

HIGH-ALUMINA CHEMICALLY-BONDED REFRACTORY CASTABLES CONTAINING LIQUID OR POWDERED BINDERS

Ana P. Luz¹, Simone J.S. Lopes¹, Daniel T. Gomes², Victor C. Pandolfelli¹

¹Federal University of São Carlos (UFSCar), São Carlos, Brazil, ²Petrobras, Rio de Janeiro, Brazil.

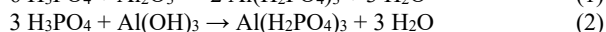
ABSTRACT

Phosphate-bonded refractories may be applied as repairing materials due to their fast setting time and good thermo-mechanical properties in the 30-1000°C temperature range. Phosphoric acid and monoaluminum phosphate (MAP) solutions are commonly used as main binder additives in chemically-bonded compositions, but solid 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 producers. 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 thermo-mechanical performance (mainly cold and hot mechanical strength, thermal shock and erosion resistance) in the 600-1000°C temperature range.

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 operate in the range of 600-815°C) usually comprise phosphoric acid or monoaluminum phosphate [MAP or Al(H₂PO₄)₃] solutions as binder source [4,5]. Based on the literature [1-3], the setting mechanism derived from the action of H₃PO₄ reaction with Al₂O₃ (above 127°C) or Al(OH)₃ at room temperature is based on the generation of Al(H₂PO₄)₃ and water (Eq. 1 and 2) into the castable mix. After that, the MAP decomposition and the precipitation of AlPO₄·xH₂O (which is usually an amorphous phase) lead to the hardening and subsequent loss of workability observed during the processing of refractory products [6-8].



Therefore, MAP can be in situ generated (when adding H₃PO₄ solution to the refractory dry-mix containing reactive alumina or aluminum hydroxide) or directly added to castables [6,8,9]. Some refractory producers prefer to work with commercial and stabilized Al(H₂PO₄)₃ solutions, whereas others find more

practical to prepare their own MAP by mixing Al₂O₃ and/or Al(OH)₃ particles with the phosphoric acid solution [9].

Nevertheless, in order to speed up the phase transformations related to the phosphoric acid and monoaluminum 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 [1,4,9]. Besides that, the incorporation of sintering additives (i.e., boron based compounds) into such complex compositions can also improve the thermo-mechanical performance of high-alumina chemically-bonded refractories in the temperature range of 500-815°C due to the in situ generation of Al₁₈B₄O₃₃ phase [6].

It is easy to realize that designing a phosphate-based castable with optimized 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 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 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.

EXPERIMENTAL

A vibratable formulation containing 86 wt% of coarse tabular alumina as aggregates (d ≤ 6 mm, Almatiss, USA) and 14 wt% of reactive aluminas (CL370C and CT3000SG, Almatiss, USA) and fine tabular alumina (d ≤ 200 μm, Almatiss, USA) 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, USA; (2) M, Magnesita Refratários, Brazil; (3) I, IBAR, Brazil)] were also processed (with binder solutions provided by the suppliers) and evaluated as reference materials. Table 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 wt% of commercial monoaluminum phosphate (MAP) solutions (Fosbind 151 or Fosbind 50, with ~35 or ~38 wt% of P₂O₅, respectively) supplied by the Prayon company (Belgium), and 1.5 wt% of dead-burnt MgO (d < 212 μm, Magnesita Refratários, Brazil) were added to the alumina dry-mix during processing.

Whereas, the combination of 6 wt% of a powdered magnesium monophosphate (M-11-57, $d < 45 \mu\text{m}$, ~60% P_2O_5 , Budenheim, Germany) plus 0.25 wt% of dead-burnt MgO and 1 wt% citric acid (PA, Synth, Brazil) were required to attain suitable flowability and hardening time of the castable containing this novel binder.

Table 1: Chemical composition of the evaluated refractories.

Oxides (wt.%)	Commercial products			Designed formulations
	<i>S</i>	<i>M</i>	<i>I</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

As two of the analyzed commercial products (*M* and *I*) contained sintering additives in their compositions (to favor an earlier sinterization/densification of the refractories microstructure during heating) and aiming to allow a fair comparison among these refractories and designed castables, the formulations elaborated in this work comprised 1 wt% of a boron-based compound (B, $d < 45 \mu\text{m}$, $\text{B}_2\text{O}_3 = 53.38 \text{ wt}\%$, under patent application [6]).

During the castable processing step, the compositions were dry-homogenized for 1 min and mixed for more 2 minutes 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 wt%) and following the mixing procedure as recommended by the suppliers.

Flowability measurements were carried out according to ASTM C860. The castable setting was analyzed based on the time required for suitable demolding of the prepared samples (150 mm x 25 mm x 25 mm) that was kept at 30°C.

Bars samples (150 mm x 25 mm x 25 mm) of the designed formulation and *S* were molded, cured at 30°C for 24h, dried at 110°C for 24h and pre-fired in the 500-815°C temperature range for 5h before testing. On the other hand, the evaluated specimens of *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, using kerosene as the immersion liquid) of the castable were attained after drying (110°C for 24h) and firing (815°C for 5h) 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, Germany) 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 for 5h) following the ASTM C704 standard (1 kg of 36 grit silicon carbide to erode specimens with 100 mm x 100 mm x 25 mm thick, leading to a weight loss that was converted to a volumetric one). Furthermore, pre-fired bars (150 mm x 25 mm x 25mm, 815°C for 5h) were submitted to a total of 10 thermal shock cycles (ASTM C1171-91) at 815°C ($\Delta T \sim 790^\circ\text{C}$). The damage caused by the thermal changes was analyzed by the elastic modulus measurements at room temperature via the bar resonance technique [10]) as a function of the thermal cycles.

RESULTS AND DISCUSSION

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 readily 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 behavior of these refractories. Table 2 points out the main binder additive (liquid or powdered) as well as the vibratable flow and setting time of each analyzed material.

Table 2: Evaluated castables (commercial and designed ones) and their binder system, initial vibratable flow and setting time.

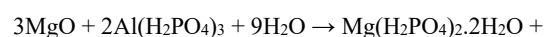
Compositions	Main binder	Added liquid (wt.%)	Initial vibratable flow (%)	Setting time (min)
<i>S</i>	Liquid activator – FORMULA*	11.6	160	150
<i>M</i>	MAP solution*	13.0	117	50
<i>I</i>	ADT 111 solution*	13.0	6	240
TA-FB151-B	Fosbind 151 = MAP solution (Prayon)	12.0	95	90
TA-FB50-B	Fosbind 50 = MAP solution (Prayon)	12.0	80	75
TA-MGP-B	Magnesium monophosphate powder (Budenheim)	6.0 (water)	137	300

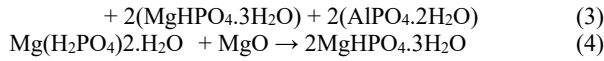
MAP = aluminum monophosphate, * liquid binder provided by the castable's supplier.

S was prepared with a liquid activator that seems to be a phosphoric acid solution with green color. This material showed a slightly heat release during mixing (measured temperature = 35°C), resulting in high flow level (160%) and overall setting time of 150 min. On the other hand, the solution used for the preparation of *M* and *I* consisted mainly of monoaluminum phosphates. Despite the suitable flow (117%) of the former, the high reactivity among the liquid binder and solid components of this castable led to a mix with short workability and setting time (~50 min). This can be a limiting aspect when considering the preparation, placing and handling of a great batch of this material. *I* castable showed longer working time (~240 min), but the main issue of this product was its reduced vibratable flow (6%), which can affect the quality of the ceramic lining due to difficulties during placing such material.

Regarding the designed castables, preliminary tests indicated that adding 1.5 wt% 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 Table 1, TA-FB151-B and TA-FB50-B presented suitable flow values (80-95%) and setting time (75-90 min). 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 mixed with alumina particles (resulting in excessive long setting time) at 30°C, it was required the incorporation of additional MgO (0.25 wt%) and citric acid (1 wt%) into TA-MGP-B composition to attain improved flow (137%) and induce the samples' hardening after around 300 min.

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 [6], in the case of the designed MAP-containing castables (TA-FB151-B and TA-FB50-B), MgO should react with $\text{Al}(\text{H}_2\text{PO}_4)_3$ giving rise to metastable/soluble component $[\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ as well as stable/insoluble ones (newberyite = $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) in the 30-110°C temperature range (Eq. 3 and 4).





The formation of a greater amount of the crystalline $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ hydrates acted speeding up the overall setting time of TA-FB151-B and TA-FB50-B (Table 2). Similar transformations should take place in the TA-MGP-B composition, however, in order to optimize 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. While 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 behavior of the chemically-bonded compositions. After testing different amounts of MgO and citric acid, it was possible to attain a composition with suitable properties (Table 2) when considering 0.25 wt% of MgO and 1 wt% citric acid in combination with 6 wt% of magnesium monophosphate binder.

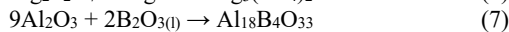
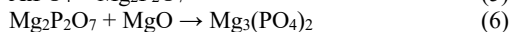
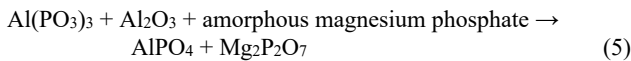
Cold and hot mechanical properties

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

Table 3: Cold mechanical strength, apparent porosity and density results of the analyzed castables.

Compositions	Drying/Firing temperatures (°C)	Cold flexural strength (MPa)	Apparent porosity (%)	Density (g/cm ³)
<i>S</i>	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
<i>M</i>	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>I</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

In general, the castables containing sintering additives, such as TA-FB151-B, TA-FB50-B, TA-MGP-B, *M* and *I*, showed higher mechanical strength than *S* in both evaluated conditions. The benefit of the boron-compound incorporation into the designed compositions could be mainly observed in the improvement of the cold mechanical strength of these samples after pre-firing at 815°C for 5h (Table 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 , $\text{Al}(\text{PO}_3)_3$ and non-crystalline magnesium phosphates. At higher temperatures (>650°C), in situ reactions involving these resulting compounds might induce the formation of AlPO_4 , $\text{Mg}_2\text{P}_2\text{O}_7$ and $\text{Mg}_3(\text{PO}_4)_2$ (Eq. 5 and 6). Additionally, the interaction of fine alumina and B_2O_3 leads to $\text{Al}_{18}\text{B}_4\text{O}_{33}$ generation (Eq. 7) [6].



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 5h. 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 values (when compared to the ones attained for the dried samples) after pre-firing step at 815°C for 5h (Table 3). The apparent porosity and density results were kept in the range of 13.6 - 20.5% and 2.77 - 3.08 g/cm³, respectively.

Regarding the HMOR and cold erosion resistance of the chemically-bonded refractories (Fig. 1), 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 $\text{Al}_{18}\text{B}_4\text{O}_{33}$ generation and other microstructural transformations favored the HMOR increase for the other compositions especially at 815°C (Fig. 1a). 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 *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 equal to 1382°C, whereas the other evaluated castables presented $T_{0.5}$ between 1496°C and 1512°C. Consequently, the other chemically-bonded refractories showed higher thermo-mechanical stability. Besides that, Fig. 1a 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.

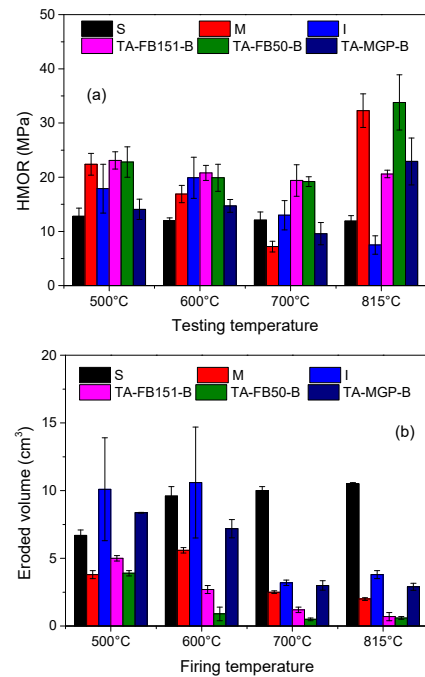


Fig. 1: (a) HMOR (3-point bending test) and (b) eroded volume of the evaluated castables. The prepared samples were pre-fired at 500°C, 600°C, 700°C and 815°C for 5h before the measurements.

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 5h (Fig. 1b). However, the binding strength among coarse and fine components of the *S* and *I* samples generated

after firing them at 500°C and 600°C, was not strong enough to prevent their erosion associated with the contact of SiC particles with the castables' surface. Due to the absence of a sintering additive in *S* composition, the attained eroded volume was still kept around 10% even when subjecting these samples to higher pre-firing temperatures (700-815°C). Thus, aiming to optimize 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 ($\Delta T \sim 790^\circ\text{C}$, Fig. 2a) pointed out that the main changes took place between 0 and 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. 2b).

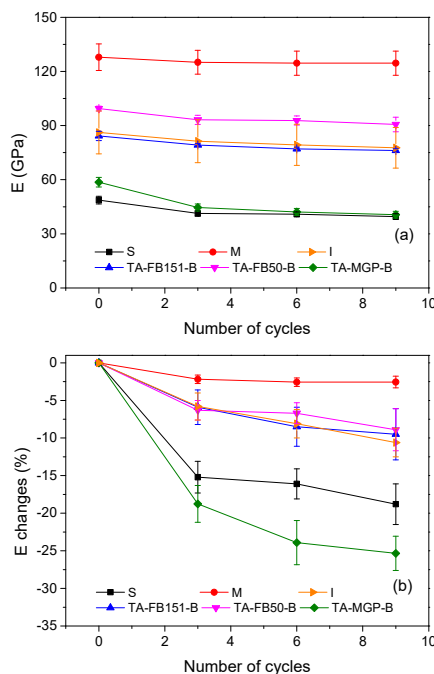


Fig. 2: (a) Elastic modulus evolution and (b) E change of the prepared castables as a function of thermal shock cycles ($\Delta T \sim 790^\circ\text{C}$). All samples were pre-fired at 815°C for 5h.

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. 2). 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 around 40 GPa (Fig. 2a) after 9 cycles. Consequently, when analyzing the *E* loss due to the thermal damage induced by the temperature variation ($\Delta T \sim 790^\circ\text{C}$), the former material had the worst performance compared to the other castables.

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 (*S*, *M* and *I*) available for

application in petrochemical industries. The combination of commercial monoaluminum 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 aluminum phosphates (mainly $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) during mixing and curing, which controls the vibratable flow and setting behavior 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 $\text{Al}_{18}\text{B}_4\text{O}_{33}$ above 600°C. In general, the formation of this aluminum 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 ingredients (coarse, fine and binder components) in a single dry-mix, which makes its handling and preparation easier.

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