

## Microtextural aspects of the chemical corrosion in Pierce-Smith converters (PSC)

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Microtextural studies are often the basis for projects proposing improvements in the quality of refractory coatings that come into contact with aggressive molten material. The material used for this analysis either comes from laboratory-level corrosion tests or from furnace walls and linings that have come to the end of their working cycle.

This article aims to evaluate the reach of the chemical wear mechanism with a microtextural study of samples that have been in industrial use. However, other wear mechanisms should be taken into consideration; acting in parallel they can be even more important quantitatively than the chemical wear itself which results from the microtextural analysis of the samples.

*Keywords:* Pierce-Smith Converter. Wear mechanisms. Refractory. Microstructure.

### Aspectos Microestructurales de la corrosión química en un convertidor (PSC)

Los estudios microestructurales han estado frecuentemente en la base de proyectos orientados a la mejora en la calidad de los revestimientos refractarios destinados a estar en contacto con metales fundidos. Los materiales empleados en este trabajo proceden de las paredes de hornos que están en la fase final de su vida útil. El trabajo intenta asociar el mecanismo de corrosión química existente con las modificaciones microestructurales encontradas en piezas utilizadas en planta. No obstante, debería considerarse que existen otros mecanismos de corrosión, que actuando en conjunción con los arriba descritos podrían ser más relevantes desde el punto de vista cuantitativo que la corrosión química detectada en los análisis microestructurales de las muestras.

*Palabras clave:* Convertidor Pierce-Smith, mecanismos de corrosión, refractarios, microestructura.

### 1. INTRODUCTION

One of the basic processes of copper pyrometallurgy involves the treatment of copper matte (molten solutions of copper and iron sulphides) or white metal (molten copper sulphide) in blister copper (copper saturated in oxygen) in Pierce-Smith Converters (PSC)<sup>1, 2</sup>. An increase in productivity of pyrometallurgical installations that obtain copper in the future can be based on the discontinuous transformation of operations in continuous work or on the average temperature increases of molten material (metals or slag) which intervene in the processes. Under these circumstances, the materials used for coatings must be able to guarantee a minimum of operational hours under maximum thermal effort conditions, both chemical and mechanical.

The microtextural analysis permits comparing us the physical and chemical parameters of samples that have been attacked and those which have not. Within the attacked samples, we have also been able to study the transformations experimented by material originally installed in the PSC, according to the distance to the solid-molten interface.

Nevertheless, even if conclusions made from the microtextural analysis were true, they do not necessarily constitute

a final and sole analysis of real wear experimented by PSC coatings.

The Nodal Wear Model (NWM), has been a tool used in the interpretation and quantitative simulation of differential corrosion processes for electric furnace linings or blast furnace hearths. Once the refractory corrosion mechanisms are known, the corresponding corrosion equations can be established which show the evolution with the wear time lining profiles<sup>2-7</sup>.

Five years ago, the Copper Group (DIMET-Concepción-Chile and Oviedo-Spain), began working on the adaptation of the NWM theory for copper pyrometallurgy. They have particularly focused their attention on the study of differential corruptions produced in PSC coatings. They develop mechanisms and equations for corrosion that affects the most damaged area in the PSCs (nozzles zone)<sup>8-10</sup>. In Table 1, the chemical, physical and mechanical characteristics are shown for magnesia – chromium refractories, material normally used at present in copper metallurgy for coating the PSC nozzle zones<sup>11, 12</sup>.

The importance of price refractory on the cost of the product finished in the extractive metallurgy of copper has

been notably inferior to the one which has meant traditionally in the iron and steelmaking industry. This circumstance has provoked that the research and development of the materials utilized by the steelmaking industry be notably superior to the one that has been carried out in the copper pyrometallurgic. For this reason, publications the works relationship with the CPS coatings will be necessarily scarce. In fact, it could say that in the last four decades, the refractory quality utilized by the CPS linings has been the same: magnesia-chromium refractories<sup>2, 11)</sup>. From ten years ago, the development in the CPS refractory materials have been fundamentally two<sup>11, 13)</sup>:

- Improvement of the direct chemical union between the matrix and dispersed phases, by means of which it was succeeded one increasing in the mechanic cold resistance the product.
- Modify the chemical characteristics of the matrix phase in such a way that their resistance to the chemical attack be similar to the one that has the dispersed constituent (MgO burned or electrofused).

## 2. EXPERIMENTAL PROCEDURE: SAMPLES AND THECNIQUES

The material used for this study, attacked and unused refractory bricks, either comes from laboratory-level corrosion tests or from furnace walls and linings that have come to the end of their working cycle.

The X-ray powder diffraction analysis to identify the mineralogical phases was made with a Philips PW 1729-1710 instrument. The machine settings were 40 mA and 45 kV (Cu- $K_{\alpha}$  radiation;  $\lambda = 1.5418 \text{ \AA}$ ),  $2\theta$  range 5-80,  $2\theta$  step scans of  $0.02^{\circ}$  and a scan step time of 1 s. The samples analyzed were previously grounded as finely as possible.

A CAMEBAX SX-50 electron microprobe analyzer with four dispersive spectrometers was used to analyze the phases of the attacked and unused refractory brick in the PSC coatings. Semi-quantitative analyses of the present elements in the refractory samples were obtained by a MEB JEOL-6100 scanning electron microscope with a secondary electrons detector and a retro-dispersive electrons detector. This instrument was also used to obtain the images to be analyzed by the image analyzer.

Electron microprobe analysis and scanning electron microscope require a very flat and well polished surface, so the refractory samples were mounted in plastic moulds (blocks of  $2 \times 1 \times 1 \text{ cm}$ ). After the pouring resin became hard, the samples were polished.

The analysis of images taken with the scanning electron microscope was carried out with a Quantimet image analyzer (typical instrument of a number of television-based, optical image analyzers) to determine porosity in the attacked and unused refractory brick.

All these instruments belong to the Scientific Technical Services of Oviedo University.

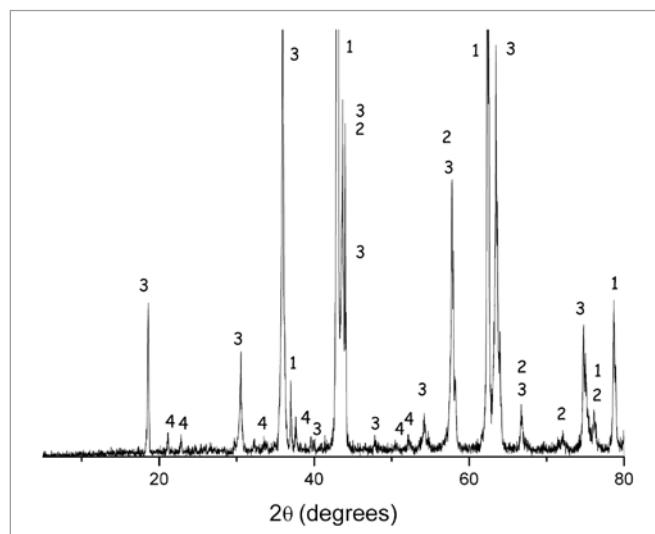


Figure 1.- X-ray diffraction pattern of unattacked refractory. Phases: 1=periclase, 2=alumina-chromite, 3=magnesio-chromite, 4=forsterite.

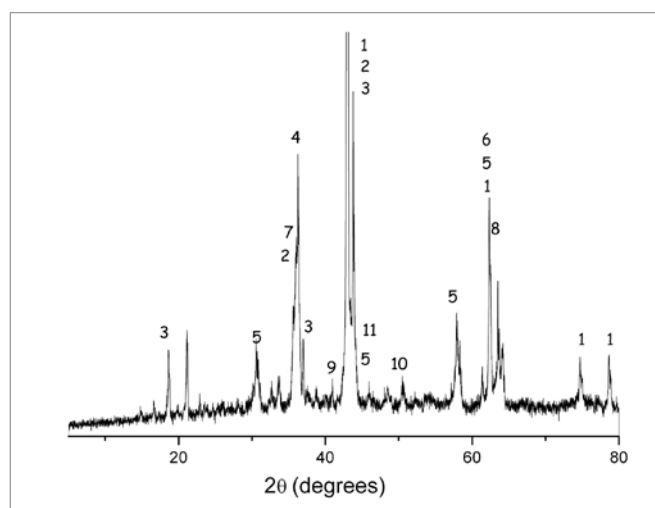


Figure 2.- X-ray diffraction pattern of attacked refractory. Phases: 1 = periclase, 2= $\text{Cr}_2\text{O}_3$ , 3=magnetite, 4=cuprite, 5=iron-chromite, 6=tenorite, 7= $\text{Cu}_2\text{O}$ , 8=magnesio-chromite, 9=hematite, 10=copper, 11= $\text{Cr}_5\text{O}_{12}$

## 3. RESULTS

The X-ray diffraction patterns obtained for the unused and attacked refractories are shown in Figures 1 and 2. The identified phases in the unused sample were the following: periclase ( $\text{MgO}$ ), forsterite ( $\text{Mg}_2\text{SiO}_4$ ), aluminian chromite ( $\text{Fe}(\text{Cr,Al})_2\text{O}_4$ ), and magnesio-chromite ( $\text{MgCr}_2\text{O}_4$ ). In the attacked sample, cupric phases (native copper, tenorite –  $\text{CuO}$ -, cuprite - $\text{Cu}_2\text{O}$ -,  $\text{Cu}_2\text{O}_3$ ) were identified in addition to mentioned ones. These phases were formed due to the chemical attack of the slag to the refractory brick. Moreover, there are some chromium and iron oxides (such as hematite – $\text{Fe}_2\text{O}_3$ - and magnetite - $\text{Fe}_3\text{O}_4$ -) that the unused sample does not have due to the high temperature condition into the converter. The X-ray diffraction analysis is a reflection of the evolution that these products have undergone in the last decade. Usually up until the end of the last century, the presence of chromite ( $\text{FeCr}_2\text{O}_4$ ) was found in the phase analyses of magnesia-chromium

TABLE 1.- CHEMICAL, PHYSICAL AND MECHANICAL CHARACTERISTICS FOR MAGNESIA – CHROMIUM REFRACTORIES.

<b>Chemical analyses (weight %)</b>	MgO	62%
	Cr <sub>2</sub> O <sub>3</sub>	18%
	Al <sub>2</sub> O <sub>3</sub>	8%
	FeO	7%
	SiO <sub>2</sub>	1%
	CaO	1%
	Antioxidants	3%
<b>Physical characteristics</b>	Density	3200 kg·m <sup>-3</sup>
	Porosity	14.5%
	Mean specific heat (25-1000 °C)	1085 J·kg <sup>-1</sup> ·K <sup>-1</sup>
	Mean thermal conductivity (25-1000 °C)	2.7 W·m <sup>-1</sup> ·K <sup>-1</sup>
	Mean dilatation coefficient (25-1000 °C)	14.4·10 <sup>-6</sup> K <sup>-1</sup>
<b>Mechanical characteristics</b>	Toughness (25-1000 °C)	0.47 MPa·m <sup>0.5</sup>
	Fracture critical tension (950 °C)	8.3 MPa
	Mean size of defects	20 μm
	Effective energy of fracture (950 °C)	10.0 J·m <sup>-2</sup>
	Elastic module (950 °C)	11 GPa

TABLE 2.- CHEMICAL ANALYSES AND STANDARD DEVIATION OF THE PHASES  $\sigma$ .

	Magnesio chromite (MgCr <sub>2</sub> O <sub>4</sub> )		Periclase (MgO)		Forsterite (Mg <sub>2</sub> SiO <sub>4</sub> )
	no attacked sample	attacked sample	no attacked sample	attacked sample	no attacked sample
Oxides	weight % ( $\sigma$ )	weight % ( $\sigma$ )	weight % ( $\sigma$ )	weight % ( $\sigma$ )	weight %
Na <sub>2</sub> O	0.06 (0.1)	0.02 (0.02)	0.03 (0.02)	0.01 (0.01)	0
MgO	24.47 (12.82)	18.42 (0.87)	86.6 (5)	85.16 (6.30)	53.45
Al <sub>2</sub> O <sub>3</sub>	17.18 (8.74)	20.34 (2.81)	0.79 (0.63)	2.18 (1.73)	0.15
SiO <sub>2</sub>	0.19 (0.36)	0.02 (0.03)	0.34 (0.08)	0.61 (0.86)	41.37
K <sub>2</sub> O	0.02 (0.04)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0
CaO	1.11 (2.78)	0.04 (0.03)	0.06 (0.08)	0.30 (0.58)	2.46
TiO <sub>2</sub>	0.74 (0.98)	0.32 (0.06)	0.04 (0.03)	0.05 (0.03)	0.03
Cr <sub>2</sub> O <sub>3</sub>	40.22 (12.13)	48.33 (2.62)	3.67 (2.17)	3.36 (3.38)	0.46
MnO	0.42 (0.17)	0.38 (0.06)	0.31 (0.16)	0.67 (0.19)	0.3
FeO	10.91 (3.69)	11.87 (0.89)	5.06 (2.63)	5.75 (3.50)	0.72
NiO	0.11 (0.07)	0.11 (0.07)	0.14 (0.05)	0.05 (0.05)	0.04
CuO	0.04 (0.05)	0.03 (0.04)	0.15 (0.11)	0.21 (0.23)	0
N° Analyses	7	17	7	11	1

materials. As shown in Figure 1, the chromite has been substituted for other species such as magnesia and aluminian chromite. The aim of these modifications has been to cause an increase in refractory properties of the matrix compounds. By doing this, the properties of the refractory matrix elements might reach – in order of magnitude – disperse characteristics: grains of periclase or of FeO solid solution in the periclase.

The electron microprobe analyses (Table 2) allowed us to verify that in the magnesio-chromite grains of the unused sample, the chrome and magnesium oxides contents are high, and the aluminum and iron oxides contents are low. CaO and SiO<sub>2</sub>, which give rise to a lower melting point of the refractory and the decreasing in brick strength, are present as impurities.

The percentages of MgO and Cr<sub>2</sub>O<sub>3</sub> are similar in both attacked and unused samples, but Al<sub>2</sub>O<sub>3</sub> and MnO are found in a lower amount in the last one.

A qualitative and then a quantitative analysis allowed us to distinguish between periclase and magnesio-chromite grains as shown in Figures 3 and 4 for the attacked and unused samples, respectively, which was essential to carry out the image analysis.

The elements scanned were: O, Mg, Cr, Al, Fe and Si in all the samples and also Cu and S, in the used sample.

A mapping of Cu and S elements revealed that they are located at the matrix and surrounding magnesio-chromite and periclase grains as it is shown in Figure 4.

The Fe content in the attacked sample is higher than in the unused one because this element is present in the chalcocite<sup>1)</sup>.

For the unused sample, 27 images were analysed in order to obtain the percentages of periclase, magnesio-chromite, and pores into the refractory bricks. The results were: 24.98 % of periclase, 59.83 % of magnesio-chromite, and 15.19 % of pores. These results agree with the manufacturer's values.

The images (240 in number) of the attacked samples analyzed named 1, 2, 3, and 4 in accordance with its position in the tuyere<sup>11)</sup>: 1 is the sample nearest to the converter (inside) and 4 is the furthest one. Table 3 shows the average percentages of periclase, magnesio-chromite and pores. The decreasing in porosity in the attacked sample (~5%) is explained as a result of the chemical attack of the slag filling the pores.

However, porosity over 25% was obtained in some of the number 4 samples since high temperatures cause breaks and these areas of the refractory brick do not suffer the slag attack.

#### 4. DISCUSSION OF THE RESULTS

The refractory brick suffered important modifications during the copper manufacturing process, both in chemical composition and textural conformation.

Matrix is the most altered side because due to the slag

TABLE 3: PERCENTAGE OF POROUS, MATRIX AND GRAINS FOR ATTACKED REFRACTORY BRICK SAMPLES.

Sample	% porous	% matrix	% grains
1	4.28	25.06	70.67
2	2.63	11.66	85.72
3	2.24	10.76	87.00
4	8.26	6.81	84.92

attack towards the refractory brick; the unused sample has a high volume of oxides of Mg and Cr, and the used refractory matrix contains important amounts of copper and Cu<sub>2</sub>S.

Porosity is also affected due to the attack of the slag filling the porous.

Grains are the less affected ones because nor periclase neither magnesio-chromite show variations from unused sample to the used one.

The refractory brick also suffered mineralogical transformations, especially in the matrix, as revealed by X-Ray diffraction and scanning electron microscope.

The problem with materials that are in contact with corrosive molten material does not generally stem from physical-chemical characteristics of disperse elements but rather from the matrix and from the capacity of molten material to interconnect, by chemical attack, all the sealed porosity of the material.

If the physical-chemical nature of the refractory matrix is very sensitive to chemical attack from molten material, the deterioration of the product is very violent and the controlling stage is the dissolution-chemical attack of the matrix. Nevertheless, if the refractory matrix property is sufficiently high, then the deterioration mechanism might be the progressive dissolution-attack on disperse phases. Obviously, a whole mixture of possibilities can fall between these two extreme situations with both wear mechanisms in force.

The discontinuous character of wear processes in refractory masonry of PSC nozzle zones, of variable depths of loosening material, gives cause to think that the chemical attack mechanisms are not the sole cause of coating deterioration<sup>14)</sup>. This conclusion can not be made as a direct consequence of microtextural analysis of attacked material. Therefore, alternative proposals to improve the coating capacity which only consider microtextural studies of samples that have been in contact with aggressive fluids (at laboratory or industrial scale), can sometimes be inefficient or even counterproductive in some cases.

The evolution analysis of the proportion of dispersed material (grains), pores and matrix of samples studied according to the position they held in relation to the solid-molten interface (Table 3) can confirm that we are dealing



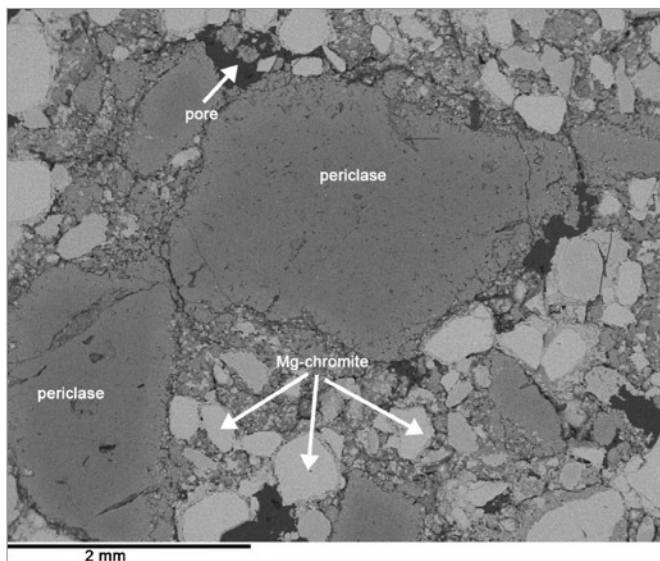


Figure 3.- SEM view of the unattacked refractory sample.

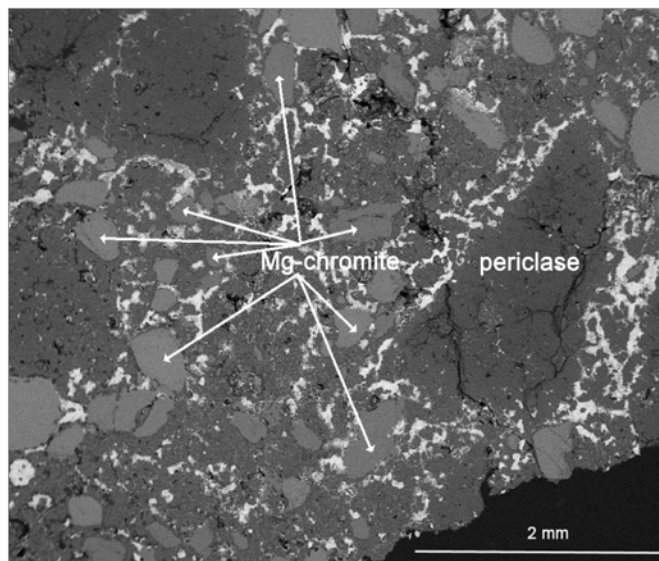


Figure 4.- SEM view of the attacked refractory sample.

with a mixed chemical attack mechanism. Nevertheless, it is estimated that the participation of the speed of the refractory matrix dissolution (90%) is far higher than that corresponding to the dissolution of dispersed elements (10%).

The zone affected by the chemical wear-dissolution of the refractory can be identified by the zone of refractory thickness for which material porosity is shown to be greatly reduced (around 5.0%) as a consequence of the molten layer infiltration capillarity. Nevertheless, as already mentioned, the refractory zone located at the end of the infiltrated layer, is affected by thermic fatigue mechanisms as a consequence of the discontinuous character of (heating-cooling processes) oxygen smelting converting in the PSC<sup>7, 8, 14</sup>).

The Nodal Wear Model (NWM) analysis has been able to determine for the first time that the participation of chemical wear is 35%. Therefore, the microtextural analysis can help decrease this quantity<sup>14</sup>).

Decreasing the contribution of chemical wear of PSC coatings in nozzle zones means that the physical-chemical matrix characteristics – which impede closed porosity material to interconnect – can reach those corresponding to dispersed grains in the material. Over the last ten years the presence of ferro-chromium and aluminium powder (in the chemical formulation of magnesia-chromium products) has been considered as a means to achieve this. However, the greater or lesser presence of these metallic additives are conditioned by the corresponding increase in price of the finished product.

Finally, it is necessary remember that the variables that influence in the mechanism of thermal fatigue refractory in the CPS are following: open porosity of material, operative variables of the conversion process and design characteristics of the copper converter<sup>14</sup>).

## 5. CONCLUSIONS

The microtextural analysis of products in contact with corrosive fluids is an essential tool in defining the controlling mechanism of refractory chemical degradation.

Improvements in quality to lengthen coating life must consider what factors control the chemical deterioration of the product, for which it is necessary: A) To confirm that the mechanisms of chemical degradation are equivalent to the observed to scale of laboratory. B) To determine whether other types of mechanisms exist and which act alongside the chemical deterioration.

Actually, improvements in magnesia-chromium products might have reached maximum if the problem analyses the chemical deterioration mechanism (only the 35 % of the material wear is attributed to these mechanisms). The cost to improve the chemical resistance might not be compensated by the corresponding increase in the number of PSC castings, having taken into account the high influence of thermic fatigue in material deterioration (65 %).

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## REFERENCES

1. J. Sancho, L.F. Verdeja, A. Ballester. *Metalurgia Extractiva. Síntesis*. Madrid, 2000; pp. 246-294.
2. L.F. Verdeja, J.P. Sancho, A. Ballester. *Materiales Refractarios y Cerámicos. Síntesis*. Madrid, 2008; pp. 274-292.
3. L.F. Verdeja, A. Alfonso, R. González. Material wear in blast furnace crucibles. *Am. Ceram. Soc. Bull.*; 77 (5): 91-96. (1998)
4. L.F. Verdeja, R. Parra, J.P. Sancho, J. Bullón. Corrosion mechanism and wear prediction of the sole of an electric arc furnace. *ISIJ*; 43(2): 192-200. (2003)
5. L.F. Verdeja, R. González, A. Alfonso, M<sup>a</sup> F. Barbés. Nodal wear model: corrosion in carbon blast furnace hearths; *Rev. Metal. Madrid*; 39(3): 183-192. (2003)
6. M<sup>a</sup> F. Barbés. El Modelo de Desgaste Nodal en la simulación y diseño de los crisoles de alto horno, Ph.D. Thesis, the University of Oviedo, Oviedo, Spain, 2004.
7. M<sup>a</sup> F. Barbés, E. Marinas, E. Brandaleze, R. Parra, L.F. Verdeja, G.A. Castillo, R. Colas. Design of Blast Furnace Crucibles by Means of the Nodal Wear Model. *ISIJ International*, Vol. 48 (2008), No. 2, pp. 134-140
8. L.F. Verdeja, R. Parra, R. Parada, A. Alfonso, C. Marcos, Ch. Goñi, M<sup>a</sup> F. Barbés. Aplicación de MDN al estudio de la corrosión de los convertidores Peirce-Smith; *Bol. Soc. Esp. Ceram. V.*; 43(2): 203-205. (2004)
9. Ch. Goñi, V. Bazán, R. Parra, J. Martínez, L. Albornoz, P. Fernández, L.F. Verdeja. Modelling of Peirce-Smith converter tuyere zone wear mechanism. In: Díaz C, Landolt C, Utigard T, editors. *Pyrometallurgy of Copper*. Quebec: Canada; 4 (2), 285-300. (2003)
10. Goñi Ch. Desarrollo y aplicación de los modelos de corrosión refractaria para un CPS, Ph.D. Thesis, The University of Concepción, Santiago de Chile, Chile, 2004.
11. J.L. Liow, P. Tsirikis, N.B. Gray. Study of refractory wear in the tuyere region of a Peirce – Smith nickel convertor; *Canad. Metall. Quart.*; 37 (2): 99-117. (1998)
12. C. Marcos, M.A. Llorca, P. Cambor, L.F. Verdeja. Caracterización de refractarios monolíticos. *Bol. Soc. Esp. Ceram.*; 41 (2): 241-251; (2002).
13. K. Goto, W.E. Lee: The direct-bond in magnesia chromite and magnesia spinel refractories. *J. Am. Ceram. Soc.* ; 78 (7): 1753-1760. (1995)
14. Ch. Goñi, M<sup>a</sup> F. Barbés, V. Bazán, E. Brandaleze, R. Parra, L.F. Verdeja: The mechanism of thermal spalling in the wear of the Pierce-Smith Copper Converter. *J. Ceram. Soc. Jpn* 2006; 114(8): 665-668.

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