

THE NODAL WEAR MODEL IN THE ANALYSIS OF WEAR AND CORROSION IN REFRACTORY MATERIALS BY MOLTEN PHASES

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ABSTRACT

The wear and corrosion phenomena in the lining of ferrous and non ferrous pyrometallurgical furnaces are complex problems where chemical, interfacial and mechanical phenomena are presents. Even a big effort to relate fundamentals understanding of wear, corrosion and other type of degradation of refractory materials, the link between this knowledge and industrial practice is still poor. Several designs are still based on trial and error tests to define the best material with the most attractive cost/performance relation.

The Nodal Wear Model is a tool that allows an analysis based on the physicochemical mechanism of the wear and corrosion combining mathematical modeling of the temperature field in the lining by FEM. It was applied with success to several ferrous applications (blast furnace crucible, torpedo car, EAF for ferroalloys production).

The paper discusses the basis of the model and shows the continuous improvement achieved in an electric arc furnace applying this model, both on productivity and extension of campaigns between the total reconstructions of the sole.

INTRODUCTION

The refractory materials used in furnaces, ovens, and transport pots or storage equipment must maintain their chemical, physical, and mechanical properties at high temperatures to resist attack for the longest possible time. The goals for general optimization for different processes are to achieve the physical chemistry transformations faster, working at a higher temperature and continuously transforming discontinuous operations. In most cases, a technical limitation to accomplishing this is the quality of the refractory materials and design of the lining.

Until now, equipment lining has been designed through trial-and-error tests to determine the material with the most attractive cost/performance relation. In addition, laboratory tests have been used to compare corrosion resistance under conditions that try to simulate an industrial environment. The Nodal Wear Model (*NWM*) presented in this paper is a tool to analyze the attack of the lining by the molten phases. Its application can help in the choice of refractory material and the design of the lining.

In industrial practice, post-mortem studies provide important support for the design and evaluation of refractory materials. However, the post-mortem analysis could provide a wrong conclusion and offers no information about the rate of corrosion.

From laboratory scale, dynamic and static laboratory tests are standard [1]. The simplest static test is the analysis of the reaction when a sample of a molten phase is poured on the surface of a refractory. So-called “finger tests” are two others types of test that could be done with different initial reactive conditions for the liquid/solid system. One such test is conducted in a molten phase by filling a hole made in a refractory. The other involves immersing a piece of refractory in the liquid. In the first case, the liquid phase could be saturated by the dissolution of a component of the refractory. This possibility is avoided in the second test, enabling the identification of a specific step of diffusion through a boundary layer.

The conclusions of these tests, which are based on the analysis of the altered microstructure of the refractory, help in understanding the corrosion/wear mechanism. However, the extrapolation to real industrial conditions must be done carefully as laboratory conditions differ from the real conditions of the process. Moreover, it is expected that within a few hours the results could be experimentally quantified by the depth of the zone attacked by the melts. In order to achieve this objective, the corrosion/wear mechanism has to be accelerated to have a measurable result in this time (2–4 h) with a penetration about 10^{-3} m. The wear process is chemically accelerated by the addition of chlorines, borines, and especially fluorines into the melts. This modification changes completely the characteristics of the melts from the real system and the rate of corrosion/wear is 50–100 times the real rate [2]. At the same time, the thermal dynamic conditions in the real process are far from those used in the tests. Thus, these tests are valid only for the comparison of the quality of different materials based on their resistance under the experimental conditions.

The Nodal Wear Model (*NWM*) is a mathematical modeling tool that complements the analysis of corrosion / wear phenomena done by the classical post mortem analysis and laboratory tests, as the previous ones mentioned. The *NWM* takes the phenomenological quantification of the individual mechanisms, each of which is thermally activated, to establish a corrosion equation that expresses the advance of the corrosion interface in units of $L \times t^{-1}$ (length by time). From the description of the geometry using a finite-element method (FEM) grid, the thermal field is obtained by choosing adequate border conditions. The surface, defined by the interface melts/refractory, is modified using the appropriate corrosion equation in the nodes of a second grid that represents this interface. The equations used in this step represent the control mechanism of the corrosion/wear.

THE FORMALIMS OF THE NODAL WEAR MODEL

The *working temperature* at the interface has been traditionally considered as the temperature of the process, that could be measure directly, T_∞ that differs from the Nodal Temperature T_i that is not possible to measure directly. The difference between both temperatures ($T_\infty - T_i$), could rise up to many decades even the thermal boundary layer δ_i is small [3]:

$$T_i = T(x_i, y_i, z_i)$$

$$T_\infty = T(x_i, \delta_x, y_i, z_i + \delta_z)$$

For the calculations explain further in the text $\delta_x = \delta_y = \delta_z$

All the parameters and variables that influence the final phenomenon of wear and corrosion are a function of T_i and ($T_\infty - T_i$). To apply the NWM a thermal field must be calculated in the lining. The mathematical solution for this problem was developed by means of a Finite Element Model with two boundaries conditions: the temperature on the shell or the temperature of the bath T_∞ , and the heat transfer between the melt and the lining, represented by the convective heat transfer coefficient. With these two know parameters and the thermal conductivity (λ) for the materials used in the lining of the furnace the complete thermal field can be calculated and so on the nodal temperature T_i .

During the operation the wear/corrosion phenomenon modifies the geometry of the lining. The thermal field before a Δt , which could represent a cycle of operation, is not longer valid since a new geometry appears and the distribution of temperature has left consolidating along this new geometry of the refractory lining on the furnace. The modification of the geometry is calculated applying to each node in the interface melt/refractory a corrosion equation expressed on Lxt^{-1} . This equation, characteristic according to the control mechanism of the wear process is formally an empiric equation based on the phenomenological analysis of the wear phenomena that allow defining the control mechanism of this very complex process. The parameters of this corrosion / wear equation are calculated from the value of $T_i, (T_\infty - T_i)$ and $(T_i - T_{i-1})$ and $(T_i - T_{i+1})$ that are the thermal difference between the node i and their adjacent ones. With this formulation, the corrosion rate in the node i expressed in units of length by unit of time is represented by Equation 1.

$$v(\text{corrosion})_i = f(T_i; T_i - T_\infty; T_i - T_{i-1}; T_i - T_{i+1}) \quad ; \quad \left[\frac{L}{t} \right] \quad (1)$$

The wear in each node is determined supposing that the temperature remains constant during the interval of time Δt :

$$(\text{Wear})_i = v(\text{corrosion})_i \Delta t \quad ; \quad [L] \quad (2)$$

As the geometry of the system has been modified, the new temperature field should be obtained solving the same FEM problem with a new geometry. The evolution of the wear/corrosion profile for the lining is obtained by means of an iterative process. If each iterative cycle takes place after a certain Δt , the calculation process for the i node in the n^{th} iteration is:

- Temperature in the i node by FEM: $T_{i,n-1}$
- Corrosion rate in the node i : $v(\text{corrosion})_i = f(T_{i,n-1}; \Delta T_{i,n-1})$
- Wear during the Δt of the iteration n in the i node: $(\text{Wear})_i = v(\text{corrosion})_i \Delta t$
- Definition of the new geometry and calculation of the new temperature field, $T_{i,n}$ in the whole refractory lining and so the nodal temperature (temperature at the interface melt/refractory).

It is important to note that the interface melts/refractory, where the attack occurs, defines a surface build by the nodes where the wear-corrosion equations are applied. This 2D grid is independent of the FEM grid used for the numeric resolution of the temperature field in the lining.

To apply the NWM it is necessary to develop corrosion equations [$v(\text{corrosion})_i$] that allow the geometry correction of the refractory lining. These corrosion equations depend on the specific mechanism considered as control step of the corrosion/wear of the lining. For the simulation and design of the Electric Arc Furnace that is presented in this study two basic mechanisms were considered: infiltration in the open porosity for the original sole of the furnace and chemical dissolution for the modified sole.

A more detailed presentation of the mathematical formalism is presented elsewhere [4].

WEAR CORROSION EQUATIONS

Infiltration

The simplification in the representation of the porous refractory microstructure as a straight-line pore of radius r is very useful for the derivation of the thermodynamics and kinetics expressions for pore infiltration. The equilibrium value of liquid rise in this capillary can be calculated by minimizing the variation in total free energy ΔF as a function of the rise, z . Setting $d(\Delta F)/dz = 0$, the following equation is obtained, giving the equilibrium rise z_e [10].

$$z_e \rho g - \frac{2\sigma_{lv} \cos \theta}{r} = P_o - P_v \quad (3)$$

Where ρ is the liquid density, g the gravity, σ_{lv} the surface energy between the liquid and the gas phase, θ the wetting angle between the liquid and the solid, P_o is the pressure applied on the liquid at the capillary entrance $z = 0$ and P_v the pressure of the vapor phase ahead of the infiltration front. If we assume that the flow of the infiltrated melt is incompressible and laminar with viscosity η the velocity u can be expressed by equation (4):

$$u = \frac{dz}{dt} = -\frac{1}{\eta} \frac{r^2}{8} \frac{dP}{dz} = -\frac{1}{\eta} \frac{r^2}{8} \frac{\Delta P_t}{z} \quad (4)$$

The total pressure drop driving infiltration is equal to the applied pressure $P_o - P_v$, minus the capillary pressure $\Delta P_c = \frac{2\sigma_{lv} \cos \theta}{r}$, and minus the hydrostatic pressure $\rho g z$. In most practical

situations, $z \ll z_e$, so ΔP_t is nearly constant during the infiltration process ($\Delta P_t \approx P_o - P_v - \Delta P_c$). After integrating equation (4) once with respect to z and then with respect to time taking $z = 0$ at $t = 0$, it gives

$$z = \left[\frac{r^2}{4\eta} \right]^{1/2} \Delta P_t^{1/2} t^{1/2} \quad (5)$$

Applying this equation, also known as Washburn's equation [4], to an industrial furnace where the height of the liquid metal and slag represents the metallostatic pressure, it can be transformed in a unidirectional equation (L/T) to apply in each of the nodes of the surface for the interface melt / lining.

$$v(\text{corrosion})_i = \frac{2(\rho_s g z_s + \rho_M g z_M + P_{atm})^2}{\gamma_{m/g} \cos \theta \eta} r^2; \left[\frac{L}{t} \right] \quad (6)$$

Assuming that the melts in the furnace are a metal and a slag the parameters of equation (6) are: ρ_s the slag density, z_s slag eight, ρ_M metal density, z_m metal eight and P_{atm} the atmospheric pressure over the bath.

Chemical Dissolution

The chemical dissolution takes place when one of the constituents of the refractory can dissolved in the melts. To obtain the nodal equation, the dissolution is considered as a process where a constituent of the refractory diffuses into the melt. If any chemical reaction occurs in the interface it is not taken into account due to the high rate of chemical reactions at high temperature, and so no chemical control is expected. The basic equations that represent these phenomena are Fick's laws of mass transfer. For a steady state condition the diffusional mass flow of the attacked species J_i , could be calculated by the well known equation:

$$J_i = k_i \Delta C_i \quad (7)$$

Where k_i is the mass transfer coefficient, ΔC_i the difference of concentrations of the specie that diffuses between the interface and the bulk of the melt. This equation can be transformed to represent this control mechanism in units of length by unit of time:

$$v(\text{corrosion})_i = k_i \Delta C_i \left(\frac{\rho_i}{\rho_g} \right) \left(\frac{100}{\%cm} \right); \left[\frac{L}{t} \right] \quad (8)$$

In Equation 8 the difference of concentration ΔC_i should be expressed in fraction; ρ_i is the nodal density of the melt in contact with the refractory; ρ_g is the bulk density of the refractory and $\%cm$ is the percentage of the constituent that dissolves. The value for the nodal mass transfer coefficient from the refractory surface to the melt is obtained by the following equation:

$$k_i = 0.332 Re^{1/2} Sc^{1/3} \left(\frac{D_i}{L} \right) \quad (9)$$

Where D_i is the diffusion coefficient of the attacked specie; L , is the lineal characteristic dimension; Re , the Reynolds number and Sc the Schmidt number, both of them chosen as the most representative of the conditions in the interface refractory – melts in the furnace. The corrosion equation that results from substituting the expression (8) in (9) is:

$$v(\text{corrosión})_i = 0.332 Re^{1/2} Sc^{1/3} \left(\frac{D_i}{L} \right) \left(\frac{\rho_i}{\rho_g} \right) \left(\frac{100}{\%cm} \right); \left[\frac{L}{t} \right] \quad (10)$$

To be able to use this corrosion equation it is necessary to know the movement of the melt in the interface with the refractory. The nodal velocity \bar{v}_i used to calculate the Reynolds number is estimate from specific conditions where the equation will be applied. It can be shown [5] that the value of \bar{v}_i can take the following forms:

$$\bar{v}_i = 6.98 \mu_i^{1/3} \rho_i^{2/3} \Delta \rho_i^{1/3} \quad (11)$$

$$\bar{v}_i = \frac{(3D_i)^{1/2}}{3} \quad (12)$$

Where μ_i and ρ_i are the viscosity and the density of the melt in the node i , $\Delta \rho_i$ is the dif-

ference of density between the node i and its adjacent node. The equation (12) is the relative velocity of the melt in the node i of the lining when the difference of temperature between two contiguous nodes of the interface melt/ceramic tends to zero, the velocity for the movement of the melt depends on the value of the diffusion coefficient of the species that diffuse D , according to: $D = \overline{v_i \bar{d}}$, where \bar{d} represents the displacement of atoms in

the melt in one second. At the same time, $D = \frac{1}{3} \bar{d}^2 f$ where f is the jump frequency of atoms in the melt. In one second, $(3 D_x)^{1/2}$ is the distance they can cross.

Another equation developed under the same analysis but not detailed in this paper is the thermal mechanical degradation. The so called thermal spalling has been applied to the study and analysis of wear and corrosion phenomena in Pierce Smith Converters [6, 7].

EXAMPLES OF APPLICATION ON THE DESIGN OF AN EAF SOLE

The electric arc furnace shown in Figure 1 and Figure 2, where an example of the thermal profile calculated by means of FEM method, is operating in the refining of ferromanganese alloys. It has a magnesite castable sole with high MgO content (% MgO > 95%). For the initial conditions of the study a continuous campaign of measurements of the sole allowed establishing the corrosion profile shown in the Figure 1. The average duration of the sole was only 19 tappings that represent a corrosion rate of $0.52 \text{ cm} \times \text{hr}^{-1}$. The control mechanism identified for the wear of the sole in this initial condition was the penetration of the alloy through the open porosity. A FEM calculation of the temperature field was done using as border conditions the outside wall temperature. The value of $18 \text{ W} \times \text{m}^{-2} \times \text{K}^{-1}$ for the convective heat transfer coefficient between the ferroalloy and the refractory lining adjust the results of the NWM to the experimental measurements of the wear in the sole [14]. The others parameters in Equation 6 are the following:

- Time of one cycle for refining: 3 hrs (Δt)
- Surface tension of ferromanganese: $\gamma_{l/s} = 0.20 \text{ N} \times \text{m}^{-1}$
- Density of ferromanganese: $\rho \text{ (Fe - Mn 80\%)} = 7125 - 0.893T \text{ (K)} \text{ kg} \times \text{m}^{-3}$
- Contact angle between ferroalloy and refractory: $\theta = 30^\circ$
- Thermal Conductivity: $\lambda = 10 \text{ W} \times \text{m}^{-1} \times \text{K}^{-1}$
- The overall size of the open pores of the refractory is between 12 and 20 microns
- The viscosity dependence on temperature of the melt used in the calculation is shown in the following Table:

Table 1: Dependence on temperature for viscosity of ferromanganese alloy: 80% Mn, 1.4% C, 0.8% Si, 0.15% P and 17.65% Fe

Temperature (°C)	975 ^[15]	1100 ^[15]	1119	1280	1400 ^[12]
Viscosity (Pa·s)	$1.0 \times 10^{12.5}$	1.0×10^8	4.3×10^7	8.2×10^5	5.0×10^{-3}

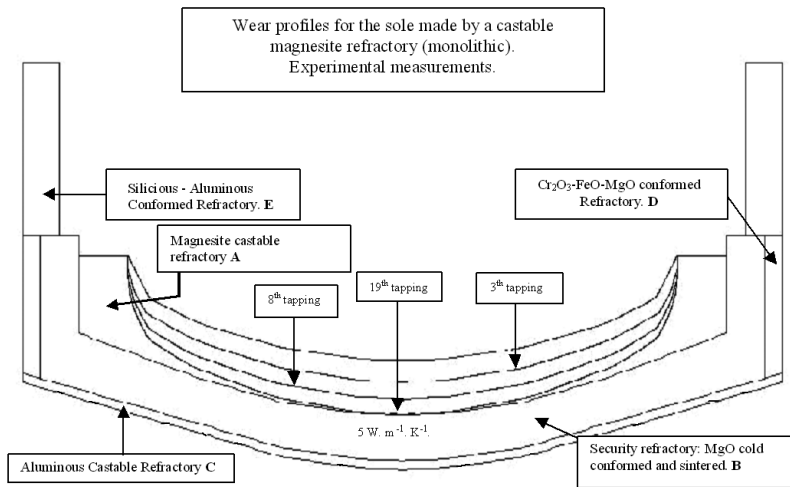


Figure 1: Lining characteristic of an electric arc furnace in ferromanganese production. Initial corrosion profiles for a monolithic magnesite sole and thermal modeling

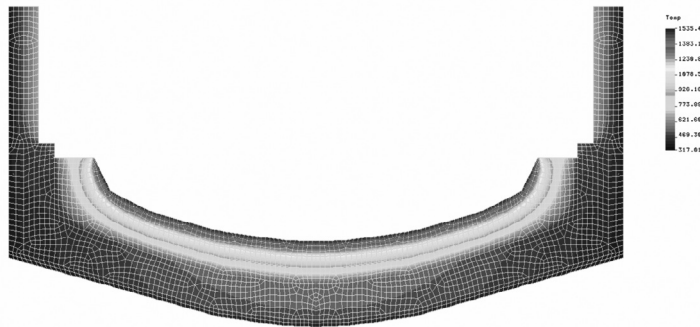
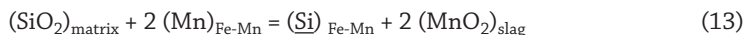


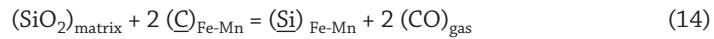
Figure 2: An example of the thermal profile in the lining of the electric arc furnace obtained by means of FEM

To extend the number of tapping many simulations were done changing the design of the sole, using other materials with a higher thermal conductivity λ .

- Region B changes from sintered magnesite ($\lambda = 5.0 \text{ W}\times\text{m}^{-1}\times\text{K}^{-1}$), to magnesia-carbon graphite refractory ($\lambda = 25 \text{ W}\times\text{m}^{-1}\times\text{K}^{-1}$). The number of tapping can be increased up to 25.
- Region B, C y D, to magnesia-carbon graphite refractory ($\lambda = 25 \text{ W}\times\text{m}^{-1}\times\text{K}^{-1}$). The number of tapping can be increased up to 33.

The second improvement in the design of the lining was the modification of the sole in order to change the physical chemistry control for the wear/corrosion. When the sole is made by a castable dolomitic material, with a very little average size of particles (less than 100 μm) and low content of impurities: (75 % MgO , 20 % CaO , 0.60 % SiO_2 , 3.80 % Fe_2O_3 , 0.30 % Al_2O_3 , others: 0.30 %), the formation of liquid reactive phases is facilitated at low temperature. Even of being a not conformed material, the open porosity is very low and the mechanism of corrosion is conditioned to the dissolution of the matrix constituent (magnesium, calcium, aluminum and iron silicates) in the melt. In this case the constituent of the refractory that is corroded by the melt is the SiO_2 by the reactions:





It was shown experimentally that this substitution of the castable magnesite by a dolomitic sole increases the number of tapping to about 45. The corrosion rate is in this case $0.27 \text{ cm} \times \text{hr}^{-1}$ (the wearing of the 30 centimeters of the sole is achieved in 45 operations of two and a half hour each), that is still far from $3.70 \times 10^{-2} \text{ cm} \times \text{hr}^{-1}$ in the case of the sole of an electric arc furnace in the production of carbon steel. The simulation procedure in this case uses $v(\text{corrosion})$ given by Equation 10.

The actual design of the lining has take into account all the simulations done and the continuous modification that has optimized the number of tapping from 19 to more than 100. The new design considers air forced convection to increase the refrigeration of the furnace (Figure 3). The results of this new design reflected the optimization summarized in Table 2.

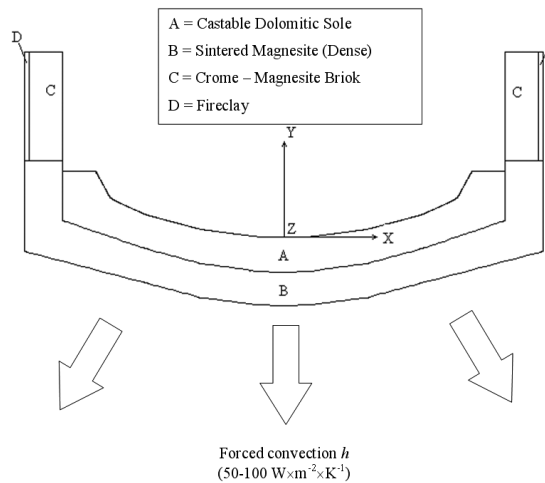


Figure 3: Actual design for the furnace

Table 2: Summary of the improvements in the operation of the Electric Arc Furnace

Year	Tapings between sole reconstruction	Productivity (Ton \times hr $^{-1}$)	Comments
1999	19	1.2	Capillary control of the wear corrosion phenomena. Magnesite sole
2000	45	1.44	Chemical control and castable dolomitic sole and higher conductivity in the security refractory
2002	1200	2.7	Chemical control and castable dolomitic sole with intensive refrigeration on the shell

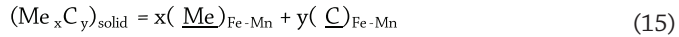
The optimization was achieved by different actions that we propose to classify in three groups:

- Diminishing of the nodal temperature, T_i at the interface refractory / liquid alloy. The actions were the use of materials with high thermal conductivity, an appropriate design of the lining to ensure a good heat transfer from furnace to the surroundings and use forced convection for the refrigeration of the shell
- Increasing the power of the furnace and the charging and tapping system
- Hot reparation of the lining “ceramic welding” without any humidity bonding.

The first one is directly related with the NWM, the two remaining are operational

optimizations but related to the optimization of the lining, specially the increase of the power that needs a more reliable sole.

Even the actual situation represents an impressed optimization if it is compared with the situation in the year 1999 it still exists an opportunity for further improvement. The simulation using the NWM has shown that the formation of a protective layer in the sole could increase the number of tapings for this furnace. One of the options to continue the research on the optimization is consider the use of carbides layers. The problem is to find in what conditions the nodal temperature T_i could be the equilibrium temperature for the following reaction:



One evident problem is the chemical specification for the refined ferromanganese that could not allow the chemical scheme for the presence of a solid protection layer on the sole.

Another way to improve the useful life of could be a new design with materials that have higher thermal conductivity to increase even more the heat loses and modify the thermal field. In the actual design the temperature in the shell is about 150°C, higher more than 100°C from the initial design. The idea is to reach a nodal temperature near the solidus temperature of the ferroalloy, about 900°C. The NWM helps to analyze and to quantify the real relevance of the insulation and clarify that a control of heat loses is needed to increase the useful life of the lining.

CONCLUSIONS

The combination of the corrosion equations with the NWM provides a tool for the analysis of the corrosion/wear phenomena in many different configurations. Even of the fact that the application of the model needs powerful computation facilities the bases for the calculations are simple.

The two step of the model require a comprehensive understanding of the mechanism that can control the corrosion/wear phenomena and a precise evaluation of the temperature field in the lining. For the corrosion/wear phenomena all the possibilities of experimental test and post mortem analysis can help to define the control step.

The border conditions for the calculation of the thermal profile that define the nodal temperature must be evaluated directly on the furnace. Some on line instrumentation are a very important support for this calculation. If it is possible to have on line measurements the application of NWM can give on line estimation of the modification of the geometry of the lining and in this sense the on line thermal measurement could be transform on a on line monitoring of the lining integrity.

Some paradigms in the analysis of the phenomena that occur in the interface of a refractory lining exist up to date. Many analyses consider the temperature at the interface melts/refractory as the bulk temperature and supposed constant the long of the lining. If we can imagine a constant field in the bath, situation far from a real condition, the differential corrosion/wear that appears in the lining of any type of furnace must produce an inhomogeneous dissipative heat transfer in the lining, and consequently the temperature in the interface can't be constant in the whole interface. Certainly the direct measure of this temperature field is almost impossible to achieve. Another consideration which is usually accepted is the fact that an insulation between the work refractory and the shell of the furnace is of advantage, due to a lower heat loses. It was proved that this configuration affects negatively the live of the refractory. When this insulation is replaced by a

material with a higher thermal conductivity, or just eliminated, the performance of the refractory that is in contact with the melts increases. In this last case the work refractory contacts with the shell by means of low rigidity polymeric joining.

Finally, it is important to underline that this model will not replace all the other analysis done on the corrosion/wear phenomena in refractory materials. More than this, the NWM needs all the information that is provided by experimental test and post mortem analysis to have a well understanding on the basic physical chemistry phenomena. In this sense and with the new materials proposed as alternative to the classic ones used in the pyrometallurgical reactors, more experimental research must be done and a combination of experimental work with the NWM is a option for the design of new materials and lining in furnaces.

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