IMPROVEMENT OF MAC BRICKS FOR STEEL LADLE WITH CAO-MgO-Al_2O_3 AGGREGATE: A NEW PERSPECTIVE FOR CEMENT APPLICATION

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ABSTRACT
Magnesia-Alumina-Carbon (MAC) and Alumina-Magnesia-Carbon (AMC) bricks have been consolidated as a product for the metal line of the steel ladles in a majority of the integrated steel shops worldwide. Spinel MgO.Al2O3 formation during ladle operation allows to an expansive reaction that can prevent metal and slag infiltration and also promotes better corrosion resistance.

The requirements for steel quality depend on the steel shop process. Refractory indication follows operational conditions of each customer in order to optimize the campaign with acceptable cost/benefit. Better performance is the driven force for searching innovative solutions to MAC bricks in order to fulfill the performance even in particular conditions, as in both Al and Si killed steel ladles.

This work presents the development of the MAC bricks with addition of a cement CaO-MgO-Al2O3 aggregate as an alternative technological solution for the ladle metal line. A comparative evaluation was performed to show the potential of this new raw material. Product properties, corrosion evaluation and customer trials are presented in this paper.

INTRODUCTION
Future steels will face some critical problems such as quality, price, customer demands and environmental and ecological concerns. Advanced technologies are needed for the production including both the modern production process and the industrial structure. One of the essential tasks in the steelmaking process is to control nonmetallic inclusions that are directly linked to the utilization of a deoxidizer that is somewhat limited due to the formation of oxides in liquid steel. [1].

Steels, when cast into ingots, can be classified into four types according to the deoxidation practice or, alternatively, by the amount of gas evolved during solidification. These four types are called killed, semikilled, capped, and rimmed steels [2]

Killed steel is a type of steel from which there is practically no evolution of gas during solidification of the ingot after pouring, because of the complete deoxidation, and formation of pipe in the upper central portion of the ingot, which is later cut off and discarded. All alloy steels, most low-alloy steels, and many carbon steels are usually killed. The continuous casting billets are also killed. Killed steel is characterized by a homogeneous structure and even distribution of chemical compositions and properties and it is produced by the use of a deoxidizer such as Al and a ferroalloy of Mn or Si. However, calcium silicide and other special deoxidizers are sometimes used [3].

Aluminun (Al) is widely accepted as a deoxidizer in steelmaking process and its addition is very convenient. A1effectively reduces oxygen content in liquid steel to low levels. For example, a content of about 4ppm oxygen is attained at 1873K with 0.02wt% soluble Al at equilibrium. However, its utilization as a deoxidant is somewhat limited due to the formation of A1containing oxides in liquid steel. It is experimentally confirmed that alumina inclusions easily form clusters [1].

Silicon (Si) is also one of the principal deoxidizers used in steelmaking and silicon content also determines the type of steel produced. Killed carbon steels may contain Si up to a maximum of 0.60wt% [3]

Most during 80´s decade steel industry had a very great improvement in quality, process control and a variety of steel types were requested with desired properties. Operational conditions became more restrict and several changes in the process were introduced. Integrated steel shops adopted world wide the BOF convertors technology for primary refining. Since then MgO-C bricks are been using as the working line. When secondary metallurgic practices started been consolidated in steel shops, steel ladles became one of the main process equipment.

Steel ladles are submitted to high temperatures effects, aggressive slags, long lasting metal permanence and many refine factors that required high quality refractory products. Alumina-silica and alumina bricks (resin bonded or pitch impregnated) became obsolete for severe applications. Nowadays, alumina-magnesia-carbon (AMC) and magnesia-alumina-carbon (MAC) bricks are been used as the current technology for the metal line, impact region and bottom for integrated steel ladle. Uncertainty of the future demand from the quality alumina raw materials was the driving force for the development of the magnesia-alumina-carbon (MAC) refractory bricks. This new line was an improvement of AMC bricks to offer better performance in the steel ladles since 2006 [4].

MAC bricks have been consolidated as a technological alternative for the metal lining of the steel ladles in a majority of the integrated steel shops in South America. Magnesia-alumina spinel formation during ladle operation allows to an expansive reaction that can prevent metal and slag infiltration and provides better corrosion resistance.

Development of MAC resin bonded bricks combines the advantages of the magnesia and spinel raw materials with low wettability of slag and molten metal from carbon. Also spinel formation occurs mainly in the hot face and closes the joints between the bricks. This expansion reaction decreases the metal and slag infiltration [4].

Despite the spinel reaction can be directly related to the ratio Al_2O_3/MgO, it is also necessary to consider the sources of alumina and magnesia used. This ratio alone cannot be used as an indicator of the spinel reaction as it can be seen that the combination of different sources of alumina gives specific results for each system [4].

Spinel formation is a combination of several factors as particle size, amount, purity and types of alumina, magnesia and carbon and additives than can promote this reaction and also the temperature and time.

One of the reason for better MAC performance compared do AMC bricks is due the formation of a dense layer on the hot face, as shown in Fig. 1. This layer is majority spinel Al_2O_3-MgO and forms only in Al killed steel. Some customers have an important production of Si killed steel in combination with Al killed steel and more wear is expected due to the directly corrosion of the brick compounds.

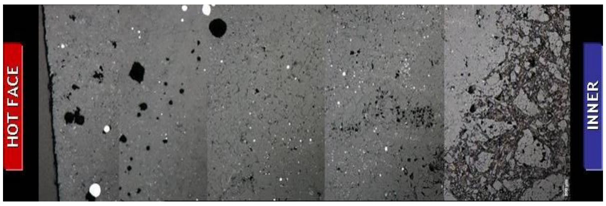

Fig. 1: Spinel Al_2O_3-MgO dense layer formed on the hot face of MAC brick.

Doloma carbon (CaO.MgO-C) brick presents a good slag resistant in Si killed steel due to the presence of free lime. In contact with slags not fully saturated with lime, a dense layer of recrystallized lime and dicalcium silicates forms on the hot face of the brick, limiting further slag penetration. Basically, the slag's reaction with the lime stops penetration, slowing down overall wear [5]. This was the motivation of using a new aggregate based on calcium magnesium aluminate (CMA) cement clinker in MAC bricks, as presented in Fig. 2.

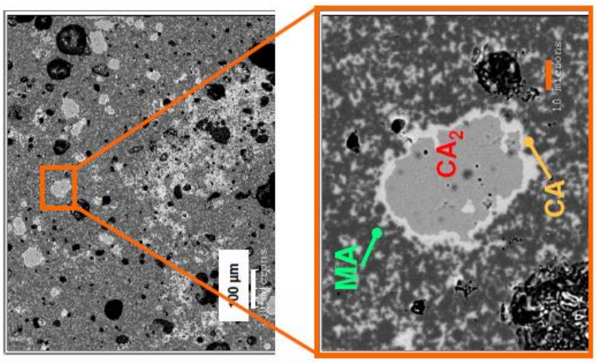

Fig. 2: Microstructure of CMA aggregate (black: pores, dark grey: MA-spinel, light grey: CA2, white: CA)

The typical chemical composition of the CaO-MgO-Al_2O_3 aggregate is 70% Al_2O_3, 20% MgO and 10% CaO. The CMA aggregate consists of a fine network of micro-MA spinel phases with embedded CA and CA2 crystallites. Some CA2 occurs as clusters of 50 to 100 µm with a thin reaction zone consisting of CA (Fig. 2). The average crystallite size of the MA spinel inside the aggregate is 3 µm. Approximately 70% of the aggregate consists of the MA-spinel while 20% are CA and 10% CA2 [6]. CMA aggregates have been prepared by crushing and sieving the MA spinel containing cement clinker. Four fractions of the CaO-MgO-Al2O3 aggregate, 0-0.09 mm (CMA 72 cement), 0-1mm, 1-3mm, and 3-6 mm have been prepared.

Comparative evaluation of the MAC bricks with addition of CaO-MgO-Al_2O_3 aggregate and the original composition were performed in different temperatures to show the potential of this new raw material. This paper presents the product properties, corrosion evaluation and customer trials in the metal line of steel ladle.

EXPERIMENTAL PROCEDURE

Two identical MAC compositions were selected to study the influence of the effect of CaO-MgO-Al_2O_3 aggregate (KERNEOS Aluminate Technologies, France) for increasing corrosion resistance in acid slag, as presented in Tab. 1. The new raw material was introduced replacing same amount and grain size distribution of fused Al_2O_3 (95.5 wt% of Al_2O_3, Elfusa Geral de Eletrofusão, Brazil). Dead burned MgO (98.5 wt% of MgO, Magnesita Refratários, Brazil), graphite content (95.0 wt% of C, Nacional de Grafite, Brazil), resin-pitch binder and antioxidant amount were kept the same for both compositions. Composition A1 is the original one.

Tab. 1: Compositions comparison between conventional MAC (magnesia-alumina-carbon) bricks (A1) and MAC with CaO-MgO-Al_2O_3 aggregate (A2).

	A1	**A2**
Fused Alumina	+++	+++
CMA aggregate	-	+
MgO Sinter	+++	+++
Graphite (%wt)	**5**	**5**
Total C (%wt)	+++	+++
Antioxidants	++	++

All prismatic samples (160mm x 40mm x 40mm) were prepared and pressed (FKL friction press, 450t, Brazil) at Magnesita R&D center and cured at 200°C/6h under a 10ºC/min heating rate. Samples were evaluated after cure and after coking at 1400ºC/5h and 1600ºC/5h (electric oven, 10ºC/min heating rate).

Physical and mechanical properties were evaluated. Bulk density and apparent porosity were measured according to ASTM C20. Cold crushing strength was carried out in universal mechanical testing equipment (EMIC, Model PC200C, Brazil) according to ASTM C133. For HMOR evaluation no previous thermal treatment were carried out and tests were performed using internal testing equipment (Magnesita, Brazil). Samples were wrapped in nickel foil to prevent oxidation. Elastic modulus was evaluated by sonic resonance method (James Instrument, Model V Meter, USA) according to ASTM C885. Permanent volumetric expansion (PVE) was measured according to ASTM C134 after firing the samples in electric furnace.

Thermal shock tests was carried out by heating prismatic samples wrapped in nickel foil in an electric oven at 1200ºC and cooling in a copper refrigerated plate. After cooling, elastic modulus was measured to evaluate the damage. Samples cured at 200ºC/6h were pre-coked at 1000ºC/5h to eliminate the volatiles before the thermal shock test.

Corrosion test was performed with octagonal prismatic samples in an induction furnace at 1700 °C/3h. Tests samples were previously coked at 1000ºC/5h to eliminate any volatile to prevent explosion and were immersed in molten steel and synthetic slag, as shown in Tab. 2. Each 30min the slag was renewed to prevent saturation.

Tab. 2: Chemical analysis of the slag used in induction corrosion test. Average composition based on customer's process of 4 months.

	(%)
MnO	**1.2**
SiO_2	**36.9**
Al_2O_3	**13.5**
CaO	**44.4**
MgO	**6.9**
Binary basicity	**1.2**
Quaternary basicity	**1.0**

RESULTS AND DISCUSSIONS

Tab. 3 shows the comparative results between conventional MAC (magnesia-alumina-carbon) bricks (A1) and MAC with CaO-MgO-Al_2O_3 aggregate (A2).

	A1	A2
After curing at 200 °C		
Density (g/cm3)	**3.09**	**3.06**
Porosity (%)	**9.1**	**9.6**
CCS (MPa)	**71.6**	**59.2**
HMOR (MPa) 1400°C	**10.6**	**10.0**
Elastic Modulus (GPa)	**65**	**60**
After coking at 1400 °C		
Density (g/cm3)	**2.95**	**2.92**
Porosity (%)	**14.5**	**14.9**
CCS (MPa)	**54.1**	**51.7**
HMOR (MPa) 1400°C	**5.9**	**6.2**
PVE (%)	**4.1**	**4.4**
Elastic Modulus (GPa)	**39**	**36**
After coking at 1600 °C		
Density (g/cm3)	**2.70**	**2.73**
Porosity (%)	**20.7**	**19.6**
CCS (MPa)	**23.8**	**23.9**
HMOR (MPa) 1400°C	**2.1**	**2.0**
PVE (%)	**14.0**	**14.0**
Elastic Modulus (GPa)	**31**	**30**

***CCS: cold crushing strength, HMOR: hot modulus of rupture, PVE: permanent volumetric expansion**

Apparent density and apparent porosity were very similar in any evaluated temperature showing no significance alteration in properties due to the introduction of the new aggregate. Even during production to customer's trial no problems were observed during pressing and storage. This was a concern as the CaO-MgO-Al_2O_3 aggregate is based on a cement composition and some hydration behavior could be expected.

Mechanical properties were also very similar at room and at high temperature. HMOR did not show any decay. These are very important results as the CaO-MgO-Al_2O_3 aggregate has less dense and higher porosity than the fused alumina.

Thermal shock resistance is presented in Fig. 3 as the decay of the relative Elastic Modulus by the number of cycles. No difference was noticed between both compositions. Mainly difference was just observed in the corrosion resistance as presented in Tab. 4 with the samples pictures after the test.

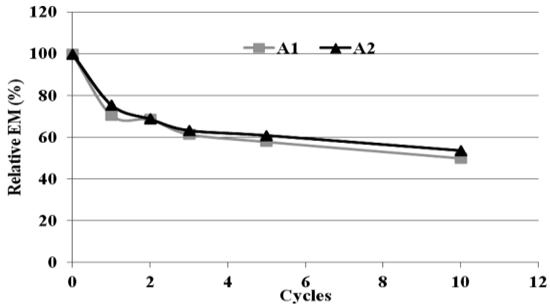

Fig. 3: Thermal shock resistance for conventional MAC (magnesia-alumina-carbon) bricks (A1) and MAC with CaO-MgO-Al_2O_3 aggregate (A2).

Tab 4.: Corrosion resistance with the samples pictures after the test for conventional MAC (magnesia-alumina-carbon) bricks (A1) and MAC with CaO-MgO-Al_2O_3 aggregate (A2).

	A1	A2
Metal Line (%)	**0.11**	**0.13**
Slag Line (%)	**33**	**26**
		

Investigation for better results for corrosion resistance for the composition A2 is been carried out by thermodynamic and physical simulation and will a subject for a complementary paper. Preliminary results showed that the presence of a stable source of CaO from the CaO-MgO-Al_2O_3 aggregate in the interface brick/slag changes the viscosity of the slag and the penetration into the brick is minimized. It is a different process from that observed with doloma-C brick where the free lime forms a dense layer of recrystallized lime and dicalcium silicates on the hot face of the brick.

STEEL SHOP TRIAL

MAC bricks with CaO-MgO-Al_2O_3 aggregate were initially tested as part of metal line in a 205t steel ladle together with conventional MAC composition in an integrated steel shop. Panel of 180° standard parallel bricks (229x152x76mm) were assembled. Normal operational conditions have steel killed with Al, Si and both metals simultaneously. Then the complete success for the new aggregate is still under the evaluation. Fig. 4 shows the ladle after a Si killed steel and is clear that a coating over the brick was formed. This result corroborates the lab corrosion test and was a driven force for continuing the trials.

As the main difference between compositions A1 and the A2 is corrosion with acid slag the perception with the real advantage for the new $CaO\text{-}MgO\text{-}Al_2O_3$ aggregate is longer than usual. The plan for the correct evaluation was to run a full 6 months production and trial at the customer full metal line. This procedure is been adopted since February 17.

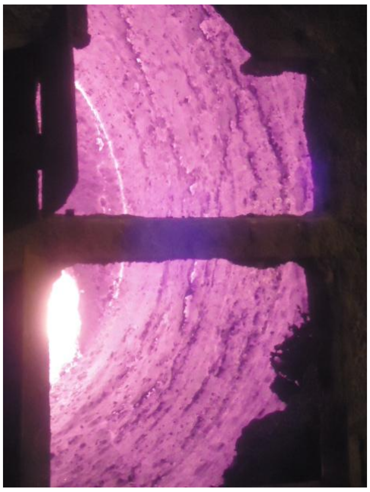

Fig. 4: MAC bricks with $CaO\text{-}MgO\text{-}Al_2O_3$ aggregate after 10 heats in a 205 steel ladle in an integrated steel shop.

SUMMARY AND CONCLUSIONS

A new development of MAC bricks was conducted by introducing a new $CaO\text{-}MgO\text{-}Al_2O_3$ aggregate for steel shops with Si killed steel. The challenge was to design refractory with positive interaction with slag from the process as this is seen one of the key successes to extend campaign life.

Comparative evaluation with original MAC brick was performed and no differences were observed on physical and mechanical properties. This is an amazing achievement because the new aggregate is replacing a denser material as fused alumina. Also thermal shock properties were very similar but corrosion in acid slag was improved with the new composition.

First customer's trials corroborated the lab results from better slag corrosion in acid environment. Trials with the new $CaO\text{-}MgO\text{-}Al_2O_3$ aggregate are longer than usual and the evaluation will run a full 6 months production. The trial at the customer full metal line in the steel ladle is running in an integrated steel shop.

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