High-Alumina Chemically Bonded Refractory Castables Containing Liquid or Powdered Binders

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Dedicated to the 10th Anniversary of refractories WORLDFORUM

Phosphate-bonded refractories may be applied as repairing materials due to their fast setting time and good thermomechanical properties in the 30–1000 °C temperature range. Phosphoric acid and Monoaluminium Phosphate (MAP) solutions are commonly used as main binder additives in chemically bonded compositions, but powdered phosphate compounds can also be applied for this purpose. This work addresses the design of vibratable high-alumina castables containing MAP (liquid) or magnesium monophosphate (powder) as binding agents. Various experimental tests (flowability, setting time, cold and hot mechanical strength, thermal shock resistance, and others) were carried out and the developed compositions were compared with commercial products of different refractory suppliers. According to the attained results, both evaluated additives (MAP solutions or magnesium monophosphate) are very effective and they have the advantage of not inducing the castables' temperature increase (such as the case of mixtures prepared with phosphoric acid) during the mixing and curing steps. Furthermore, the addition of a sintering additive (boron-based compound) to the evaluated formulations resulted in enhanced thermomechanical performance (mainly cold and hot mechanical strength, thermal shock and erosion resistance) in the 600–1000 °C temperature range.

1 Introduction

In order to maximize the operational time of petrochemical units, chemically-bonded refractories have been commonly used as repairing materials due to their short setting time (when compared to products containing hydraulic binders) and other interesting properties, such as high green mechanical strength, good adhesion, reduced risk of cracking under high heating rates after curing, etc. [1–3]. Consequently, proper selection of refractory repairing materials is an important issue for applications at high working temperatures, as severe damage to the original ceramic linings may lead to thermal energy losses and safety concerns for the operational personnel and process.

The available high-alumina phosphate-bonded refractory castables designed for Fluid Catalytic Cracking units (FCC which equipment operates in the range of 600–815 °C) usually comprise phosphoric acid or monoaluminium phosphate [MAP or $Al(H_2PO_4)_3$] solutions as binder source [4, 5]. Based on the literature [1–3, 6], the setting mechanism derived from the action of H_3PO_4 reaction with Al_2O_3 (above 127 °C) or $Al(OH)_3$ at room temperature is based on the generation of $Al(H_2PO_4)_3$ and water (eq. 1–2) into the castable mix. After that, the MAP decomposition and the precipitation of $AlPO_4 \cdot xH_2O$ (which is usually an amorphous phase) result in hardening and subsequent loss of workability observed during the processing of refractory products [7–9].

$$6\ H_3PO_4 + Al_2O_3 \rightarrow 2\ Al(H_2PO_4)_3 + 3\ H_2O \qquad \text{(eq. 1)}$$

$$3\ H_3PO_4 + Al(OH)_3 \rightarrow Al(H_2PO_4)_3 + 3\ H_2O \qquad \text{(eq. 2)}$$

Therefore, MAP can be in situ generated (when adding H_3PO_4 solution to the refrac-

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tory dry-mix containing reactive alumina or aluminium hydroxide) or directly added to castables [7, 8, 10]. Some refractory producers prefer to work with commercial and stabilized $Al(H_2PO_4)_3$ solutions, whereas others find more practical to prepare their own MAP by mixing Al_2O_3 and/or $Al(OH)_3$ particles with the phosphoric acid [10].

Nevertheless, in order to speed up the phase transformations related to the phosphoric acid and monoaluminium phosphate interaction with the castables' raw materials, the addition of setting agents (i.e., MgO, CaO, calcium aluminates, etc.) to the compositions should also be considered. Such additives induce an acid-base reaction, resulting in the formation of amorphous/crystalline phosphates that affect the refractory hardening and other properties [1, 4, 10]. Besides that, the incorporation of sintering additives (i.e., boron based compounds) into such complex compositions can also improve the thermomechanical performance of high-alumina chemically-bonded refractories in the temperature range of 500–815 °C due to the in situ generation of $Al_{18}B_4O_{33}$ phase [7].

It is easy to realize that designing a phosphate-based castable with optimised features is not a straightforward task, due to the many components and their important roles in the various phase transformations expected to take place during service. Additionally, the refractory producers must provide not only the dry-mix but also the liquid component (acid solution) to end-users and these two materials should be mixed and processed on site. Consequently, there are some concerns related to logistic issues (mainly storage and transportation) associated with these acid solutions and care must be taken when handling phosphoric acid, for instance, as this is a highly corrosive material. Thus, an alternative and desired route would be the development of chemically-bonded refractories containing powdered phosphates (i.e., MAP or magnesium monophosphates) instead of liquid ones. In this latter case, water could be used as the liquid phase and the mixing step of the chemically-bonded compositions would be similar to the one applied for the preparation of traditional cement-containing materials.

Considering these aspects, this work addresses the design of improved vibratable high-alumina castables containing MAP (liquid) or magnesium monophosphate (powder) as binding agents. Various experimental tests (flowability, setting time, cold and hot mechanical strength, thermal shock resistance, and others) were carried out and the developed compositions were compared with commercial products of different refractory producers.

2 Materials and techniques

A vibratable formulation containing 86 mass-% of coarse tabular alumina as aggregates (d ≤ 6 mm, Almatis, USA) and 14 mass-% of reactive aluminas (CL370C and CT3000SG, Almatis/US) and fine tabular alumina (d ≤ 200 µm, Almatis/US) as main matrix components, was designed according to Alfred's particle packing model (q = 0,26) [5]. Besides that, three high-alumina commercial products [(1) S, Stellar/US (2) M, Magnesita Refratários/BR; (3) I, IBAR/BR)] were also processed (with binder solutions provided by the suppliers) and evaluated as reference materials.

Tab. 1 points out the overall chemical composition of the commercial and designed castables.

Different binding systems (liquid or powdered) were added to the tested formulation. In the case of the liquid additives, 12 mass-% of commercial monoaluminium phosphate (MAP) solutions (Fosbind 151 or Fosbind 50, with ~35 or ~38 mass-% of P_2O_5, respectively) supplied by Prayon company/BE, and 1,5 mass-% of dead-burnt MgO (d < 212 µm, Magnesita Refratários/BR) were added to the alumina dry-mix during processing. Whereas, the combination of 6 mass-% of a powdered magnesium monophosphate (M-11-57, d < 45 µm, ~60 % P_2O_5, Budenheim/DE) plus 0,25 mass-% of dead-burnt MgO and 1 mass-% citric acid (PA, Synth/BR) were required to attain suitable flowability and hardening time for the castable containing this novel binder.

As two of the analysed commercial products (*M* and *I*) contained sintering additives in their compositions (to favour an earlier densification of the refractories microstructure during heating) and aiming to allow a fair comparison among these refractories and designed castables, the formulations prepared in this work comprised 1 mass-% of a boron-based compound (B, d < 45 µm, B_2O_3 = 53,38 mass-% [7]).

During the castable processing step, the compositions were dry-homogenized for 1 min and mixed for more 2 min in a rheometer, by adding MAP solutions or distilled water to the dry powders. The commercial refractories were also prepared in the same equipment, but considering the addition of the provided liquid solutions (11,6–13 mass-%) and following the mixing procedure as recommended by the suppliers.

Flowability measurements were carried out according to ASTM C860. The setting time was analysed based on ultrasonic measurements (equipment IP-8 and software UltraTestLab V3, UltraTest/DE) to follow the propagation velocity of ultrasonic wave in wet mixtures of the castables in order to estimate their workability [11]. These analyses were performed at room temperature (~25 °C) for 24 h.

Bars samples (150 mm × 25 mm × 25 mm) of the designed formulation and *S* were moulded, cured at 30 °C for 24 h, dried at 110 °C for 24 h and pre-fired in the 500–815 °C temperature range for 5 h before testing. The evaluated specimens for materials *M* and *I* were provided by the refractories' suppliers, and they were subjected to the same processing steps mentioned above.

The cold flexural strength (ASTM C133-97) and apparent porosity (ASTM C380-00, us-

Tab. 1 Chemical composition of the evaluated refractories

Oxide [mass-%]	Commercial Product			Designed Formulation
	S	*M*	*I*	
Al_2O_3	94,8	94,3	94,0	94,8
SiO_2	–	0,2	0,6	–
CaO	0,8	0,6	–	–
Fe_2O_3	0,1	0,3	0,1	0,1
P_2O_5	3,8	3,9	2,8	3,6–4,6

Tab. 2 **Evaluated castables (commercial and designed ones) and their binder system and initial vibratable flow values**

Composition	Main Binder	Added Liquid [mass-%]	Initial Vibratable Flow [%]
S	Liquid activator – FORMULA*	11,6	160
M	MAP solution*	13,0	117
I	ADT 111 solution*	13,0	6
TA-FB151-B	Fosbind 151 = MAP solution (Prayon)	12,0	95
TA-FB50-B	Fosbind 50 = MAP solution (Prayon)	12,0	80
TA-MGP-B	Magnesium monophosphate powder (Budenheim)	6,0 (water)	137

MAP = aluminium monophosphate, *liquid binder provided by the castable's supplier.

ing kerosene as the immersion liquid) of the castable were attained after drying (110 °C for 24 h) and firing (815 °C for 5 h) steps.

Hot modulus of rupture (HMOR) was measured at 500 °C, 600 °C, 700 °C and 815 °C (using samples pre-fired for 5 h at the same testing temperature) in HBTS 422 equipment (3-point bending test, Netzsch/DE) based on the ASTM C583-8 standard. Cold erosion resistance of the refractories was also evaluated (using samples fired at 500, 600, 700 and 815 °C respectively for 5 h) following the ASTM C704 standard (1 kg of 36 grit silicon carbide to erode specimens with 100 mm × 100 mm × 25 mm thick, leading to a weight loss that was converted to a volumetric one).

Furthermore, pre-fired bars (150 mm × 25 mm × 25 mm, 815 °C for 5 h) were submitted to a total of 10 thermal shock cycles (ASTM C1171-91) at 815 °C (ΔT~790 °C). The damage caused by the thermal changes was analysed by the elastic modulus measurements at room temperature via the bar resonance technique [12, 13]) as a function of the thermal cycles.

3 Results and discussion

3.1 – Flowability and setting time

The main challenge to develop chemically-bonded castables with suitable flowability and setting time is associated with finding a proper balance between the amount/concentration of the acid (phosphoric acid or phosphate-based compounds) and basic components (i.e., CaO, MgO) added to the mixture. Due to the fast acid-base reaction that takes place during the compositions mixing and curing steps, the selection of the binder system plays an important role in the rheological behaviour of these refractories. Tab. 2 points out the main binder additive (liquid or powdered) as well as the vibratable flow of each analysed material.

S was prepared with a liquid activator that seems to be a phosphoric acid solution with green colour. This material showed a slightly heat release during mixing (measured temperature = 35 °C), resulting in high flow level (160 %) and the beginning of its setting took place ~4 h (Fig. 1 a). On the other hand, the solution used for the preparation of *M* and *I* consisted mainly of monoaluminium phosphates. Despite the suitable initial flow (117 %) of the former, the high reactivity among the liquid binder and solid components of this castable resulted in short workability (vibratable flow drop was identified after 15 min reaching values of ~40 %). Even with the flow level decrease of the *M* refractory, the ultrasonic measurements only detected a significant raise of the propagation wave velocity in the fresh castable mix above 10 h (Fig. 2 a), which indicates that a long period of time is still required for the full hardening of the samples. Castable *I* showed short working time (ultrasonic propagation velocity presented a major increase around 1–2 h) and this behaviour allied to its reduced vibratable flow (6 %) can affect the quality of the ceramic lining due to difficulties during placing such material.

Regarding to the designed castables, preliminary tests indicated that adding 1,5 mass-% of the selected MgO to the MAP-bonded compositions would allow the in situ transformations to evolve under a compatible rate and without excessive heat release (mix temperature ~30 °C), as commonly observed in phosphoric acid-bonded materials [9]. As shown in Tab. 1, TA-FB151-B and TA-FB50-B presented suitable flow values (80–95 %) and the setting/hardening of these compositions was

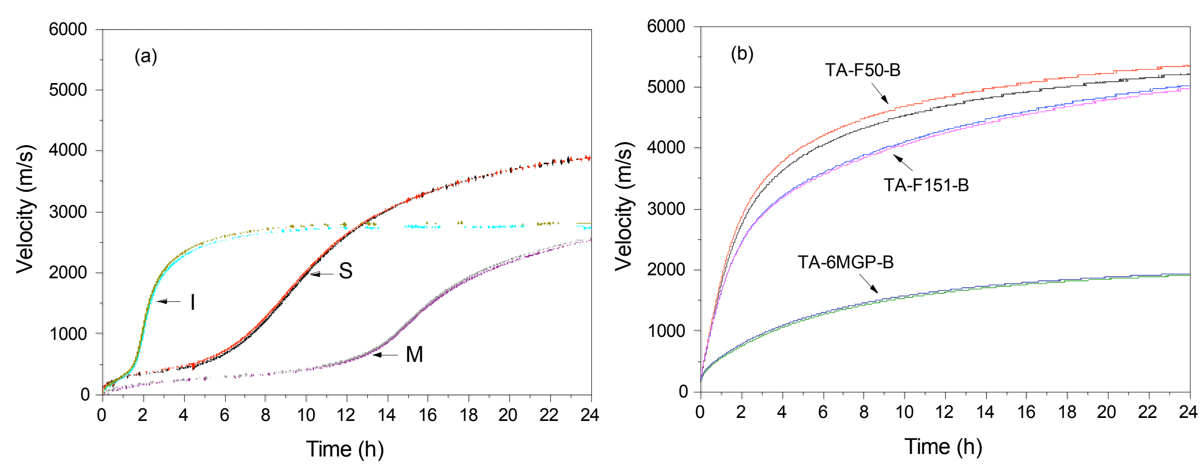

Fig. 1 a–b **Ultrasonic propagation velocity measured during the evaluation of wet mixtures of (a) the commercial, and (b) the designed phosphate-bonded castables at room temperature (~25 °C) for 24 h**

observed after approximately 75–90 min (Fig. 1 b). However, despite some attempts to increase the vibratable flow levels of such compositions, it was difficult to improve this property due to the higher viscosity of these binders (Fosbind 151 and Fosbind 50, viscosity = 60–100 Pa · s at ~20 °C) when compared with phosphoric acid (viscosity = 47 Pa · s at ~20 °C).

On the other hand, the main advantage of using magnesium monophosphate (MGP) in the TA-MGP-B composition was the fact that this powder was directly added to the dry-mix and the castable preparation was very similar to the one used for cement-bonded refractories, with the addition of water as the liquid phase.

Due to the low reactivity of MGP when only mixed with alumina particles (resulting in excessive long setting time) at 30 °C, it was required the incorporation of additional MgO (0,25 mass-%) and citric acid (1 mass-%) into TA-MGP-B composition to attain improved flow (137 %) and induce the samples' full hardening close to 5 h (Fig. 1 b).

Basically, the setting time of chemically bonded refractories are related to the acid-base reactions that take place during the mixing and curing steps of these materials. According to previous studies by the authors [7], in the case of the designed MAP-containing castables (TA-FB151-B and TA-FB50-B), MgO should react with $Al(H_2PO_4)_3$ giving rise to metastable/soluble component $[Mg(H_2PO_4)_2\cdot 2H_2O]$ as well as stable/insoluble ones (newberyite = $MgHPO_4\cdot 3H_2O$ and $AlPO_4\cdot 2H_2O$) in the 30–110 °C temperature range (eq. 3–4).

$$3MgO + 2Al(H_2PO_4)_3 + 9H_2O \rightarrow Mg(H_2PO_4)_2\cdot 2H_2O + 2(MgHPO_4\cdot 3H_2O) + 2(AlPO_4\cdot 2H_2O) \qquad (3)$$

$$Mg(H_2PO_4)_2\cdot H_2O + MgO \rightarrow 2MgHPO_4\cdot 3H_2O \qquad (4)$$

The formation of a greater amount of crystalline $MgHPO_4\cdot 3H_2O$ and $AlPO_4\cdot H_2O$ hydrates acted speeding up the overall setting time of TA-FB151-B and TA-FB50-B (Tab. 2). Similar transformations should take place in the TA-MGP-B composition, however, in order to optimise the rheological features of this castable not only MgO but also a small amount of citric acid (which is a retarded agent) had to be incorporated into the dry-mix. Whereas the addition of dead-burnt magnesia (setting agent) to the mix induces faster generation of the insoluble phosphate-bases phases, the formation of complex compounds based on citrate anion (due to the presence of citric acid) and Al^{3+} prevents these cations from interacting with phosphate ions and, consequently, delays the precipitation of some crystalline hydrates [6, 8].

Thus, even small contents of this retarder additive may significantly affect the setting behaviour of the chemically-bonded compositions. After testing different amounts of MgO and citric acid, it was possible to attain a composition (TA-MGP-B) with suitable properties (Tab. 2 and Fig. 1 b) when considering 0,25 mass-% of MgO and 1 mass-% citric acid in combination with 6 mass-% of magnesium monophosphate binder.

3.2 Cold and hot mechanical properties

Tab. 3 presents the cold flexural strength, apparent porosity and density of the refractories after drying (110 °C for 24 h) and firing (815 °C for 5 h).

In general, the castables containing sintering additives, such as TA-FB151-B, TA-FB50-B, TA-MGP-B, *M* and *I*, presented higher mechanical strength than *S* in both evaluated conditions. The benefit of the boron-compound incorporation into the designed compositions could be mainly observed by the improvement of the cold mechanical strength of these samples after pre-firing at 815 °C for 5 h (Tab. 3).

Based on thermogravimetric and XRD analyses (results not shown here) [6], these high-alumina phosphate-bonded systems should present the decomposition of the main hydrated phases between 80 °C and 300 °C, leading to the generation of $AlPO_4$, $Al(PO_3)_3$ and non-crystalline magnesium phosphates. At higher temperatures (>650 °C), in situ reactions involving these resulting compounds might induce the formation of $AlPO_4$, $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ (eq. 5–6). Additionally, the interaction of fine alumina and the B_2O_3 source leads to $Al_{18}B_4O_{33}$ generation (eq. 7) [6].

$$Al(PO_3)_3 + Al_2O_3 + \text{amorphous magnesium phosphate} \rightarrow AlPO_4 + Mg_2P_2O_7 \qquad \text{(eq. 5)}$$

$$Mg_2P_2O_7 + MgO \rightarrow Mg_3(PO_4)_2 \qquad \text{(eq. 6)}$$

$$9Al_2O_3 + 2B_2O_{3(l)} \rightarrow Al_{18}B_4O_{33} \qquad \text{(eq. 7)}$$

These transformations are responsible for the enhancement of TA-FB151-B, TA-FB50-B, TA-MGP-B castables properties after firing at 815 °C for 5 h. Such results are very promising considering that fluid catalytic cracking units (FCC) commonly operate in the range of 600–815 °C and this latter temperature is used as the standard reference value to select refractory materials for the petrochemical industry.

All tested castables presented small changes in their apparent porosity and density

Tab. 3 Cold mechanical strength, apparent porosity and density results of the analysed castables

Composition	Drying/Firing Temperature [°C]	Cold Flexural Strength [MPa]	Apparent Porosity [%]	Density [g/cm³]
S	110	8,2 ± 1,9	17,2 ± 0,2	2,92 ± 0,01
	815	7,9 ± 0,5	18,5 ± 0,3	2,90 ± 0,01
M	110	14,4 ± 1,4	17,2 ± 0,4	3,05 ± 0,02
	815	40,9 ± 3,0	13,6 ± 0,.2	3,08 ± 0,01
I	110	11,9 ± 2.8	19,1 ± 0,8	3,07 ± 0,02
	815	20,3 ± 2,0	18,3 ± 0,7	3,07 ± 0,02
TA-FB151-B	110	13,6 ± 1,8	14,9 ± 0,3	2,91 ± 0,01
	815	27,8 ± 1,2	14,4 ± 0,1	2,91 ± 0,01
TA-FB50-B	110	11,6 ± 0,9	20,1 ± 0,2	2,79 ± 0,01
	815	24,4 ± 1,1	19,0 ± 0,3	2,77 ± 0,02
TA-MGP-B	110	7,9 ± 1,4	20,1 ± 0,3	2,83 ± 0,01
	815	19,7 ± 1,8	20,5 ± 0,2	2,82 ± 0,02

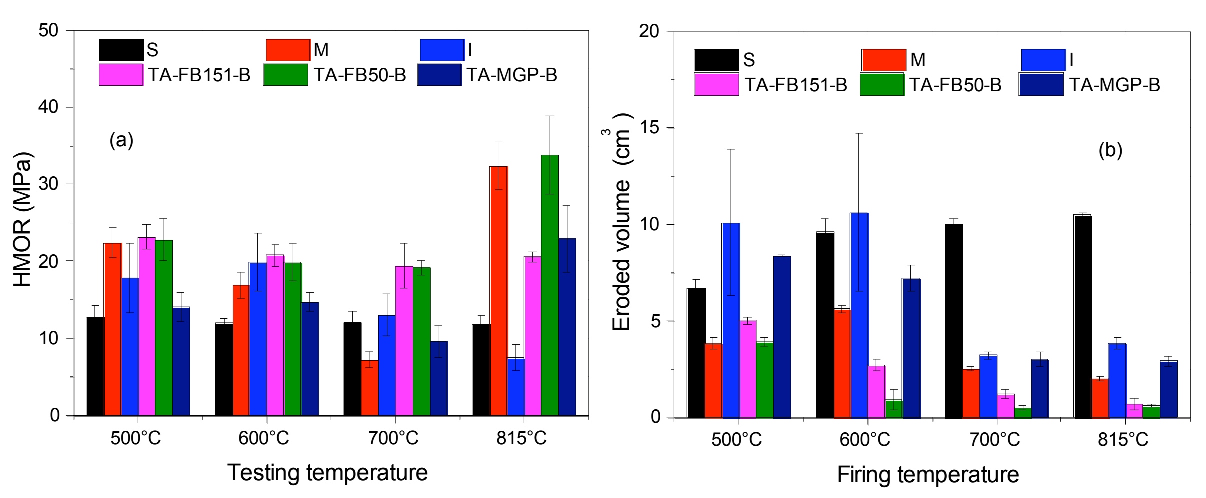

Fig. 2 a–b HMOR (3-point bending test) (a); and eroded volume of the evaluated castables (b); the prepared samples were pre-fired at 500 °C, 600 °C, 700 °C and 815 °C for 5 h before the measurements

values (when compared to the ones attained for the dried samples) after pre-firing step at 815 °C for 5 h (Tab. 3). The apparent porosity and density results were kept in the range of 13,6–20,5 % and 2,77–3,08 g/cm^3, respectively.

Regarding to the HMOR and cold erosion resistance of the chemically bonded refractories (Fig. 2), the mechanical measurements (3-point bending tests) carried out at 500 °C and 600 °C indicated that the MAP-bonded compositions (*M*, *I*, TA-FB151-B and TA-FB50-B) showed a better performance than *S* and TA-MGP-B. *S* material (sintering additive-free) roughly presented the same mechanical strength values (~12 MPa) in the 500–815 °C, whereas the $Al_{18}B_4O_{33}$ generation and other microstructural transformations favoured the HMOR increase for the other compositions especially at 815 °C (Fig. 2 a). The exception was *I* refractory, as this castable showed significant drop of its mechanical strength at 700 °C and 815 °C, which might be related to an excess of sintering additive contained in this composition, resulting in liquid phase generation and the samples' softening at high temperatures. The lower thermal stability of composition *I* was also confirmed in refractoriness under load experiments (results not shown here), where the maximum recommended temperature ($T_{0,5}$) attained for this material was 1382 °C, whereas the other evaluated castables presented $T_{0,5}$ in the range between 1496–1512 °C. Consequently, the other chemically-bonded refractories showed higher thermomechanical stability. Besides that, Fig. 2 a highlights that the highest HMOR values attained at 815 °C were (MPa): TA-FB50-B = 33,8 ± 5,1; *M* = 32,3 ± 3,1; TA-MGP-B = 22,9 ± 4,3 and TA-F151-B = 20,6 ± 0,7.

The faster and improved sintering/densification of the designed castables containing the boron-based compound also led to an expressive reduction in TA-FB151-B, TA-FB50B and TA-MGP-B samples eroded volume after pre-firing at 700–815 °C for 5 h (Fig. 2 b). However, the binding strength among coarse and fine components for the *S* and *I* samples generated after firing them at 500 °C and 600 °C, was not strong enough to prevent their erosion based on the standard evaluation technique.

Due to the absence of a sintering additive in *S* composition, the attained eroded volume was still kept around 10 % even when

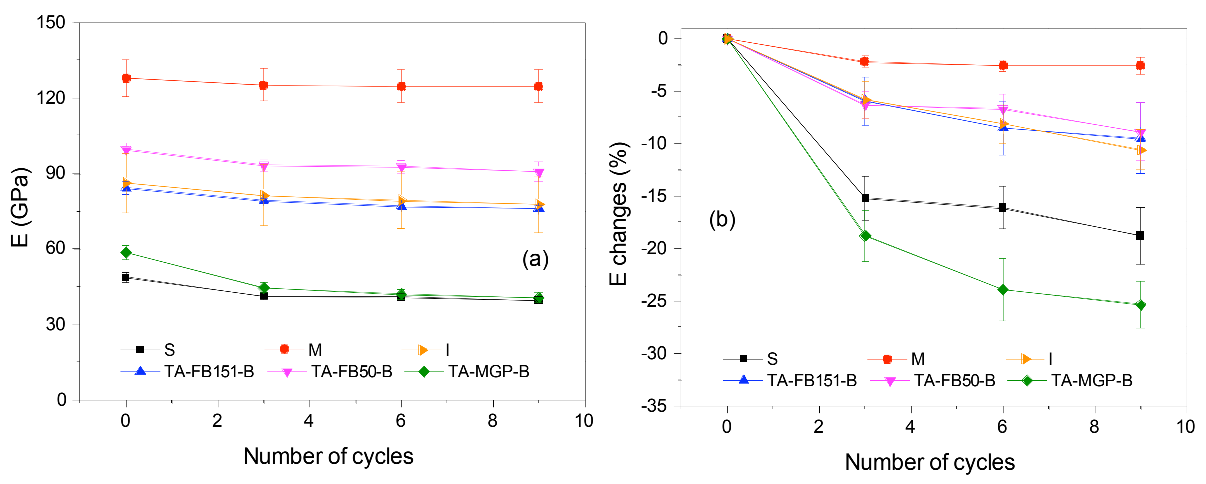

Fig. 3 a–b Elastic modulus evolution (a), and exchange of the prepared castables as a function of thermal shock cycles (ΔT ~790 °C) (b); all samples were pre-fired at 815 °C for 5 h subjecting these samples to higher pre-firing temperatures (700–815 °C). Thus, aiming to optimise the erosion resistance of chemically bonded compositions at intermediate temperatures (500–815 °C), it is recommended the use of sintering additives to induce earlier phase transformations and, consequently, the formation of strong ceramic bonds among the castables' matrix compounds.

The elastic modulus evolution of the evaluated refractories as a function of the thermal shock cycles (ΔT ~790 °C, Fig. 3 a) pointed out that the main changes took place between 0–3 cycles. *M* was the material that presented the highest stiffness value (~125–128 GPa) and after a total of 9 thermal cycles, a slightly damage could be detected in this material as the E loss (percentage decay compared to the initial elastic modulus values measured before thermal shock tests) was equal to –2,6 % (Fig. 3 b). TA-FB50-B, TA-FB151-B and *M* also presented high E values in the range of 74–99 GPa and the stiffness change of these samples after the various evaluated cycles was around –9,5 % (Fig. 3).

Although TA-MGP-B (composition containing the powdered magnesium monophosphate binder) showed higher initial elastic modulus (58,9 GPa) than *S* (48,7 GPa), these both refractories presented final stiffness values close to 40 GPa (Fig. 3 a) after 9 cycles.

Consequently, when analysing the E loss due to the thermal damage induced by the temperature variation (ΔT ~790 °C), the TA-MGP-B had the worst performance compared to the other castables.

4 Conclusions

Based on the presented results, vibratable high-alumina chemically-bonded refractory castables containing liquid or powdered binders were successfully designed, resulting in similar or even superior performance when compared to three equivalent commercial products (*S*, *M* and *I*) available for application in petrochemical industries. The combination of commercial monoaluminium phosphate solutions (MAP, Fosbind 151 and Fosbind 50) and dead-burnt magnesia (setting agent) resulted in compositions with the most promising properties.

The interaction of these components with the fine alumina of the castables' matrix plays an important role giving rise to in situ generation of magnesium and aluminium phosphates (mainly $MgHPO_4·3H_2O$ and $AlPO_4·2H_2O$) during mixing and curing, which controls the vibratable flow and setting behaviour of these compositions. The addition of a boron-based sintering compound to the designed refractories (with liquid or powdered binder) induced faster sintering/densification of the resulting microstructure with the generation of $Al_{18}B_4O_{33}$ above 600 °C.

In general, the formation of this aluminium borate led to the increase of the samples stiffness, mechanical strength, erosion and thermal shock resistance.

Although the castable containing magnesium monophosphate (powdered binder) presented higher E drop during the thermal shock measurements, the overall performance of this composition was better than some of the commercial products (i.e., *S* and *I*). Additionally, TA-MGP-B castable has the advantage of having all components (coarse, fine and binder) in a single dry-mix, which makes its handling and preparation easier.

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