

Design of Self-Flow Chemically-Bonded Castables*

S. J. S. Lopes, A. P. Luz, D. T. Gomes, V. C. Pandolfelli

The strength derived by using phosphate-based binders is related to the in situ generation of new phases, which takes place during the refractories' initial processing steps. Considering the fast reaction rate of acid-base transformations, their exothermic feature and difficulties to optimise particle dispersion in acid medium, phosphate-bonded products are usually placed via gunning, hand packing or vibration. This work focused on developing high-alumina self-flow chemically-bonded castables for petrochemical/aluminium industries, based on adding sodium polyphosphates and phosphoric acid and monoaluminium phosphate solutions. Flowability, working and setting time, cold and hot mechanical strength, porosity and thermal shock measurements were carried out in order to evaluate the performance of the designed refractories. According to the results, the presence of sodium polyphosphates improved the castables' flowability, resulting in maximum free-flow of 120–160 %. When compared to a vibratable phosphate-bonded commercial product, the developed castables containing H_3PO_4 and MAP solutions presented higher mechanical strength and thermal shock resistance, in addition to their self-flow behaviour.

Introduction

Chemically-bonded refractories have been investigated over the years due to their short setting time, high green mechanical strength, good adhesion and improved spalling resistance when subjected to high heating rates after the curing step [1, 2]. Such ceramic products have also been widely used in petrochemical/aluminium industries, as they present suitable properties in the temperature range (25–1000 °C) required by this process. Nevertheless, the placing methods used for phosphate-bonded refractories are mainly via vibration or gunning [2, 3] and, according to the consulted literature, no publications concerning the design of self-flow castables for these systems could be found.

It is highly desirable to develop chemically-bonded compositions presenting high free-flow levels, as various benefits may be achieved during their preparation, including:

- faster placing of the ceramic lining,
- no need of highly trained operational staff, among others. The main difficulty to attain these self-flow refractories is associated with particle dispersion in acidic medium and in situ transformations [reactions among acidic salts (liquid or solids)] or phosphoric acid solutions (H_3PO_4) with

basic or amphoteric oxides [3, 4] that already take place during their mixing step. Sodium polyphosphates have been commonly used as dispersant in ceramic systems. They present great potential for application in self-flow phosphate-bonded castables and these molecules may act based on:

- the electrostatic mechanism derived from their adsorption on the oxide surface;
- steric repulsion due to the long polyphosphate chains, and
- withdrawal of multivalent cations that preferentially adsorb on particles surface and lead to the system flocculation, due to the decrease of the electrical double layer thickness [5].

The withdrawal of cations from the liquid medium is commonly followed by significant viscosity drop for solutions containing such additives and metallic ions, as Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , and others [6] can be complexed by the chain endings and middle groups of these molecules. Furthermore, polyphosphates can be easily hydrolysed and different parameters (i.e., temperature, pH, ionic force and concentration of uni- or multivalent cations in the liquid medium) will affect the reaction rate of such transformation [7]. Based on the data presented above, the present work aimed to design

self-flow high-alumina castables bonded with phosphoric acid and/or monoaluminium phosphate solutions for petrochemical/

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Tab. 1 Polyphosphate additives selected for the preparation of high-alumina chemically-castables

| Additive | Bulk Density [g/cm ³] | Chain Length [Units Number] | P ₂ O ₅ Content [mass-%] | Na ₂ O Content [mass-%] | Solution pH 1 [mass-%] |
|----------|-----------------------------------|-----------------------------|--|------------------------------------|------------------------|
| Budit 3H | 0,9 | >30 | 70,5 | 27,5 | 3,0 |
| Budit 6H | 0,6 | 28 | 68,0 | 29,5 | 5,7 |

aluminium industries, using MgO as setting agent and sodium polyphosphates as dispersant additives.

Experimental

A self-flow castable composition comprised by 85 mass-% of coarse and fine tabular alumina ($d < 6 \mu\text{m}$, Almatís/DE) and 15 mass-% of reactive aluminas (CL370 and CT3000 SG, Almatís/DE) was designed according to the Alfred's particle packing model ($q = 0,21$). Two binding systems were evaluated:

- 2,8 mass-% of dead-burnt magnesia ($d < 212 \mu\text{m}$, 98,2 mass-% MgO, Magnesita Refratários S.A./BR) + 14 mass-% of phosphoric acid solution ($\text{H}_3\text{PO}_4 = 48 \text{ mass-%}$ concentration) obtained by diluting the original 85 mass-% H_3PO_4 liquid provided by Fosbrasil Company/BR);
- 2,5 mass-% of dead-burnt magnesia and 14 mass-% of a mixture comprising 25 % of commercial monoaluminum phosphate (MAP) solution (35 mass-% of P_2O_5 , Fosbind 151, Prayon/BE) and 75 % of phosphoric acid (48 mass-% concentration). MgO was incorporated to the dry components of the compositions. The raw materials were dry-homogenized and wet-mixed in a rheometer for 6 min.

Two commercial sodium polyphosphates (Tab. 1) supplied by Budenheim/DE as well as citric acid (PA, Synth, Diadema/BR) were selected as promising dispersants for the alumina-based chemically-bonded castables.

The castable's flowability level and temperature were analysed right after the compositions processing, whereas the setting time (complete hardening) was followed by a manual inspection of the moulded samples that were kept at 30 °C. The workability of the compositions was determined based on the standard flow-table apparatus as a function of time (ASTM 1446-11) and the mixtures were kept in plastic bags between each measurement.

The working time was defined as the time measured from the end of the mixing step up to the moment when the castable's free-flow level dropped to values lower than 55 %. These measurements were conducted for the most promising compositions containing 0,5 mass-% of sodium polyphosphates and the ones prepared with low amounts (0,10, 0,15 and 0,25 mass-%) of citric acid +0,5 mass-% of Budít 3H or 6H.

Aiming to better understand the rheological behaviour of the castables and the influence of adding dead-burnt magnesia to these mixtures, the free-flow and temperature evolution with time were determined for the following compositions:

- additive-free,
- 0,5 mass-% Budít 6H,
- 0,5 mass-% Budít 3H + different MgO contents (0, 0,26, 0,28 and 3,0 mass-%, respectively).

In this case, free-flow values were evaluated without keeping the castables inside plastic bags between the measurements, which would prevent monitoring the spreading progress during short time intervals (2 min). Four compositions were selected for further thermo-mechanical characterization. The cold flexural strength (ASTM C133-97) and apparent porosity (ASTM C830-00, using kerosene as the immersion liquid) measurements of the dried (110 °C for 24 h) and fired (815 °C for 5 h) castables were carried out.

Cold erosion resistance of the refractories was 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). Hot modulus of rupture (HMOR) was measured at 500 °C, 600, 700 and 815 °C respectively (using samples pre-fired for 5 h at the same testing temperature in HBTS 422 equipment

(3-point bending test, Netzsch/DE) based on ASTM C583-8 standard.

Furthermore, pre-fired refractories (815 °C for 5 h) were subjected to a total of 9 thermal shock cycles (ASTM C1171-91) at 815 °C ($\Delta T \sim 790 \text{ °C}$). The damage resulted from the temperature changes was evaluated by the elastic modulus measurements at room temperature using the bar resonance technique (which is based on sample excitation and detecting the correspondent vibration spectrum with piezoelectric transducers) as a function of the thermal cycles (0, 3, 6 and 9).

Results and discussion

Flowability and temperature evolution of compositions without dispersant additives and containing 0,5 mass-% of Budít 3H or 6H were monitored in short time intervals (Fig. 1). The free-flow tests were carried out without keeping the mixtures after each measurement in plastic bags and, therefore, their continuous spreading (cumulative flow) was followed with time.

Fig. 1a indicates that additive-free (without sodium polyphosphates) compositions prepared with phosphoric acid solution did not present important changes in their free-flow value with time even when changing the added MgO content. Moreover, the temperature increase only took place in refractories containing magnesia (Fig. 1b), due to the exothermic acid-base reaction (which is responsible for the materials' hardening) [1]. No precipitation of insoluble phosphate phases was expected to be observed in the MgO-free composition, as alumina dissolution in H_3PO_4 solution has low reaction rate below 127 °C [1].

Castables with Budít 3H or 6H (without MgO) presented high free-flow values (Fig. 1c and 1e) and this behaviour is related to the dispersing effect of these additives due to electrosteric mechanism [5]. Alumina dispersion via multivalent cation withdrawal should not be very effective in this case, as the presence of Al^{3+} ions in the liquid medium would be required. Besides that, cations complexation usually takes place in lower extension for trivalent species, as they preferentially occur at the endings of the polyphosphate chains [6].

The different flowability levels of the castables containing Budít 6H and Budít 3H (without MgO, Fig. 1c and 1e) are ex-

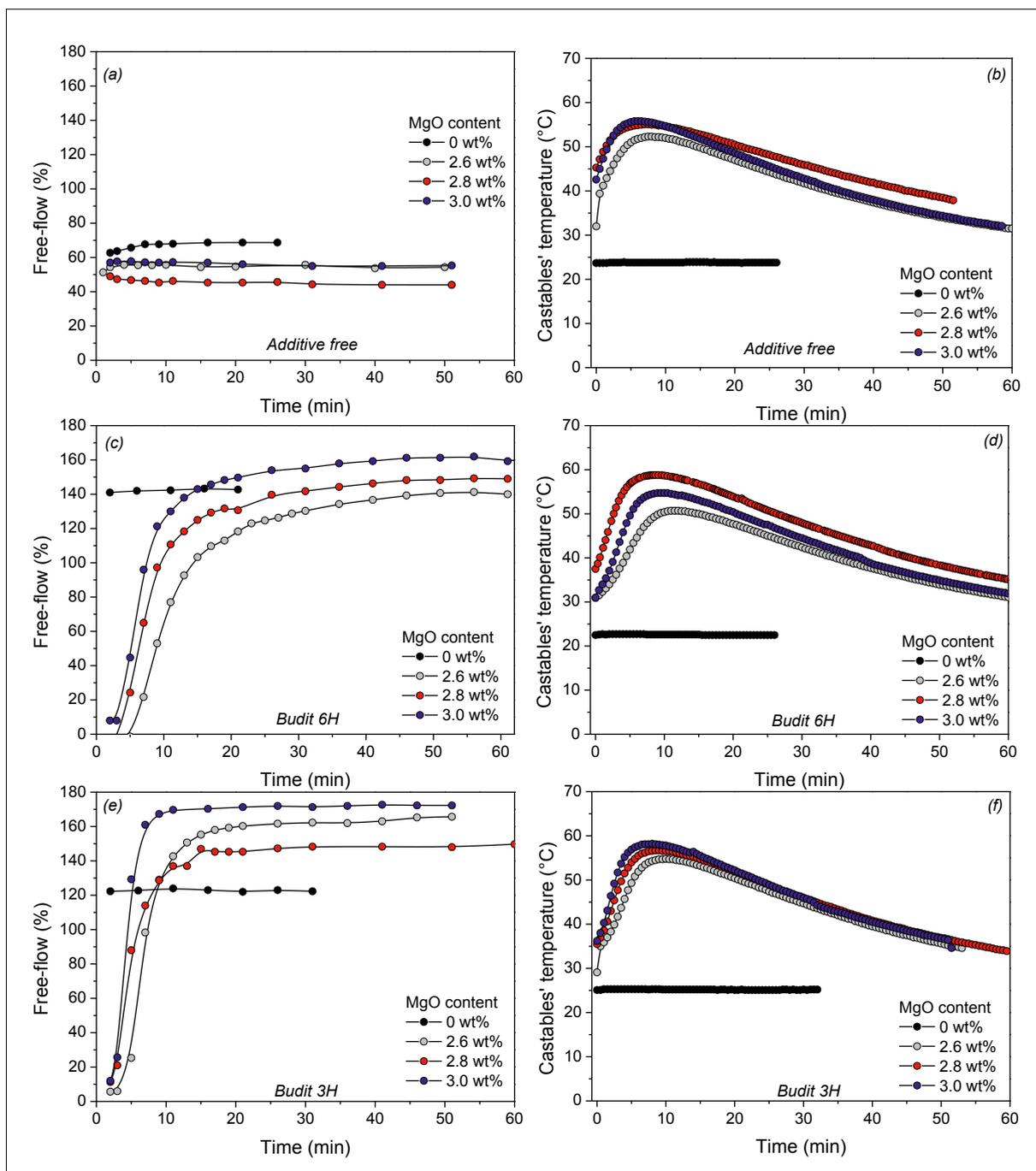


Fig. 1 a–f Cumulative free-flow (a, c and e), and temperature evolution (b, d, and f) of the castables as a function of time; the prepared compositions contained 0, 2, 6, 2, 8 or 3, 0 mass-%, respectively of dead-burnt magnesia with 0 or 0,5 mass-% of Budite 6H or 3H and 14 mass-% of H_3PO_4 solution

plained by the greater trend of the latter to undergo hydrolysis when in contact with aqueous medium (as observed by the ^{31}P NMR measurements, results not shown here). Thus, Budite 3H-containing compositions must present higher concentration of short chain fragments than the ones with Budite 6H. Based on the important role of the steric mechanism to induce alumina disper-

sion, the greater length of Budite 6H chain fragments generated in the castable mixture tends to be the main feature that favoured the highest free-flow level (~140%) attained for this additive.

The combination of MgO and polyphosphates (Fig. 1c and 1e) led to distinct behaviour, as although the initial flowability of the compositions was low (close to zero),

significant changes were observed as time progressed and the maximum free-flow attained was even higher than the one of the magnesia-free castable (i.e. Fig. 1e). The reduced initial flow (at $t = 0$) presented by the castables may be associated with the high ionic strength of the liquid medium due to MgO dissolution (releasing Mg^{2+} ions) in H_3PO_4 .

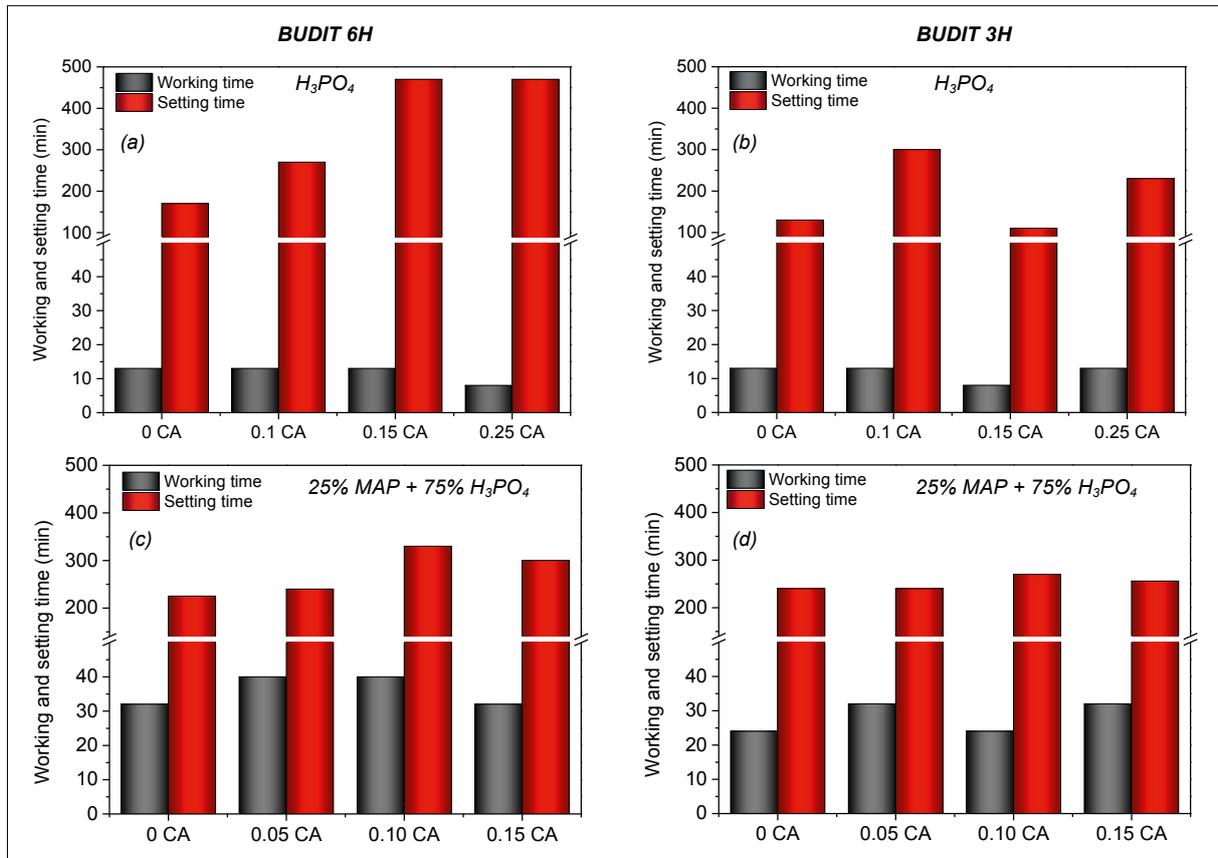


Fig. 2 a–d Working and setting time of the designed high-alumina castables containing 0,5 mass-% of (a and c) Budit 6H or (b and d) Budit 3H and different citric acid (CA) amounts (0–0,15 mass-%); two different binding system were evaluated: addition of 14 mass-% of H_3PO_4 solution (concentration of 48 mass-%) or 14 mass-% of a mixture containing 25 % MAP and 75 % H_3PO_4 solutions; setting agent was 2,5–2,8 mass-% MgO

Furthermore, Mg^{2+} cations should rapidly react with this acid component, resulting in the precipitation of solid compounds [2]. The further increase of the free-flow values with time can be explained by the Mg^{2+} complexation via the polyphosphate chains [6], which becomes more important with the increase of the bivalent ions and phosphorus content in the evaluated medium. Van Wazer and Callis [8] reported that the complexation effectiveness is greater when smaller phosphate-based anions (i.e., $P_2O_7^{4-}$) are available in the liquid.

Additionally, the heat release (due to the acid-base reaction, resulting in temperature increase – Fig. 1d and 1f), should also play a role in the progress of the free-flow values with time, as shorter phosphate chain fragments tends to be formed due to the molecules hydrolysis at higher temperatures [7–8].

Consequently, higher content of phosphate anions with short chain length can be generated with the castable's temperature

increase, favouring a more effective complexation of the Mg^{2+} cations.

The improved free-flow results observed for the Budit 3H-containing compositions with MgO (Fig. 1e) are also associated with the greater extent of the hydrolysis reaction of this additive with the binder solution (H_3PO_4) and the further generation of phosphate anions (i.e. $P_2O_7^{4-}$, as detected in the ^{31}P NMR measurements) that should readily interact with Mg^{2+} species and give rise to magnesium-phosphate complexes. Therefore, the maximum flowability level should be attained when a significant PO_4^{3-} ions content is available in the composition and, due to their low complexing power, a further step will consist on the precipitation of magnesium-phosphate-based insoluble phases that should reduce the castable's working time and induce its hardening.

When measuring the castables' working (defined as the time when actual free-flow <55 %) and setting time (complete hardening), the refractories bonded with H_3PO_4 so-

lution +2,8 mass-% MgO presented short workability (~10–15 min, Fig. 2a and 2b) even when small amounts of citric acid (CA, retarder agent) was incorporated into the mixtures. As pointed out in Fig. 2a and 2b, the CA addition mainly affected the setting behaviour of the moulded samples as this additive acts delaying the precipitation of insoluble phosphate compounds [1].

From the application point of view, the short working time (~10–15 min) and high temperature (~55 °C) of the self-flow H_3PO_4 -bonded castables during processing are important issues, as:

- short working time can prevent the correct installation of these materials in large scale,
- the heat release and high temperature of the mixtures can result in safety problems for the operational staff specially when working in confined environments.

Hence, a suitable alternative to optimise these properties (based on preliminary tests) consisted of using a mixture of

Tab. 2 Thermomechanical performance of the evaluated compositions and a commercial vibratable chemically-bonded castable (reference)

| Properties | Temperature [°C] | Castables* | | | | |
|--|------------------|------------|-----------------------------------|-----------------------------------|---------------------------------------|---------------------------------------|
| | | Reference | 6H-H ₃ PO ₄ | 3H-H ₃ PO ₄ | 6H-MAP-H ₃ PO ₄ | 3H-MAP-H ₃ PO ₄ |
| Cold Flexural Strength [MPa] | 110 | 8,2 ± 1,9 | 8,4 ± 0,9 | 8,5 ± 1,0 | 11,2 ± 1,0 | 12,6 ± 1,3 |
| | 815 | 7,9 ± 0,5 | 8,3 ± 0,6 | 8,0 ± 0,5 | 10,8 ± 1,0 | 10,6 ± 0,9 |
| Apparent Porosity [%] | 110 | 17,2 ± 0,2 | 16,0 ± 0,5 | 19,2 ± 0,7 | 14,4 ± 0,4 | 15,1 ± 0,2 |
| | 815 | 18,5 ± 0,3 | 20,4 ± 0,3 | 22,3 ± 0,2 | 19,9 ± 1,2 | 17,2 ± 0,3 |
| Eroded Volume [cm ³] | 500 | 6,7 ± 0,4 | 9,5 ± 0,9 | 7,9 ± 0,3 | 10,1 ± 0,7 | 5,6 ± 0,6 |
| | 600 | 9,6 ± 0,7 | 10,5 ± 0,6 | 8,9 ± 0,6 | 9,7 ± 0,2 | 5,9 ± 0,6 |
| | 700 | 10,0 ± 0,3 | 10,4 ± 0,6 | 8,0 ± 0,5 | 10,0 ± 0,8 | 5,6 ± 0,3 |
| | 815 | 10,5 ± 0,1 | 9,3 ± 1,1 | 7,1 ± 0,7 | 9,8 ± 0,9 | 7,5 ± 0,8 |
| HMOR [MPa] | 500 | 12,8 ± 1,5 | 8,8 ± 0,7 | 10,0 ± 0,4 | 14,9 ± 0,8 | 12,4 ± 1,2 |
| | 600 | 12,0 ± 0,5 | 9,0 ± 0,4 | 8,7 ± 0,8 | 12,4 ± 0,9 | 10,6 ± 1,4 |
| | 700 | 12,1 ± 1,5 | 9,9 ± 0,3 | 8,9 ± 0,8 | 11,2 ± 0,9 | 10,9 ± 0,3 |
| | 815 | 11,9 ± 1,0 | 8,5 ± 0,6 | 8,6 ± 0,6 | 10,4 ± 0,5 | 10,4 ± 1,6 |
| Elastic Modulus after Thermal Shock Cycles (ΔT ~790°C) | Cycles | | | | | |
| | 0 | 48,7 ± 2,0 | 36,7 ± 1,6 | 44,3 ± 1,7 | 44,6 ± 0,7 | 49,6 ± 1,4 |
| | 3 | 41,3 ± 1,5 | 31,0 ± 1,5 | 39,0 ± 1,8 | 37,5 ± 0,6 | 43,7 ± 2,4 |
| | 6 | 40,9 ± 1,2 | 30,7 ± 1,2 | 37,4 ± 1,8 | 36,5 ± 1,4 | 42,6 ± 2,4 |
| | 9 | 39,6 ± 1,6 | 30,3 ± 0,6 | 37,2 ± 2,2 | 35,0 ± 0,6 | 42,2 ± 2,9 |

* Compositions containing Budit 3H or 6H also comprised 0,10 or 0,05 mass-% of citric acid, respectively

25 mass-% monoaluminium phosphate (MAP) + 75 mass-% H₃PO₄ solutions as liquid binder. As pointed out in Fig. 2c and 2d, MAP + H₃PO₄ addition resulted in significant improvements of the refractory's working time, as the free-flow level of such materials was kept above 55 % for 30 min (average). A small decrease of the maximum temperature (12,3 °C and 2,7 °C for the castables with Budit 6H and 3H, respectively) and high free-flow levels (90–110 %) could still be obtained when adding MAP to the binder solution.

High-alumina castables containing phosphoric acid and 0,5 mass-% Budit 3H or 6H as well as the compositions prepared with MAP, H₃PO₄ solutions and 0,5 mass-% Budit 3H or 6H were evaluated and compared with a commercial high-alumina vibratable refractory (reference, Thermbond 18BL, Stellar/US) commonly used in petrochemical industries (Tab. 2).

When only phosphoric acid was used as binder, similar mechanical strength values as the ones for the commercial vibratable castable were attained independently on the added dispersant (Budit 3H or 6H). The decrease of the modulus of rupture, fol-

lowed by the porosity increase for the fired samples (815 °C for 5 h), is related to the hydrates' decomposition that usually takes place around 150 °C 0,5 [4] during the refractories heating.

MAP addition to the mixture containing Budit 3H (3H-MAP-H₃PO₄) improved its erosion resistance when compared to the one bonded with H₃PO₄ (Tab. 2). This enhanced performance points out the potential of such refractory to be applied in Fluid Catalytic Cracking (FCC) units of petrochemical industries.

The same trend observed in the cold mechanical strength measurements was also kept during the HMOR tests (Tab. 2), as the H₃PO₄-bonded compositions presented lower hot modulus of rupture than the ones bonded with MAP + H₃PO₄. Moreover, the latter showed similar performance as the reference material.

Another important property of the castables is their thermal shock resistance that was evaluated along 9 cycles at 815 °C (ΔT~790 °C). Based on the absolute E-values attained after 9 thermal cycles, the following sequence of values was obtained: 3H-MAP-H₃PO₄ (42,2 GPa) > Ref-

erence (39,6 GPa) > 3H-H₃PO₄ (37,2 GPa) > 6H-MAP-H₃PO₄ (35,0 GPa) > 3H-H₃PO₄ (30,3 GPa). The highest damage (E-loss ~ -20,87 %) due to the temperature changes was detected for the 6H-MAP-H₃PO₄ composition. According to the attained results, 3H-MAP-H₃PO₄ castable proved to be the most promising self-flow refractory and, in general, it presented superior performance when compared to the commercial vibratable phosphate-bonded product (reference).

Conclusions

Self-flow phosphate-bonded castables containing sodium polyphosphate dispersants were developed in this work. Both additives analyzed (Budit 3H and 6H) helped in increasing the free-flow levels (>100 %) of the compositions after 15 min since the end of the mixing step.

The most efficient dispersant (Budit 3H) induced faster and higher flow increase due to the generation of phosphate ions with short length chain as a consequence of the molecules' hydrolysis (as pointed out by the ³¹P NMR analyses). The optimization of the castables' working time (up to 30 min) was

only accomplished when mixing two different binder solutions (MAP and H_3PO_4) and using this blend as the main binding system.

Based on the thermo-mechanical properties of the designed compositions, the self-flow castable bonded with MAP and H_3PO_4 and containing Budit 3H presented superior performance (especially higher erosion and thermal shock resistances), even when compared to a commercial vibratable phosphate-bonded product selected as reference.

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