Engineering Failure Analysis 78 (2017) 161–168

Contents lists available at ScienceDirect

Engineering Failure Analysis

journal homepage: www.elsevier.com/locate/engfailanal

A statistical and post-mortem study of wear and performance of MgO-C resin bonded refractories used on the slag line ladle of a basic oxygen steelmaking plant

Ronaldo Adriano Alvarenga Borges, Guilherme Frederico Bernardo Lenz e Silva *

University of São Paulo, Department of Metallurgy and Materials, São Paulo, Brazil

ARTICLE INFO

Article history:
Received 13 July 2016
Received in revised form 24 March 2017
Accepted 26 March 2017
Available online 28 March 2017

Keywords:
MgO-C refractories
Wear mechanism
Steelmaking ladle
Post-mortem analysis

ABSTRACT

Refractories are essential materials used in steelmaking equipment. Understanding their wear mechanisms is important to promote safe, low-cost and high-performance steel processing. In the present work, a wear and performance evaluation of MgO-C refractories from steelmaking ladles was performed using statistical and post-mortem analyses to identify the main causes of degradation and failure. The post-mortem analysis showed that the main wear mechanism involved in the degradation process was the chemical corrosion of magnesia grains facilitated by the addition of nepheline fluxing, which is linked to the production method of steel grades with low sulfur content. Chemical corrosion of magnesia grains in the refractories used for ladle slag lines was intensified by the sodium-rich calcium-aluminum silicate slag reactions that dissolve magnesium, decreasing life of the equipment. A statistical evaluation of steelmaking shop ladles during 2015 (approximately 6700 heats) showed the main cause of degradation of the refractory ladle to be totally linked to the manufacturing process of low-grade sulfur steels.

1. Introduction

Among the various types of materials used in the steel industry, we can highlight refractory materials, which are widely used as coating equipment and as pig iron and steel transport/treatment vessels in steelmaking plants around the world. The intensive use of refractories in steelmaking plants is due to the properties these compounds exhibit such as high starting melting point, high structural strength at high temperatures and in highly corrosive environments, and an intensive stability in temperature variations [1–5]. Virtually all major industries producing materials such as iron and steel, cement, glass, chemicals and petrochemicals use some sort of refractory ceramic material in the coating of its reactors for protection and wear, as working temperatures (some above 1000 °C) are high [1]. Refractories are responsible for limiting the wear corrosion and reducing heat losses from the molten steel reactors and, in general, it would be virtually impossible to manufacture such materials without the use of any type of refractory ceramic material that can withstand the extreme conditions that the reactors are subjected to in terms of temperature, pressure and aggressive chemicals [1].

In general, coating wear is caused by various factors that may act in independent or combined ways. Corrosion by liquid metal and slag, metal and slag infiltration, sudden changes in temperature (thermal shock), excessive compression of the structure,

* Corresponding author.
E-mail address: guilhermelenz@usp.br (G.F.B. Lenz e Silva).

http://dx.doi.org/10.1016/j.engfailanal.2017.03.020
1350-6307/

Table 1
Refractory structure composition of the steel treatment ladles in accordance with the chemical specifications.

Slag line		Metal line		Bottom ladle		Bottom ladle (jet's impact region)	
Substance	Wt. (%)	Substance	Wt. (%)	Substance	Wt. (%)	Substance	Wt. (%)
MgO	85–90	MgO	75–80	Al_2O_3	~79	Al_2O_3	~88
C	11–13	Al_2O_3	20–25	MgO	~6	MgO	~6
		C	5–8	C+ others	~15	C	~6

oxidation of the carbon in refractory brick, and erosion caused by impact are the main refractory degradation factors [6,7]. Furthermore, according to [8], the wear of the refractory slag line is from chemical, thermal and mechanical events. Generally, the degradation process starts with a chemical event due to chemical potential differences between compounds of the refractory and slag and ends with thermomechanical events depending on the conditions to which the refractory is exposed and the type of reactor project.

The post-mortem analysis is one of the most useful tools for determining the root causes of the failures of coatings and for understanding the wear mechanisms involved. This technique is performed by conducting a systematic characterization of a refractory product after the end of its lifetime [9]. According to [10], the post-mortem analysis is the one of main tools to determine refractory in service and to provide information that can point the way to better service.

Through the post-mortem analysis of the refractory samples, it is possible to determine the chemical reactions that occur during the corrosion process, as evaluated by optical microscopy, X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) and cathodoluminescence (CL) microscopy [4,11]. Some works such as [4,11,12] show how post-mortem analysis can be utilized to identify the mechanisms and phenomena of the corrosion and chemical dissolution of the refractory by slag.

The objectives of this work are to analyze the degradation phenomena and wear mechanisms that occur in the slag line region of the steel treatment ladle (Table 1 and Fig. 1) of an oxygen steelmaking plant using the post-mortem analysis' technique. In addition, this work tries to understand if this degradation process is linked to typical metallurgical refining treatment processes that occur in the plant using a statistical process analysis of an operational database. Table 2 shows the main steps used in a typical post-mortem refractory analysis.

2. Materials and methods

For the experimental part, refractory samples from a steel treatment ladle in operation were collected after the end of its lifetime. For this study, samples were collected from only the slag line region because of the level of wear in this region. After the collection of the samples, they were prepared and analyzed by optical and electron microscopy for the post-mortem study. From the observations and chemical analyses, it was possible to identify the degradation phenomena and possible wear mechanisms that govern the performance ladle over its lifetime.

The sample collection was conducted using a hydraulic machine (known as a hydraulic remover), as illustrated in Fig. 2.

After the collection, the samples were taken to a laboratory where they were prepared for microscopic analysis. The preparation steps were sampling, cutting and mounting using epoxy resin impregnation under vacuum and after curing, sequential

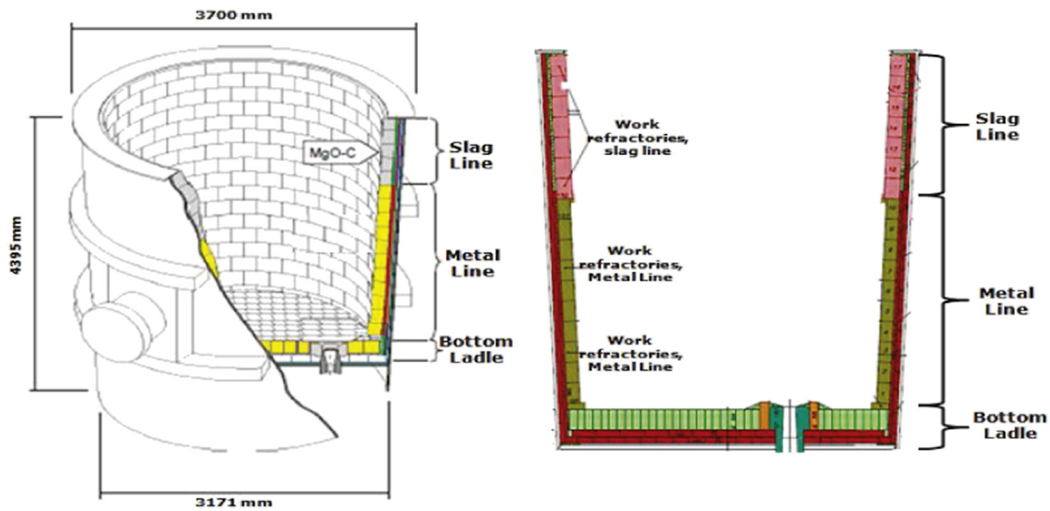

Fig. 1. Image and structure of the steel treatment ladle with different regions.

Table 2
Main steps in a post-mortem study of refractories [9].

Step	Task	Observation and variables
Definition of a post-mortem study	Research of operating conditions related with macro and microstructure modifications of refractories	Operating time, metallurgical treatments, power on-off processing time, volume and flow of gases, average load transported, temperature (average, maximum and minimum), operational interferences and mechanical interventions, types of metallurgical slags, fluxing and treatments routes.
Collection of the samples	Collection and sample identification (positioning of each collected sample in the metallurgical reactor)	Type of mechanical devices for sample collection (use of pneumatic devices, hydraulic, water, etc.) and standby time (operation output - sample collection).
Handling	Packaging, and handling of samples (sending)	Time of packaging and transportation of the samples. Special packing must be used when the refractories could react with water (water steam, relative humidity and/or environment water) Photographic survey of the conditions received samples (optical, display initial conditions: formats, presence of cracks, rusted areas, reacted area, presence of metals and slag, etc.
Definition of the tests	Initial analysis and definition of the tests to be performed. Mechanical testing, chemical, physical, optical and electron microscopy with microanalysis, etc.	Porosity, density, chemical composition, determine the mineralogical phases, reflected microscopy using light microscopy of polished section, etc.
Evaluation and conclusions about wear mechanisms	Analysis, statistical modeling and diagnosis of failure	Integrated discussion (user and suppliers of refractories) and definition of future approaches to improve quality and performance of materials.

grading with kerosene. The final polishing step was performed using a fine (<2 μm) diamond abrasive slurry. Then, the microstructural and chemical analyses of the ladle's slag line refractory samples were performed to identify the microstructures and the chemical compounds of interest. Reflected light stereomicroscope was used (LUPA ZEISS STEMI 2000-C) to identify the structures of interest to be analyzed by electron microscopy (SEM; Philips XL-30).

Fig. 2. Images of refractory demolition and sample collection from the ladle slag and metal line at the end of its lifetime (samples length range size from 110 to 229 mm).

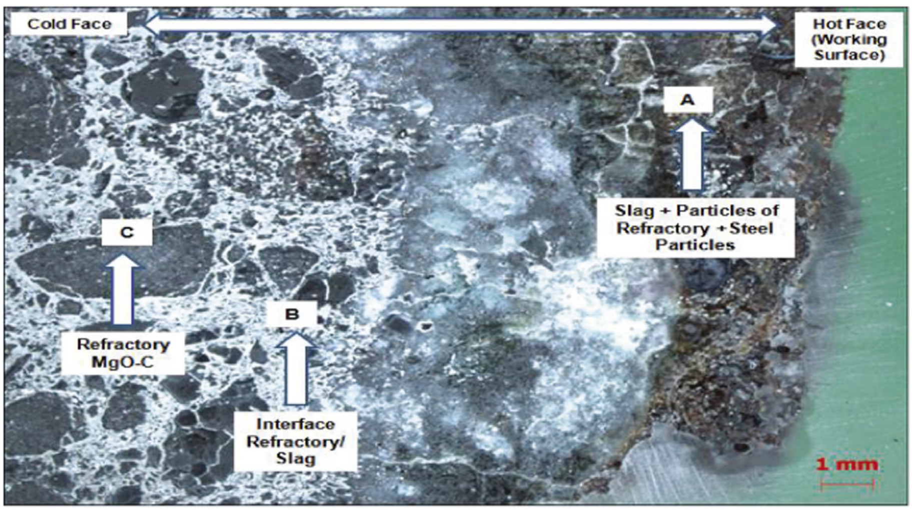

Fig. 3. Micrograph of the slag line ladle refractory sample using reflected light microscopy.

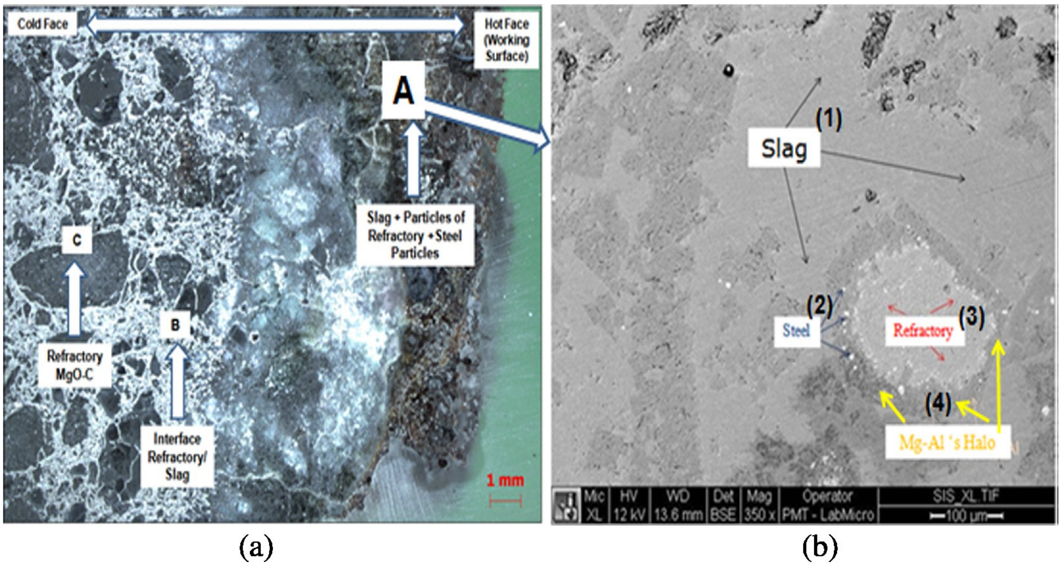

Fig. 4. (a) Region A amplification using a (b) back-scattered micrograph image (BEI) showing the MgO refractory grains surrounded by slag and steel particles, illustrating the corrosion process.

3. Results

Fig. 3 shows an image of a refractory slag line sample obtained using in the reflected light stereomicroscope. We can identify three distinct regions, namely, A-slag region (slag + particles of refractory + steel particles), B-interface region (interface refractory/slag) and C-refractory region (refractory MgO-C).

Fig. 4b shows a magnification of region A, the slag region (slag + particles of refractory + steel particles).

The presence of regions identified in Fig. 4 (region A) described above can be confirmed by chemical analysis using SEM-EDS (Fig. 5 and Table 3). The characterization of the three areas (A, B and C) noted in Fig. 4 and the possible phenomena and wear mechanisms involved were determined. In the slag region (slag + refractory particle + steel particles), it was observed that

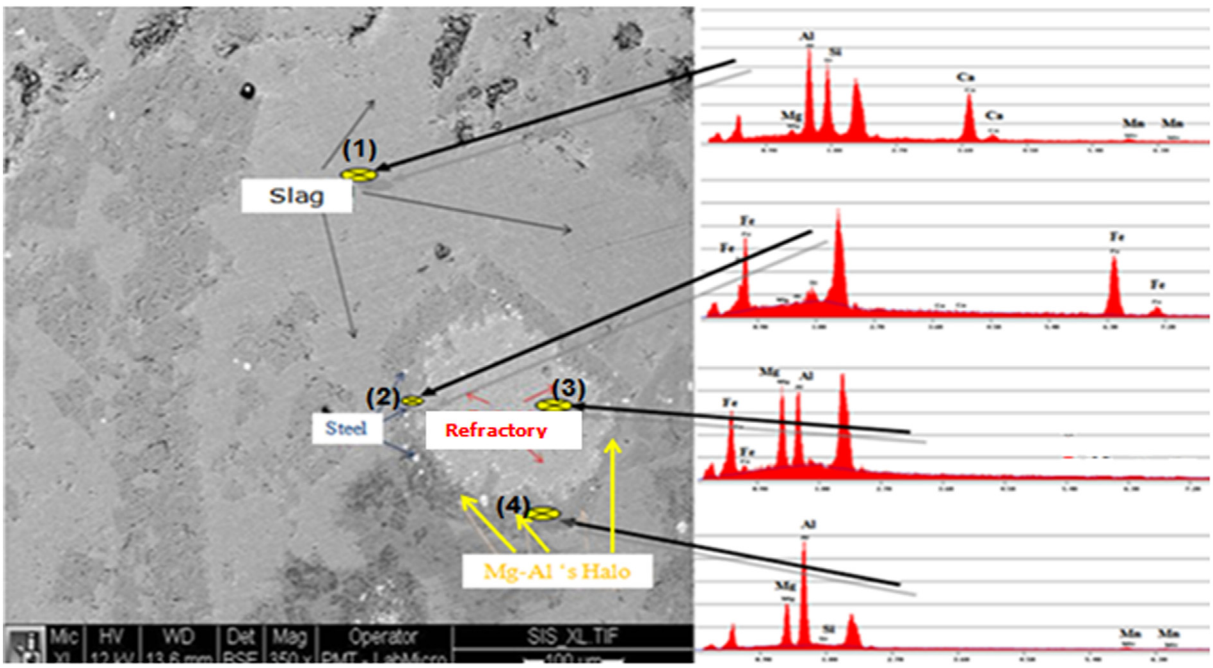

Fig. 5. Region A amplification using a back-scattered micrograph image and SEM-EDS chemical analysis.

Table 3
Chemical analysis of the regions 1, 2, 3 and 4 mentioned in Figs. 4 and 5 using SEM-EDS.

Slag (1)		Steel (2)		Refractory (3)		Mg-Al's halo (4)	
Substance	Wt. (%)	Substance	Wt. (%)	Substance	Wt. (%)	Substance	Wt. (%)
MgO	1.68	Fe	~100.00	MgO	31.88	MgO	22.02
Al_2O_3	28.44			Al_2O_3	35.32	Al_2O_3	66.49
SiO_2	29.45			FeO	32.80	SiO_2	2.01
CaO	33.59					MnO	9.48
MnO	6.84						
Total	100.00	Total	100.00	Total	100.00	Total	100.00

there appears to be a multiphase region with multiple components; in addition, there were steel particles infiltrated into this region, and the refractory was being dissolved by the slag.

In the interface region B (refractory/slag) observed in Figs. 3 and 4, there were observed refractory grains of MgO, probably electrofused, being corroded by slag infiltration into the refractory matrix (Figs. 6 and 7). Fig. 6 is the amplification of the interface region B, and Fig. 7 shows the different constituents of this area. Table 4 shows the results of the chemical analysis of the interface region.

Furthermore, an analysis was also performed on the region between the electrofused MgO grains (slag shown in Fig. 7), and it was found to have the typical composition of slag (Table 4), which confirms the above, referring to the attack of the grain of the refractory material by slag. This refractory wear mechanism of the slag line seems to be the predominant phenomenon in the steel ladle region.

Another relevant fact to be discussed from the analysis of Fig. 7 and Table 4 is the presence of sodium in the slag. As the manufactured steels, do not contain this chemical element, it is supposed that it should arise from the addition of nepheline (sodium, potassium, aluminum silicate $(Na,K)AlSiO_4$), a slag-fluidizing compound, added to lower the melting point of the slag. The addition of this material contributes in a significant manner to the refractory wear by slag corrosion, as it makes the slag extremely aggressive to the refractory. Nepheline is added in this steelmaking plant when low-sulfur steel (sulfur <60 ppm) is being produced to reduce the slag melting point and decrease the basicity (BB - binary basicity or BB_{LF} - ladle furnace basicity) to optimize the desulfurization process. The metallurgical refining route/treatment to produce this steel is call "Dessulfurado" or Desulfurized.

A statistical analysis of the participation of the Dessulfurado route (%) in the lifetime of the ladles reveals the negative impact of nepheline use and Dessulfurado route use (%) (Table 5 and Figs. 8 and 9). A statistical evaluation of steelmaking shop ladles during 2015 (approximately 6700 heats) was made using an operation database to correlate the metallurgical treatment refining route Dessulfurado with degradation of the refractory ladle. Table 5 shows the high consumption of nepheline in the Dessulfurado metallurgical treatment route, and Fig. 8 shows the negative correlation of Dessulfurado route and ladle's lifetime. A statistical analysis of Fig. 9 confirms all these results and includes comments.

Fig. 9 shows the differences between the averages (live and %Dessulfurado) of Block 1 and Block 2, Block 3 and Block 4, and the 1° Quartile to the 3° and 4° Quartiles. These differences can be observed in Tables 6 and 7, where the ANOVA (variance analysis) is performed to prove the real negative impact of the production of Dessulfurado steel with nepheline utilization on the ladle life. The statistical parameter test used was F and *t* (Student). If F was observed to be larger than a critical F or the quotient (F_observed / F_critical) is >1, the averages are different.

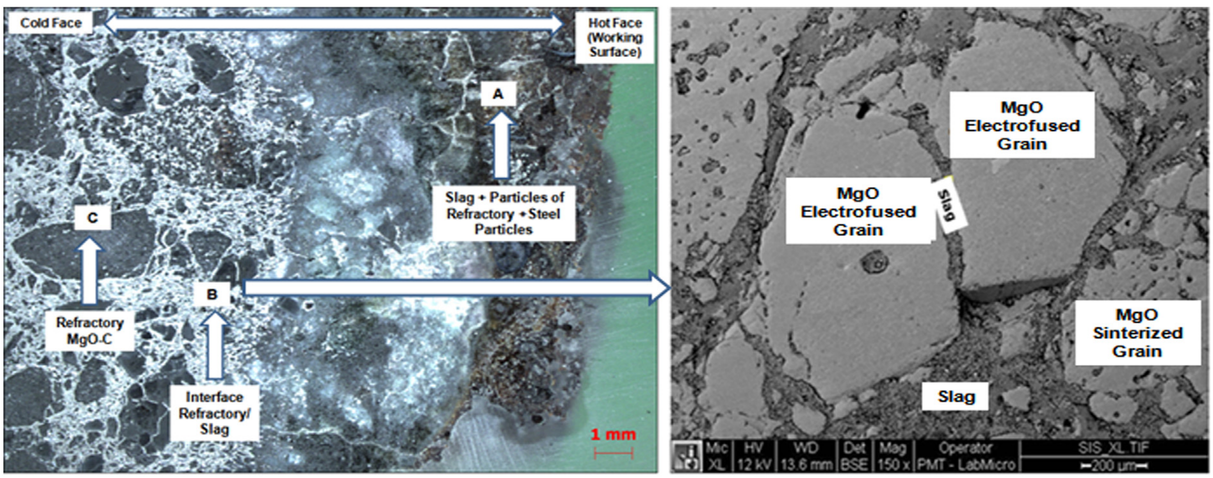

Fig. 6. Region B amplification using a back-scattered micrograph image showing the MgO refractory grain surrounded by slag illustrating the corrosion process.

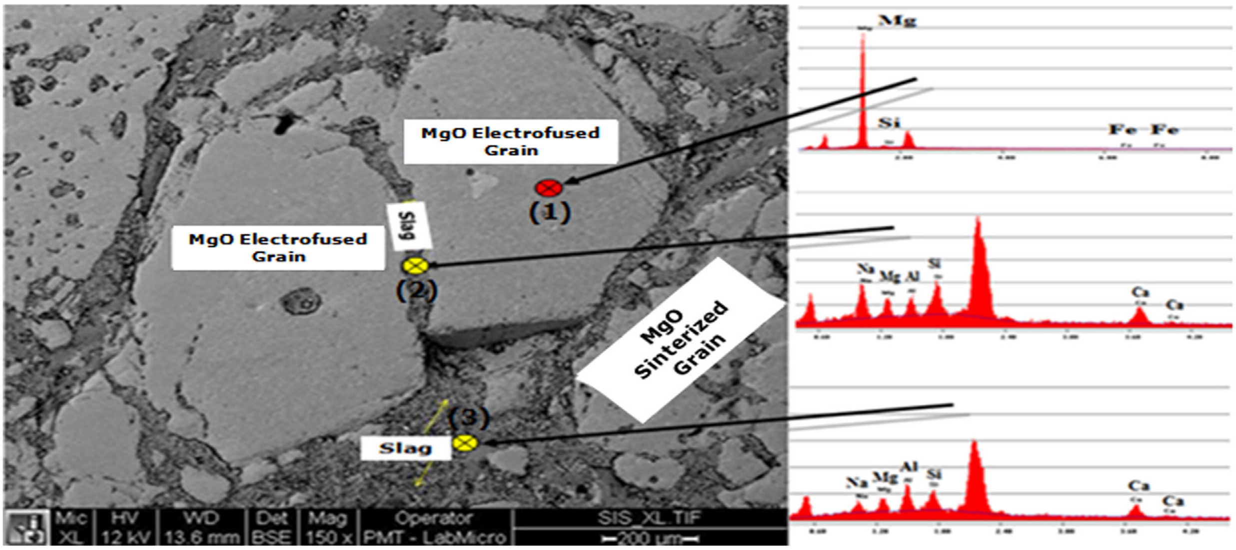

Fig. 7. Amplification and chemical analysis by SEM-EDS of interface region B. MgO electrofused grains (refractory) are being corroded by slag infiltration into the refractory matrix.

The analysis of Block 1 (Fig. 9) with Block 2 (where the reference is the median of the data) verifies that there was a 16% increase in the average ladle lifetime with a corresponding decrease of 32% in the average participation of the Dessulfurado route. The comparison of the best performance (175 runs/heat with 5% of the Dessulfurado route participation) to the worst result (92 runs with the participation of 11% of the Dessulfurado route) reveals an even greater difference (a 47% reduction in the average lifetime of the ladle).

When considering the average life of the ladles (154 runs), it appears that there is a 21.5% increase in the life expectancy of the ladles when compared to the average life of Block 3 (135 runs/heats) in relation to Block 4 (164 runs/heats), for a reduction of 31.9% in the percentage reduction in the share of the Dessulfurado Block route 3 (7.5%) relative to that of Block 4 (5.1%).

Analysis by quartiles shows, in principle, a reduction of the lifetime upon increasing the percentage of the Dessulfurado route for all quartiles. However, performing an analysis of the variance between quartiles (F test; to reject the null hypothesis that the

Table 4
Chemical analysis (SEM-EDS) of the grains in the region of the interface proving that they are refractory MgO grains and chemical analysis of the interface region (slag) between the electrofused MgO grains. The slag if high in sodium, probably from nepheline additions.

Chemical composition of MgO electrofused grains (1)		Chemical composition of slag (2)		Chemical composition of slag (3)	
Substance	Wt. (%)	Substance	Wt. (%)	Substance	Wt. (%)
MgO	95.04	Na_2O	14.38	Na_2O	6.57
SiO_2	1.70	MgO	12.27	MgO	12.57
FeO	3.26	Al_2O_3	13.99	Al_2O_3	26.50
		SiO_2	31.21	SiO_2	28.21
		CaO	28.16	CaO	26.15
Total	100.00	Total	100.00	Total	100.00
Infiltrated slag basicity		$BB_{(Binary)}$	0.90	$BB_{(Binary)}$	0.93
		$BB_{(Ladle\ furnace)}$	1.14	$BB_{(Ladle\ furnace)}$	0.99

Where: $BB = CaO / SiO_2$ and $BB_{LF} = (CaO + 1.40 * MgO) / (SiO_2 + 0.6 * Al_2O_3)$.

Table 5
Specific consumption of nepheline for the groups of steel in this steelmaking plant.

Groups	Specific consumption
High carbon	0.49 kg/t.
Low sulfur (Dessulfurado)	1.14 kg/t.
Common	0.15 kg/t.
Degassed	0.06 kg/t.
Double refining (Dessulfurado)	1.06 kg/t.
Peritectic	0.53 kg/t.
UBC-general	0.02 kg/t.

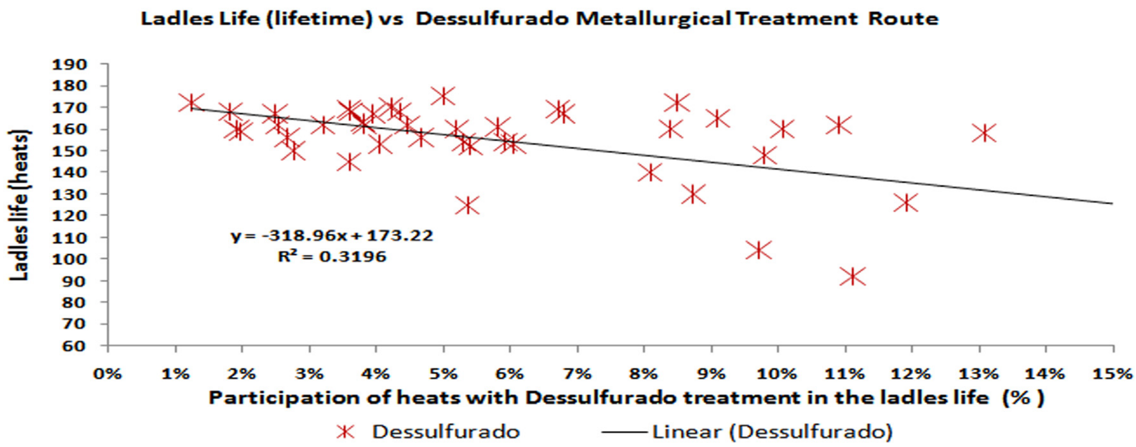

Fig. 8. Correlation between ladle life and participation % of metallurgical route Dessulfurado.

means are equal, the F observed must be greater than the critical F or the ratio of F observed/critical F must be >1) shows a real loss of life among only the Quartiles 3 and 4 compared to 1. The remaining variance (ANOVA) is indicated in Tables 6 and 7.

For region C in Fig. 3, no important results were found.

4. Discussion of the results

The results of the post-mortem tests show that the refractory structure degradation process of the analyzed steel treatment ladle slag line is the chemical corrosion by the slag formed during the secondary refining process of the steels. This phenomenon, as shown in the various figures above, is facilitated by the addition of nepheline (a high-capacity compound used for fluidizing slag with high corrosive power against refractory structures). The nepheline is used when the steelmaking plant produces low-sulfur steel (metallurgical route Dessulfurado) and negatively impacts the ladle life. In addition, there is slag infiltration between the refractory grains, causing high-porosity intragrains, that further promote the slag infiltration mechanism and facilitate the corrosive processes between the refractory and slag (due to the larger contact area with the higher porosity of grains). Furthermore,

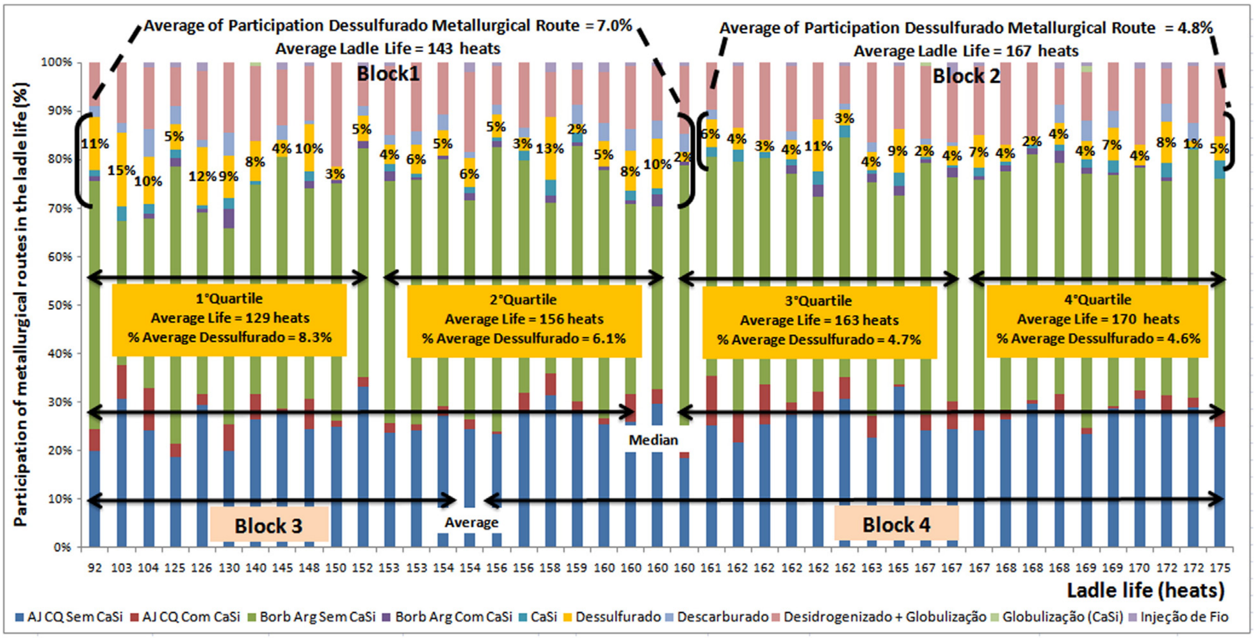

Fig. 9. Influence of % participation of metallurgical Dessulfurado group/route in the ladle life.

Table 6
Variance analysis (ANOVA) to compare the differences between the averages of the lifetime of ladles.

Quotient: (F_observed / F_critical)	Life_1° Quartile	Life_2° Quartile	Life_3° Quartile	Life_4° Quartile	Life_Block 2	Life_Block 4
Life_1° Quartile	1	4.419	6.699	8.635	NR	NR
Life_2° Quartile	–	1	7.497	28.497	NR	NR
Life_3° Quartile	–	–	1	9.585	NR	NR
Life_4° Quartile	–	–	–	1	NR	NR
Life_Block 1	NR	NR	NR	NR	6.699	NR
Life_Block 3	NR	NR	NR	NR	NR	9.111

Symbol (–) Reciprocal aij = aji. Symbol (NR) Unrealized.

Table 7
Variance analysis (ANOVA) to compare the differences between averages of the % of Dessulfurado route (%DS).

Quotient: (F_observed / F_critical)	%DS_1° Quartile	%DS_2° Quartile	%DS_3° Quartile	%DS_4° Quartile	%DS_Block 2	%DS_Block 4
% DS_1° Quartile	1	0.498	1.471	1.691	NR	NR
% DS_2° Quartile	–	1	0.265	0.355	NR	NR
% DS_3° Quartile	–	–	1	0.004	NR	NR
% DS_4° Quartile	–	–	–	1	NR	NR
% DS_Block 1	NR	NR	NR	NR	1.239	NR
% DS_Block 3	NR'	NR	NR	NR	NR	1.353

Symbol (—) Reciprocal aij = aji. Symbol (NR) Unrealized.

if this ladle's slag is rich in iron oxides, the carbon of the MgO-C refractory may be oxidized by iron oxide causing structural degradation.

5. Conclusions

It follows, therefore, that for the optimum performance life of a steel ladle, it is necessary to rationalize the use of fluidizing additions to slag containing sodium, in this case, nepheline. This addiction is correlated to production of low-sulfur steel that negatively impacts the performance of the ladles. In addition, analyses using the post-mortem technique can reveal the phenomena involved in the degradation of refractory structure equipment such as the steel ladle of the steelmaking. The chemical corrosion mechanism was the main factor of degradation and, consequently, the life of the steel ladle.

Acknowledgments

The authors thank the steelmaking company that provided the data and samples for this study.

References

[1] European Refractories Producers' Federation, Refractory Ceramics and Industrial Minerals are Critical for European Industry, Bruxelles, May 2009.
[2] W.E. Lee, R.E. Moore, Evolution of in situ refractories in the 20th century, J. Am. Ceram. Soc. 81 (6) (1998) 1385–1410.
[3] W.E. Lee, W.M. Rainforth, Ceramic Microstructures: Property, Control by Processing, Chapman and Hall, London, UK, 1994.
[4] M. Karakus, R.E. Moore, Cathodoluminescence (CL) microscopy application to refractories and slags, J. Miner. Mater. Charact. Eng. 1 (1) (2002) 11–29.
[5] Refractories Handbook, The Technical Association of Refractories, Japan, 10th ed., 1998.
[6] M. Bilgiç, Parameters Effecting Life Time of Refractory in Steelmaking, Department of Material Science and Engineering, Sweden, 2005 (21 pp.).
[7] M. Nicolae, I. Vilciu, E.D. Stoica, Research on the mechanism of damage line bricks in the slag LF, Int. J. Eng. 9 (2011) 117–120.
[8] R.A. Mattila, J.P. Vatanen, J.J. Harkki, Chemical wearing mechanism of refractory materials in a steel ladle slag line, Scand. J. Metall. 31 (2002) 241–245.
[9] Guilherme F.B. Lenz e Silva, Introdução à Siderurgia, cap. 9 – Refratários para Siderurgia, ABM Associação Brasileira de Metalurgia, Materiais e Mineração, 2007 (428 pp., Org. por Marcelo B. Mourão).
[10] D. Thomas, Analytical Challenges in Refractory Materials, The Southern African Institute of Mining and Metallurgy, Analytical Challenges in Metallurgy, South Africa, May 2009.
[11] R.P. Ornelas, et al., Post-mortem study of refractory concretes exposed to corrosive effect of synthetic slag of petroleum coke, J. Mater. Sci. Eng. 4 (10) (2010) 24–33.
[12] J. Bennett, et al., An analysis of the cause of failure in high chrome oxide refractory materials from slagging gasifiers. Albany Research Center, Albany, USA, 2005 97321 DOE/ARC-2005-008.