DEVELOPMENT OF MGO-ULC BRICK TO RUHRSTAHL HERAEUS LOWER VESSEL *

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Abstract
For the purpose of extend the life cycle of the RH lower vessel campaign, increase operational safety and reduce CO_2 emissions, ultra-low carbon (ULC) refractory bricks were developed, which have a low carbon content (≤ 1.8%wt) using a special type of graphite for application in the throat region of the RH lower vessel. Initial tests carried out in partnership with RHI Magnesita indicated significant improvements. The results show that the performance achieved with the MgO-ULC lining surpasses that of the magnesia-chromite bricks traditionally used, indicating a longer life cycle potential. In addition, it was found that it is possible to produce ultra-low carbon steels under these new conditions. At the same time, interest is growing in the development of new materials for lining RH degassing vessels. Traditionally, the RH vessel is lined with chrome-magnesium materials, a choice driven by the needs of the process, which aims to reduce the carbon contained in the liquid steel. Refractory linings that deviate from the chrome-magnesian composition are rare, highlighting the need for innovation in this sector.
Keywords: Degasser; RH; Ruhrstahl Heraeus; MgO-ULC.

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1 INTRODUCTION

The steel industry, seeking to meet rigorous quality standards, relies on the Ruhrstahl Heraeus (RH) degasser to promote deep decarburization and cleaning of steel. The RH degasser is a partial-quantity liquid steel treatment plant, which means that part of the steel contained in the ladle is transported into the equipment. Circulation is conducted through two refractory pipes (up and down), in this case, each pipe is composed of two refractory structures, called the throat and snorkel, as illustrated in Figure 1:

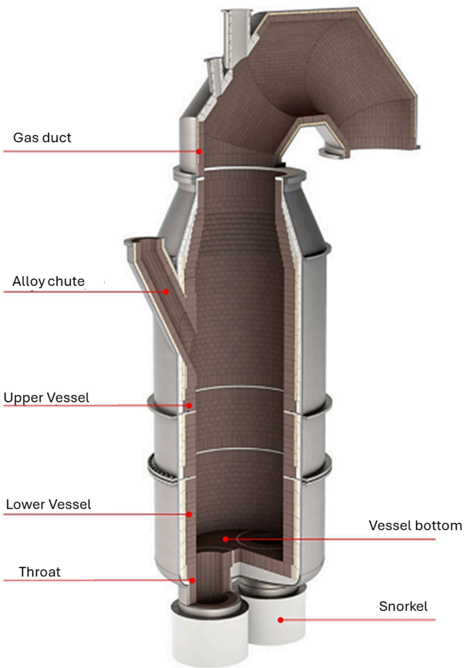


Figure 1. Regions of the RH vessel, adapted from [1,2]

1.1 THE CIRCULATION PROCESS

When argon is injected through the ascent snorkel, the steel from the ladle is sucked into the vessel, due to the principle of gas-induced circulation. The expansion of the argon due to its low temperature raises the column of liquid steel in the region of this leg, creating a difference in potential energy in relation to the column of the other leg, causing the liquid steel to descend into this leg.

The liquid steel that enters the vessel, subjected to the action of the vacuum, loses not only the argon drag, but also other gases dissolved in the bath (CO, N_2, H_2). In this way, the refined steel returns more purified to the ladle. The cyclical continuity of these stages allows the steel to circulate through the vessel and ladle, degassing and homogenizing the bath. [3]

In this context, the refractories used in RH vessels face complex challenges, including exposure to high temperatures, the corrosive action of slag and the challenge of achieving increasingly shorter treatment times. It is therefore essential to use high quality products to guarantee the necessary performance and durability in a way that does not interfere with the final quality of the steel. [4]

1.2 REFRACTORY WEAR MgO-Cr_2O_3

The refractories used for RH degassers are of the basic magnesia-chromium type, due to their high thermal stability and resistance to corrosion by slag. They can be semi-alloyed, alloyed, or direct alloyed, depending on the wear mechanism present in the specific region of the equipment.

During the treatment process, both the refractory and the casing are heated internally and externally. Radiation from the steel bath in the ladle heats the casing from the outside, while the liquid steel heats the refractory from the inside. This heating generates significant tensile stresses near the inner face in the throat area, the region that connects the inside of the vessel with the steel ladle and can result in gaps in the joints between the bricks there. During the circulation of the hot steel, these openings can remain, especially due to the downward expansion of the bottom of the vessel, which can allow the steel to infiltrate. As a result, over the course of the campaign, the throats can suffer structural fragmentation caused by frequent thermal oscillations, leading to a reduction in the useful life of the campaign. [5]

In ultra-low carbon steels, quality requirements are becoming more stringent, demanding ever lower carbon contents or in extremely narrow ranges. Despite the advantages of chrome-magnesian bricks, liquid oxide corrosion represents a severe form of degradation that reduces the useful life of these materials. Against this backdrop, MgO-ULC brick was evaluated as a new lining for the throats of the lower RH vessel.

RH slag can form in the vessel due to the dragging of slag from the steel ladle during the immersion of the legs and the dissolution of FeO. As the decarburization reaction proceeds, the FeO concentration decreases continuously to supply oxygen to the steel. After decarburization, aluminum is added to deoxidize the liquid steel containing high oxygen content, with this, the FeO content decreases and the Al_2O_3 content increases. [6]

1.3 REFRACTORY WEAR MgO-ULC

MgO-C is commonly used in refractories for basic oxygen furnace (BOF), electric arc furnaces (EAF) and steel ladles. Refractories in this category have the advantage of excellent resistance to penetration by slag, due to the low wettability of the carbon during contact with the oxides present in it. In addition, MgO-C refractories are highly resistant to thermal shock. These characteristics make it better evaluated than magnesia-chromite refractories. [6]

In addition to better property indices, the advantages of using MgO-C to replace chrome-magnesian fired bricks can be varied, such as: shorter production lead time; lower average cost; energy savings for the customer during the preheating stage - since MgO-C requires a preheating curve of no more than 16 hours. For chrome-magnesian bricks, the curve can be up to 60 hours. In addition, MgO-C bricks are much easier to recycle compared to chrome-magnesian bricks, and in the event of disposal, there is no risk associated with the presence of Cr^{+6}.

However, there are three concerns in the application of MgO-C bricks that limit them from being widely used in RH degassers, among them carbon capture during the treatment of ultra-low carbon steel and high-temperature oxidation. For these reasons, a new magnesia carbon material with a particular type of graphite was developed, enabling the fixed carbon content to be lower than 1.8%wt, and is categorized as MgO-Ultra Low Carbon (MgO-ULC).

2 DEVELOPMENT

2.1 MATERIALS

The lining currently used in the working area of Ternium BR's lower RH vessel consists of a conventional type of chrome-magnesian refractory brick (MgO-Cr_2O_3), which is fired and re-fired. In contrast, the product developed for evaluation is an MgO-ULC refractory brick, which is resined, cured and contains a special type of graphite, contributing to a fixed carbon content of only 1.8% by weight. Table 1 shows the specifications of these two materials discussed in this development.

Table 1. Specification of the two products: MgO-Cr_2O_3 and MgO-ULC

Product	Al_2O_3 (%)	MgO (%)	Cr_2O_3 (%)	Carbon (%)	Binder
MgO-Cr_2O_3	6,8	62,3	20,5	0,0	Ceramics
MgO-ULC	0,3	97,5	0,0	1,8	Resin

Before starting the tests at Ternium BR, laboratory experiments were carried out to evaluate and compare the physical, mechanical, and chemical characteristics of the MgO-Cr_2O_3 and MgO-ULC products. These experiments followed the internal protocols of the RHI Magnesita Research and Development Center, located in Contagem, Brazil. Of the five scheduled tests, three were completed. At the end of each test, the lining was thoroughly inspected to measure the thickness of the remaining refractory material to assess the condition of the lining. With the information collected, it was possible to calculate wear rates and identify potential for improvement.

To increase the life cycle of the lower vessel, it was decided to install the MgO-ULC material in both throats, the area that currently has the lowest lining potential. The other areas received the traditional MgO-Cr_2O_3 material.

Figure 2 shows the assembly of the refractory lining. In the regions where the MgO-ULC was mounted, it was recommended that an antioxidant paint be applied to prevent the material from oxidizing during heating.

Figure 2. Refractory installation photos

2.2 METHODS

To analyze the possible impact of the ULC lining on the decarburization process, an in-depth analysis was made of all the runs that passed through the RH, and an equation was applied to represent the kinetics of the carbon removal equation. Using a simplified model, which can be adjusted to experimental results, it was possible to calculate the kinetics of the reaction, as defined by Equation 1: [9,10]

$$C(f) = Co\, e^{(-Kt)} \tag{1}$$

- C: final carbon content (ppm)
- Co: initial carbon content (ppm)
- K: decarburization kinetic constant (min^{-1})
- t: decarburization time (min)

Using this equation, it was possible to obtain the values of the apparent decarburization constant for the treatment of 84 runs, for steels up to 30 ppm, 50% of which occurred in RH's with routine material and the other half of the runs in RH's with test material. The selected runs contained similar final and initial carbon ppm values, as well as process conditions that could be grouped together.

The initial carbon content considered in all the runs is the result collected after pouring in the BOF process, and the final carbon content considered is the result of the last sample after decarburization in the RH, until reaching the carbon range set for each grade.

3 RESULTS AND DISCUSSIONS

3.1 COMPARATIVE ANALYSIS OF THE PHYSICAL PROPERTIES OF BRICKS $MgO\text{-}Cr_2O_3$ AND MgO-ULC

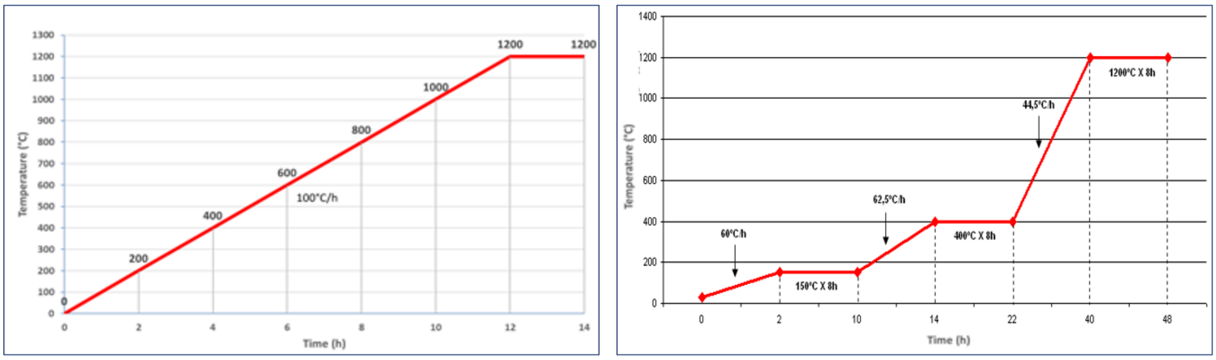
The physical and mechanical properties are shown in Table 2:

Table 2. Physical and mechanical properties

Properties	$MgO\text{-}Cr_2O_3$	MgO-ULC
Bulk Density [g/cm^3]	3,33	3,17
Bulk Density red.atm. (1000ºC)	-	3,10
Apparent Porosity (%)	12,5	6,00
Apparent Porosity red.atm. (1000°C)	-	9,5
Cold Crushing Strength [N/mm^2]	130	85,0

3.1 ADVANTAGES OF USING MgO-UCL MATERIALS IN RH

The complex routine of a steel mill constantly requires time reductions to complete each stage, whether it be assembly, preheating or heating. MgO-ULC materials, when compared to $MgO\text{-}Cr_2O_3$ materials, can reduce the assembly heating time by up to 70% compared to the current method. This also contributes to a significant reduction in CO_2 emissions. Figure 3 shows a comparison of the heating curves indicated for each of the materials.



Recommended heating curve for the MgO-ULC
Recommended heating curve for the MgO-Cr2O3

Figure 3. Comparison of heating curves

Other advantages include a reduction in manufacturing costs, lead time and the carbon footprint (CO_2 footprint). MgO-ULC is a cured material, unlike $MgO\text{-}Cr_2O_3$, which requires a firing step. This additional step increases the cost of the product, increases production time and increases the carbon footprint. With the complete migration of the working lining of the lower vessel to the MgO-ULC material, there was an approximate 50% reduction in the carbon footprint, considering the production and preheating of the equipment.

3.2 PERFORMANCE

The main motivation for using the MgO-ULC lining was to reduce thermoclase failures and lower the wear rate. The objective is to improve the thermomechanical behavior of the material and extend the service life of the equipment. Currently, the areas that determine the end of the lining's use are the throats, especially the riser throat. During the operation of the vessel, it was observed that the throats remained in excellent condition, showing a lower wear rate and providing greater operational safety.

Figures 4 and 5 show the photographic records obtained during the visual inspections.

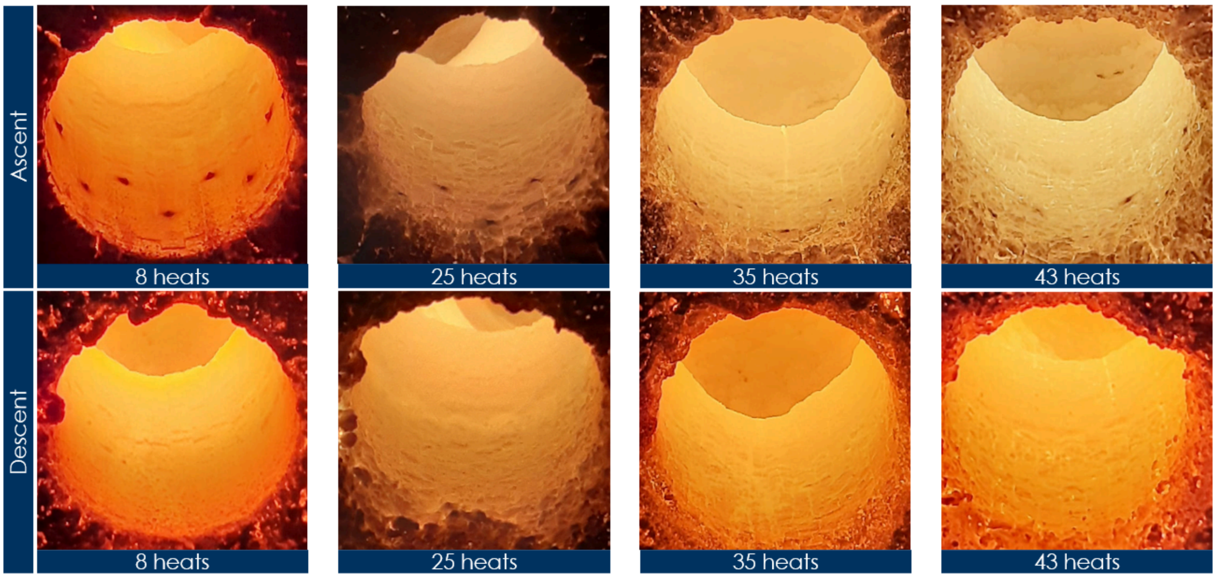


Figure 4. Visual inspections during the test.

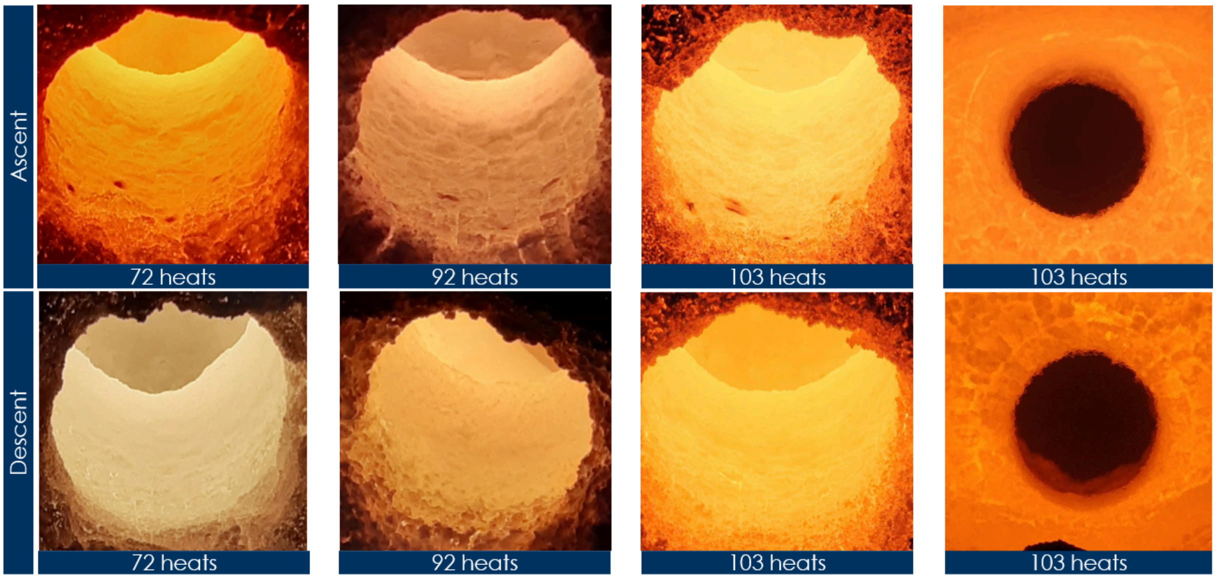


Figure 5. Visual inspections during the test.

When comparing the behavior of the different materials, the MgO-ULC exhibits a lower wear rate and no chipping, in contrast to the MgO-Cr_2O_3 lining of the snorkels. This behavior was expected due to the presence of carbon, whose function is to improve thermomechanical performance and reduce slag wettability.

Figure 6 shows the lining of the bottom, throats and snorkels after the end of the campaign:

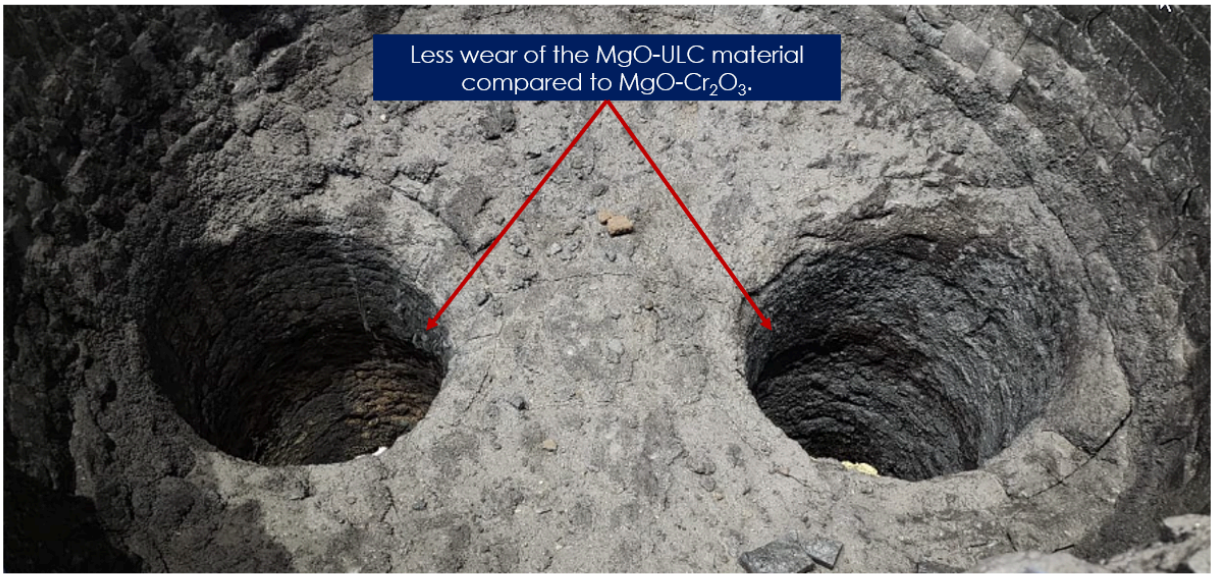


Figure 6. Revestimento após término da campanha.

Figures 7 and 8 illustrate the wear profiles of vessels coated with MgO-ULC and $MgO-Cr_2O_3$, respectively, which operated for similar periods and under comparable process conditions. The wear profile was measured using a laser scanner.

MgO-ULC - VI#10 - 110 heats				
Rhythm (heat/day)	Total Vacuum Time (min)	Average Vacuum Time (min)	Total Oxygen (Nm^3/h)	Average Oxygen per Heat (Nm^3/h)
9,4	3876	35,3	19736	179,41

$MgO-Cr_2O_3$ - VI#05 - 108 heats				
Rhythm (heat/day)	Total Vacuum Time (min)	Average Vacuum Time (min)	Total Oxygen (Nm^3/h)	Average Oxygen per Heat (Nm^3/h)
7,7	3927	36,36	20852	193,07

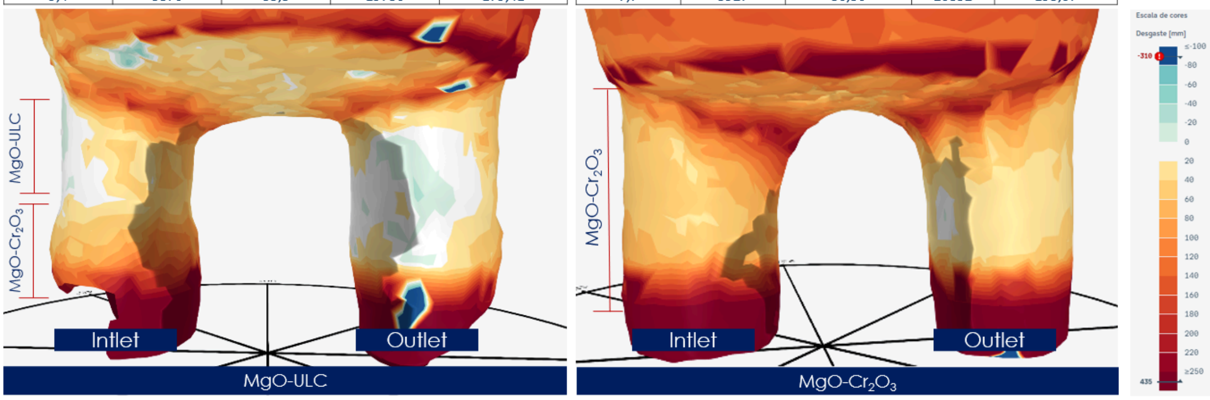


Figure 7. Lining wear profile side view.

MgO-ULC - VI#09 - 110 heats				
Rhythm (heat/day)	Total Vacuum Time (min)	Average Vacuum Time (min)	Total Oxygen (Nm³/h)	Average Oxygen per Heat (Nm³/h)
10,0	3782	34,3	24409	221,9

$MgO-Cr_2O_3$ - VI#09 - 101 heats				
Rhythm (heat/day)	Total Vacuum Time (min)	Average Vacuum Time (min)	Total Oxygen (Nm³/h)	Average Oxygen per Heat (Nm³/h)
9,2	3739	37,0	23389	231,6

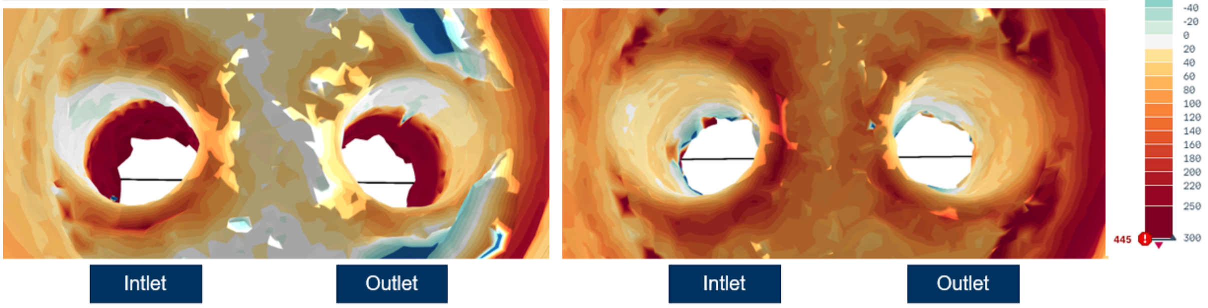


Figure 8. Lining wear profile top view.

Figure 9 shows a comparison between the MgO and $MgO-Cr_2O_3$ linings.

Figure 9. Comparison between the MgO and $MgO-Cr_2O_3$.

Decarburization on the cold side of the lining did not affect the performance of the material, which remained intact and showed good mechanical resistance. This mechanism is inherent to the process and poses no risk to the operation.

The ULC material showed fewer cracks perpendicular to the hot face than the $MgO-Cr_2O_3$ material and, consequently, a lower infiltration rate.

Figure 10 shows a historical and comparison of the wear rates of vessels lined with MgO-ULC and $MgO-Cr_2O_3$.

Materials	Project (mm)	Wear (mm)	Remaining (mm)	Performance (heats)	Wear Rate (mm/heat)
MgO-ULC	200	50	150	110	0,45
MgO-ULC	200	50	150	103	0,49
$MgO-Cr_2O_3$	200	70	130	129	0,54
$MgO-Cr_2O_3$	200	55	145	98	0,56
$MgO-Cr_2O_3$	200	80	120	121	0,66
$MgO-Cr_2O_3$	200	75	125	113	0,66
$MgO-Cr_2O_3$	200	75	125	112	0,67
$MgO-Cr_2O_3$	200	75	125	109	0,69
$MgO-Cr_2O_3$	200	125	75	126	0,99
$MgO-Cr_2O_3$	200	125	75	122	1,02
$MgO-Cr_2O_3$	200	150	50	126	1,19
$MgO-Cr_2O_3$	200	175	25	129	1,36

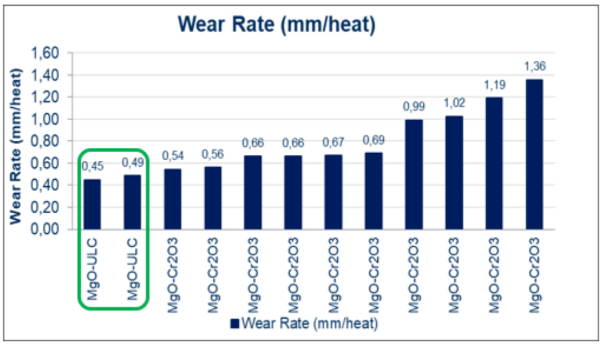


Figure 10. Wear rate historical.

3.3 COMPARATIVE ANALYSIS OF DECARBURATION

By applying Equation 1, it was possible to know the decarburization kinetic constant for all the runs and establish a comparison between the process in the test application scenario and the routine scenario. Figure 11 shows a comparison of the carbon removal behavior between the RH's that used $MgO-Cr_2O_3$ lining (routine) and MgO-ULC. The analysis was carried out using the data from the runs which had a maximum concentration of 30ppm of carbon contained in the bath, as these are more critical steels.

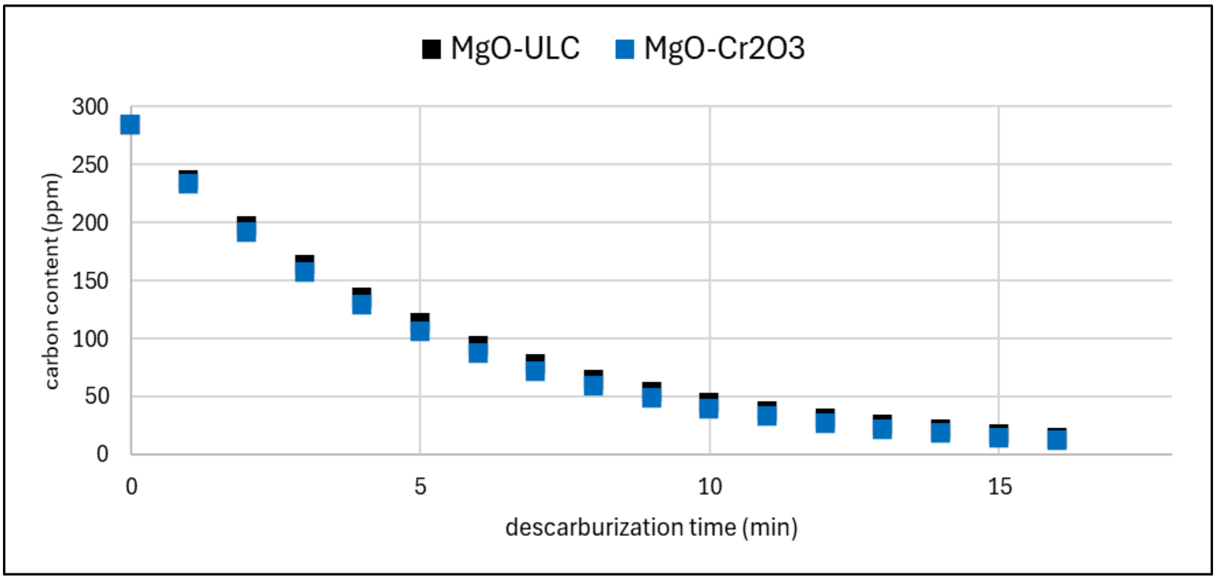


Figure 11. Comparison of decarburization curves during degassing in ULC-coated vessels and $MgO-Cr_2O_3$ lining vessels

The scale on the y-axis of Figure 11 (0.0 to 300.0 ppm) indicates the average carbon variation calculated through the decarburization kinetic constant, with the carbon variation in relation to time (x-axis). As you can see, there is a small difference in the ppm of carbon obtained, which becomes smaller as the process progresses. From the point of view of process quality, there was no significant impact on the production of these steels, a factor that confirmed the operational safety of the production of ultra-low carbon steels on a large scale with the ULC lining present in the throats of the equipment, maintaining quality levels of steel within expected parameters.

4 CONCLUSION

To extend the useful life of the lower vessel campaign of the RH degassers, the MgO-ULC refractory with 1.8% carbon by weight applied to the vessel throats proved to be efficient from the point of view of material performance, proving to be superior to chrome-magnesian.

The percentage of carbon contained in the MgO-ULC material proved to be negligible during the process and did not affect the quality of the steels produced. Therefore, with the statistical analysis of the samples and operational data, we concluded that the MgO-C brick linings had no negative influence on the decarburization rate and achieved a 35% higher lifetime lining performance, paving the way for greater application opportunities for RH degassers and the potential to achieve longer campaigns.

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