Matrix Engineered ULC High Alumina-Spinel Castable Developments for Steelmaking Applications

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Abstract

With the crisis of raw materials punishing the refractory world, it was no different for the Brazilian market to seek innovations and new opportunities to mitigate the constant price increases of those inputs. Manufacturers, as well as refractory users, have been working on development efforts aimed mainly to reduce dependence on some refractory raw materials, as well as promoting other gains, either in specific consumption or in the reduction of the final cost of the production processes, through rational use of refractory linings. In complete alignment with the market, Saint-Gobain Performance Ceramics and Refractories has been working on the development of a complete line of high alumina-spinel castables, with ultra-low cement content, engineered matrix and reduced water requirements, for various applications, such as steel ladle, where monolithic products mean reduction of specific consumption, due to the possibility of a partial repair of the refractory line, and lower thermal losses, due to lower thermal conductivities compared to conventional products containing carbon. This paper will present the results obtained in those developments, showing the microstructural engineering evolution of these concretes, and results obtained in labs and practical application in a large steel ladle in Brazil. That new concrete family has shown superior performance in corrosion and spalling resistances during operation, being a perfect option to meet market expectations for more efficient refractories.

1. Introduction

The application of alumina-spinel products has been deeply spread through steel making equipment, especially in case of steel ladle bricks and castables[1). In some cases, their application has allowed to reach gains beyond the refractory technology itself, but also improving environmental aspects, reducing specific consumption and promoting energy saving to steelmaking production[2).

Alumina-Spinel products have been deeply investigated[3). Despite the origin of spinel source, if it came from "in situ" spinel formation", or from spinel addition, those products have very good properties, which results usually in a higher performance during steelmaking applications.

Based on those aspects, development efforts have been given to a new generation of matrix engineered alumina-spinel castables, with interesting characteristics, as:

- Optimized grain size distribution;
- Lower size spinel sources;
- Special calcined aluminas;
- Optimized rheological properties.

As main results, the developed products have better properties than regular ones, especially considering corrosion and thermal shock resistance[1), as well as free flowing with very low amount of water, as low as 4%.

The objective of the present paper is to show some of those developed products, correlating their good properties with the new engineered matrix, where spinel is spread homogenously.

2. Experimental Procedure

Table 1 shows a summary of products conception, in terms of raw materials sources and maximum grain sizes.

Table 1 Formulation basis of regular and developed products.

Product	A	B	C	D	E
Raw Material:					
White F. Alumina	+++	+++++	+++++	+++	+++
Tabular Alumina	++			++	++
Calcined Alumina	+	+	+	+	+
CAC	+	+	+	+	+
"in situ" Spinel		+			
Synthetic Spinel A			+	+	+
Synthetic Spinel B				+	+
Others	+	+	+	+	+
Maximum grain size	8mm	8mm	8mm	8mm	8mm
MgO content (%)	0,0	6,0	4,0	4,0	4,0

Water content of castables were determined according application needs. After mixing, flow table test was performed o compare flowability.

All products were submitted to different heat treatments (400 °C, 1000 °C and 1500 °C). After each heat treatment, products were characterized to obtain physical properties, thermal shock resistance (from residual elastic modulus) and hot modulus of elasticity. A dynamic slag attack test, considering a high FeO slag with $CaO/SiO_2 = 3$, at 1650 °C, was done to compare castables corrosion resistance.

A post mortem analysis was done for casted block applied to at steel ladle bottom. Micro structure EDS and physical properties were evaluated for that sample.

3. Results

3.1 Mixing properties

Castables were mixed using a planetary mixer. Water amount was added until castables reach consistency to be applied, as they are produced for industrial application. Values of water amount, flowability and green density are presented in **Table 2**.

Table 2 Water content and flowability.

Product	A	B	C	D	E
Water content	5,5	6,8	7,0	4,0	4,3
Free flow (mm)	140	n.a.	n.a.	215	230
Flow table (mm), after dropped 15 times	174	134	135	238	240
Volumetric density (g/cm^3)	3,11	3,12	3,06	3,32	3,10

After mixing, castables were casted in aluminum molds to obtain the probes for testing.

3.2 Characteristics after heat treatment

After demolding, the probes were heat treated at different temperatures for testing, in an oxidizing atmosphere, for 5 hours. Test results are presented in **Table 3**.

Table 3 Castables characteristics after heat treatments (T°C x 5 hours).

Product	A	B	C	D	E
After 400°C					
A.D. (g/cm^3)	3,05	3,04	2,97	3,25	3,08
A.P. (%)	14,5	19,8	21,0	11,2	12,4
M.O.R. (MPa)	21,9	3,4	6,0	15,2	8,9
C.C.S. (MPa)	80,4	28,0	23,7	72,6	45,4
L.D.V. (%)	-0,2	-0,1	-0,1	+0,1	0,0
After 1000°C					
A.D. (g/cm^3)	3,01	2,99	2,94	3,26	3,06
A.P. (%)	20,2	23,9	24,8	**12,5**	14,4
M.O.R. (MPa)	13,8	5,2	8,8	14,9	14,2
C.C.S. (MPa)	80,7	28,3	34,7	98,7	56,9
L.D.V. (%)	-0,1	0,0	-0,1	0,0	-0,1
After 1450°C					
A.D. (g/cm^3)	2,97	2,79	2,86	3,25	3,06
A.P. (%)	18,9	26,2	25,0	12,6	17,4
M.O.R. (MPa)	30,1	8,4	16,4	35,7	26,8
C.C.S. (MPa)	138,3	28,6	76,3	160,1	154,4
L.D.V. (%)	+0,4	+2,4	+0,7	+0,2	-0,1
H.M.O.R. (MPa) at 1400°C	10,2	4,8	5,3	**19,5**	18,2
Slag test					
-Corrosion index	1,4	2,2	1,8	1,0	1,0
-Average infiltration (mm)	6,2	4,0	4,2	0,0	0,0

The thermal shock resistance was evaluated for probes heat treated at 1450 °C. Elastic dynamic modulus was evaluated before and after thermal shock at different temperatures (400, 800, 1000 and 1200 °C). Products that have a low modulus of elasticity decay are considered to be more resistant to thermal shock. **Fig. 1** shows the results of elastic modulus decay after thermal shock for castables.

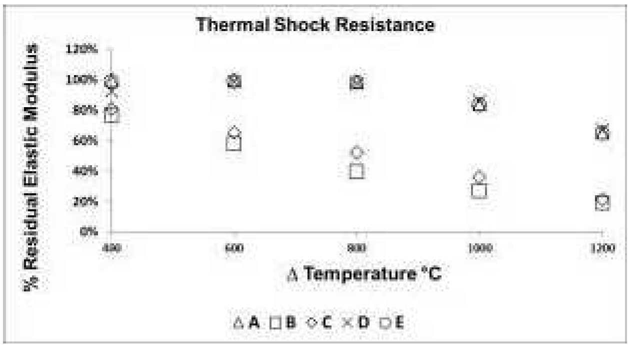

Fig. 1 Elastic modulus decay for castables, after thermal shock resistance at different temperatures.

Corrosion resistance was evaluated with probes heat treated at 1450 °C. Results are presented at **Table 3**, and sectioned probes after slag test are showed in **Fig. 2**.

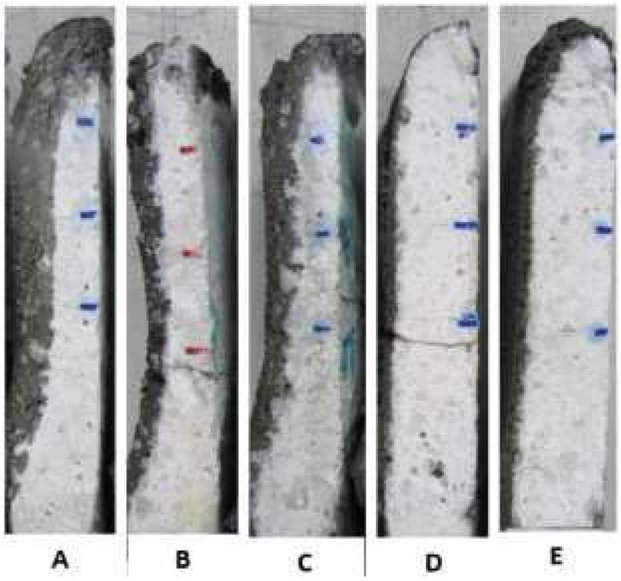

Fig. 2 Castables aspect after slag corrosion test, considering a high FeO content slag with CaO/SiO2 = 3, at 1650 °C.

4. Discussion

The current study has evaluated two different concepts for high alumina castables. Product A is a conventional vibrated high alumina castable, with no MgO sources. Products B to E are different alumina-magnesia castables, which magnesia source were varied. While castable B has a free source of MgO, to promove "in situ" spinel formation, castables C to E have different sources of synthetic spinel. Castable B and C are applied by vibration, while castables D and E are self-flowing.

From the results in **Table 3**, it can be seen that castables A, D and E, with a lower requirement of water presented lower porosities after heat treatment. Castables D and E also presented higher cold mechanical resistance after heat treatment at 1450°C, and also hot mechanical resistance at 1400 °C. Those castables received the addition of a second spinel type B.

Castable B, with a free MgO source, presented a higher linear dimensional variation after 1450°C, as a result of "in situ" spinel formation, while the other castables are more stable.

That dimensional stability seems to interfere on the thermal shock resistance, once the more stable castables A, D and E presented better results.

From the slag resistance test, results showed that MgO presence is effective to increase slag penetration. Castables with higher porosity can show lower wear resistance, even with MgO addition. Special source of spinel B has showed high efficiency for overall slag resistance, once castables D and E presented the best results.

Considering the presented results, mainly due lower porosity after 1000 °C and higher HTMOR, castable D was elected to be applied for a trial at a bottom steel ladle. That initial trial was conducted with a pre-shaped block, as an initial step for a complete monolithic bottom trial. Results will be presented on next topic.

5. Steel Ladle Trial

5.1 Instalation

Castable D was chosen to be applied in a field trail. A brick lined free carbon steel ladle of 190 ton of capacity received a casted block, which was installed according **Fig. 3a** and **3b**. The casted block dimension was defined as 800mm x 400mm x 229mm. 229mm is the thickness of steel ladle bottom outside impact pad.

After installation, the steel ladle was heated up until 1000 °C, according to customer's standard. The steel ladle operation was followed to evaluate casted block performance considering spalling and wear behavior. No spalling was observed during steel ladle campaign. Steel ladle bottom, after 42 heats and 109 heats are also presented in **Fig. 3c** and **3d**, respectively. Steel ladle finished operation after 115 heats, that is the campaign target for customer. Steel mix was considered usual according to customer's operation.

During steel ladle demolishing, the casted block was evaluated for wear. The minimum thickness found for casted block was 110 mm. A sample was taken for post mortem analysis.

5.2 Post mortem analyses

A photo of sectioned sample is presented in **Fig. 4**. As can be seen, the samples presented an altered layer of approximately 13mm. A crack can be observed and was resulting from demolishing process.

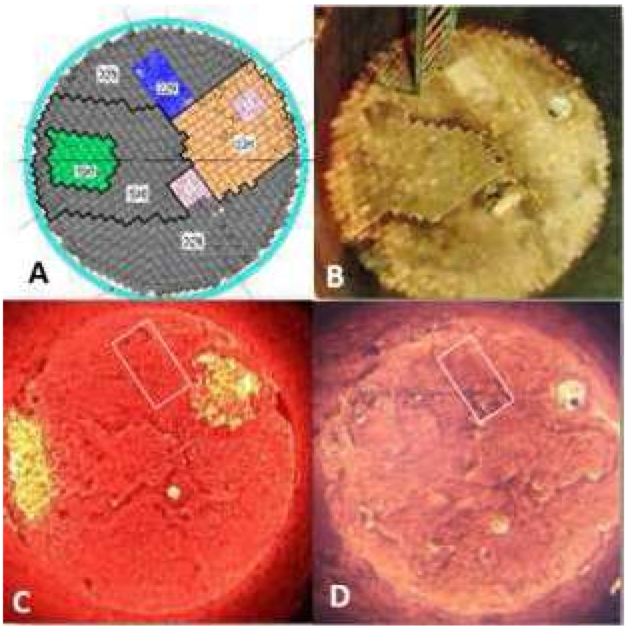

Fig. 3 Casted block installation (blue area) on steel ladle bottom (A and B). Casted block aspect after 42 heats (C) and after 109 heats (D).

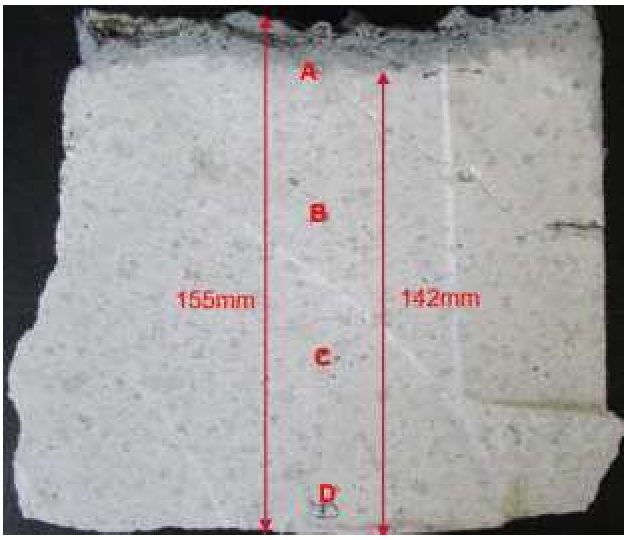

Fig. 4 – Casted block sample cut surface.

Physical properties were evaluated for regions A, B, C and D and showed in **Table 4**. As can be seen, the castable retained homogeneity of properties along thickness, once density, porosity and mechanical strength showed relative small variation.

Chemical variation was identified only for hot face (region A) and are relative from SiO_2, CaO and Fe_2O_3 impregnation, from hot face to cold face. That aspect could be better visualized through **Fig. 5**, where microstructural EDAX scanning is presented for hot face (A), showing transition between altered and unaltered regions.

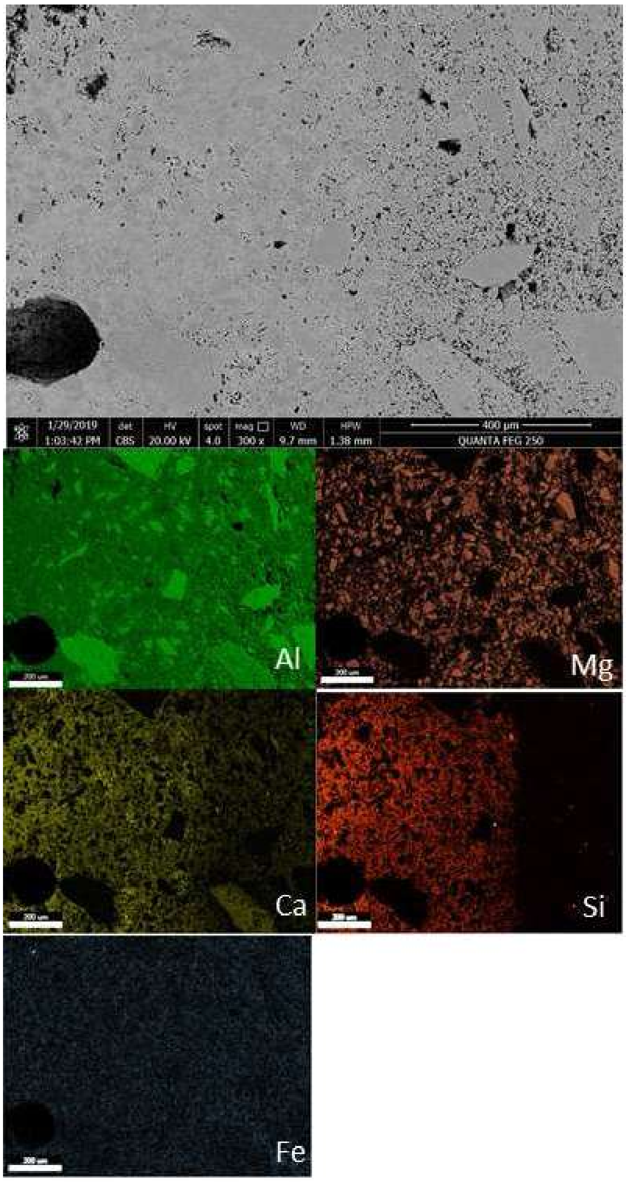

Fig. 5 EDAX image of casted block (region A), showing the interface between altered (left) and unaltered region (right).

Table 4 Physical properties for casted block sample after usage.

Sample region	A	B	C	D
Bulk density (g·cm^{-3})	3,21	3,22	3,24	3,26
Aparent porosity (%)	13,9	14,3	13,6	12,9
C.C.S. (MPa)	177,1	170,2	n.a.	143,2

n.a.: not avaliable.

However, that impregnation is kept close to the hot face, showing a similar behavior observed for castables D and E during slag tests (**Fig. 2**).

6. Conclusion

Evaluated Al_2O_3-MgO castables, with adjusted grain size distribution, new special sources of fine spinel, and lower water requirements, demonstrated excellent thermal mechanical characteristics, including hot mechanical resistance and thermal shock resistance, as well as better corrosion resistance.

Among those new generation castables, castable D was applied in a field test, as casted block for a steel ladle. After 115 heats application on steel ladle bottom region, the casted block demonstrated remarked homogeneity through the thickness, good mechanical integrity, small thickness of the impregnated layer, what contributes for a very good performance. The result certainly enables the product for future testing of total monolithic bottom, which is expected soon and the results will be presented in a forthcoming publication.

References

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3) A.P. Luz, M.A.L. Braulio, V.C. Pandolfelli. Refractory Castable Engineering, FIRE Compendium Series, (2015).