CARACTERIZAÇÃO DE TIJOLO REFRATÁRIO DE MgO-C PARA PANELA DE AÇO DA ARCELORMITTAL PECÉM*

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Resumo

A caracterização e seleção apropriada dos refratários podem levar a melhorias no desempenho do revestimento refratário, implicando nos seguintes benefícios: uniformização do perfil de desgaste e, consequentemente, redução do consumo específico de refratário e aumento da disponibilidade do equipamento para operação. Neste trabalho são apresentados e discutidos os resultados de caracterização de tijolo refratário de MgO-C para a linha de escória de panela de aço. As principais técnicas de caracterização utilizadas para caracterização de amostras de tijolo antes e após uso foram difratometria de raios X (DRX) e microscopia eletrônica de varredura (MEV) com auxílio da espectroscopia de energia dispersiva de raios X (EDS). Através das análises das amostras post-mortem os principais meios de degradação dos refratários de magnésia-carbono são por dissolução química intergranular da escória nos grãos de MgO e consequentemente dispersão dos grãos para o banho de escória.

Palavras-chave: Refratários; Tijolos; Panela de Aço; Linha de Escória.

CHARACTERIZATION OF MgO-C BRICK FOR STEEL LADLE FROM ARCELORMITTAL PECÉM

Abstract

The characterization and correct selection of refractories can lead to improvements in the performance of the refractory lining, resulting in the following benefits: uniformity of the wear profile and, consequently, reduction of the specific consumption of refractory and increased availability of the equipment for operation. In this work, the results of the characterization of MgO-C refractory brick for the steel ladle slag line are presented and discussed. The main characterization techniques used for brick characterization before and after use were X-ray diffraction (XRD) and scanning electron microscopy (SEM) with the aid of energy dispersive X-ray spectroscopy (EDS). Through the analysis of post-mortem samples, the main means of degradation of the magnesia-carbon refractories are by intergranular chemistry of the slag in the MgO grains and consequently dispersion of the grains to the slag liquid.

Keywords: Refractories; Bricks; Steel Ladle; Slag Line.

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1 INTRODUCTION

In the last years, the refractory industry has been adjusting to the new reality of the steelmaking with a view mainly to developing new materials that meet the requirements inherent in steel production and refining, in addition to reducing costs, rationalizing resources and obtaining high quality products. The MgO-C refractories have stood out due to their excellent properties in terms of corrosion resistance, thermal shock, durability and flexibility in the face of current operational demands. One of the main applications of this material consists of refractory lining to steel ladle that transport liquid metal throughout the refining processes in steelmaking plants. However, due to the growing demand for high quality and clean steels, metallurgical processes are becoming increasingly aggressive towards refractories, especially in the slag line area. In this case, understanding the wear mechanisms involved in this area is important for the development of materials with high performance in terms of availability and operational safety in the face of requests of different natures that are imposed on the refractory lining during the steel production process.
In this context, theoretical and practical aspects related to the physical, thermal and mechanical properties of the commercial MgO-C refractory brick for the slag line area are presented and discussed. The objective is to study the predominant wear mechanisms in MgO-C bricks, seeking alternatives to reduce or inhibit such mechanisms by improving the characteristics and microstructural properties, aiming at high operational performance in the face of requests of various natures imposed on the refractories of the slag line of steel ladle.

1.2 Steel Ladle

One of the main applications of MgO-C bricks is to refractory lining of steel ladles in steelmaking plant that transport liquid metal throughout the refining processes. Thus, the design of the lining and the selection of materials are carried out by area, that is, based on regions of the pan that present similar physical and chemical demands, Figure 1.

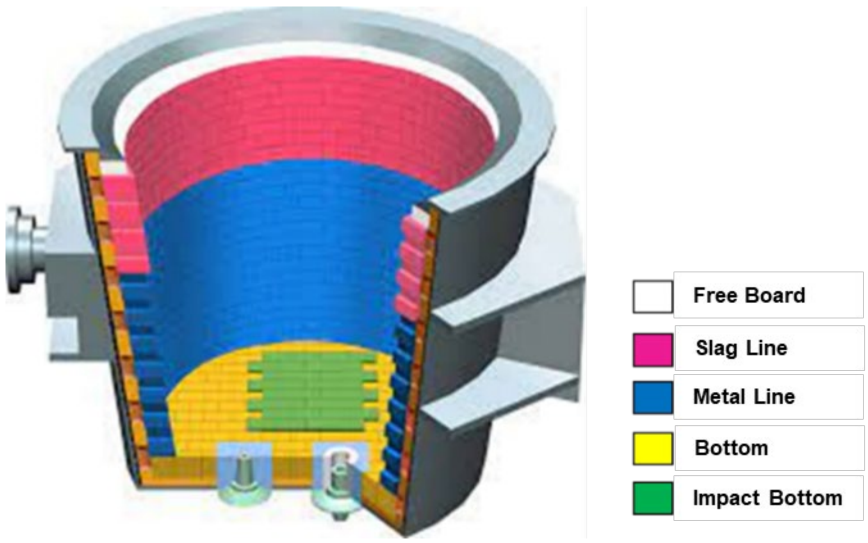


Figure 1. Schematic drawing of refractory lining for steel ladle.

This procedure has the function of guarantee a better balance of the wear of the refractories, preventing that one region has greater wear than the other, which can cause premature stops and unavailability of the equipment [1, 2]. Therefore, refractories must not only have high chemical and physical resistance to high temperatures, but also remain intact during operation under various operating conditions [2]. Thus, for the technological evolution of these inputs to occur, it is necessary to consider the impacts not only of the raw materials used in the manufacturing stage (aggregates of MgO, carbon, binders and antioxidants), but also the installation of the lining and the conditions operational (such as slag basicity, slag viscosity, heating, etc.), which are differents from one plant to another. Additionally, thermodynamic modeling and laboratory tests are some of the tools used to evaluate the wear mechanisms and predict the performance of these materials. Thus, the next sections of this literature review are devoted to the main characteristics of the MgO-C refractory and the wear mechanisms involved in the steel ladle slag line.

1.2 MgO-C Refractories

The MgO-C refractories are considered a high-performance material due to their excellent physicochemical properties, being found in quantities and costs compatible with the needs of steel metallurgy processes [3, 4]. Its first applications were carried out between 1975 and 1980 [1, 2] in Japan in the form of bricks and since then it has become a reference in the steel industry due to its refractoriness, high thermal conductivity, excellent thermal and thermal shock resistance, low slag wettability and high absorption of thermomechanical stresses [4].
MgO-C bricks are manufactured using the following raw materials: magnesia aggregates (sintered or electrofused), natural lamellar graphite, organic binder (tar, pitch or phenolic resin) and metallic additives [3, 4, 5]. In Figure 2 there is a schematic illustration of the disposition of the components contained in this type of refractory.

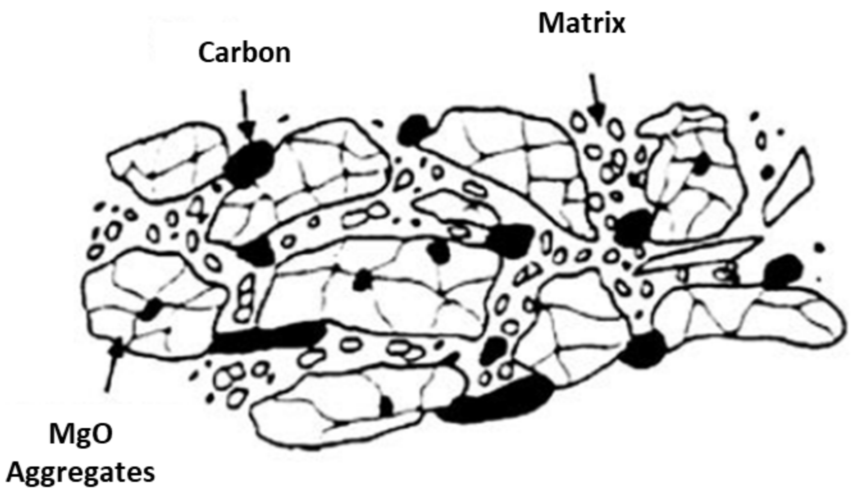


Figure 2. Schematic illustration of the structure and constituents of MgO-C refractories [2, 5].

MgO-C refractory bricks are basically composed of small magnesia grains (50 - 500µm), magnesia aggregates (1 - 7 mm) and graphite lamella (50 - 500µm in length) bonded to a resin or pitch [5, 6, 7]. Normally, in commercial bricks, the amount of magnesia is around 80 to 93% by weight. Graphite, on the other hand, varies from 7 to 20% by weight and antioxidants, when added, can reach up to 8% by

weight. The use of graphite in refractory bricks is mainly motivated by the increase in resistance to penetration of the slag, due to the low wettability by the slag that gives graphite and high chemical stability against the slag. In addition, the high thermal conductivity and low thermal expansion increase the resistance to thermal shock.
According to the literature [8, 9], corrosion of refractories located in the area that is in contact with the slag results from 3 primary mechanisms. The first is the dissolution or diffusion of the refractory material, in this case magnesia, into the liquid slag. Another mechanism is the penetration of the slag into the refractory, which causes mechanical and chemical effects. The third mechanism is erosion, which is associated with the movement of gases and slag. The literature also adds that the chemical corrosion of refractory bricks begins with the penetration of the slag through the pores, followed by the removal of the matrix, which causes the grains to become loose and later to be pulled out of the refractories.

2 DEVELOPMENT

2.1 Materials and Methods

The table 1 presents the samples taken from commercial bricks from the MgO-C system that were used to determine the physical and chemical properties.

Table 1. Identification of the studied samples.

Description	Original Brick	Post Mortem Brick
Ladle Area	Slag Line	Slag Line
Quality Material	MgO-C	MgO-C
Amount Sample	1	2

The information contained in the technical data sheet of the brick studied is presented in table 2.

Table 2. MgO-C Brick Data Sheet Information.

Equipment	Ladle	
Area	Slag Line	
Product Description	MgO-C Brick	
Chemical analysis	Typical value	Assured value
MgO (%)	78,0	72,0
T.C (%)	15,5	12,0
Physical Properties	Typical value	Assured value
Bulk Density (g/cm^3)	2,98	2,93
Apparent Porosity (%)	3,0	4,5
Cold Crushing Strength (kg/cm^2)	430	300

2.1.1 Mineralogical Analysis

The mineralogical characterization was carried out aiming to identify the crystalline phases present in the refractory bricks. The technique used was the qualitative analysis of phases by X-ray diffraction, using X-ray diffractometer.

2.1.2 Microstructural Analysis

Scanning electron microscopy (SEM) analyzes were performed to evaluate the original characteristics and understand how the mechanisms responsible for wear occur in the refractory brick.

2.1.3 Post Mortem Analysis

Brick sampling took place during the demolition of Steel Ladle #4 after the end of its campaign after 113 heats (Figure 3). During sampling of the refractory lining, the collected materials were identified according to the application position (Table 1).

Figure 3. Steel Ladle #4 after 113 heats.

2.2 Results and Discussion

2.2.1 Mineralogical Analysis

The phase composition of the brick sample from the slag line is presented in Figure 4. The results indicated that the brick is constituted, essentially, by magnesia (MgO) and carbon (C), as previously discussed, these phases govern the main properties and characteristics of MgO-C bricks. Also there is the presence of a residual amount of kyanite (Al_2SiO_5). Studies show kyanite as a phase that can be used to control the volumetric stability of refractories at high temperatures [10].

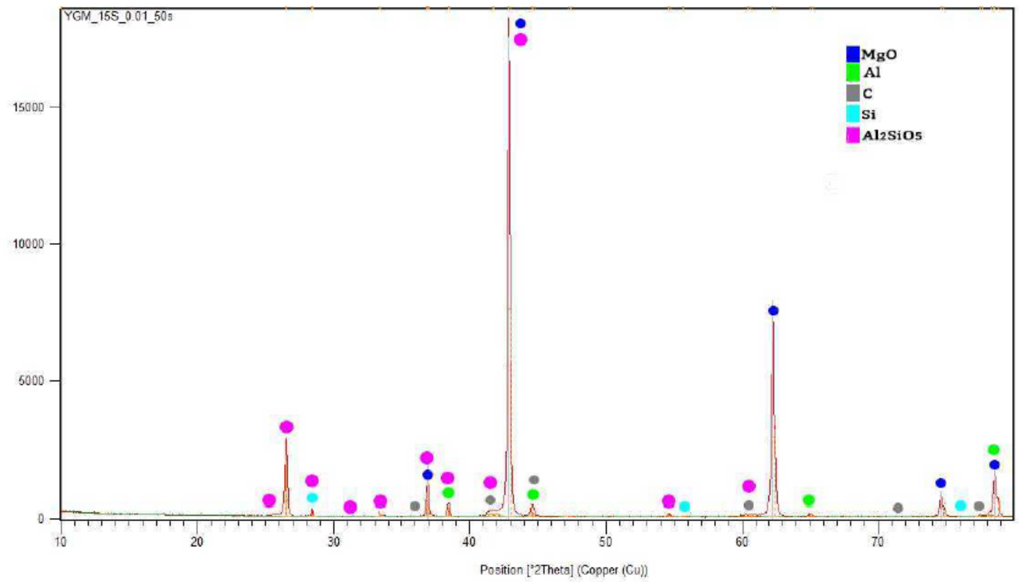


Figure 4. Diffractogram of MgO-C Brick (original sample).

The diffraction lines pointed to the presence of metallic aluminum (Al) and metallic silicon (Si) as antioxidants. The type and amount of antioxidants are essential to adapt the properties of the bricks to the mandatory ones imposed on the refractory lining. For example, increasing the antioxidant content provides high resistance to oxidation, but affects resistance to resistance and favors the influence of cracking. Thus, there is an adequate range of antioxidants that provides a compromise between chemical and physical properties, Figure 5 [11].

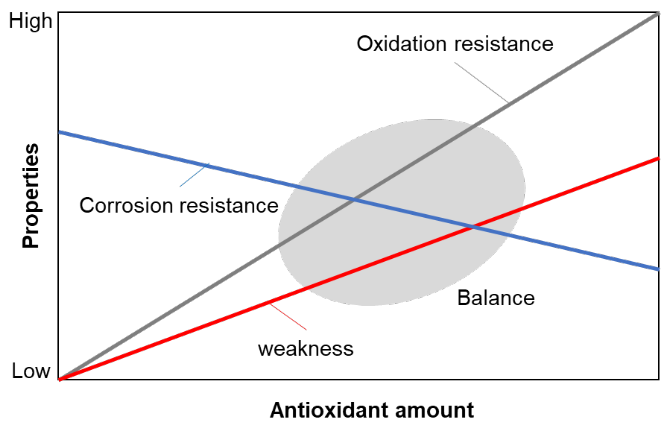


Figure 5. Effect of antioxidant content on the properties of carbon-containing bricks [11].

2.2.2 Microstructural Analysis

The microstructure of the MgO-C refractory before its industrial use (in natura) is shown in Figure 6. It can be seen that the material has a microstructure of sintered and electrofused grains bonded in a resin matrix. There is also a wide particle size distribution, with the largest particles exceeding 1 mm. This distribution is a positive factor in relation to packaging, resistance to thermal shock and chemical resistance [6, 7]. The presence of porosity inside the aggregates of large particles and sintered grains is easily observed, which potentially represents a lower resistance to slag attack, as well as a greater reaction potential. It is also observed in some acute angle aggregates, where the cubic crystallization of MgO grains is well defined.

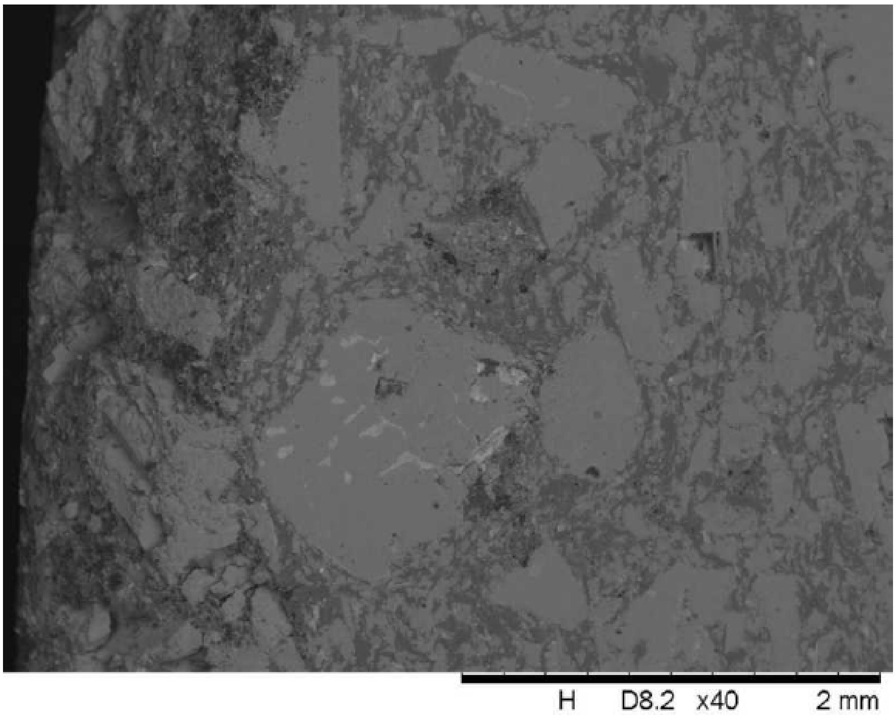


Figure 6. Microstruture MgO-C Brick.

Small-crystal magnesia sinter has a larger grain boundary area relative to its volume and, for this reason, is more prone to dissociation into the slag. According to Takanaga [12], the periclase crystal size has a significant influence on the brick corrosion rate of the MgO-C system, Figure 7.

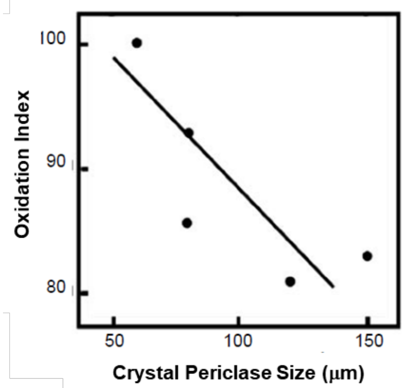


Figure 7. Influence of crystal periclase size on the corrosion resistance of MgO-C bricks [12].

According to mapping results (Figure 8), metallic aluminum (Al) and metallic silicon (Si) are finely dispersed in the matrix, including well-distributed graphite lamellae. Al and Si X-ray diffraction lines were observed, as discussed previously, due to the concentration of these phases.

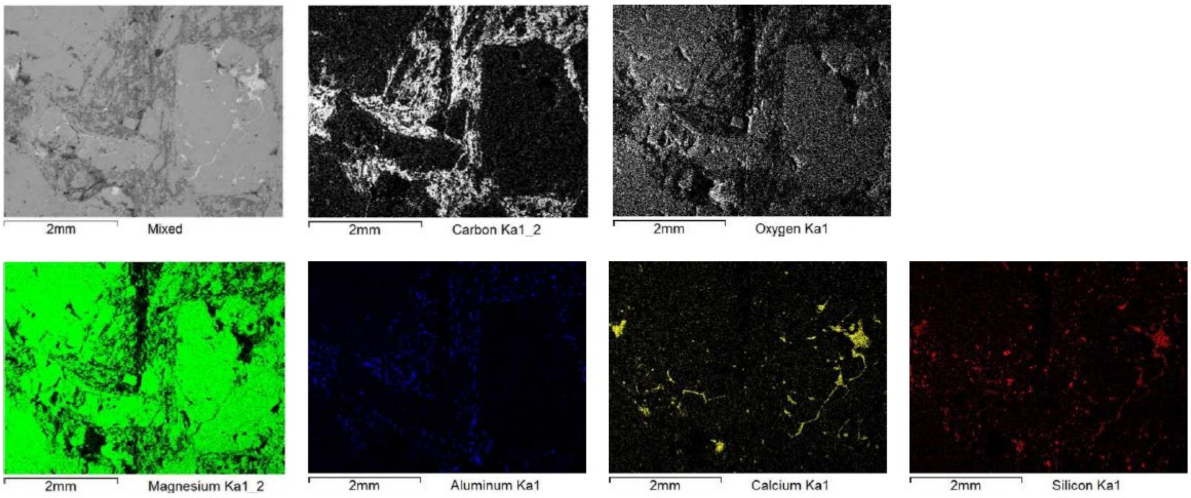
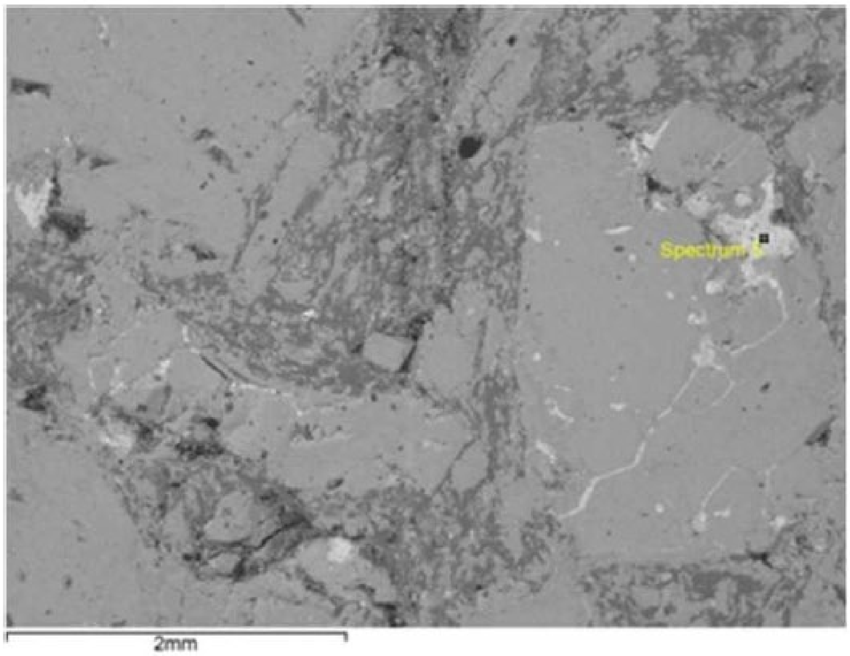
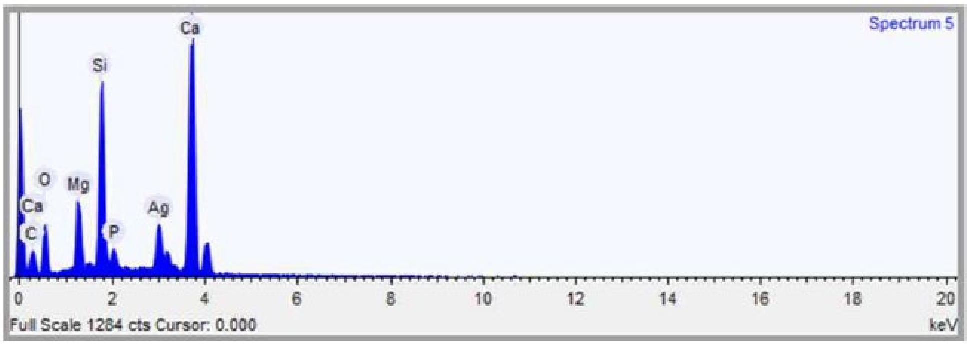


Figure 8. Mapping results of the microstructure of the MgO-C brick.

In Figure 9, the microstructure of the magnesia grains (9.a) is analyzed, which contains phase impurities composed of calcium silicate (Si - Ca) in the grain boundaries, according to the results of EDS (9.b).



(9.a)



(9.b)

Figure 9. Microstructure showing the magnesia grain (9.a) and EDS results in the magnesia grain boundary region (9.b).

2.2.3 Post Mortem Analysis

Figure 10 shows the sample after the industrial use of the MgO-C brick with the study regions highlighted, including the description of the respective analysis carried out. It was observed that the post mortem brick had cracks close to the hot face, possibly caused by the thermal stresses to which the bricks were subjected during operation.

Figura 10. MgO-C Brick after use (113 heats).

Table 3 presents the results of the properties and characteristics before the hot face (Working Side) and cold face (Back Side). There was an increase in apparent porosity when compared with the technical specification values for the brick from 4.5% (original) to 8.6% (after use). This result is associated with the emergence and growth of pores in the microstructure due to the formation of new phases in the microstructure, as well as carbon oxidation. Similarly, there was a difference in mechanical resistance comparing the reference values (430 kg/cm^2) with the result of the brick after use (303 and 368 kg/cm^2). This difference is justified by the increase in the porosity of the material.
In terms of chemical composition, the results of the sample of the hot face of the brick (Working Side) indicated that there was a penetration of slag due to the high contents of CaO (21.16%) and Al_2O_3 (21.58%) and low concentration of MgO (41.16%). Similarly, X-ray diffraction results pointed to the presence of typical slag phases on the hot face of the brick. On the contrary, the cold face of the brick presented results of chemical composition and mineralogical composition closer to

the original characteristics of the material, indicating that this region remained relatively preserved.

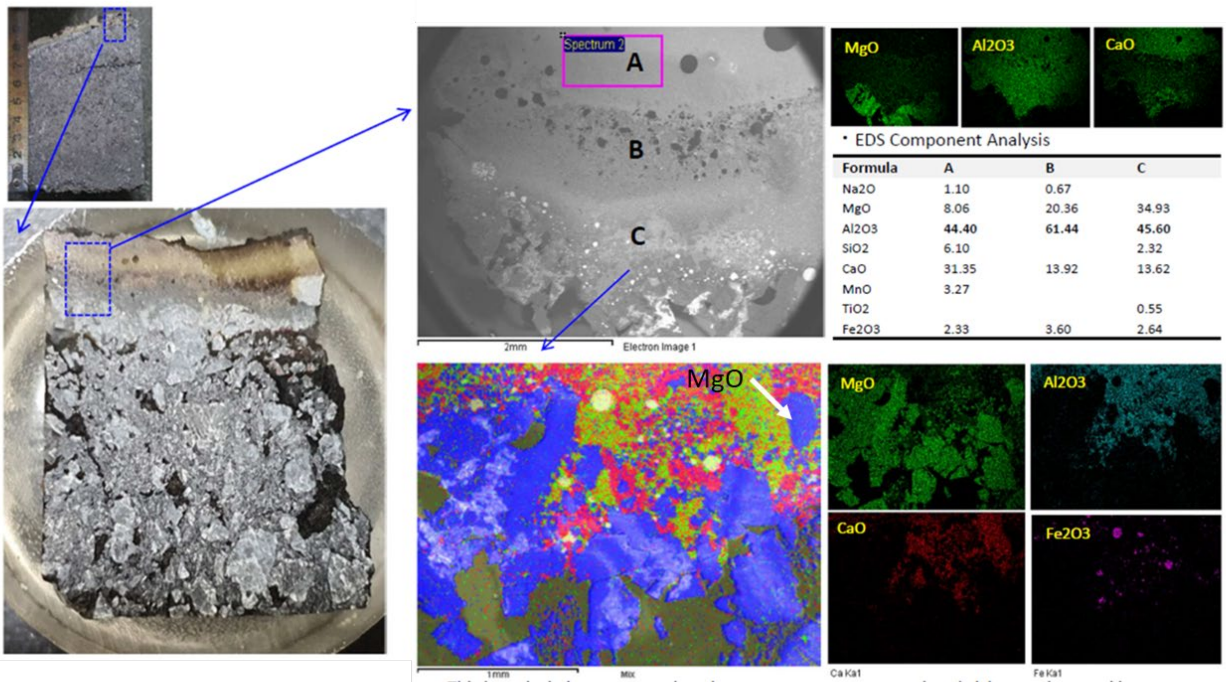
Table 3. Post Mortem Results.

Samples		Slag Line Brick	
		Working Side	Back Side
Bulk Density (g/cm^3)		2.97	2.99
Apparent Porosity (%)		8.6	8.6
Cold Crushing Strengths (kg/cm^2)		368	303
Chemical Composition (%)	SiO_2	4.11	0.91
	Al_2O_3	21.58	2.84
	Fe_2O_3	1.65	0.36
	CaO	21.16	0.86
	MgO	41.16	80.83
	C	7.13	14.19
Mineralogical Characterization	MgO	P	P
	C	P	P
	Al	-	-
	Si	-	-
	$MgAl_2O_4$	P	P
	$Ca_{12}Al_{14}O_{33}$	P	-
	Ca_3SiO_5	P	-
Label: P = Present Phase			

In the microstructure analysis of the brick after use (Figure 11), it is possible to observe a reduction of the original resin/carbon matrix, through the retraction of the dark area, confirmed in the results of the chemical analysis that revealed a reduction in the amount of carbon, Work Side (7.13%) and Back Side (14.19%). In turn, the EDS results indicated the absence of antioxidants, which contrasts with the matrix analysis of the same new material (Figure 8). The reduction of carbon means greater wettability of the refractory by liquid phases such as slag [6, 7]. This is a key factor for the occurrence of a chemical reaction, which may explain the slag attack on the brick. It should be noted that the macroscopic analysis of the brick shows the contact zone of the slag quite degraded, while the opposite zone may be reasonably preserved, even with the presence of carbon.

There was penetration of slag on the hot face of the brick, which is evidenced in the results of the EDS microprobe analysis of the points (A, B, C) identified in the micrograph (Figure 11). The chemical attack of the slag on these refractories is observed, which occurs preferably in the matrix, pulling out the magnesia aggregates, or which causes wear of the refractories. In this attack, pore formation also occurs. Accentuated wear of the matrix was also identified, where it is possible to clearly observe the magnesia aggregates that are giving off from the matrix. The analysis with EDS showed that zones that remain unaltered coexist in a brick, which contrast with zones completely taken over by slag, even with the absence of MgO (points A and B). The micrograph of point C followed by EDS suggests a typical chemical attack by dissolution from the matrix on the slag (containing elements CaO and Fe_2O_3), also showing a grain of MgO-C wholly loose and dispersed in the slag.

In general, to minimize refractory dissolution, the slag is saturated with magnesium oxide. However, instead of minimizing saturation, it may contribute to the dissolution of the phase present in magnesia grain boundaries, which are likely to dissolve more easily due to their lower refractoriness compared to MgO. Thus, the aggregates are attacked intergranular dispersing the grains to the liquid slag [13].



Formula	A	B	C
Na2O	1.10	0.67	
MgO	8.06	20.36	34.93
Al2O3	**44.40**	**61.44**	**45.60**
SiO2	6.10		2.32
CaO	31.35	13.92	13.62
MnO	3.27		
TiO2			0.55
Fe2O3	2.33	3.60	2.64

Figure 11. Microstructure of the MgO-C brick after use, showing the regions of interest and the results of the EDS microanalysis.

3 CONCLUSION

The laboratory characterization results showed that the microstructural design had a significant influence on the properties of the magnesia-carbon (MgO-C) system brick. The post mortem study suggested as the main wear mechanism the chemical attack of the slag on this refractory, which occurs preferably in the matrix, pulling out the magnesia aggregates, which causes the wear of the refractories. In this attack, pore formation also occurs. The degradation of MgO-C refractories results from the intergranular chemical dissolution of the slag in the grains. This effect is favored by the presence of impurities, SiO_2 and CaO, in the grain boundaries from the raw material of magnesia aggregates, showing that the quality of the raw material in the manufacture of the refractory is one of the determining factors for the useful life of these materials.
Although the wear of refractory bricks in the slag line is inherent to the steel production process, efforts are always made to reduce this wear as much as possible in order to extend the lifetime of the steel ladle. Chemical corrosion due to slag attack is the determining factor in refractory degradation. In addition, thermal factors such as temperature, thermal gradients, thermal expansion and thermoclase can be aggravating, but normally they are not decisive in material degradation.
In summary, optimizing refractory lining performance requires a systematic approach to evaluate wear mechanisms and directing efforts to improve refractories quality and metallurgical processes.

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