Selection of binders for *in situ* spinel refractory castables

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Abstract

The expansive behavior of alumina–magnesia refractory castables is usually associated with *in situ* spinel formation. Nevertheless, when bonded with calcium aluminate cement (CAC), this class of materials can present additional expansion reactions due to CA_2 and CA_6 formation. Considering that these reactions impart a further contribution to the material's overall volumetric change, the objective of this work has been to analyze the effect of partial or complete replacement of CAC by hydratable alumina (HA). Taking into account that this substitution would affect various castable processing steps, properties such as the mechanical strength (during curing, intermediate or high temperatures), linear change behavior during heating, creep and thermal shock resistance were evaluated. In general, CAC-containing castables led to better mechanical strength and thermal shock resistance, whereas HA-containing castables presented higher creep resistance, lower apparent porosity and better volumetric stability. Due to the substantial reduction of the overall expansion of alumina–magnesia castables, the addition of hydratable alumina was pointed out as an interesting alternative to attain designed expansion levels.
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1. Introduction

Alumina–magnesia castables are widely known for their expansive behavior, due to *in situ* spinel ($MgAl_2O_4$) formation at temperatures higher than $1000\,°C$.[1–3] Various parameters can affect this reaction: the MgO[1,3] and alumina[4] grain sizes, the microsilica content,[5,6] the refractory aggregates nature,[7] among others. In addition, the binder system selected for this class of castables might influence their volumetric stability, as a consequence of its reactions and sinterability at high temperatures.

Calcium aluminate cement (CAC) is the typical binder used in *in situ* spinel refractory castables, showing benefits such as suitable working, setting and demoulding time and also corrosion resistance.[8] Nevertheless, CAC additions in these castables may lead to further expansion, attributed to CA_2 and, mainly, CA_6 formation.[5,9,10]

Acicular calcium hexaluminate crystals can enhance properties such as thermal shock and creep resistance,[11] as their needle-like shape can act as *in situ* whiskers, increasing the material's toughening. Despite these advantages, the excess of CA_6 formation with such morphology might lead to mechanical damages due to cracking, requiring control of the calcium aluminate cement content, as presented in previous work by the authors.[9]

A possible alternative to inhibit CA_6 expansion is the calcium aluminate cement replacement with hydratable alumina. Commercial hydratable alumina products are based on the rehydration ability of ρ-Al_2O_3, a metastable phase which presents hydraulic setting at room temperature.[12] Zhang and Li[13] analyzed the effect of alumina polymorphism on the synthesis of spinel ($MgAl_2O_4$) from 1000 to $1600\,°C$ and observed that the use of γ or ρ-Al_2O_3 led to shrinkage during spinel formation, whereas α-Al_2O_3 resulted firstly in expansion followed by a smaller contraction. This result was attributed to the higher density of α-Al_2O_3 when compared with γ or ρ-Al_2O_3.

Furthermore, in the presence of silica, a metastable SiO_2–Al_2O_3 liquid can be formed at temperatures close to $1250\,°C$,[14] providing densification of alumina systems bonded with hydratable alumina. This effect can counterbalance the *in situ* spinel expansion, affecting the volumetric stability of alumina–magnesia refractory castables.

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Considering these aspects, the objective of this paper is to analyze the effect of partial or total replacement of calcium aluminate cement with hydratable alumina on the expansion behavior of alumina–magnesia castables. As the binder system affects processing steps such as curing and phase development at intermediate (350–1000 °C) and high (1150–1500 °C) temperatures, these stages were evaluated by means of mechanical strength, apparent porosity, assisted sintering extent, thermal shock and creep resistance. The results obtained indicated that calcium aluminate cement and hydratable alumina played different roles in the processing of castables, including the volumetric stability behavior, suggesting an alternative route for designing the alumina–magnesia expansion of castables.

2. Experimental procedure

Two binders were selected and a total of 6 wt% of them were added to the castables [calcium aluminate cement (CAC) Secar 71 (Kerneos, France), containing 30 wt% CaO, and a hydratable alumina (HA) AlphaBond 300 (Almatis, USA)]. Additionally, compositions containing both binders were also prepared with different CAC/HA ratios: 4 wt% cement + 2 wt% hydratable alumina (4C2H) or 2 wt% cement + 4 wt% hydratable alumina (4C2H).

Vibratable castables were designed using the Alfred particle packing model ($q = 0.26$).[15] The castables' matrix comprised 6 wt% of dead-burnt magnesia (<45 µm, 95 wt% MgO, $CaO/SiO_2 = 0.37$, Magnesita S.A., Brazil), 1 wt% of microsilica (971U, Elkem, Norway), 7 wt% of reactive alumina (CL370, Almatis, USA) and 15 wt% of fine tabular alumina (<200 µm, Almatis, USA). To complement the compositions, coarse tabular alumina was used as aggregate ($d \leq 6$ mm, Almatis, USA). General information about the selected raw materials is presented in Table 1. The water content for a suitable moulding increased with the hydratable alumina content: 3.9 wt% for 6 wt% CAC (6C), 4.5 wt% for 4C2H, 5.0 wt% for 2C4H and 5.3 wt% for 6 wt% HA (6H).

The castables were cast into 40 mm × 40 mm cylindrical molds and the mechanical strength was evaluated after curing at 50 °C (in a humid environment – 100% of relative humidity – for castables containing CAC – 6C, 4C2H and 2C4H – and at room conditions – 40% of relative humidity – for the one bonded with hydratable alumina – 6H), at different lengths of time (1, 3, 5 and 7 days). Mechanical strength tests were also carried out after firing at intermediate temperatures (1 day curing at 50 °C,

1 day drying at 110 °C and a heat treatment for 5 h at 350, 600, 800 and 1000 °C at a rate of 1 °C/min). The mechanical evaluation was conducted according to the ASTM C496-90 standard (Splitting Tensile Strength of Cylindrical Concrete Specimens) in MTS testing equipment (MTS Systems, Model 810, USA).

Following that, samples were molded (25 mm × 25 mm × 150 mm) to evaluate the modulus of rupture after firing at 1150, 1300 and 1500 °C for 5 h (heating rate = 1 °C/min). Their permanent linear expansion (PLE) was measured by the percentage difference between the initial and the final length (before and after heat treatment) divided by the initial sample dimension. The 3-point bending test was carried out according to the ASTM C133-94 standard and was performed in the same MTS equipment described above. SEM analyses were conducted (SEM, Hitachi S-510, Tokyo, Japan). The apparent porosity for the mechanical strength samples was also evaluated by the Archimedes technique in kerosene (after heat treatment at intermediate and high temperatures).

To assess spinel and CA_6 formation, an assisted sintering technique was carried out in refractoriness-under-load equipment (Model RUL 421E, Netzsch, Germany). Cylindrical samples were prepared according to 51053 DIN standard (height and external diameter = 50 mm and central inner diameter = 12.4 mm), cured at 50 °C and dried at 110 °C for one day, followed by a pre-firing at 600 °C for 5 h before testing. For this test, samples were heated up to 1500 °C under a heating rate of 3 °C/min and kept at this temperature for 5 h. The compression load applied was 0.02 MPa. Creep tests were also performed on samples previously calcined at 600 °C and fired at 1550 °C for 24 h. The creep measurements were carried out at 1450 °C for 24 h under a constant compression load of 0.2 MPa. In order to analyze the effect of liquid formation, thermodynamic simulations were performed (FactSage, Thermfact and GTT-Technologies, Universidade Federal de São Carlos, FAI).

Additionally, thermal shock tests were conducted using multiple cycles for samples (25 mm × 25 mm × 150 mm) previously fired at 1300 and 1500 °C. The furnace temperature was kept constant at 1025 °C and the dwell time at this temperature was 15 min. After this period, the samples were thermal shocked in air, leading to a temperature gradient close to 1000 °C. Subsequently, the elastic modulus was evaluated, using the resonance method (ASTM C-1198). Following that, the samples were returned to the furnace and the same procedure was repeated for 10 cycles.

Table 1
General characteristics of the raw materials used.

Raw materials	Physical properties		Chemical composition (wt%)							
	D_{50} (µm)	SSA (m²/g)	Al_2O_3	Na_2O	SiO_2	MgO	CaO	Fe_2O_3	K_2O	C
Tabular alumina	*Several ranges (from 6–3 to 0.2–0 mm)*		99.5	≤0.4	≤0.02	–	–	–	–	–
Reactive alumina	2.5	3.0	99.7	0.1	0.03	–	0.02	0.03	–	–
Dead-burnt MgO	10	1.3	0.35	–	1.21	95.3	0.44	1.74	–	–
Microsilica	0.15	22	0.4	0.1	97.5	0.1	0.2	0.1	0.3	0.5
Calcium aluminate cement	20	1.2	≥68.5	–	<0.8	<0.5	≤31	<0.3	–	–
Hydratable alumina	4	160	>88	<0.5	<0.3	–	<0.1	–	–	–

3. Results and discussion

3.1. Binder effects in the different processing steps of Al₂O₃–MgO castables

The mechanical strength throughout the curing time at 50 °C was affected by the amount and sort of binder used. As shown in Fig. 1, the castable containing 6 wt% of hydratable alumina presented better results up to the 5th curing day. This aspect might be related with the reaction between magnesia and alumina, leading to hydrotalcite [$Mg_6Al_2(CO)_3(OH)_6 \cdot (4H_2O)$] formation,[16–18] which can strengthen the material due to the generation of hydrogen bridges. Nevertheless, as the density of hydrotalcite is even lower than that for brucite ($\rho_{hydrotalcite} = 2.18$ g/cm³ and $\rho_{brucite} = 2.54$ g/cm³),[19] its formation can cause more expansion damage than the MgO hydration itself. As a consequence, the mechanical strength of the sample containing hydratable alumina decreased on its 7th day of cure. This result is also related to the low porosity and permeability levels provided by the hydration of this binder, due to the formation of bayerite and boehmite gel, reducing the room available for accommodation of the expansive products (brucite and hydrotalcite).[20]

Concerning the calcium aluminate cement-bonded castable (6C), the mechanical strength was not as high as that presented for hydratable alumina, but its increasing strength trend must be highlighted, resulting in a better performance after 7 days of curing. This enhancement in the mechanical strength is caused both by CAC and MgO hydration.[21] Reducing the CAC content from 6 to 4 wt% and adding 2 wt% of hydratable alumina (4C2H) resulted in a lower modulus of rupture up to the third day of curing. Nevertheless, this composition attained a high level of mechanical strength after 7 days. Furthermore, as all the castables bonded with CAC were cured in a humid environment, the mechanical strength for the castable 2C4H (2 wt% CAC + 4 wt% HA) resulted in worse behavior, as hydratable alumina develops its strength better when cured at normal room conditions.[22]

The hydratable alumina-bonded castable (6H) presented a continuous decrease in mechanical strength at intermediate temperatures (Fig. 2a). This behavior is not ideal for applications of
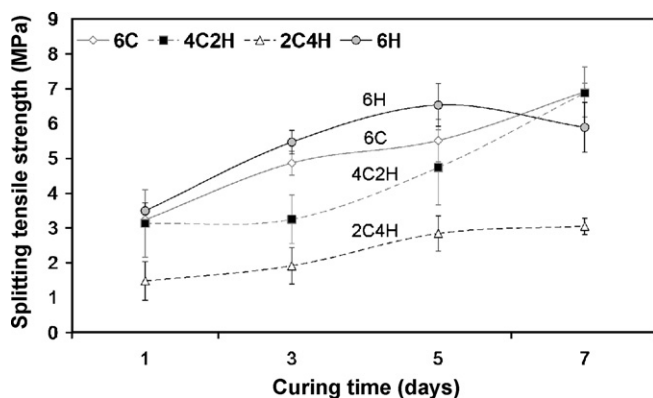
Fig. 1. Splitting strength with the curing time at 50 °C for alumina–magnesia castables containing 6 wt% CAC (6C), 4 wt% CAC + 2 wt% HA (4C2H), 2 wt% CAC + 4 wt% HA (2C4H) or 6 wt% HA (6H).
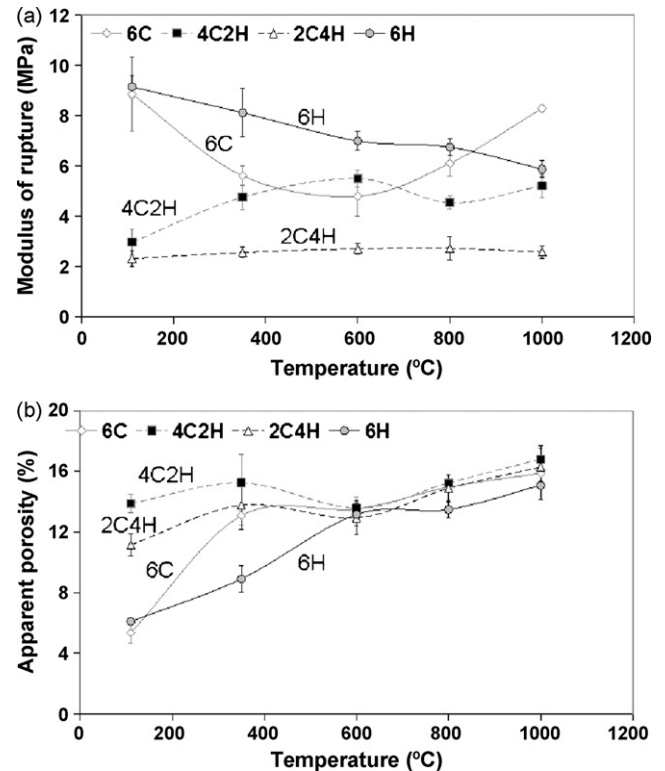
Fig. 2. (a) Mechanical strength and (b) apparent porosity at intermediate temperatures (350, 600, 800 and 1000 °C) of alumina–magnesia castables containing 6 wt% CAC (6C), 4 wt% CAC + 2 wt% HA (4C2H), 2 wt% CAC + 4 wt% HA (2C4H) or 6 wt% HA (6H).

alumina–magnesia castables in steel ladles, as lower mechanical strength at this temperature range can induce cracks due to the thermo-mechanical stresses that can be generated during the first heat-up. Nevertheless, the results obtained are higher than the other compositions in the 110–800 °C range. This reduction of mechanical strength is associated with the alumina phase transformations (boehmite–gamma–delta–theta–alpha)[13] and is in tune with the results presented by Altun.[23] The cement hydrates decomposition led to a decrease in the splitting tensile strength up to 600 °C for the 6C composition, but afterwards this castable strengthened, due to the calcium aluminate formation[24] and their bonding effects.

The castables containing mixtures of calcium aluminate cement and hydratable alumina (4C2H and 2C4H) presented lower levels of mechanical strength, similar to the curing stage. The low splitting tensile strength observed after 1 day drying at 110 °C can be correlated with the high level of apparent porosity detected for these two castables compared to the samples bonded with CAC (6C) or HA (6H), as shown in Fig. 2b. This figure also points out the lower porosity in the hydratable alumina-bonded castable up to 600 °C, consistent with its lower permeability.[20] From 600 to 1000 °C, all the castables tend to present similar porosity values, indicating that the mechanical strength performance was set by other factors, such as formation of phases and their intrinsic properties or coarsening of their pores at constant porosity.
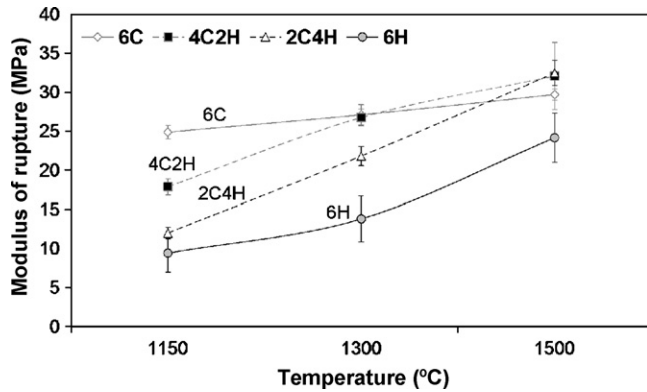
Fig. 3. Mechanical strength after firing at high temperatures for 5 h (1150, 1300 and 1500 °C) for alumina–magnesia castables containing 6 wt% CAC (6C), 4 wt% CAC + 2 wt% HA (4C2H), 2 wt% CAC + 4 wt% HA (2C4H) or 6 wt% HA (6H).

The continuous mechanical strength loss observed for the hydratable alumina castable (6H) at intermediate temperatures reflected on the development of this property at higher temperatures (after firing at 1150, 1300 and 1500 °C for 5 h) (Fig. 3). Nevertheless, a latter increase in the mechanical strength was detected. At high temperatures, the compositions containing CAC and HA (4C2H and 2C4H) strengthened and, after firing at 1500 °C, presented better results than the others containing only cement or hydratable alumina. This behavior might be related to the phases developed at high temperatures and also with the hydratable alumina sintering behavior, as will be presented in the next section. In previous work,[9] it was shown that lower calcium aluminate cement contents led to better mechanical strength, due to a controlled CA_6 formation. In order to analyze the influence of hydratable alumina and complement the results presented before, the assisted sintering technique was carried out.

3.2. Binder effects on the expansion behavior of Al_2O_3–MgO castables

As calcium aluminate cement (6C) induces the expansion of alumina–magnesia castables,[9] its replacement by hydratable alumina (6H) led to a noteworthy reduction on the overall expansion of this class of castables (Fig. 4a). The range of expansion attained indicates the effect of matrix raw materials on the volumetric stability of alumina–magnesia castables. This expansion reduction for the 6H composition is associated with: (i) the higher densification due to the use of ρ-alumina in spite of α-alumina,[13] (ii) the shrinkage, especially in the presence of silica[14] and (iii) the absence of expansion related to CA_6 formation.

This third aspect can be observed by the expansion rate (Fig. 4b) of alumina–magnesia castables bonded with calcium aluminate cement (6C) or hydratable alumina (6H). Conversely to the two expansion peaks that appeared in the CAC composition (related to spinel and CA_6),[9] the HA castable presented only a small upwards peak close to 1100 °C, as
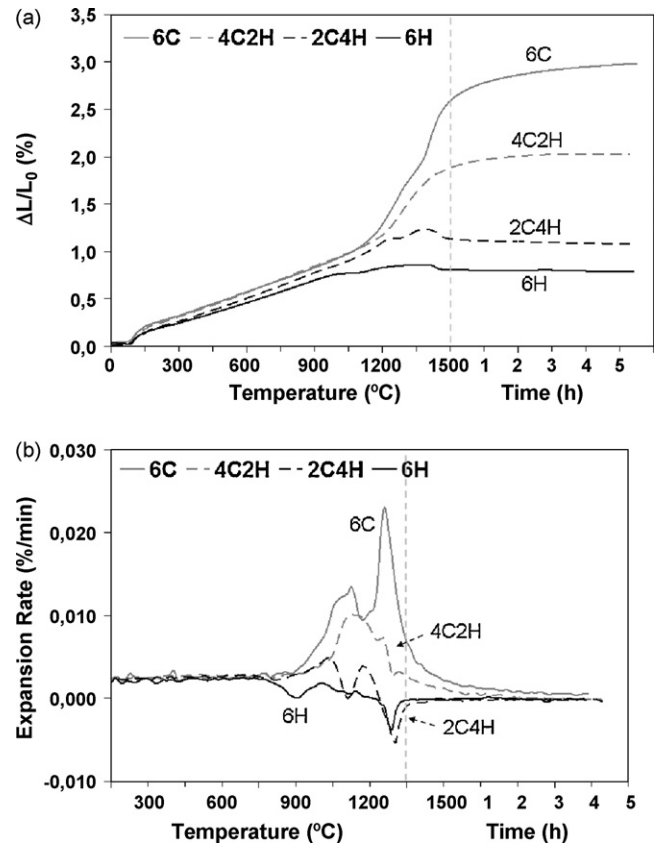

Fig. 4. (a) Expansion behavior and (b) expansion rate of alumina–magnesia castables containing 6 wt% CAC (6C), 4 wt% CAC + 2 wt% HA (4C2H), 2 wt% CAC + 4 wt% HA (2C4H) or 6 wt% HA (6H).

a consequence of spinel formation. However, it was much lower than that presented in the castable 6C, due to the sinterability of hydratable alumina. Compositions containing cement and hydratable alumina seemed an interesting route for reducing the overall expansion of *in situ* spinel refractory castables.

In order to better understand the hydratable alumina behavior, two other castable compositions were produced and their assisted sintering curves were attained. A hydratable alumina-bonded alumina castable (HAC–MgO free) and an alumina–magnesia castable (ISC – *in situ* spinel castable – binder free) were compared with the hydratable alumina-bonded alumina–magnesia castable (6H). Fig. 5a shows the dimensional change profiles for these compositions. The castable bonded with HA (HAC) presented a high shrinkage at temperatures above 1000 °C (∼−0.8%), whereas the one containing only magnesia (ISC) resulted in ∼2% expansion. As a consequence of shrinkage and expansion effects, the overall result of the alumina–magnesia castable bonded with hydratable alumina was an intermediate value (∼1%). The derivative curves of these castables (Fig. 5b) also highlight that the hydratable alumina shrinkage counterbalances the expansion of *in situ* spinel formation. This HA feature is opposite to that presented by CAC, where the $MgAl_2O_4$ and CA_6 formation led to a higher overall expansion of a CAC-bonded alumina–magnesia castable (6C).
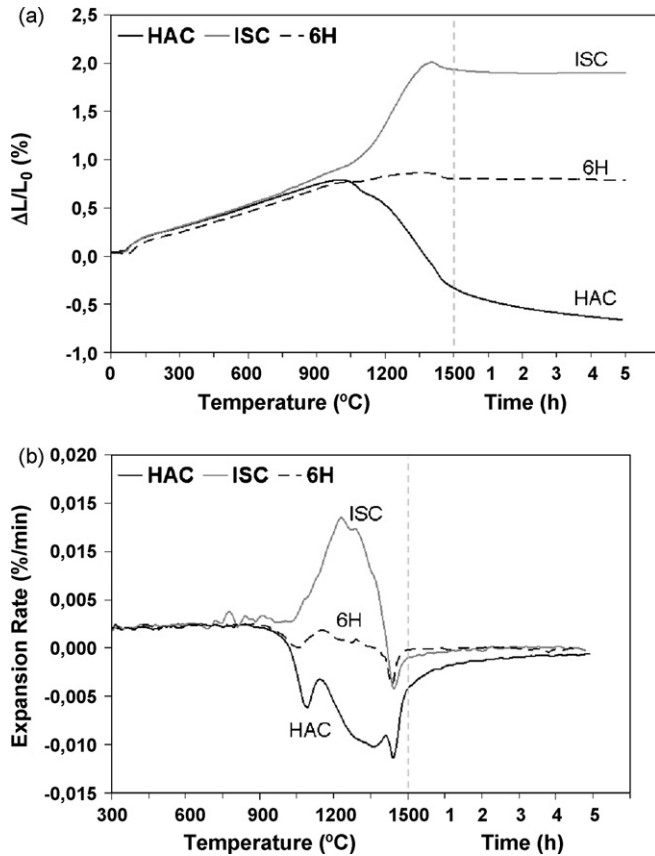
Fig. 5. (a) Expansion behavior and (b) expansion rate of the hydratable alumina-bonded castable with no MgO (HAC), the alumina–magnesia castable with no binder (ISC) and the alumina–magnesia castable containing hydratable alumina (6H).
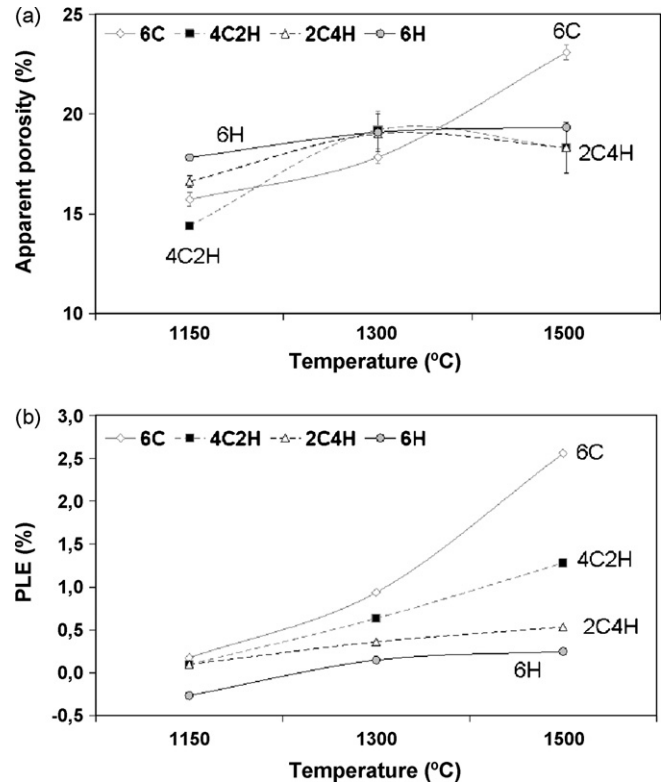

Fig. 6. (a) Apparent porosity and (b) permanent linear expansion (PLE) of alumina–magnesia castables fired at 1150, 1300 and 1500 °C for 5 h, containing 6 wt% CAC (6C), 4 wt% CAC + 2 wt% HA (4C2H), 2 wt% CAC + 4 wt% HA (2C4H) or 6 wt% HA (6H).

Back to the former compositions, the apparent porosity (AP) of the castables prepared only with CAC or HA or their mixtures were also evaluated (Fig. 6a). The CAC-bonded castable (6C) was the only one that increased the apparent porosity at 1500 °C, suggesting that a high CA_6 formation may cause mechanical damages to the castable.[9] This statement is supported by the permanent linear expansion (PLE), shown in Fig. 6b. Conversely, even with the increase in the expansion, both castables, 4C2H and 2C4H, presented a decrease of AP at 1500 °C. The sample containing only hydratable alumina (6H) kept an almost constant AP value from 1150 to 1500 °C.

Concerning the microstructural features, different behaviors were observed for the castables containing only CAC (6C) or hydratable alumina (6H) after firing at 1300 °C for 5 h (Fig. 7). The CAC-containing sample presented regions where Ca–Al–Si were close together, indicating that phases such as gehlenite and anorthite were developed, as discussed in a previous paper from the authors.[5] Conversely, as there was no CaO available in the castable bonded with hydratable alumina (6H), an interaction between SiO_2 and MgO was detected. According to Braulio et al.,[1] forsterite (Mg_2SiO_4) was developed in alumina–magnesia castables, at high firing temperature (1500 °C) and due to the magnesia availability at this temperature. This reaction result in shrinkage, which was

observed in the hydratable alumina-bonded alumina magnesia castable sintering profile (Fig. 4a), as forsterite formation is usually carried out at temperatures roughly above 1000 °C and is followed by such behavior.[25,26] Despite these differences related to the silica interaction with other matrix components, in both castables, the spinel (MA) was already detected at this temperature.

Due to the different expansion behaviors, these castables also developed particular microstructures, after firing at 1500 °C (Fig. 8). Whereas the calcium aluminate cement led to the CA_6 formation and coarse spinel grains, the hydratable alumina castable resulted in a denser microstructure and finer spinel grains. Based in the literature, this latter behavior is related to the reaction between magnesia and the α-alumina produced by the transformation of ρ-alumina,[13] and also due to the lower liquid phase content, as no CaO was available to form low-melting point phases[22] by its reaction with silica and alumina.

3.3. Binder effects on the thermo-mechanical behavior of Al_2O_3–MgO castables

The main microstructural features that affect the creep resistance of refractory castables are: (i) the content, composition and location of liquid phases, (ii) the apparent porosity and (iii) the size, morphology and location of crystalline phases.
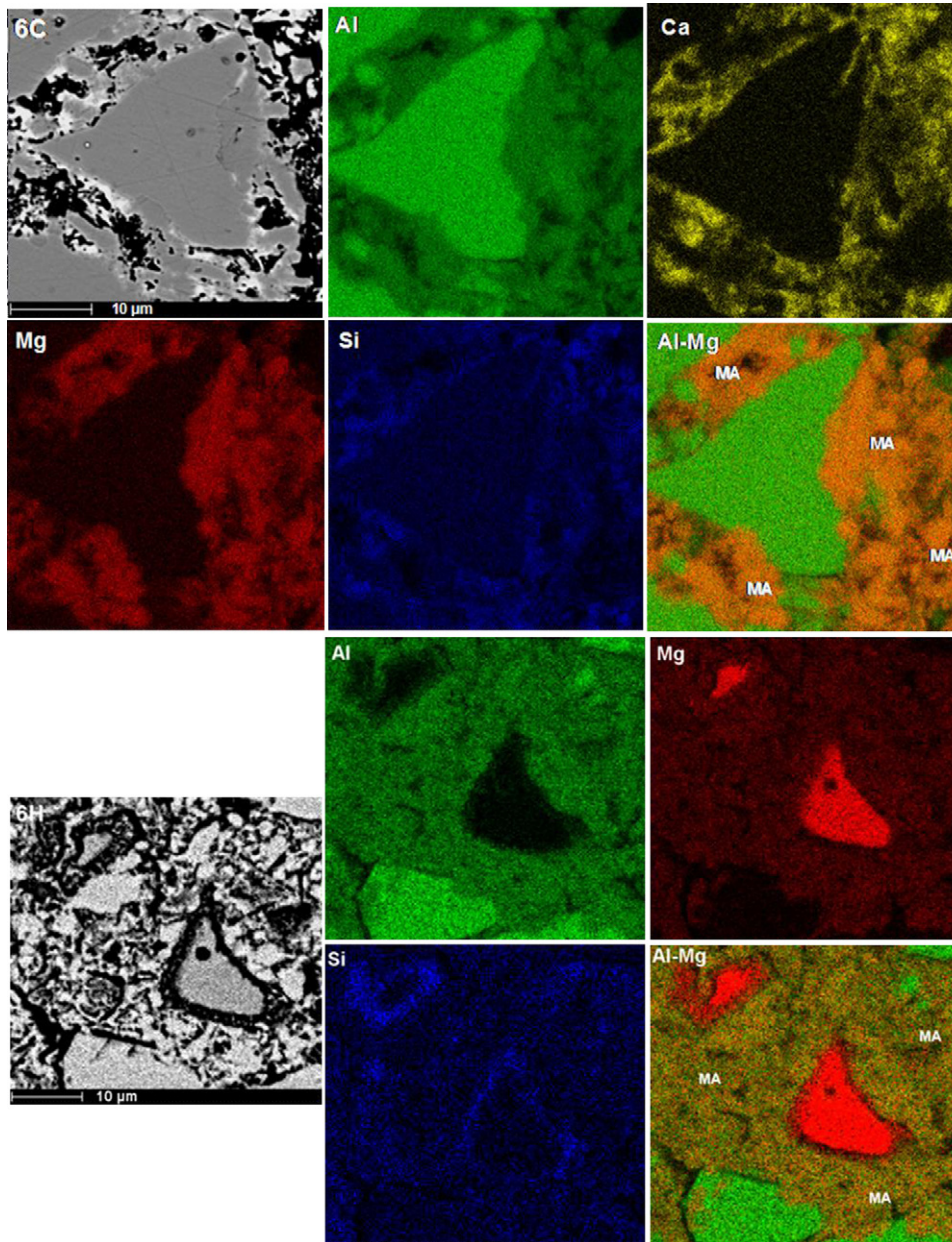
Fig. 7. Microstructural evaluations of alumina–magnesia castables bonded with 6 wt% CAC (6C)[1] or HA (6H), after firing at 1300 °C for 5 h (MA—spinel).

Considering the apparent porosity (ii) lower creep for the castables containing hydratable alumina (6H, 2C4H and 4C2H) should be expected as they present lower values after sintering at 1500 °C for 5 h (Fig. 6a). On the other hand, based on item (iii), the sample containing 6 wt% CAC (6C) should be the best one, as spinel grains were larger (>20 μm) than in the sample containing hydratable alumina (<10 μm) (Fig. 8). In addition, this castable presents higher CA_6 content, which would also improve the material's toughening.[9,11] Nevertheless, Fig. 9 indicates a better behavior for the castable 6H, whereas all the castables presenting CAC resulted in approximately close behavior and a higher creep deformation, after 24 h at 1450 °C.

To better understand this result, thermodynamic simulations were performed and the expected equilibrium phases at 1450 °C were obtained. The castable containing 6 wt% of hydratable alumina resulted in no liquid phase at this temperature: 76 wt% alumina, 16 wt% spinel ($MgAl_2O_4$) and 7 wt% sapphirine ($Mg_4Al_{10}Si_2O_{23}$). Conversely, all the CAC-containing castables presented liquid phases at 1450 °C, as listed below:

- Composition 6C (6 wt% CAC): 4 wt% liquid (comprising 8 wt% MgO, 23 wt% SiO_2, 21 wt% CaO and 48 wt% Al_2O_3), 65 wt% alumina, 20 wt% spinel and 11 wt% CA_6;
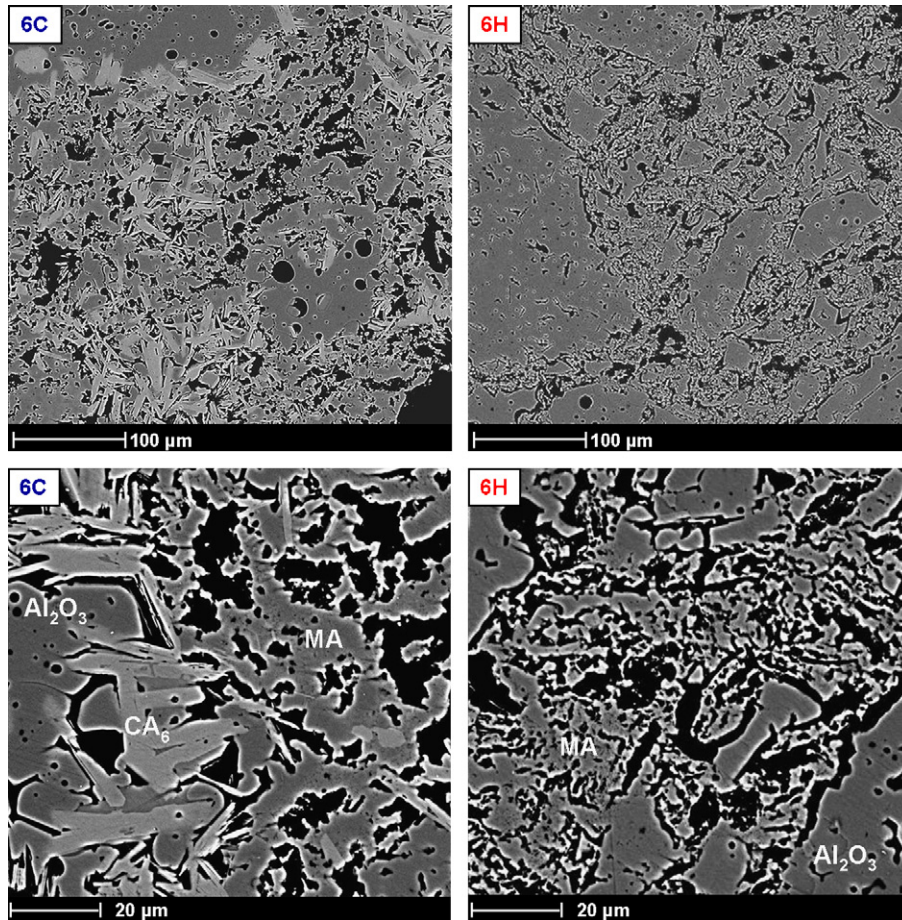
Fig. 8. Microstructural evaluations of alumina–magnesia castables bonded with 6 wt% CAC (6C)[7] or HA (6H), after firing at 1500 °C for 5 h (MA—spinel).

- Composition 4C2H (4 wt% CAC and 2 wt% HA): 4 wt% liquid (comprising 8 wt% MgO, 23 wt% SiO_2, 21 wt% CaO and 48 wt% Al_2O_3), 72 wt% alumina, 20 wt% spinel and 3 wt% CA_6;

- Composition 2C4H (2 wt% CAC and 4 wt% HA): 3 wt% liquid (comprising 9 wt% MgO, 29 wt% SiO_2, 17 wt% CaO and 45 wt% Al_2O_3), 76 wt% alumina and 20 wt% spinel.

According to these thermodynamics predictions, it could be asserted that the presence of liquid phase played the most important role in the creep behavior of the alumina–magnesia castables analyzed. The close predicted values of liquid phase and composition for all castables containing CAC led to similar overall deformations.

As all the castables containing CAC presented similar creep behavior, thermal shock analyses were only carried out on the castables containing 6 wt% CAC (6C) and 6 wt% hydratable alumina (6H), after firing at 1300 and 1500 °C for 5 h (Fig. 10). For the castables fired at 1300 °C, the thermal shock results of the castable containing CAC were better. As a consequence of the HA sintering delay, the thermal shock behavior of the 6H composition was worse after firing at 1300 °C, due to a poorer bonding linkage between the formed phases. Nevertheless, for the samples fired at 1500 °C, the thermal shock results were similar, regardless of the binder system, due to the sintering of the hydratable alumina containing castable at this temperature (Fig. 5).
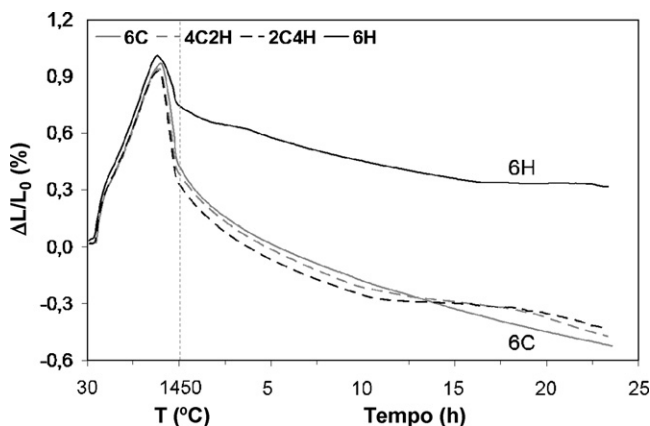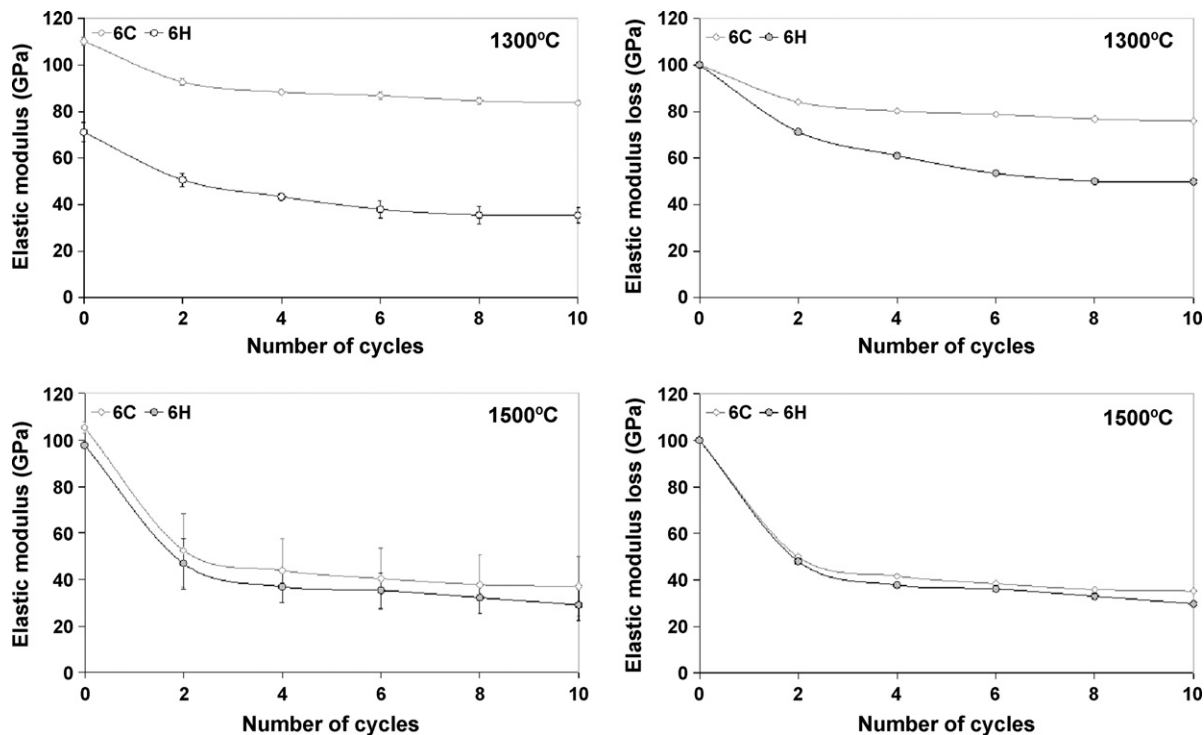

Fig. 9. Creep resistance (24 h at 1450 °C) of alumina–magnesia castables pre-fired at 1450 °C for 24 h, containing 6 wt% CAC (6C), 4 wt% CAC + 2 wt% HA (4C2H), 2 wt% CAC + 4 wt% HA (2C4H) or 6 wt% HA (6H).

Fig. 10. Thermal shock resistance (absolute and percentage elastic modulus loss, $\Delta T = 1000\,^{\circ}C$) of alumina–magnesia containing 6 wt% CAC (6C) or 6 wt% HA (6H), after firing at 1300 or 1500 °C for 5 h.

4. Conclusions

The present study indicated benefits and drawbacks of calcium aluminate cement or hydratable alumina additions to alumina–magnesia castables. In general, CAC-containing castables performed better regarding mechanical strength and thermal shock resistance. Nevertheless, they attained higher *in situ* expansion, due to the CA_6 formation. An efficient way to control the volumetric stability can be achieved by the addition of hydratable alumina, as its shrinkage behavior counterbalances the *in situ* spinel expansion. Furthermore, this binder led to higher creep resistance and also low apparent porosity levels, which can be useful to reduce the slag infiltration. Additionally, a full systemic analysis concerning the best binder to be applied on this class of castables would only be completed after assessment of corrosion resistance, where the performance of castables would depend very much on slag composition.

Acknowledgements

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