

REPORT

Chrome Free Unfired Magnesite Brick – A Really Environmentally Friendly Product for RH Degassers –

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Abstract

The companies' commitment to zero CO₂ emissions by 2050 has promoted a huge effort in the search for alternatives to replace conventional products, aiming to drastically reduce the carbon footprint. In refractory industry, for example, materials produced at low temperatures have been researched to replace high temperatures fired bricks, with significant CO₂ emissions in their processing. This is the case of MgO-Cr₂O₃ products, used as refractory lining at RH degassers. In addition to the environmental appeal for CO₂ reduction, the elimination of chromium is also a pursued objective, mainly due to the possibility of contamination of the environment by Cr⁺⁶. Additionally, new possibilities for safe recycling can be explored with the absence of chromium. This work presents the efforts in the development of unfired Cr-free alternative refractories for application in RH degassers, to contribute with environmentally friendly products.

1. Introduction

Currently around 70% of consumed refractories in the world are used by the steel industry, of which 1/3 are consumed during secondary refining operations¹⁾. The introduction of continuous casting, the growing demand for "ultra clean" steels²⁾ and the increased use of scrap as a raw material require additional treatment steps. Degassing – the main example of which is the Ruhrstahl Heraeus (RH) process – is one of these additional stages, incorporated for the elimination of hydrogen, carbon and oxygen, in addition to the homogenization of liquid steel.

Evidently, the stability of the refractories lining inside of equipment for steel refining is crucial for

cleanliness of the final product, which includes minimizing its wear and eventual incorporation of refractory particles into the metal bath. In addition, the correct selection of lining material extends the operating cycle of the asset and avoids interruptions in production. For this, understanding the wear mechanisms of refractories subject to RH Degasser operation is essential.

Despite its performance when it comes to high corrosion resistance as a result from direct bonding between chromium ores and magnesium aggregates through which the grains are predominantly joined by a solid-state diffusion mechanism, current magnesite-chrome refractory linings have been replaced due to the toxicological and environmental risks associated

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with Cr^{6+} . Aiming at finding a potential substitute, compositions containing spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$ have been the focus of multiple studies to verify their applicability in industrial processes such as steel degassing (RH³⁾, VOD⁴⁾, copper refining⁵⁾ and cement production⁶⁾.

Focusing mainly on thermal shock and corrosion, this work proposes to compare laboratory trials results between a proposal of new product unfired and based on $\text{MgO}-\text{Al}_2\text{O}_3$ without chromium in its composition with current fired with chromium content in RH operation. Initially, an exposition will be made of the physical-chemical, thermal and mechanical properties to which the lining is submitted during the industrial process. Based on these mechanisms, the experimental results of thermal shock and corrosion resistance tests will be discussed.

2. Experimental Procedure

Following the purpose of this paper to evaluate a more environmentally friendly product as an alternative to standard fired magnesia-chrome containing materials, a composition (here named as U1 presented on Table 1) of high-grade fused magnesia, high MgO content magnesia sinter and

fused spinel of different grain sizes were made as the proposed formulation. Grain sizes of mentioned raw materials was defined to provide an optimized grain sized distribution and higher densification. Due to thermal cycles and high FeO content slag the refractory lining of RH Degassers are submitted, two main properties of the product are necessary to achieve good field performance: high thermal shock resistance and high corrosion resistance. Aiming at having a product with high performance in both properties, ceramic additives were used in the mix and a chemical binder, activated at lower temperatures (below 500°C), was used to provide non-fired bricks, in order to reduce CO_2 emissions.

Table 1 also presents two different chemical analysis of direct-bonded $\text{MgO}-\text{Cr}_2\text{O}_3$ products as commercial references, currently applied as RH Degassers lining: CR1 for lower vessel critical areas, such as impact pads, throat, and RH snorkels, and CR2 for RH lower vessel non-critical areas. Both are for high performance comparison available in the market as reference value of standard fired refractory bricks.

Physicochemical properties measurements, presented on Table 2, were conducted on U1 sample

Table 1 Detailed description of samples used in this paper

Samples	U1	CR1	CR2
Components:			
Fused magnesia (~5.0 mm)	80.5	-	-
Magnesia sinter (~1.0 mm)	2.5	-	-
Fused spinel (~1.0 mm)	12.5	-	-
Ceramic additive A	2.0	-	-
Ceramic additive B	0.5	-	-
Chemical binder	2.0	-	-
Chemical analysis / %			
MgO	83.0	65.0	67.0
Cr_2O_3	<0.0	23.5	16.1
Al_2O_3	9.3	3.3	7.9
SiO_2	0.5	1.8	2.0
Fe_2O_3	0.1	5.5	7.0
Other	7.1	0.9	0.0

Table 2 Physicochemical properties

Properties	U1	CR1*	CR2*
After baking (200°C)			
Bulk density / $\text{g} \cdot \text{cm}^{-3}$	3.12	-	-
Apparent porosity / %	8.8	-	-
Cold crushing strength / MPa	84.8	-	-
Module of rupture / MPa	18.3	-	-
After firing ($1,000^\circ\text{C}$)			
Bulk density / $\text{g} \cdot \text{cm}^{-3}$	3.07	-	-
Apparent porosity / %	13.8	-	-
Cold crushing strength / MPa	43.9	-	-
Module of rupture / MPa	4.4	-	-
After firing ($1,450^\circ\text{C}$)			
Bulk density / $\text{g} \cdot \text{cm}^{-3}$	3.07	3.21	3.08
Apparent porosity / %	13.9	15.9	17.5
Cold crushing strength / MPa	37.1	54.1	34.8
Module of rupture / MPa	5.0	5.9	4.4
Hot modulus of rupture at $1,400^\circ\text{C}$ / MPa	2.2	7.6	5.9

*As CR1 and CR2 are commercial products used as reference, their samples were already fired.

after baking at 200 °C and after heat treatments at 1,000 °C and 1,450 °C, to analyze the evolution of properties at different temperatures. As CR1 and CR2 are commercial products, the samples taken as received were used as comparison for properties after 1,450 °C heat treatment. After each heat treatment conducted in reduced atmosphere, Bulk Density and Apparent Porosity were performed following the standard ABNT NBR 16661, Cold Crushing Strength follows standard ABNT NBR 10059, Modulus of Rupture follows standard ABNT NBR 5014 and Hot Modulus of Rupture standard ABNT NBR 9642.

Before thermal shock resistance characterization, samples were submitted at 1,450 °C in reduced atmosphere for 5 hours. Then 10 cycles of thermal shock at 1,000 °C for 1 hour each and air (forced convection) until reach room temperature were conducted with sonic elastic modulus measurement after cycles 1, 2, 4, 6, 8 and 10. All materials were compared considering the residual percentage of the original Young Modulus.

FactSage 8.0 software was selected to simulate the both F2 and C2 slags/refractory interface selecting FactPs, FToxid and Ftmisc databases for calculations. Equilibrium condition of a hypothetical interface varying from 100 % of slag to a 100 % of refractory was simulated, showing what phases could be expected for at a simulated condition considering an operation at 1,700 °C and 0.04 atm (approximately vacuum condition inside the RH).

The RH Degasser slag changes throughout the operating cycle, starting from a normal steel ladle slag, evolving into a FeO-rich slag, and ending up in a CaO/Al₂O₃ slag system⁷⁾. Corrosion resistance

was then determined using a rotary slag test kiln, at 1,680 °C (±20 °C), using two slag compositions: a FeO rich slag (F2) and a CaO/Al₂O₃ slag (C2). For each trial, the slag was renewed, resulting in a two corrosion stages with new slag. The slag chemistry analysis is presented in Table 3.

In addition, as the absolute values of wear at samples submitted to the rotary kiln corrosion trial was too low, a more aggressive test was necessary trying to have a more representative of RH Degasser real operational conditions. The purpose of the lance erosion test was to evaluate FeO resistance at a high temperature (~2,000 °C) with an irradiation time of 30 seconds. The oxygen gas flows through a steel pipe which at high temperatures generates FeO that will erode the refractory brick. The volume of the eroded hole was measured by filling the eroded hole with silicon carbide grains and converting the volume from its weight.

3. Results and Discussion

As previously presented, Tables 1 and 2 showed that the developed formulation of unfired brick has a lower porosity than commercial MgO-Cr₂O₃ products which can impact on slag penetration. The different heat treatments applied to the developed product showed a good evolution of cold mechanical resistance, with the values after heat treatment at 1,450 °C at the same level as those observed for the MgO-Cr₂O₃ products. However, the developed product presented lower value of hot mechanical resistance when compared to commercial products containing chromium. As an isolated case, these lower values may not have great influence on refractory performance, but when associated with the resistance to thermal shock and to cracks appearance by thermomechanical stress, it becomes an important property to be achieved. These phenomena are very common in critical regions of RH Degasser, such as the throat and snorkels, especially in those cracks that occur at the interface between volumes impregnated with slag and volumes that still unaltered, which greatly contribute to the structural spalling of the bricks in

Table 3 Chemical analysis of FeO rich slag (F2) and CaO/Al₂O₃ slag (C2)

Compounds	F2	C2
Fe ₂ O ₃	39.3	-
CaO	34.2	40.4
Al ₂ O ₃	16.8	55.8
SiO ₂	6.5	-
MgO	3.2	3.8

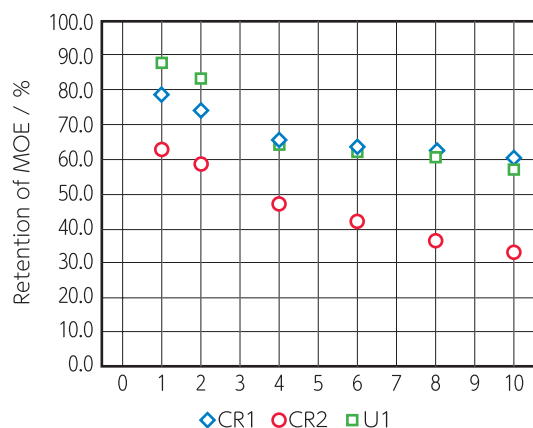


Fig. 1 Percentage values of modulus of elasticity/young's modulus after 10 cycles of thermal shock at 1,000 °C.

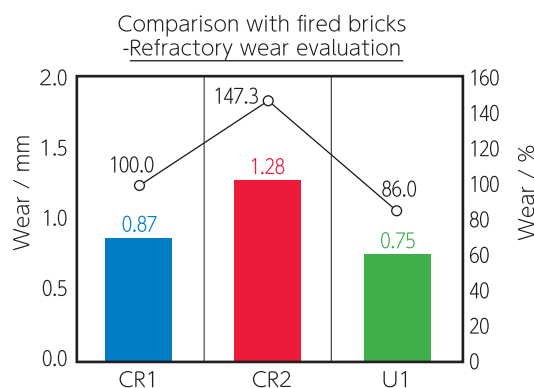


Fig. 2 Absolute and relative wear values after a FeO rich slag (F2) corrosion test in rotary kiln.

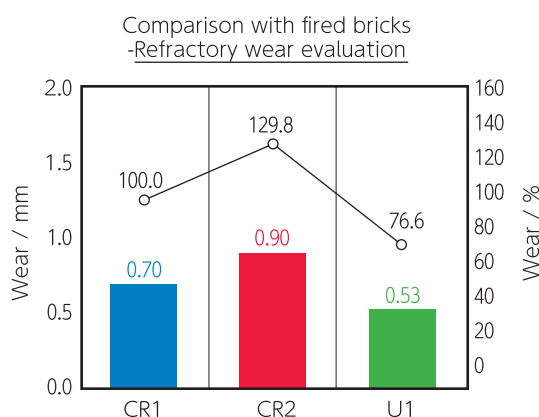


Fig. 3 Absolute and relative wear values after a CaO/Al₂O₃ rich slag (C2) corrosion test in rotary kiln.

operation.

As seen in Fig. 1, the thermal shock resistance test showed that the developed unfired product (U1) showed a very similar behavior to the commercial product containing chromium used in the critical parts of the RH furnace (CR1) and better performance than commercial chromium containing product used in the less noble regions (CR2). This shows the effectiveness of the ceramic additives on improving the thermal shock characteristics of the developed material.

In both cases, using F2 or C2 slags, the developed formulation proved to be more resistant in the corrosion test when compared to fired references as

shown in Figs. 2 and 3.

After achieving good results at thermal shock and corrosion resistance tests, U1 proposal formulation and CR1 reference were selected for a simulation of phases in equilibrium at the slag/refractory interface, at temperature and pressure similar to the operating conditions, using Factsage 8.0 thermodynamic simulation software. The results are shown in Figs. 4, 5, 6 and 7.

Simulation using the FeO-rich slag, shown in Fig. 4, indicates that the interface of the commercial product containing chromium shows an initial solubilization of the refractory of about 17 %. After this point, MgO saturation occurs becoming stable. The saturation of chromium spinel, on the other hand, occurs later, in a fraction around 20 % of refractory. During all simulated fractions, there is a small evolution of the gas phase, rich in O₂. There is no precipitation, in equilibrium, of phases other than those initially present in the refractory.

The simulation (Fig. 5) for U1 formulation results on initial refractory solubilization, at the FeO-rich slag interface, close to 15 %. The additives ceramic phases A and B are completely solubilized, and the system, in equilibrium, presents, for proportions above 15 % of refractory, 2 immiscible slags. The spinel phase only becomes stable in a proportion of above 90 % refractory. There is also a presence of gas phase rich in O₂ in practically all refractory

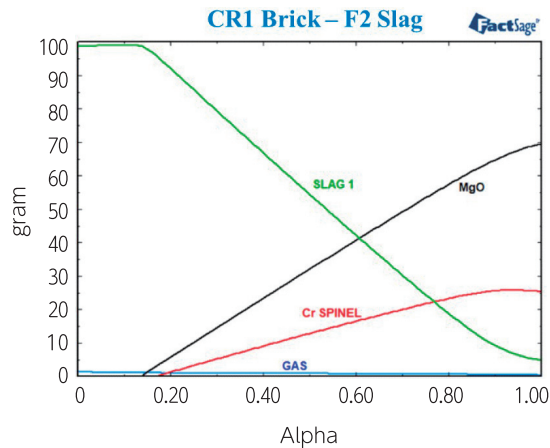


Fig. 4 Equilibrium phases, at 1,700 °C and 0.04 atm, simulated by FactSage 8.0, considering chemical analysis of chromium containing CR1 brick, into hypothetical slag F2/brick interface, varying from 100 % slag (Alpha = 0) to 100 % refractory (Alpha = 1).

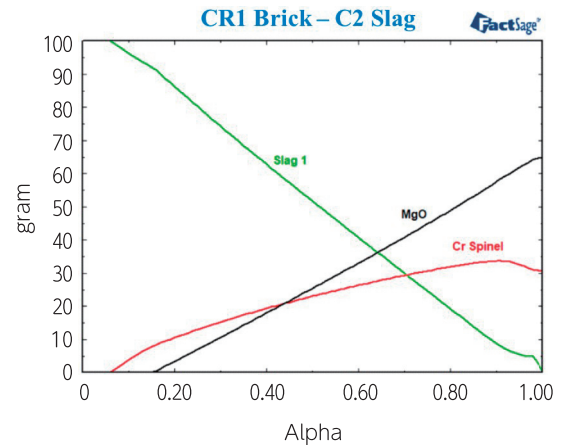


Fig. 6 Equilibrium phases, at 1,700 °C and 0.04 atm, simulated by FactSage 8.0, considering chemical analysis of chromium containing CR1 brick, into hypothetical slag C2/brick interface, varying from 100 % slag (Alpha = 0) to 100 % refractory (Alpha = 1).

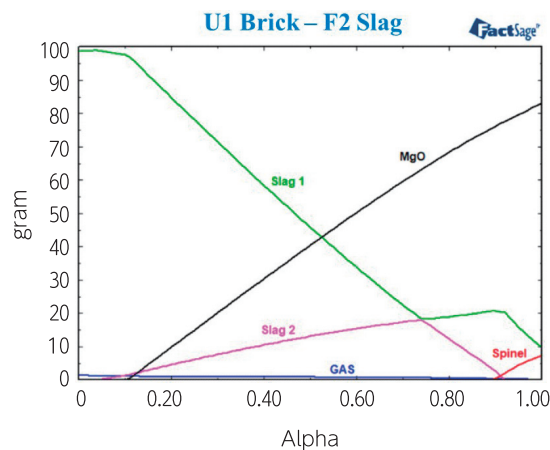


Fig. 5 Equilibrium phases, at 1,700 °C and 0.04 atm, simulated by FactSage 8.0, considering chemical analysis of unfired chromium free U1 brick, into hypothetical slag F2/brick interface, varying from 100 % slag (Alpha = 0) to 100 % refractory (Alpha = 1).

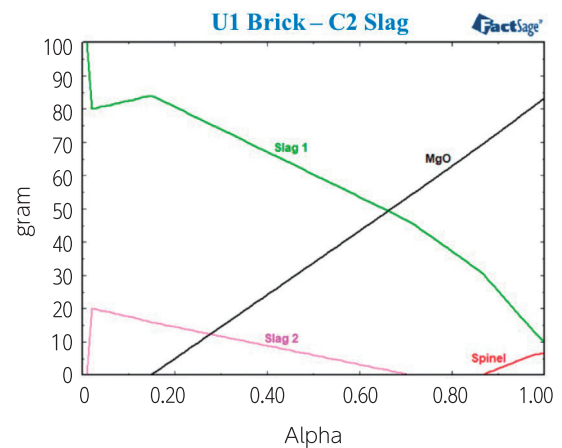


Fig. 7 Equilibrium phases, at 1,700 °C and 0.04 atm, simulated by FactSage 8.0, considering chemical analysis of unfired chromium free U1 brick, into hypothetical slag C2/brick interface, varying from 100 % slag (Alpha = 0) to 100 % refractory (Alpha = 1).

proportions.

Fig.6 illustrates the simulation of interface between CR1 brick with the C2 slag ($\text{CaO}/\text{Al}_2\text{O}_3$). The commercial refractory containing chromium (CR1) has a lower solubility when compared with the simulation done with F2 slag, with chromium spinel already saturating the slag from about 7 % of refractory fraction. No gas phase was detected.

In the case of the refractory/slag interface for formulation U1, showed at Fig.7, the initial solubilization is much higher than for the product containing chromium, around 18 %. Again, the additive ceramic phases A and B are not stable at all refractory ratios, and two immiscible slags are present up to the 70 % refractory ratio. No gas phase is present at equilibrium conditions, and the

spinel phase only becomes stable from a proportion of 88% refractory.

From achieved results at corrosion tests and in the phase equilibrium simulations, it is possible to indicate that the presence of two immiscible slag phases, present in the $\text{MgO-Al}_2\text{O}_3$ system, combined with the complete solubilization of additive ceramic phases A and B in these same slags, play a key role in the improved corrosion and slag penetration resistance.

Visual observation of the bricks after corrosion attack lance test, shows cracks in the holes of CR1 and CR2 bricks, but not in U1, according to the appearance and cross section surfaces. Fig. 8 shows the detailed images of cross sections of the three products after lance teste and corresponding volume values caused by erosion.

The depth and volume of melt loss was the lowest for U1 unfired bricks when compared to CR1 and

CR2. The appearance and cross sections surfaces of the fired bricks CR1 and CR2 showed cracks around the melted holes unlikely unfired bricks. The thermal shock is considered to be high because the lance melt damage test rapidly reaches very high temperatures, around $2,000^\circ\text{C}$. Therefore, it is considered that the unfired bricks with excellent heat spalling resistance have not presented cracks.

In addition, the amount of erosion loss tended to be lower for unfired bricks than for fired ones which can be justified by lower porosity of unfired compared to the fired ones. Contrariwise, the porosity of unfired bricks increases when heat treatment is applied. Therefore, the FeO resistance of unfired bricks used and heated in an actual furnace may differ from the trend of the lance erosion test results. Although fired bricks were also included in the comparison, caution should be exercised in comparing the test results of this study.

Ultimately all performed tests results indicate the good performance of unfired new development as a potentail substitution of fired chromium-based standard bricks. When we remove the heat treatment at high temperatures from the production process of the refractory bricks, there is potential of reduction of 357,1 kg of CO_2 emission per ton of brick due to removal firing step maintaing only baking⁸⁾.

4. Conclusions

Highlighting toxicological and environmental risks associated with hexavalent chromium in $\text{MgO-Cr}_2\text{O}_3$ fired bricks – widely used in steel degassing equipment, such as in the Ruhrstahl Heraeus (RH) process – refractories based on $\text{MgO-Al}_2\text{O}_3$ have been considered in the literature as potential substitutes. Throughout this work, several characterizations were carried out, seeking to evaluate the feasibility of a refractory based on $\text{MgO-Al}_2\text{O}_3$ for the lower vessel RH.

The present paper showed a successful development based on $\text{MgO-Al}_2\text{O}_3$ proposal suitable with some of the most important properties conferred by chromium-containing products currently applied in RH degasser. This new product was developed using

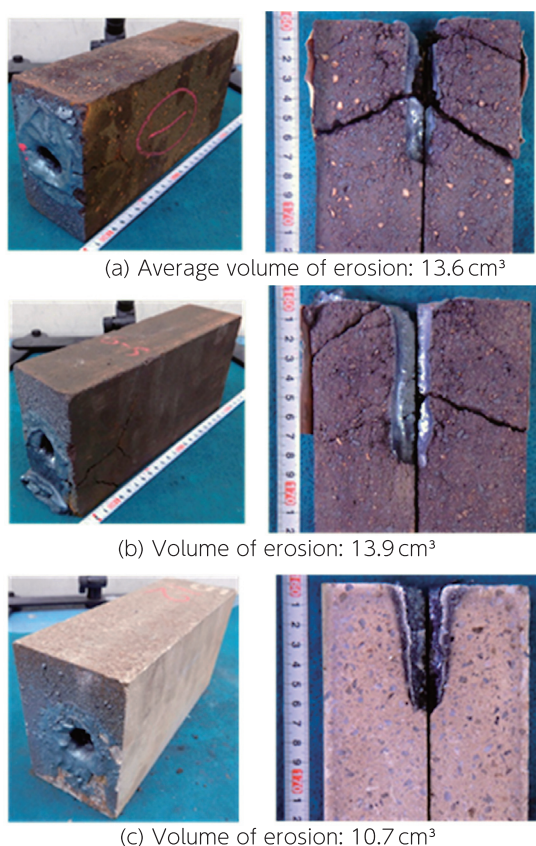


Fig. 8 Cross section surfaces of (a) CR1, (b) CR2 and (c) U1 bricks after corrosion attack by lance test.

a lower heat treatment temperature, reducing CO₂ emissions in comparison to traditional chromium containing materials.

Satisfactory levels of resistance to thermal shock were achieved, compatible with a commercial reference product containing chromium, used in critical regions of the RH furnace, such as throat and snorkel.

A major corrosion resistance was achieved by new product, mainly by the addition of ceramic additives that, through their solubilization, provided lower

extension in the impregnation by the evaluated slags. Even in more harsh conditions trials, the new product performance exceeded fired bricks on thermal shock resistance associated with higher temperature corrosion resistance.

Future studies aiming at focusing on improvement of hot mechanical resistance, necessary to prevent the appearance of cracks in current commercial products, due to the very characteristic thermomechanical effects present during the operation of RH degasser.

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