CONSTRAINING EFFECTS ON HIGH-ALUMINA CALCIUM MAGNESIUM ALUMINATE-BONDED CASTABLES FOR STEEL LADLES

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ABSTRACT

The main features of magnesium aluminate spinel ($MgAl_2O_4$) are related to its chemical stability and the volumetric expansion that takes place during its *in situ* formation. Although the volume increase can close joints and generate compressive stresses, it can also spoil the refractory's performance if not properly designed. In order to master the expansion and improve the corrosion resistance to basic slag, a unique binder (CMA72) obtained by co-sintering calcium oxide, magnesia and alumina has been recently developed, aiming to homogeneously attain ultra-fine spinel throughout the refractory matrix. Regarding the studies associated with the expansive behavior of spinel-forming castables, they are usually conducted in free-expansion environments, which is not in tune with the working structural conditions that involve limited room for volumetric change. Considering that the restrained expansion can act as a strengthening mechanism by reducing the castables' porosity levels, the results attained in lab-scale conditions (expansion-free situation) may not represent the practical ones, when the compositions are applied in steel ladles. In this context, this work addressed the evaluation of thermo-mechanical properties after firing the castables under constraint, for compositions containing different amounts of *in situ* formed spinel and CMA72 binder. Besides this design issue, a very relevant processing condition, that is the curing temperature, was also analyzed, aiming to highlight the importance of considering other parameters to attain a suitable performance in use rather than concentrate only on the material's design. The results for the two expansion conditions and for the curing temperature change were remarkably different, pointing out that the constrained expansion procedure should be adopted for the development and evaluation of advanced spinel-forming castables' compositions, whereas processing conditions may be considered aiming to improve the working life of steel ladle linings.

INTRODUCTION

Magnesium aluminate spinel (MA) is well known by its expansive formation [1] and also by its excellent resistance to basic slag [2], making it an essential compound for steel ladle refractory products. Therefore, both topics were extensively explored in the literature [3]. Even though relevant for understanding the mechanisms that are involved in the associated reactions (MA formation and refractory's corrosion), most of the studies do not consider that the expansion is restrained by structural ladle design conditions, affecting the microstructural development of the composition and the overall properties.

Considering this aspect, Soudier and colleagues [4] analyzed the corrosion behavior of spinel-forming castables under a partially constrained expansion situation, by using electrofused Al_2O_3 crucibles to inhibit the materials' full volumetric change during the thermal treatment. With a similar approach, Sako et al. [5] evaluated the slag corrosion resistance of Al_2O_3-MgO cement-bonded castables fired with or without constraint, indicating that the penetration indexes were reduced for the restrained expansion environment, because of the resulting lower volume of pores in the castables' microstructure.

These later studies have drawn their attention mainly to the corrosive slag attack, whereas other important properties were not tracked. In this sense, the current study addressed the thermo-mechanical evaluation of high-alumina castables, containing distinct amounts of *in situ* spinel and calcium magnesium aluminate cement (CMA72), a binder developed to reduce the expansion associated with the *in situ* spinel generation and, thus, provide an uniform distribution of ultra-fine spinel in the castable´s matrix, enhancing even more the corrosion resistance of this sort of refractory [6, 7]. The compositions were evaluated under free-expansion or constrained environment, to figure out the impact of the microstructural changes caused by these likely situations.

Besides this design issue, another important practical subject is the placing temperature, as the curing of hydraulic binders is very sensitive to this parameter [8]. Because of different hydrate formation, it is expected that the phases generated at high temperatures (CA_2 and CA_6, also expansive reactions) may present distinct features (for instance, distribution and morphology), imparting an effect on the castables' behavior. As CMA72 is a hydraulic binder, this work also analyzed the impact of changing the curing temperature (8, 30 or 50°C), as this parameter, similarly to the constraining effect, may change the expansive behavior of these castables, the final microstructure after firing at a high temperature (1500°C) and the refractories' properties.

MATERIALS AND TECHNIQUES

Three Al_2O_3-MgO castables were prepared for the evaluation of the constraining effect after firing, for samples cured for 1 day at different temperatures (8, 30 or 50°C, in a humid environment). Table 1 shows details of the formulations. Tabular alumina grains (T-60, D ≤ 6 mm, Almatis, Germany) were used as coarse aggregates, whereas calcined and reactive aluminas (AC44B6, D_{50} = 2.5 µm and P1525B, D_{50} = 0.7 µm, Alteo, France), dead-burnt magnesia (98 wt% MgO, D ≤ 45 µm, Magnesita, Brazil) and microsilica (971U, Elkem, Norway) comprised the matrix. Calcium magnesium aluminate (CMA72, ~ 70 wt% Al_2O_3, ~ 10 wt% CaO, ~ 20 wt% MgO, Kerneos, France) was used as the binding agent. Refpac 200 (Kerneos, France) was added to ensure suitable dispersion during mixing. The compositions had different contents of binder. The higher the CMA72 amount, the lower the MgO content in order to have similar spinel amounts after firing at 1500°C.

Table 1 - CMA72-bonded Al_2O_3-MgO-SiO_2 formulations.

	Compositions / contents (wt%)		
Raw material	**IS - 6M6CMA**	**IS - 4.5M12CMA**	**IS - 3M18CMA**
Tabular alumina	75	74	73
Fine alumina	11.5	8	4.5
Dead-burnt magnesia	6	4.5	3
Microsilica	0.5	0.5	0.5
CMA72	6	12	18
Refpac 200	1	1	1
Water	4.4	4.5	4.5

Prismatic samples (150 x 25 x 25 mm^3) were prepared for permanent linear change (PLC), thermal shock and hot modulus of rupture tests, whereas cylinders ($D_{external}$ = 50 mm, $D_{internal}$ =

12.5 mm, height = 50 mm) were produced for the assisted sintering technique experiments. The samples were cured at distinct temperatures for 24h, dried for 24h at 110°C and calcined at 600°C for 5h. After that, they were either fired at high temperatures (1000, 1300 or 1500°C for 5h) or used for the preparation of the constraining experimental condition. For the later, a high-alumina cement-bonded composition (6 wt% CAC, Secar71, Kerneos, France) was designed and cast around the Al_2O_3-MgO-SiO_2 CMA72-bonded bar specimens, aiming to impose a certain degree of constraint, as presented in Fig. 1. After firing at 1500°C for 5h, the samples were withdrawn for thermal shock and HMOR evaluations.

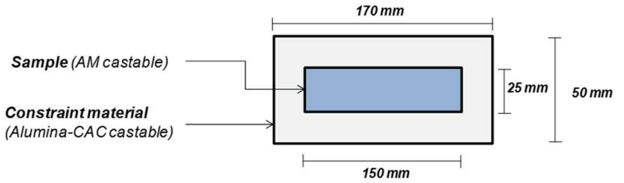

Fig. 1 - Sketch of the Al_2O_3-MgO bar configuration, embedded by an alumina-calcium aluminate cement castable, to induce a certain degree of constraint during expansion.

The castables' expansion (without constraint) was evaluated by two techniques: (1) permanent linear change (PLC), which is measured by the percentile difference between the initial and final lengths (before and after heat treatment) divided by the initial sample's dimension, and (2) assisted sintering technique, carried out in a refractoriness-under-load equipment (Model RUL 421E, Netzsch, Germany). Cylindrical samples were prepared per the 51053 DIN standard and heated up to 1500°C under a heating rate of 3°C/min and kept at this temperature for 5h. The applied compressive load was 0.02 MPa.
For the thermo-mechanical analyses (for samples with or without constrain), hot modulus of rupture evaluation (at 1450°C for samples previously fired at 1500°C for 5h) was conducted (3-point bending test, according to the ASTM C583-8 standard, HBTS 422 equipment, Netzsch, Germany). Regarding the thermal shock tests, the refractories were subjected to 8 thermal cycles (heating-cooling). The samples were placed into a furnace previously heated up to 1025°C (ΔT = 1000°C) and kept at this temperature for 15 min. Afterwards, they were suddenly cooled down at room temperature. Elastic modulus measurements were conducted after every even cycle (0, 2, 4, 6 and 8), using the bar resonance method (ASTM C-1198).

RESULTS AND DISCUSSION

Fig. 2 shows the permanent linear change results for the three compositions (Table 1) after firing at 1000, 1300 or 1500°C for 5h (initial curing at 50°C). The castable IS-6M6CMA presented the highest increase in the PLC from 1000 to 1300°C, due to its greater magnesia content and, thus, *in situ* spinel formation. Conversely, the IS-3M18CMA showed the highest PLC raise from 1300 to 1500°C, which is associated with its CMA72 content, leading to higher calcium dialuminate (CA_2) and hexaluminate (CA_6) formations. Table 2 lists the expected amount of *in situ* spinel, CA_2, CA_6 and liquid formed after the whole phase transformations (at 1500°C). The results were attained based on thermodynamic simulations (procedure described elsewhere [9]) and considered only the castables' matrix compositions (D < 200 µm). The material IS-6M6CMA resulted in the highest spinel content, but the presence of CA_2 was not predicted. Conversely, for the castables with greater amounts of CMA72 (12 or 18 wt%), a higher content of calcium aluminates was identified. It is worth noticing that the composition with intermediate CMA72 (IS - 4.5M12CMA) content showed higher CA_6 amount than the other with more binder (IS - 3M18CMA), whereas the later presented a higher quantity of CA_2 rather than CA_6. Although different reactions took place in these castables, the overall PLC after firing at 1500°C was close, pointing out that not only the spinel formation / expansion may be considered when evaluating the dimensional changes, but also the calcium aluminate generation (CA_2 and CA_6). Shrinkage and eventual warping during cooling may be also considered when analyzing these PLC results.

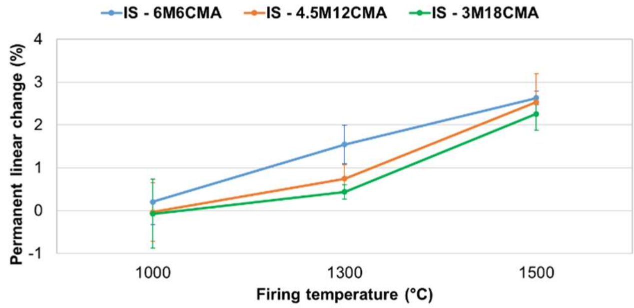

Fig. 2 - Permanent linear change (PLC) of the evaluated compositions containing different amounts of MgO and CMA72, after firing for 5h at 1000, 1300 or 1500°C.

Table 2 - Expected formed phases and their relative contents in the castables' matrix, by thermodynamic simulations, considering firing at 1500°C.

	Compositions / phase content (wt%)		
Phases	**IS - 6M6CMA**	**IS - 4.5M12CMA**	**IS - 3M18CMA**
Spinel ($MgAl_2O_4$)	86.5	74.1	69.3
CA_2	0	4.2	15.3
CA_6	8.9	16.4	10.1
Liquid	4.6	5.3	5.3

Aiming to better understand the impact of these phase transformations, assisted sintering tests were conducted (Fig. 3a), highlighting the share of each one of these reactions. Differently than the PLC results (close values after firing at 1500°C), the overall expansion levels were distinct, which can be related with the difference of the techniques, as the PLC also considers the cooling step and, thus, distinct displacements (due to phase mismatches or even related to samples' bending due to shrinkage) may be taken into account. The highest assisted sintering expansion value was observed for the IS - 4.5M12CMA composition, which shows intermediate spinel content, but the highest CA_6 one. The castable that displayed the lowest expansion level had less CMA72 (and CaO), indicating that even a composition with high spinel formation can be relatively dimensionally stable. On the other hand, higher amounts of CMA72 can reduce the overall linear change, as, besides the expansive reactions (mainly CA_2 and CA_6 in this case), shrinkage may occur (due to the combined presence of SiO_2 - CaO - Al_2O_3 - MgO, that can result in higher amount of liquid phase, as indicated in Table 2), counterbalancing the expansion induced by these phase generations. The derivative of the assisted sintering curves (Fig. 3b) indicates the temperature at which the main expansive phases take place and also the rate of their formation [10]. Although the composition IS - 3M18CMA presented higher CA_2 and lower CA_6 amounts (predicted by the thermodynamic simulation) when compared with IS - 4.5M12CMA, it showed the lowest CA_2 peak and the highest CA_6 one. This aspect indicates that the evaluation of the expansion rate may be based on morphological features, reaction speed and the castables' likelihood for accommodating the formed grains in the microstructure instead of considering the content of the generated phases.
After analyzing the expansive behavior, the thermo-mechanical properties were evaluated. Fig. 4 indicates the hot modulus of rupture of samples fired at 1500°C for 5h, with free-expansion allowance or suppressed by the Al_2O_3-CAC castable. For all

castables, the restrained environment induced an increase in the HMOR values. The higher the amount of CMA72 (and thus CA_6), the greater was the resultant improvement (26% for IS-6M6CMA, 61% for IS-4.5M12CMA and 185% for IS-3M18CMA), pointing out that the addition of this binder can either help to enhance the corrosion resistance or to improve the hot mechanical behavior.

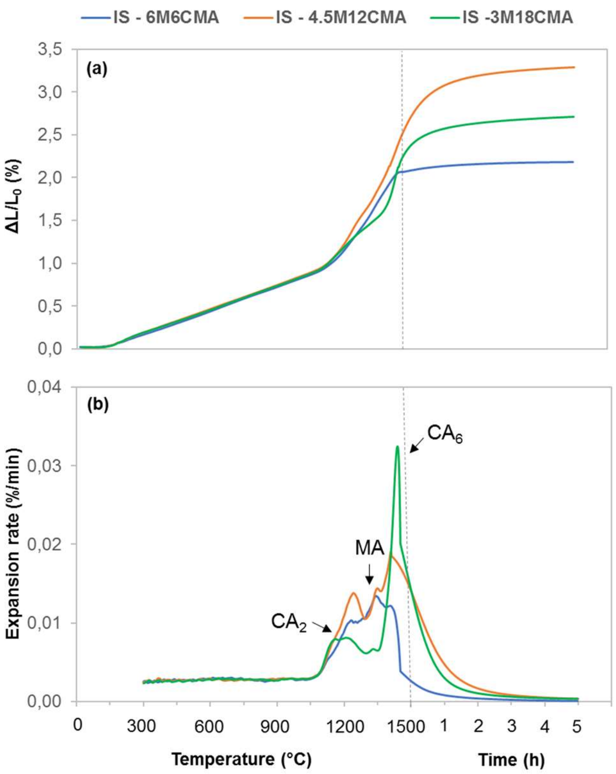

Fig. 3 - (a) Expansive behavior and (b) expansion rate of the compositions containing different amounts of MgO and CMA72, during firing up to 1500°C for 5h.

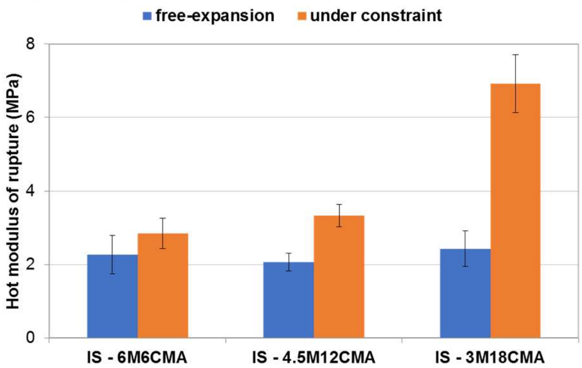

Fig. 4 - Hot modulus of rupture at 1450°C for compositions containing different amounts of MgO and CMA72, cured at 50°C and fired at 1500°C for 5h.

Similar results were observed for the thermal shock resistance evaluation (Fig. 5). The initial MOE values were increased when the samples were fired under constraint. However, the percentage loss as a function of the number of cycles (Table 3) considerably increased for the expansion under constraint (UC) condition when compared with the free-expansion one (FE), which may be a consequence of the reduction in the volume of pores [5], that usually act as crack deflectors, improving the refractory fracture energy. These results point out the importance of the expansion under constraint evaluation and the need for new techniques that can simulate this condition, as selecting the materials by considering only free-expansion environments may lead to wrong interpretations and inappropriate selection of castables for steel ladles. Regarding the distinct compositions, no difference was detected when they were evaluated without any constraint. Conversely, for the restrained expansion condition, the castable with the highest expansion level (IS - 4.5M12CMA) showed the greatest initial MOE value and the lowest MOE percentage decrease. Nonetheless, the opposite situation (lowest initial MOE and percentage MOE loss) was not detected for the castable with the lowest expansion level (IS - 6M6CMA). This may be a consequence of the different microstructures formed for these compositions (distinct contents of spinel and calcium aluminate phases, their distribution and morphologies).

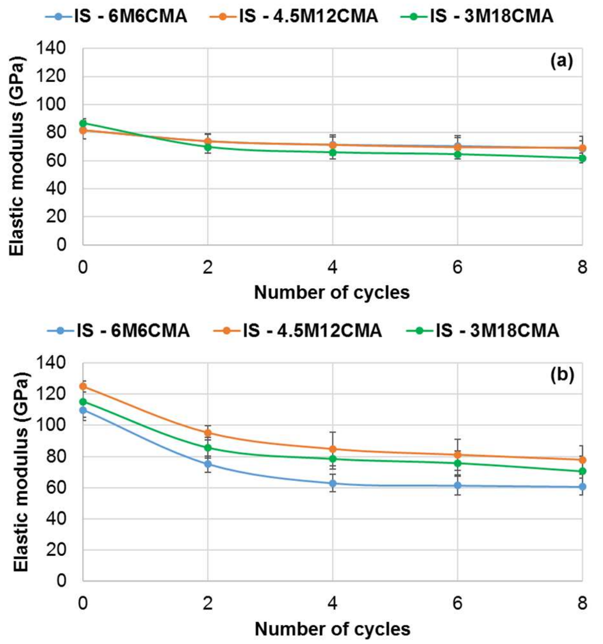

Fig. 5 - Elastic modulus values as a function of the number of thermal shock cycles for compositions containing different amounts of MgO and CMA72, after firing at 1500°C for 5h with (a) free-expansion (FE) or (b) under a constrained environment (UC).

Table 3 - Elastic modulus before (0 cycles) and after (8 cycles) the thermal shock, for the distinct compositions with different MgO and CMA72 contents, previously fired at 1500°C for 5h in a free-expansion (FE) or constrained (UC) environment.

Compositions	MOE (0 cycles)	MOE (8 cycles)	% loss
IS-6M6CMA (UC)	109.9 ±7.3	60.7 ± 6.3	45
IS-6M6CMA (FE)	81.9 ± 6.6	68.8 ± 5.3	16
IS-4.5M12CMA (UC)	125.0 ± 3.6	77.9 ± 9.1	38
IS-4.5M12CMA (FE)	81.5 ± 5.9	69.1 ± 8.3	15
IS-3M18CMA (UC)	115.2 ± 9.9	70.6 ± 9.5	39
IS-3M18CMA (FE)	86.6 ± 3.2	61.8 ± 3.5	29

Besides designing issues, processing conditions may be critical for the microstructural development and resulting castables' properties. A well-known example for calcium aluminate cement-bonded compositions is the curing temperature, that affects the hydrate formation kinetics and, thus, the green mechanical strength, the drying behavior, the materials' permeability and so on. Considering this aspect, castable IS-4.5M12CMA (with intermediate MgO and CMA amounts, but with the highest expansion level after the assisted sintering evaluation) was selected and cured at different temperatures for a day (8, 30 or 50°C). Fig. 6 indicates the assisted sintering technique profiles, highlighting that changing the initial processing conditions and, thus, the binder hydration, affects the microstructural development (formed phases, their rates of generation and distribution) at high temperatures. It is interesting to notice that the expansion was not only affected by the CA_6 generation (above 1350-1400°C), but also by the CA_2 and MA formation in the range of 1100-1350°C, meaning that not only CaO-containing phases are influenced by this parameter, but also other phases such as the magnesium aluminate spinel. The higher the curing temperature, the greater the overall linear expansion was.

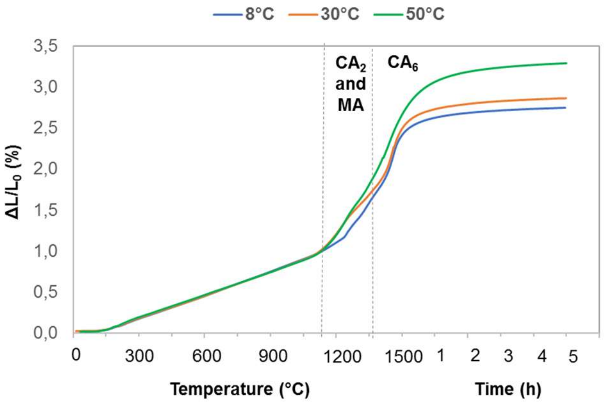

Fig. 6 - Expansive behavior of the IS - 4.5M12CMA composition, after curing at 8, 30 or 50°C for 24h and firing at 1500°C for 5h.

As a consequence of this distinct microstructural development, different HMOR values were observed at 1450°C (for samples fired at 1500°C) when changing the curing temperature (Fig. 7). The lower the temperature (lower expansion), the higher the hot mechanical strength level. For the firing under constraint, this effect is even more relevant: whereas the average HMOR increase was of 106% (3.4 to 7.0 MPa) for the 8°C condition, it was of only 57% (2.1 to 3.3 MPa) for the 50°C one, pointing out the relevance of considering application and design issues for suitable materials' evaluation.

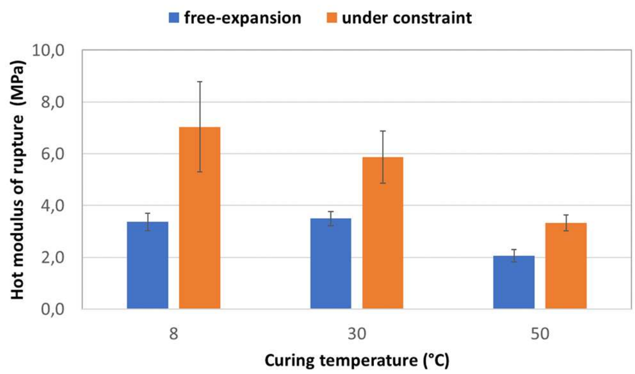

Fig. 7 - Hot modulus of rupture at 1450°C for the IS - 4.5M12CMA composition, after curing at 8, 30 or 50°C for 24h and firing at 1500°C for 5h.

Varying the curing temperature also affected the thermal-shock behavior (Table 4). For the free-expansion (FE) condition, the castable cured at 8°C showed a slightly higher initial MOE value, but the greatest MOE % loss. On the other hand, for the constrained expansion environment (UC), it presented the lowest MOE % loss, even though it has not attained the highest initial elastic modulus value. This aspect indicates how complex it is to master the microstructure / properties and that it does not only depend on the selected raw materials but also to the processing and design issues, pointing out the complexity of refractory materials and of their selection for industrial applications.

Table 4 - Elastic modulus before (0 cycles) and after (8 cycles) the thermal shock, for the composition IS - 4.5M12CMA cured at 8, 30 or 50°C for 24h and fired at 1500°C for 5h in a free-expansion (FE) or constrained (UC) environment.

Composition	MOE (0 cycles)	MOE (8 cycles)	% loss
Curing at 8°C (UC)	106.1 ± 7.7	78.3 ± 12.6	26
Curing at 8°C (FE)	85.6 ± 4.7	53.2 ± 6.3	38
Curing at 30°C (UC)	138.6 ± 4.5	72.4 ± 5.0	48
Curing at 30°C (FE)	81.4 ± 2.6	57.5 ± 5.9	29
Curing at 50°C (UC)	125.0 ± 3.6	77.9 ± 9.1	38
Curing at 50°C (FE)	81.5 ± 5.9	69.1 ± 8.3	15

FINAL REMARKS

This work indicated the relevance of evaluating design and processing parameters to obtain the best performance in industrial applications. The Al_2O_3-MgO castables bonded with CMA72 showed different effects for both the constraining expansion environment and the curing temperature. Adding greater amounts (12-18 wt%) of this binder may not only improve the corrosion resistance, but also the hot mechanical strength and thermal shock behavior. Based on the conducted evaluation, it was noticed how important it is to consider materials' selection-processing-design to improve the properties of steel ladle refractories and, thus, their working life. Novel tests to attain this target are essential and may be a subject of continuous studies for the next upcoming years.

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