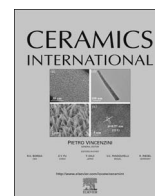




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Self-flowing high-alumina phosphate-bonded refractory castables

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ABSTRACT

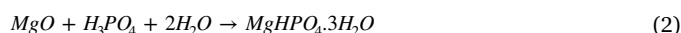
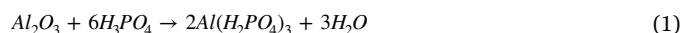
Phosphate refractories have a great potential to be applied in petrochemical industries as they present suitable properties at the temperature range used in fluid catalytic cracking units. This study addresses the development of high-alumina self-flowing castables bonded with H_3PO_4 solution (48 wt% concentration) or a mixture of phosphoric acid and monoaluminum phosphate (MAP) solutions, using MgO as a setting agent. Two polyphosphates (Budite 3H and 6H) and citric acid were evaluated as dispersant additives for these castables. The compositions were characterized by measuring their free-flow and temperature evolution over time, working and setting times, cold and hot mechanical strengths, drying behavior and explosion resistance, eroded volume and thermal shock resistance. The results indicated that high flowability (free flow > 100%) could be attained when adding the selected polyphosphates to the mixtures, whereas citric acid acted mainly as a retarder agent for the castables' setting. Moreover, free-flowing compositions with a suitable working time were obtained when combining H_3PO_4 +MAP solutions as main binders. The thermo-mechanical tests pointed out that the most promising designed refractory (containing mixture of H_3PO_4 +MAP and 0.5 wt% of Budite 3H) presented similar or even a better performance than a benchmark commercial vibratable product used in petrochemical units.

1. Introduction

Chemically-bonded refractories have been investigated over the years due to their short setting time, high green mechanical strength, good adhesion and, improved erosion and spalling resistances when subjected to high heating rates after the curing step [1,2]. These are key features for petrochemical industries as they will extend the equipment's service life lined with such refractories [3]. The placing methods commonly used for phosphate-bonded products are vibration or gunning [4–7] and, according to the consulted literature, no publications concerning the design of self-flowing castables for these systems could be found. However, it is highly desirable to develop chemically-bonded castables presenting this rheological feature, which would allow faster placing and no need of highly trained operational staff, among other advantages.

The main difficulty to attain self-flowing phosphate-bonded refractories is related to particle dispersion in acidic medium and in situ chemical transformations that already take place during the mixing step. The binding effect of such materials are provided by reactions between acidic salts (liquid or solids) or phosphoric acid solutions (H_3PO_4) with basic or amphoteric oxides (such as alumina, magnesia, zirconia and others) [7,8]. H_3PO_4 in combination with alumina and

magnesia are the main raw-materials used in chemically-bonded refractories and the likely reactions among these components are presented as follows:



Monoaluminum phosphate [MAP or $Al(H_2PO_4)_3$] can be obtained by Eq. (1) above 127 °C [9] or by reacting H_3PO_4 and $Al(OH)_3$ in the 25–90 °C temperature range [4]. On the other hand, the interaction between magnesia (basic oxide) and H_3PO_4 (Eq. (2)) can take place at room temperature, giving rise to newberite ($MgHPO_4 \cdot 3H_2O$) and heat as a consequence of the exothermic nature of this transformation [10]. This latter reaction is commonly induced by the high dissolution rate of MgO in acidic medium [10] and, for this reason, this oxide is widely used as a setting agent for high-alumina chemically-bonded castables [4,6].

When H_3PO_4 solution with high P_2O_5 concentration (~35 wt%) is used to prepare refractory compositions, the liquid medium will initially present extreme low pH (~1) and high ionic concentrations, which according to Greenwood, Kendall and Shin et al. [11,12] can affect the dispersion efficiency of many organic additives commonly used in ceramic systems. These studies also reported that anchoring

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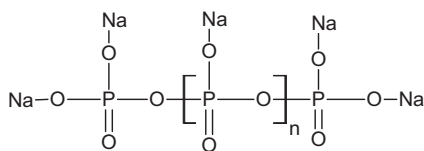


Fig. 1. Chemical structure of a linear sodium polyphosphate.

organic dispersants presenting a COOH functional group (which is dissociated as COO⁻) may be limited or even prevented in alumina suspensions in acidic pH (where positive charges are generated on the particles' surface). In such a condition (low pH), the charges contained in the polymeric chains are shielded by the great ionic force of the liquid medium and by the highly tangled or flattened conformation of these molecules.

Polyalcohols can be suggested for chemically-bonded castable's dispersion, as they act via electrostatic mechanism in acidic pH. However, according to Lyon et al. [13], these additives give rise to complex compounds in the presence of Al³⁺ cations, which inhibit all likely reactions instead of inducing alumina dispersion. For instance, PO₄³⁻ and HPO₄²⁻ (responsible for generating insoluble phases after interacting with alumina) will compete with H₂PO₄⁻ and R^{X-} (the latter is derived from the anion provided by the organic additive) in order to lead to the formation of additional compounds in the liquid medium. Consequently, the polyalcohols may prevent the formation of insoluble phosphates (i.e. AlPO₄) and postpone the refractory setting.

Sodium polyphosphates have been commonly used as a dispersant in ceramic systems [14]. Their molecules may comprise linear (Fig. 1), branched or cyclic structures and they are a great potential for applications in self-flowing phosphate-bonded castables. The dispersion induced by these compounds can be explained according to: (i) the electrostatic mechanism derived from the molecules' adsorption on the oxide surface; (ii) steric repulsion due to the long polyphosphate chains, and (iii) removal of multivalent cations that preferentially adsorb on the particles' surface and lead to the system flocculation due to the decrease in the electrical double layer thickness [14–16]. The latter route takes place due to the complexing action of such cations, which are orders of magnitude higher than for monovalent ions (i.e. Na⁺).

The withdrawal of multivalent cations by the polyphosphate chains is associated with the significant viscosity drop observed for solutions containing such additives and metallic ions, which can be mainly identified in the presence of bivalent cations (Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺ and others) [17] that are complexed by the chain-end and middle groups of these molecules. In the case of trivalent ions (such as Al³⁺), investigations using nuclear magnetic resonance spectroscopy (NMR) of ³¹P and ²⁷Al indicated that these cations should bond preferentially with the chain-end groups of the polymeric chains [18] and, consequently, the complexing effect should take place at a lower intensity than for the bivalent ions.

Furthermore, polyphosphates can be easily hydrolyzed 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 a transformation [19]. In highly acidic pH, the hydrolysis is favored and, regardless of the solute concentration, the polymeric chain split should take place at the molecule's endings and branching locations as the activation energy for breaking these points is lower at the temperature range of 25–90 °C [20]. Therefore, as the hydrolysis reaction occurs, the solution containing these additives will present shorter chain fragments and HPO₄²⁻ or PO₄³⁻ release into the liquid.

Based on the information presented above, this study aims to evaluate the influence of polyphosphate additives on the free-flowing behavior of high-alumina castables bonded with phosphoric acid and/or monoaluminum phosphate solutions, using MgO as a setting agent and citric acid as a retarder additive. After preliminary tests, the most promising compositions were optimized and characterized in order to

attain a self-flowing chemically-bonded castable with suitable properties for applications in the petrochemical field.

2. Experimental

A self-flowing castable composition consisting of 85 wt% of coarse ($d < 6 \mu\text{m}$, Almatis, Germany) and fine tabular alumina ($d < 45 \mu\text{m}$, Almatis, Germany) and 15 wt% of reactive aluminas (CL370C and CT3000SG, Almatis, Germany) was designed according to Alfred's particle packing model ($q=0.21$) [21].

Two binding systems were evaluated: (1) 2.8 wt% of dead-burnt magnesia ($d < 212 \mu\text{m}$, 98.2 wt% MgO, Magnesita Refratários S.A., Brazil) and 14 wt% of phosphoric acid solution (H₃PO₄=48 wt% concentration) obtained by diluting the original 85 wt% H₃PO₄ liquid provided by Fosbrasil Company (Brazil); (2) 2.54 wt% of dead-burnt magnesia and 14 wt% of a mixture comprising 25% of commercial monoaluminum phosphate (MAP) solution (35 wt% of P₂O₅, Fosbind 151, Prayon, Belgium) and 75% of phosphoric acid (48 wt% concentration). While preparing the castables, the MgO was firstly added to the dry components. After that, the raw-materials were dry-homogenized for 1 min in a rheometer and mixed for another 2 min (45 rpm) while adding 75% of the phosphoric acid solution. The remaining liquid was added after complete homogeneization of the materials. Finally, wet-mixing was carried out for 3 min under 55 rpm.

Three commercial sodium polyphosphates (Table 1) supplied by Budenheim (Germany), as well as citric acid (PA, Synth, Diadema, Brazil) were selected as promising dispersants for the alumina-based H₃PO₄-containing castables. Zeta potential measurements (ZA500, Matec Applied Sciences) of additive-free or 1 wt% dispersant-containing Al₂O₃ suspensions (10 wt% of solids) were carried out by titrating 0.5 mol L⁻¹ H₃PO₄ solution into the prepared suspensions in order to attain the zeta potential versus pH profiles for each analyzed composition.

Castable compositions based on binding system 1(MgO+H₃PO₄) were prepared to evaluate the role of the selected sodium polyphosphates (Buditec 3H and 6H) or citric acid (evaluated amounts =0, 0.5 or 1.0 wt%) in the castables' rheological and mechanical properties. The castable's flowability level and temperature were analyzed immediately after the composition processing, whereas the setting time (complete hardening) was followed by a manual inspection of the molded 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 that 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 wt% of sodium polyphosphates and the ones prepared with low amounts (0.10, 0.15 and 0.25 wt%) of citric acid +0.5 wt% of Buditec 3H or 6H.

In order to identify the stability of the polyphosphate additive in aqueous medium, ³¹P NMR analyses of Buditec 3H and 6H solubilized in D₂O [0.65% (m/v)] were carried out using an Avance III Bruker 14,1T (600 MHz) spectrometer, considering two different times: t=0 and 1.5h.

Table 1
Polyphosphate additives selected to prepare high-alumina chemically-castables.

Additives	Bulk density (g/cm ³)	Chain length (number of mer units)	P ₂ O ₅ content (wt%)	Na ₂ O content (wt%)	Solution pH (1 wt %)
Buditec 3H	0.9	> 30	70.5	27.5	3.0
Buditec 6H	0.6	28	68.0	29.5	5.7
Buditec 8H	0.6	7	63.5	33.5	7.6

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