PS Converter: Post-morten Analysis of Refractory Materials

/ ISMAEL PÉREZ PINA (1,3), IGNACIO MORENO-VENTAS BRAVO (1, 2*), GUILLERMO RÍOS RANSANZ (3).

(1) Departamento de Ciencias de la Tierra. Facultad de Ciencias Experimentales. Universidad de Huelva.
(2) Departamento de Ciencias de la Tierra. Facultad de Ciencias Experimentales. Universidad de Huelva. Centro de Investigación en Química Sostenible (CIQSO). Universidad de Huelva.
(3) Atlantic Copper S.L.U. Avda. Francisco Montenegro s/n. Huelva.

INTRODUCTION

Refractory materials are widely used in the lining of furnaces to produce metals via pyrometallurgical processes from natural ores and/or recycled scraps. Depending on the process, refractory materials can be made of many different components in order to match them to the specific conditions of the molten bath inside the furnace (Petkov, 2007). This work is focused on the refractory used in the copper industry, which is of magnesia-chromite type.

This refractory is made of raw materials ranging from minerals as: chromite from ore, magnesia, electrofused magnesia-chromite and electrofused magnesia. Among these raw materials, many of them come from mine and others from manufacturing processes like electrofusion in order to purify them and increase their refractory properties to better face the severe conditions in the furnaces not only caused by the high temperature but also by the chemical attack from molten bath (mainly the slags). The main challenges a refractory material must face are the following (Petkov, 2007; Goñi, 2004):

1.- High temperature (>1250ºC).
2.- Formation of new components (olivine, spinel) on refractory hot face (Bazán, 2012).
3.- Thermal shocks, mainly in batch processes like emptying and replenishment of the Pierce-Smith converter.
4.- Spalling effect due to the developing of micro-fractures at the hottest end of refractory bricks.
5.- Mechanical shocks and mechanical erosion provoked by the movement of the molten bath within the furnace.

Different phases present in refractory will be shown in this study for two scenarios: brand new and after working cycle in copper making furnaces (conversion stage).

This work is focused on the study of refractory bricks after a working campaign.

PROCESS CONDITIONS

The Pierce-Smith converter type is the most widely used furnace in the copper industry for the conversion of the matte, which come from the smelting stage.

The main aim of the conversion is the iron and sulphur removal, transforming the matte into blister copper. After this, the pyrometallurgycal process continues through firing and electro refining. The conversion reactions consist in two separately steps named slag blow and copper blow (Davenport, 2002):

$FeS + O_2 + SiO_2 \rightarrow Fe_2SiO_4$ (slag) + SO_2
$3\ FeS + 10\ 02 \rightarrow Fe304$ (slag) + $3\ SO2$
$Cu_2S + O_2 \rightarrow 2Cu$ (blister copper) + SO_2

The sequence of them is governed by the Gibbs energy according to the Ellingham diagram (Fig. 1). Minor elements present in ore are removed within the process.

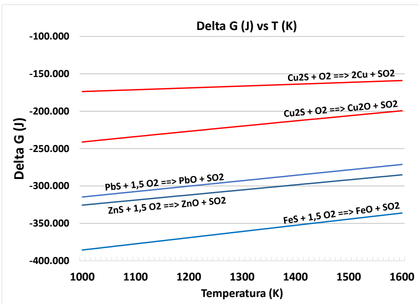

fig 1. Ellingham diagram for main reactions in the conversion step for copper making (from Fact Sage).

All reactions are exothermic, so the generated energy keeps the bath molten (autothermic). To go further, cold material is added during the process (scrap and reverts) in order to keep the temperature in the range of 1200-1350ºC because the higher working temperature, the shorter life for refractory.

The gas, which contains SO_2, is removed continuously to acid plant in order to produce sulphur acid. On the other hand, the slag (fayalite and magnetite) is removed via skimming through the mouth of the converter. At the end of the conversion process, the blister copper is also removed (Davenport, 2002).

PIERCE-SMITH CONVERTER

The main elements of the converter are the followings (Fig. 2):

1.- Horizontal cylinder with roughly 10m length and 4m diameter lined inside with refractory materials.
2.- 45-55 tuyeres in the lower part through air is injected to the bath.
3.- A mouth in the middle of the cylinder of 2 x 2 m. It is used to introduce the matte, silica, reverts and scrap as well as to remove the products (slag, blister copper and gas).
4.- The cylinder rolls on four wheels.

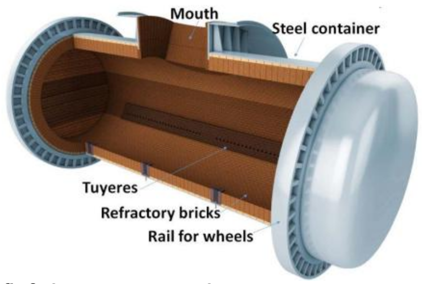

fig 2. Converter drawing (Open inside view)

Due to the wear of refractory bricks, it is necessary to reline the refractory according to the wear. The most damaged area is around the tuyeres and the upper part of them, because of the

palabras clave: Refractario, Cobre, Convertidor. | *key words:* Refractory, Copper, Converter.

* corresponding author: bravo@uhu.es

movement of the bath due to the bubbling and splashing.

The fabrication process for refractory consists in:

1.- Mixing of the raw materials; that were previously crushed and grinded.
2.- Making the bricks by pressing (2000-2500 tn/cm²).
3.- Heat treatment at 1800ºC.

ANALITICAL METHODS

For this study, samples from brand new refractory have been taken as well as samples from refractory after working campaign in a converter (a campaign is composed by 250 batches). The samples were taken from refractory bricks as is shown the Fig. 3.

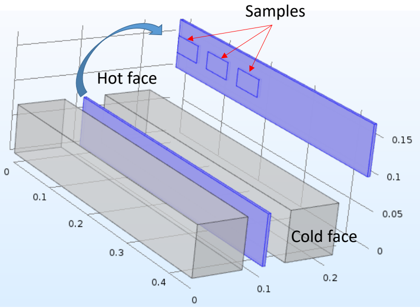

fig 3. Scheme of sampling from a refractory brick.

Those samples have been polished and analyzed using both Scanning Electron Microscopy and energy dispersive X-ray microanalysis (SEM-EDS).

RESULTS

Brand-new refractory

According to the back-scattered electron (BSE) images, we can check the association between the raw materials present in the brick after the making up. Electrofused magnesia-chromite is present in two different ways: as grain or as a ring perfectly associated around pure magnesia grains. Chromite from ore is found as delivered grains.

In most cases we find monticellite filling both the intergranular and intraganular spaces; it was not in the raw materials so we can conclude that it was formed during the making up process of the brick as result of melting reactions.

Refractory after working conditions

The post mortem carried out for this study shows that new phases have been formed depending on the studied area of the converter.

In bottom areas, copper is the only one present material, which has interacted with the brick (Fig.4 & Table 1). This interaction appears as infiltration thanks to the open porosity. This effect can reach 25 cm, from the inner face. The length of the copper filled pores depends on the temperature profile of the brick (the limit is the solidus temperature of copper).

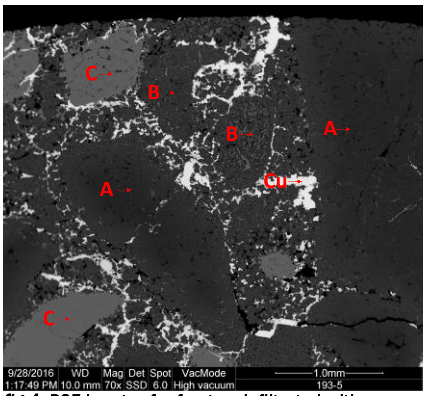

fig 4. BSE image of refractory infiltrated with copper. A=Magnesia, B= electrofused Mg-Cr, C=Chromite from ore; In white is the infiltrated Cu.

Wt%	A	B	C
O	36.9	36.0	36.2
Mg	56.7	51.3	12.6
Cr	3.5	8.5	40.3
Fe	2.2	4.2	5.4
Al	0.7		5.5

Table 1. EDS of main components in fig 4.

Regarding other areas, usually the slag penetrates the brick through both the open pores and micro-fractures, reacting with the refractory's solid phases, promoting the refractory wear (Fig.5 & Table 2). This is the main reason for refractory degradation.

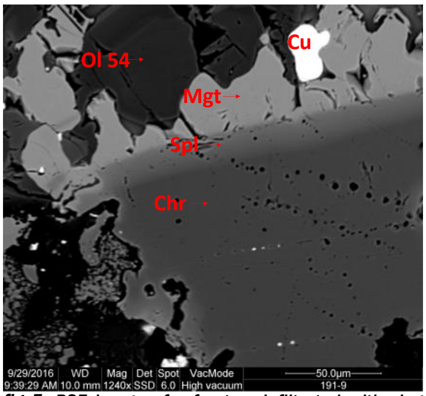

fig 5. BSE image of refractory infiltrated with slag and the new formed phases. Chr: chromite from ore; Spl: magnesia-chrome spinel; Mgt: magnetite; Ol54: olivine Mg# 54.

Wt%	Chr	Spl	Mgt	Ol54
O	36.2	33.1	27.9	39.3
Mg	13.3	7.9	1.3	11.5
Cr	40.0	36.5	1.2	
Fe	4.2	17.0	69.6	22.0
Al	6.3	5.5		
Si				27.2

Table 2. Analysis of main components from fig 5.

The resulting reaction between the melted slag and the refractory materials produces a new formation of olivine in slag's veins, and new generation of refractory's spinels. After brick wearing, spinels are mainly magnesioferrite, chromite and magnesiochromite, Present magnetite comes from the slag.

CONCLUSIONS

During operation in conversion furnaces, phases from the molten bath (mainly copper and slag) penetrate into the refractory materials through the open porosity. Infiltrated copper reaches deeper areas in the refractory; its infiltrating capacity is longer than of the slag. The higher solidus of the slag system prevents it to penetrate more deeply in the refractory brick.

Regarding chemical attack, copper does not react with refractory materials; by contrast, great attack is carried out by the slag-refractory interaction. We can conclude that refractory disappears as a consequence of this attack by means of both dissolution of magnesia in slag and formation of new phases (olivine, spinel).

ACKNOWLEDGMENTS

We deeply thank Atlantic Copper SLU for the funding of this research work and the support for sampling.

REFERENCES

Petkov, V. (2007): Degradation Mechanisms of copper anode furnace refractory linings. Doctoral thesis, Leueven Univ., Heverlee.
Davenport, G.W., King, M., Schlesinger, M., Biswas, A. (2002): Copper, Elsevier Science.
Goñi, C. (2004): Desarrollo y aplicación de modelos de corrosión refractaria para un convertidor Pierce Smith. Doctoral thesis, Universidad de Concepción, Chile.
*Bazán, V., Brandaleze, E., Parra, R., Goñi, C. (2012): Penetration and dissolution of refractory of magnetite-chrome by fayalite slag. DYNA **79**(173), 48-55.*