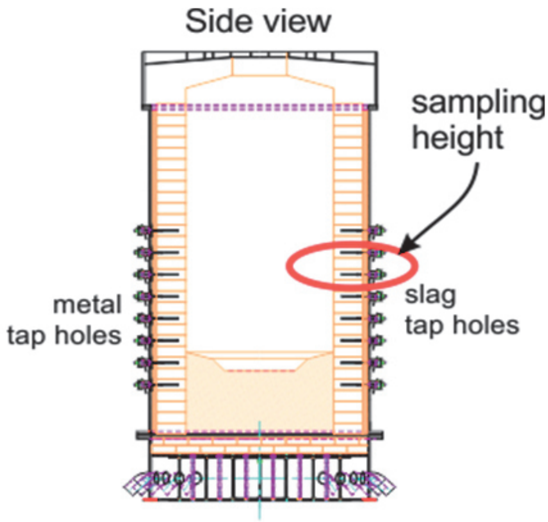


Fig. 1 Example of a thermal state of the furnace during one shift modelled with FLUENT (left), and side view of the used furnace (right)

2.2. Dig-Out and sample preparation

A large collection of samples has been taken at all levels on one side of the furnace. Observations of each led us to choose a particular bloc of freeze lining for detailed characterization. The thickness of the freeze lining varies with the height in the furnace, but also with the distance from the slag tap hole. In order to make interpretations, we choose a level where we assumed that a liquid slag was permanently present during the four weeks of the pilot campaign: the slag tap hole level (**Fig. 1**). To avoid thermal disturbances in tap hole proximity, a zone in some distance to the tap hole was chosen to be a more representative zone of the furnace. The sample taken comprises the complete thickness of the oxide skull, from refractory brick to the hot face in contact with the liquid slag (20 cm long). It was cut into two pieces (too large for SEM observations), and embedded in Specifix resin. Afterwards, the blocks were polished using a Struers RotoForce-3/RotoPol-31 device with silicon carbide paper disks successively from 220 µm down to a 5 µm medium-grain size. The polishing process was finalized on a diamond covered drape (1 µm grain size). Polished sections were then carbon coated (25 nm thick) to render them conductive for SEM analysis.

3. THERMODYNAMIC MODELLING

Thermodynamic calculations were performed by using the MTData® software to simulate oxides and mattes systems. In combination with MTData®, a ThermoCalc® software package was also used to study steel making, alloys and super-alloys processes. The chemical compositions of the slag and the metal tapping were used in combination with estimated temperatures of the hot liquids inside the furnace in order to model and predict the phases inside the furnace, assuming that the process is in equilibrium.

3.1. Analytical methodology

During the pilot essay, slag was tapped every 4-5 hours. A complete analytical chain was installed to support its monitoring from sampling, crushing and homogenization of each step of tapping, to XRF analysis after fusion of the sample. This whole analytical process provides chemical analysis before the next tapping step.

3.2. SEM-Qemscan methodology

A FEI Quanta 650F microscope, coupled with two 30 mm² Brucker EDS detectors, was used at ERAMET Research for Qemscan measurements. The Qemscan software provides pixel by pixel chemical analyses which are used to attribute each pixel to a mineral to construct a dedicated database. Due to the large size of the block, a specific kind of measurement has to be launched (BSE centroid), leaving only few unidentified pixels (dark squares of “Others” in the mapping, **Fig. 2**). Nevertheless, high resolution mineralogical mapping allows identifying very few amounts of minor phases, and statistic data on mineral relationships.

4. RESULTS

4.1. SEM observations and Qemscan mapping

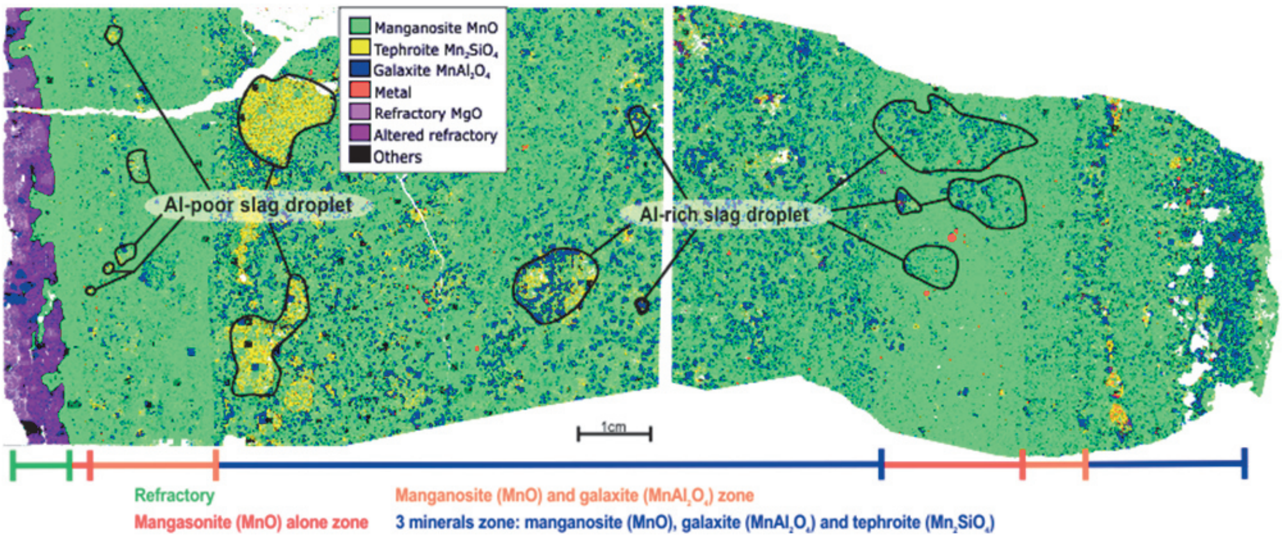


Fig. 2 Qemscan mapping trough freeze lining from refractory bricks (left) to slag contact (right)

Qemscan mapping led to the identification of different zones (**Fig. 2**): a manganosite (MnO) alone zone, a manganosite-galaxite ($MnAl_2O_4$) zone, and a three minerals (manganosite-galaxite-tephroite, Mn_2SiO_4) zone (**Fig. 2**). Two complete successions of these three zones can be seen in the sample. This freeze lining is in thermodynamic equilibrium with the slag in contact, a change in the mineralogical content of the solid part of this equilibrium follows a change of at least one other parameter, which can be the temperature or the slag chemistry. Sharp and abrupt transitions between zones imply a quick change of these parameters.

In some areas within the skull, round-shaped oxide assemblages appear, sometimes reaching sizes of more than 1 cm (**Fig. 2**). Mineralogically, these droplets are rich in tephroite and poor in manganosite. The overall chemical composition is therefore richer in silica compared to the remainder of the freeze lining. Textural relationships in those parts show that manganosite has dendritic shapes suggesting a quick crystallization.

These droplets represent liquid slag trapped during skull crystallization, and frozen in it at the end of the pilot campaign when the temperature decreases drastically. Along the freeze lining, a dramatic mineralogical change occurs in theses slag droplets, containing only tephroite at the beginning (left part, **Fig. 2**), and tephroite + galaxite at the end (right part, **Fig. 2**).

5. DISCUSSION

5.1. Thermodynamic evolution

The mineralogy of the simple systems, such as e.g. MnO-CaO-Al_2O_3-SiO_2-system, are roughly known for decades [1], and thermodynamic modelling of ferromanganese slag is currently consistent with observations [2, 3]. Thermodynamic modelling applied to tapped slag describes the crystallization path followed by the liquid from liquidus to solidus conditions (**Fig. 3**). Manganosite is the first phase to crystallize at just below 1600 °C, resulting in an enrichment of silicon and aluminum in the liquid. Below 1300 °C, galaxite followed by tephroite are the next phases to crystallize. These two different phases appear at very close temperatures and the crystallization path ended at the invariant point defined by the common crystallization of manganosite, galaxite and tephroite at 1250 °C.

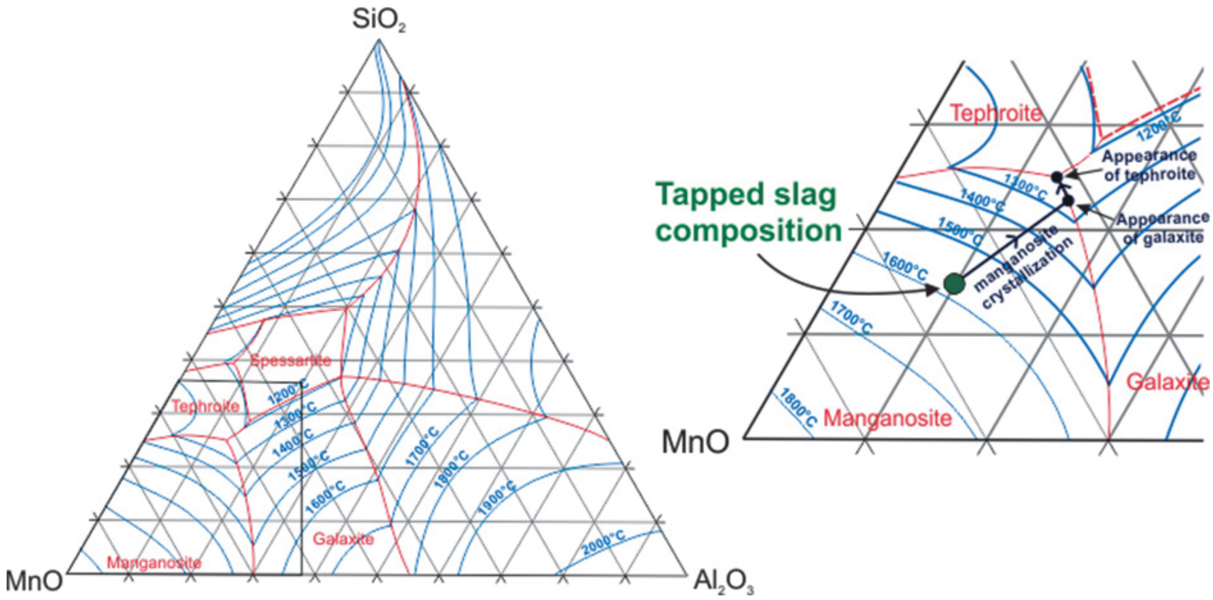


Fig. 3 Phase diagram on MnO-Al_2O_3-SiO_2 system (data from MTData® calculations)

5.2. Chemistry - mineralogy - thermic measurement correlation

The characterization of the sample showed alternations of zones characteristic of high temperatures (just below 1600 °C) and lower temperatures (approx. 1250 °C). The question to which we need to respond is how the history could be aligned to these observations of abrupt changes during the furnace operation.

The temperature evolution inside the lining during the pilot campaign can be explained by means of **Fig. 4**:

- During the three first day, the lining temperature took days to stabilize at the beginning of the pilot, but remained always above the average temperature of later operating conditions. During this period the first layer of freeze lining was formed, this could explain the monomineralic manganosite layer, that is typical for high temperature.
- During the normal conditions of pilot essays, the temperature of the lining decreased to between 200 °C and 300 °C.

- A thermal incident occurred a few days before the end of the pilot campaign, and the temperature inside the lining reached the starting temperature of the pilot. We will see later that was probably associated with a loss of some part of the freeze lining. Nevertheless, another high temperature layer is seen in the freeze lining (manganosite alone zone, like at the beginning) showing that the low temperature layers have not disappeared. The chronological timeline of the freeze lining is therefore probably broken, but it is not possible to establish the thickness of the missing parts.

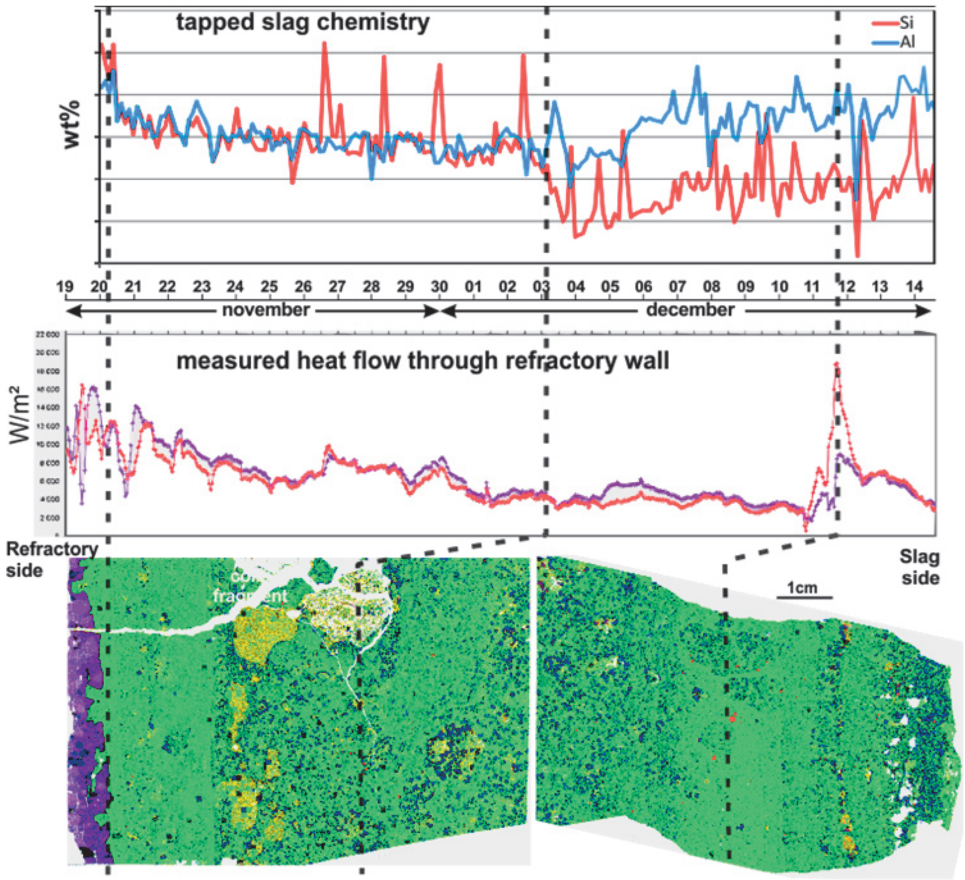


Fig. 4 Correlations between tapped slag chemistry, measured heat flow through refractory wall and mineralogical equilibria in freeze lining

During the pilot campaign, a change of chemistry of the charge was performed (change of aluminum/silicon ratio) to change the slag properties [4]. This caused an increase of the tapped slag aluminum/silicon ratio. Trapped slag droplets observed in **Fig. 2** show the same chemical change. All the significant evolutions in the operating parameters (temperature variation, slag chemistry change) are recorded within the oxide layers of the skull.

5.3. Freeze-lining stability prediction

Mineralogically alternating layers, and local zones of weakness (trapped slag droplets,…) can provide pertinent information to understand and predict physical or chemical destruction of parts of freeze lining. Liquid slag droplets trapped into the oxide skull of the lining are not randomly dispersed (**Fig. 2**). These droplets are absent in the first layer (dense manganosite only zone), and are small in the manganosite-galaxite layers. Large amounts of slag droplets are localized in the three minerals zone, and the second manganosite alone zone (**Fig. 2**). The phenomenon occurs indeed at either a low temperature, or when the already crystallized skull begins to melt. These droplets are the starting points of a mechanic and thermal weakness causing parts of the lining to fall into the furnace.

6. CONCLUSION

This detailed study of freeze lining structures and mineralogy provides information on the entire life of a furnace, with only few gaps during drastic changes of operating parameters. Undoubtedly the story line can be shortened or cut by melting processes, but these phenomena do not seem to be predominant enough to suppress a major part of the history. These observations can be introduced to numeric modelling a numerical modelling, based on on-line thermic measurement, to predict the thickness evolution of a freeze lining.

With a precise temperature monitoring of the furnace, mineral crystallizations on the refractory walls can be predicted in terms of mineralogy and liquid content. The stability of a freeze lining is directly linked to liquid proportions trapped in it, as well as to the solidus temperature of its mineralogical content. Improving the stability a freeze lining is one of the key points to improve the life time of a furnace.

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