Challenges for BOF Impact Pad: Redesign Flexible Binder for Improving Performance



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Walter Cassete, RHI Magnesita, Contagem, MG, Brazil The decarbonization and transformation of integrated basic oxygen furnace steelmaking is currently an important challenge. As a charge material with zero CO_2 emissions, steel scrap is essential to the decarbonization process. As the amount of steel scrap charged to converters increases, it promotes higher wear of refractories installed on scrap impact zones. A new generation of carbo-resins with low-emission binder system was first introduced for improving flexibility in cold processing, similar to pitch-bonded bricks processed at hot conditions. This work presents a complete comparative evaluation of the novel redesigned flexible binder MgO-C brick against the original resin-pitched one. Customers' performance is highlighted.

Introduction

The steel industry is one of the largest industrial CO2 emitters, with a current global production of about 1,850 mtpa, 70% of which is through the basic oxygen furnace (BOF) route. It accounts for up to 9% of worldwide carbon dioxide emissions. The BOF is an autothermal process where hot metal and scrap are used as charging materials. The decarbonization and transformation of integrated BOF steelmaking is an important challenge for the near future. Steel scrap is a charge material without new CO_2 emissions, whose availability is expected to grow significantly and will be essential to the decarbonization process. Fig. 1 shows the specific CO₂ emissions per ton of output product for the different starting raw materials in steel production.¹ Hot metal presents the largest contribution with around 1.5 tons of CO_2 per ton of liquid steel. Direct reduced iron (DRI) with natural gas has less than half the emission of hot metal via the blast furnace (BF) process. Future hydrogenbased direct reduction is already approaching close to zero. The only source of raw material for steelmaking with zero CO_2 emissions is steel scrap. Therefore, an increased usage of steel scrap, which can be recycled infinite times, will play an important role in

the decarbonization of the steel industry alongside direct reduction–based steelmaking.¹

Another approach to reducing CO₂ emissions is to increase the metallic Fe input to the production system. It is known that scrap works as a CO_2 diluent when introduced in iron ore-based steelmaking. Scrap is a key supplementary charge material in oxygen steelmaking converters, but scrap can also be utilized in ironmaking to decrease the use of reducing agents and also the specific CO₂ emissions. At moderate scrap rates, the reduction of CO₂ emissions is favored by increased scrap additions to the oxygen converter. In order to balance the actual heat capacity of the bath, an increased scrap melting capacity can be taken into account. Per each ton of refined steel, 50 Nm³ of oxygen are consumed. The furnace temperature is in the order of 1,650°C due to the exothermic nature of the fusion reactions. The pig iron is in the range of 65-90%; the offgases are CO rich and can be recovered or combusted into CO_2 . An increase in the tapping temperature is expected to occur with the increase in scrap rate.²

Additionally, as the amount of steel scrap charged to converters increases for reducing carbon footprint, it promotes a higher wear of refractories installed on impact pad zones of these vessels. These trends are being observed for most BOFs around the world, mainly when slag splashing is not adopted properly or hot patching repair is not performed in advance.

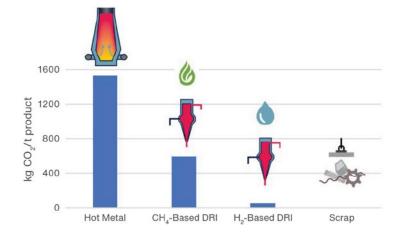
The essential goal in the development of refractory lining designs for basic oxygen furnaces is to obtain the lowest possible refractory cost per ton which is compatible with desired metallurgical and operating parameters. The development of a balanced lining with different refractory qualities, thicknesses or combinations are assigned to different areas based on continuous study of the wear patterns.³ A progression of lab studies and field trials enables a practical compromise among desired properties of the bricks to optimize performance and reduce lining costs. In the long run, the balance of refractory is achieved when evaluated properties are close to real applications.⁴

Refractory, as a ceramic material, usually exhibits high compressive strength when compared to metals. The compressive strength is found to increase significantly under dynamic loading conditions. The increase in strength is usually attributed to the combined effects of confining pressure and strain rate. Due to their high strength and enhanced high-temperature properties, MgO-C bricks can be employed under impact areas to understand the fracture behavior under impact loading conditions.⁵

In general, the scrap impact zone is the most heavily stressed area in the BOF lining. Scrap weight ranges from each customer, size vessel and BOF types. A single piece can weight up to 6 tons and fall from 5–12 m and stress the MgO-C bricks. The stresses in a scrap impact area of a BOF require the use of bricks with high fracture toughness with optimal thermoshock resistance. The strength to withstand these harsh conditions is promoted using structure-reinforcing antioxidants that decrease porosity

Figure 1

Specific CO_2 emissions per ton of output product for the different starting raw materials in steel production.¹



due to carbide formation. This is good for mechanical resistance, but with a side effect that increases the elastic module and the brittleness of the bricks. To remedy this situation, the key point to addressing toughness of the product is to redesign the binder concept.

MgO-C refractory bricks can be designed for a range of properties. They are extensively used in the working lining of BOFs and can be seen as true composites, formulated with organic and inorganic components to create a high-performance product. Magnesia confers thermal, mechanical and chemical oxidation resistances, while carbon sources enhance the ability to support thermal shock, toughness and slag corrosion. To reduce carbon oxidation, fine metal powders such as Al, Si and Al-Mg are commonly used.⁶

Organic binders are employed in the formulation of MgO-C bricks. The most desired feature is their ability to induce the generation of a high char yield after pyrolysis. Such ability is associated with the molecular configuration and chemical composition of their mere unities. For instance, the presence of oxygen atoms in the resin's backbone and high contents of aliphatic carbon segments favor the rupture of the polymeric structure, leading to the formation of volatile compounds and preventing char yield. High-carbon-yield pitches, mainly tar pitch, were first used as a binder. Due to the high content of aromatic hydrocarbons (PAHs), with carcinogenic properties they were replaced by phenolic resins (novolak and resol). However, this new binder may have a negative effect on the stiffness and the thermal shock resistance because of the nature of glassy carbon formed after tempering and low crystallinity at higher temperatures.^{6,7}

More recently, "eco binders," also called "soft-bonding binders," with low toxicity appeared as modified pitches. These alternative binders are obtained through certain treatments of coal tar pitch in order to minimize PAH

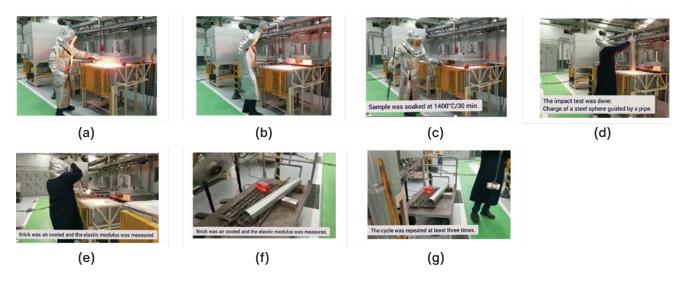
> content. Dehydrogenating agents are used to chemically break the benzene rings, which favors high-yield carbonization. Included in this last group are binder systems known as "carbonaceous resin," which is composed of units of highly polymerized hydrocarbons that results in a high C/H ratio after tempering at high temperature; the structure is similar to a "semicoke" with all the advantages of a pitch.⁶

> Increased scrap amount and/or weight challenge the new refractories to combine in ecologically friendly solutions. Among other factors, the wear of MgO-C bricks in service conditions is affected by the amount and distribution of carbon coming from the organic binders. The features of the condensed C-C network formed from the binder pyrolysis when temperature rises also affect the brick performance in service due to the

74 Technical Article

Figure 2

Impact test for composition evaluation: Furnace at 1,400°C (a), charging the brick for soaking (b), brick is soaking for 30 minutes (c), impact generated by a metallic sphere guided by a pipe (d), brick removed from the furnace (e), brick is air cooled for elastic modulus measurement (f) and cycle is repeated for a minimum of three times (g).



transformation of pitches and phenolic resins and the carbonization mechanism of eco binders. 6

The impact pad needs a unique approach for MgO-C development. Solid scrap impact acts as an instant mechanical stress, like thermal shock that results in thermal stress. So, a new evaluation test was developed for differentiating the tentative compositions, as shown in Fig. 2: (a) furnace at 1,400°C, (b) charging the brick for soaking, (c) brick is soaking for 30 minutes, (d) impact generated by a metallic sphere guided by a pipe, (e) brick removed from the furnace, (f) brick is air cooled for elastic modulus measurement and (g) cycle is repeated for a minimum of three times. A new generation of carbo-resins with a low-emission binder system was first introduced for improving flexibility in cold processing, similar to pitch-bonded bricks processed at hot conditions.

This work presents the comparative evaluation of physical and thermomechanical properties and corrosion resistance of novel redesigned flexible binder MgO-C brick against the original resin-pitched one. Customers' performance in field trials is also highlighted.

High-Flexible (HI-FLEX) Binder System

Compositions

The novel binder system is based on a unique combination of thermosetting carbonaceous materials with distinct carbon yields and softening temperatures. It allows for C-C bonding that can be generated already during the BOF preheating and starting the reactions with metals in different stages than pure resin and even resinpitch-bonded bricks. Phenolic compounds are minimized to a very low level, which also makes the new binder an environmentally friendly option. Two commercial MgO-C brands with standard resin-pitch design and the new binder system were evaluated. Table 1 shows the compositions. All compositions present the same amount of fused MgO and graphite content. Additives are also very similar regarding to the types and amounts. The main target was to highlight the potential of each binder used.

All samples were pressed in the plant under standard fabrication for BOF bricks at room temperature. The novel binder does not require any special equipment or heating process. After tempering at 200°C, samples were sent for evaluation at the R&D department. Samples were characterized as being received from the plant and

Table 1

MgO-C Bricks With Standard Resin-Pitch Binder (Brand A) and New Binder System (Brand B)

	Brand A	Brand B
Fused MgO/total MgO (%)	+++++	+++++
Graphite	++++	++++
Additives	++	++
Binder system	Resin-pitch	New binder system

after firing at 1,400°C for 5 hours and 1,600°C for 5 hours. The heating treatment was performed in an electric furnace; the rate was 215°C/hour until 1,170°C and after that, the temperature increases 41°C/ hour until 1,400°C and 1,600°C. Bulk density and apparent porosity were evaluated by the Archimedes principle with liquid immersion method, following ASTM C20. Brick dimensions were measured before and after firing with digital calipers to measure the permanent volumetric expansion (PVE). Cold crushing strength (CCS) was carried out in Kratos ECC using a 100 kN load cell (JIS R 2206 5013) on 50 x 50 x 50 mm³ specimens. Elasticity modulus was measured using an ultrasound equipment (James Instruments - model C-4902 "V" Meter of 150 kHz) according to ASTM C885.

A corrosion test was performed with octagonal prismatic in an induction furnace at 1,700°C for 3 hours after thermal treatment of 1,000°C for 5 hours to eliminate any volatile of the tempered bricks. Specimens were immersed in steel with synthetic slag that was renewed every 30 minutes to avoid saturation. Microstructure analysis was done after induction corrosion test using an optical microscopy (Carl Zeiss – Model: AXIO-Imager.A1m). The impact test was evaluated according to Fig. 2, also after 1,000°C for 5 hours.

Results

Results of the physical and mechanical properties and corrosion resistance for both brands are presented in Table 2. After tempering at 200°C for 5 hours, the new binder system presents a slightly open porosity due to the minimal amount of phenolic binder, which is responsible for a glassy carbon formation with lower wettability at room temperature. Bulk density also follows the same behavior. Cold and hot mechanical results also reflect the brittleness of phenolic resin and showed the same trend as the physical properties. The most expressive result is the reduction of the elastic modulus (EM) that is associate to the capacity for stress absorption and the main target for impact pad bricks. As far as the characterization proceeds to higher temperatures, physical and CCS are becoming closer for both binders, but the EM always is lower for the new system to improve flexibility.

Table 2

Results of Physical and Mechanical Properties and Corrosion Resistance of MgO-C Bricks With Standard Resin-Pitch Binder (Brand A) and New Binder System (Brand B)

	Brand A	Brand B
Binder system	Resin-Pitch	HI-FLEX
After tempering 200°C		
Bulk density (g/cm ³)	2.96 ± 0.01	2.90 ± 0.04
Apparent porosity (%)	4.7 ± 0.2	6.4 ± 0.6
Hot modulus of rupture after 1,400°C (MPa)	12.3 ± 1.1	10.1 ± 1.0
Cold crushing strength (MPa)	37 ± 3	32 ± 2
Elastic modulus (GPa)	40 ± 0	27 ± 1
After coked 1,000°C		
Metal line corrosion (%)	4.4 ± 0.2	3.3 ± 0.2
Slag line corrosion (%)	15.6 ± 0.1	15.4 ± 0.3
After coked 1,400°C		
Bulk density (g/cm ³)	2.91 ± 0.02	2.90 ± 0.03
Apparent porosity (%)	9.6 ± 0.5	9.4 ± 0.4
Hot modulus of rupture after 1,400°C (MPa)	13.8 ± 1.1	11.1 ± 0.4
Permanent volumetric expansion (%)	0.64 ± 0.02	1.91 ± 0.03
Cold crushing strength (MPa)	35 ± 1	30 ± 2
Elastic modulus (GPa)	41± 1	28 ± 1
After coked 1,600°C		
Bulk density (g/cm ³)	2.81 ± 0.08	2.88 ± 0.02
Apparent porosity (%)	12.0 ± 0.6	10.8 ± 0.3
Hot modulus of rupture after 1,400°C (MPa)	12.6 ± 1.3	10.3 ± 2.0
Permanent volumetric expansion (%)	2.50 ± 0.05	2.05 ± 0.04
Cold crushing strength (MPa)	33 ± 3	30 ± 3
Elastic modulus (GPa)	24 ± 0	16 ± 3

76 Technical Article

Figure 3

Impact test results for MgO-C bricks with standard resin-pitch binder (Brand A) and new binder system (Brand B) as a decay of the elastic modulus is plotted with the number of cycles.

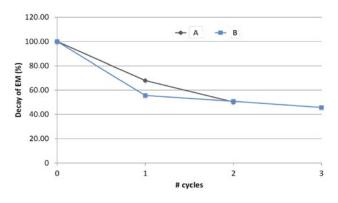
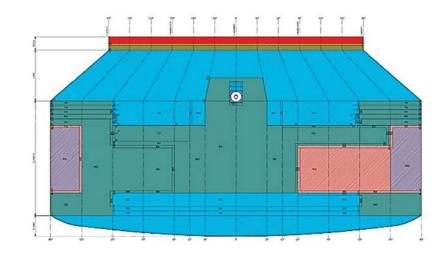


Figure 4

Impact test samples after three cycles for MgO-C bricks for standard resinpitch binder (Brand A) (a) and new binder system (Brand B) (b).



Figure 5



Design of the 226-ton basic oxygen furnace (BOF), highlighting MgO-C bricks with the new binder for the impact zone (in purple).

Permanent volumetric expansion (PVE) indicates the overall expansion of the products, and it is an indirect measurement of the interaction between aggregates and matrix. The system presents the fast stability when compared to resin-pitch binder, which means that the expansion for closing joints started at 1,400°C. At 1,600°C, PVE indicates that the reactions with antioxidants fully finished, and it happened faster for the novel binder due to the high carbon yield.

A corrosion test performed in an induction furnace at 1,700°C presented very similar results for both brands as they are based on the same fused magnesia quality and high-grade graphite content. Over 1,600°C, the physical properties are quite close, which also minimizes infiltration.

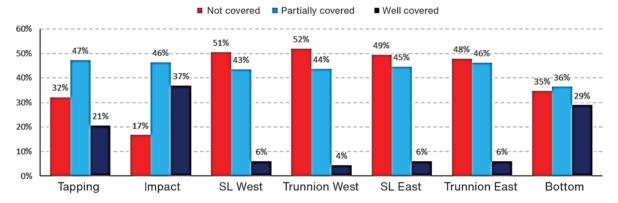
The impact test is presented in Fig. 3. The decay of the elastic modulus is plotted with the number of cycles. As

expected, the better toughness behavior is shown by the novel binder system compared to resinpitch one. Minimizing the glassy carbon in the binder favored the stress absorption with the improvement of the thermomechanical properties as presented in Fig. 4. Resin-pitch-bonded brick failed with a broken specimen. The new binder withstood the three cycles with just a minor crack. Field trials were planned for validation at the customer site.

Customer Trial

The first trial was conducted in a 226-ton BOF in the impact zone with the novel binder, as shown in Fig. 5. Other regions remain with the original MgO-C bricks bonded with the resin-pitch system. The total campaign was 3.647 heats. An indicator was developed to follow the coverage index of the refractory lining by slag in different regions of the BOF converter. This indicator was established based on visual inspections of the linings carried out during operation, and it was classified as: "well covered", "partially covered" or "not covered." During this period, the first 1,340 heats of the campaign were processed, 12% of which were visually assessed to determine the slag coverage of the lining, representing 161 heats.

Figure 6



Slag coverage index for the regions for the 226-ton BOF that carried out the first trial of the new binder at the impact zone.

Fig. 6 illustrates this indicator, highlighting that the impact region lined with the new binder showed the best protection index compared to other regions. Although the impact and tapping pad regions generally have the best indicators due to slag coating protection treatments such as slag splashing and slag coating, a direct comparison between these regions reveals that the "well covered" index in the impact region is 82% higher than in the tapping pad, while the "no coverage" index in this region is 89% higher than in the impact region.

Fig. 7 provides a photographic history of the hot inspections of the refractory lining in the impact zone throughout the converter campaign in the three main moments of the BOF: starting the campaign (one heat), over the middle of the campaign (2,019 heats) and the last one (3,647 heats). Overall, the visual analysis of the

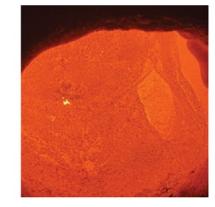
new binder showed satisfactory performance, with no failure attributed to the material and ending the campaign without any exposure of the permanent lining. It was noted that the coating adherence was quicker in the impact zone than in other areas due to the porosity at lower temperatures.

At the end of the campaign, the remaining lining is measured by the lining evaluation scan (LES) before the demolition, as shown in Fig. 8. The measurement data was processed and the images in Fig. 9 are generated based on the level of wear of the refractories. Table 3 shows the minimum residuals found in each region of the BOF, as well as the respective wear rates and performance potential. The impact region with the novel binder had a minimum end-of-campaign residual of 111 mm, corresponding to a wear rate of 0.244 mm per heat.

Figure 7

Hot inspections of the refractory lining in the impact zone throughout the converter campaign in the three main moments of the BOF: Starting the campaign (one heat) (a), over the middle of the campaign (2,019 heats) (b) and the last one (3,647 heats) (c).







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(b)

78 Technical Article

Figure 8

Measurement the remaining lining by the lining evaluation scan (LES).



The performance potential of this region, considering a safety residual of 100 mm, was 3,692 heats, with a performance potential of 4,102 heats if considering permanent exposure. The target to improve the impact area was achieved as the weak area was displaced to the west trunnion.

Summary and Conclusions

As the amount of steel scrap charged to converters increases in order to reduce carbon footprint, it promotes higher wear of refractories installed on impact pad zones. To remedy this situation, the key point to addressing toughness to the product is to redesign the binder concept.

A new binder system was designed in a unique combination of thermosetting carbonaceous materials with distinct carbon yields and softening temperatures with C-C bonding generated during the BOF preheating and starting the

reactions with metals in different stages than pure resin and even resin-pitch-bonded bricks. Phenolic compounds are minimized to a very low level to increase flexibility.

The first trial was conducted in a 226-ton BOF in the impact zone with the novel binder. Overall, the visual analysis showed satisfactory performance, with no failure attributed to the material and ending the campaign without any exposure of the permanent lining. It was noted

Figure 9

3D laser scan images generated based on the level of wear of the refractories by LES.

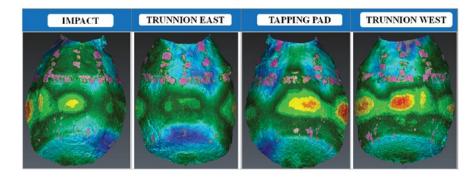


Table 3

Summary of Lining Evaluation Scan Measurements by Region

BOF regions	Wear rate (mm/heat)	Potential with 100 mm residual (heats)	Potential with permanent exposure (heats)
Tapping pad	0.200	3,507	4,008
Impact zone	0.244	3,692	4,102
Trunnion east	0.181	4,421	4,973
Trunnion west	0.253	3,366	3,672
Slag line east	0.170	4,698	5,286
Slag line west	0.229	3,713	4,149
Bottom	0.140	5,057	5,770

that the coating adherence was quicker in the impact zone than in other areas due to the porosity at lower temperatures.

This novel binder system will be expanded to other areas of BOF as flexibility is required and it is more environmentally friendly because of its contribution to increase scrap demand in real operation and less polluting than resin and resin-pitch binders.

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