Selection of dispersants for high-alumina zero-cement refractory castables

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Abstract

This article reports on the evaluation of novel short-chain molecules to improve the dispersion of zero-cement high-alumina refractory castables. Two approaches were investigated to enhance the dispersing efficiency of short-chain compounds: (a) the increase of the density of dissociable sites per molecule and (b) the improvement of the adsorption ability of the molecule at the usual pH range of high-alumina castables. Gallic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid were selected based on these requisites and evaluated as potential dispersants with the help of zeta potential analysis, rheological measurements and free-flow tests. Results indicate that such compounds are able to efficiently disperse zero-cement high-alumina castables, enabling a reduction of their water consumption for a given fluidity level.
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1. Introduction

Several recent studies have shown the importance of the dispersion of matrix fine particles on the development of high-performance refractory castables.[1–4] The appropriate dispersion of particles enables the production of highly fluid castables with minimal water content, rendering refractory materials with superior mechanical properties before and after firing.

Refractory castables are usually dispersed through the electrosteric mechanism, in which charged molecules are adsorbed on the particle surface to form steric and electrical double layers that prevents the close approximation of particles. Effective particle dispersion is accomplished when the thickness of these layers is sufficiently high to overcome the action of the attractive van der Waals forces. Nevertheless, an excessive increase of these layers must also be avoided, since it can lead to the entrapment of a considerable amount of water around particles, increasing the castable effective solid loading and decreasing its flowability.

The surface adsorption of long-chain molecules (polyelectrolytes) is one of the approaches most often used to provide a thick steric layer around particles (usually > > 1 nm) and promote efficient dispersion. However, it has been observed that such long-chain molecules seem to be not appropriate for the dispersion of zero-cement high-alumina castables, since they may induce "bridging" and "depletion" flocculation among fine particles (matrix).[4] These mechanisms usually take place when the interparticle distance in the matrix is of the same order of magnitude of the dispersant molecular length. As a result of their markedly high solid loading (> 80 vol.%), refractory castables usually display very short interparticle distances. Therefore, short-chain molecules capable of providing an electrical double layer sufficiently thick to prevent particle coagulation tend to be suitable dispersants for zero-cement high-alumina castables.

Previous studies have shown that citrate molecules fulfill these requirements, enabling the preparation of highly fluid castables with minimal water contents.[1–5] However, the major disadvantage of this dispersant is that it adsorbs preferentially on the alumina surface at acid pH values,[6] which results in a low adsorption efficiency at the usual pH range (8 < pH < 10) of zero-cement high-alumina castables. Therefore, a lower surface electric

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potential and a more pronounced screening effect due to non-adsorbed ions in solution are expected at neutral to basic pH values, reducing the dispersing ability of citrate molecules at these pH conditions.

Taking into account these aspects, the main objective of this paper is to investigate novel short-chain molecules that could improve the dispersion of zero-cement high-alumina castables by increasing the electrical potential near the particle surface and extending the range of action of the electric double layer. Two approaches were evaluated to enhance the dispersing ability of short-chain molecules: (a) the increase of the number of dissociable groups along the dispersant molecule and (b) the improvement of the adsorption efficiency of the dispersant at the usual pH range of high-alumina castables. Both approaches tend to increase the surface electric potential of particles at the castable pH range. In the second case, a reduction of the screening effect of non-adsorbed ions that compress the electric double layer is also expected.

Since the adsorption ability of dispersants was one of the features investigated to improve castable dispersion, an overview about this topic is presented in the following section.

2. Background

The adsorption ability of anionic molecules on the surface of oxide particles in aqueous suspensions is greatly dependent on the pH value of the aqueous medium, since the pH conditions control the type and density of charges on the particle surface and along the adsorbing molecule.[6–8] A recent study on alumina particles[8] has indicated that such pH dependence is significantly influenced by the dissociation constants (pK_a values) of the functional groups that constitute the adsorbing molecule. It has been observed that maximum adsorption occurs at a pH range near to the pK_a values of the molecule dissociable groups. Less adsorption is expected to take place at pH values lower than the pK_a value due to the absence of dissociated anchoring groups on the molecule. At pH values higher than the pK_a value, on the other hand, although the functional groups are expected to be fully dissociated, the adsorption of anionic molecules is limited by the lower density of positively charged sites on the alumina surface. In addition to the pK_a value, the spatial arrangement of the functional groups also exerts a marked influence on the adsorbing ability of anionic molecules. Carboxyl groups (–COOH), for instance, are known to form very stable configurations with the positive sites of alumina surface.[8]

Most of the anionic molecules used to disperse alumina-based suspensions and castables display carboxyl (–COOH),[4–16] phosphonyl [–PO(OH)$_2$ or –PO(OH)O–],[17] sulfona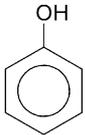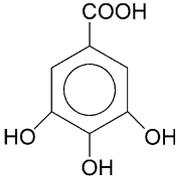te (–SO$_3$–)[18] and/or hydroxyl (–OH)[4–6,8–10,12,13] functional groups as main dissociable sites along the molecule structure. Compounds displaying carboxyl groups (e.g. polyacrylate salts) present typically low pK_a values (Table 1) and, therefore, are expected to adsorb preferentially at acid pH conditions on the alumina surface. Molecules containing predominantly hydroxyl groups, on the other hand, display much higher pK_a values (Table 1), which favor surface adsorption at basic pH values.[19,20] Finally, molecules containing phosphonyl groups (e.g. polyphosphate salts) may exhibit a wide range of pK_a values (from low to intermediate values), which would lead to maximum adsorption from acid to slightly basic pH conditions. Obviously, these pK_a-value ranges are susceptible to variations depending on the molecule side groups and, therefore, should only be considered as general guidelines for the selection of dispersants.

Due to the predominance of carboxyl groups on its molecular structure, the citrate molecule exhibit low pK_a values (3.48, 4.50, 5.82) and, thus, adsorbs in a larger extent on alumina surface at lower pH values (Fig. 1), as well illustrated by Hidber et al.[6,8]

Therefore, if the aim is to improve the adsorption ability of the dispersant at the usual pH range of high-alumina castables ($8 < pH < 10$), one should choose molecules displaying functional groups with intermediate to high pK_a values. In an attempt to fulfill this requirement, gallic acid (3,4,5-trihydroxybenzoic acid) was evaluated in this study as a potential dispersant for high-alumina castables (Table 1). Such aromatic compound displays one carboxyl (–COOH) and three hydroxyl (–OH) groups along the benzene ring, which would favor adsorption on alumina surface at basic pH values. Adsorption curves obtained by Hidber et al.[8] for 2,3,4-trihydroxybenzoic acid on alumina surface strengthens this expectation, since almost complete adsorption of this compound was observed at the basic pH range (Fig. 1). Furthermore, the absence of (–OH) groups in the ortho position of the benzene ring (Table 1) is expected to further aid the adsorption of gallic acid, since this steric configuration prevents the occurrence of unfavorable electrostatic repulsion between the carboxylate ion and the alumina surface.[8]

As previously mentioned, the second approach used to improve the dispersing ability of short-chain molecules was the increase of the density of dissociable sites along the molecule structure. This alternative was investigated in this study by evaluating 2-phosphono-butane-1,2,4-carboxylic acid as potential dispersant for high-alumina castables. This organic compound possesses one phosphonyl and three carboxyl groups along the molecule, which provide a higher charge density per molecule in comparison to citric acid. According to Liu et al.,[21,22] this molecule also adsorbs in a greater extent on the alumina surface at basic pH values if compared

Table 1
Molecular structure and dissociation contants (pK_a values) of the short-chain molecules investigated in this work and of other compounds chosen as examples

	Compound	Structure	pK_a values[a]
Examples			
	Formic acid	CH_3–COOH	3.75
	Polyacrylic acid		~4.75
	Methanol	CH_3—OH	15.5
	Phenol		10.0
	Methane phosphonic acid		2.38, 7.74
Molecules evaluated			
	Citric acid		3.48, 4.50, 5.82, > 14
	3,4,5 Trihydroxybenzoic acid (gallic acid)		4.26, 8.7, 11.45, > 14
	2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTCA)		3.74, 4.23, 5.14, 6.80, 9.05

[a] Most of the pK_a values listed were obtained at an ionic strength of 0.1 M and a temperature of 25 °C,[19] except for the values for gallic acid which were determined at 20 °C.[20]

with citric acid. This may be attributed to the presence of phosphonyl groups that broaden the molecule pK_a range towards higher values (Table 1). Liu et al. have also shown that such higher adsorption efficiency combined with a superior density of charged sites per molecule have enabled the preparation of alumina colloidal suspensions displaying apparent viscosity significantly lower than those dispersed with citric acid.[21]

3. Experimental procedure

3.1. Materials

Commercially available monohydrate gallic acid (188 g/mol, Mallinckrodt, Paris, KY, USA), anhydrous citric acid (192 g/mol, Labsynth, Diadema, SP, Brazil) and 2-phosphonobutane-1,2,4-tricarboxylic acid (270 g/mol,
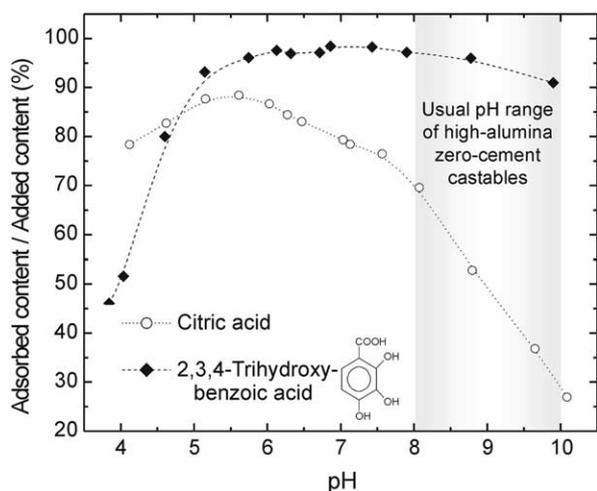
Fig. 1. Adsorption behavior of citric acid and 2,3,4-trihydroxybenzoic acid on alumina surface as a function of pH (data obtained by Hidber et al.[8]).

Table 2
Composition of the high-alumina zero-cement castable evaluated in the present study

Raw materials		Content (wt.%)
White fused alumina (aggregates)	4–10	14.9
	8–20	5.0
	20–40	14.5
	< 8	6.5
Tyler mesh # range	< 40	6.0
	< 60	13.0
	< 200	15.1
Calcined aluminas (matrix)	A-3000 FL	15.0
	A-1000 SG	10.0

grade Bayhibit AM, Bayer AG, Leverkusen, Germany) were the dispersants evaluated in this work. Gallic and citric acids were tested in powder form, whereas the 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) was used in the form of 50 wt.% aqueous solution, as provided by the supplier. The content of dispersant added to the suspensions and castables is expressed throughout the paper in terms of mass of additive per the total surface area of calcined alumina particles (mg/m^2).

White fused alumina (grade EK8R, BET specific surface area < 0.05 m^2/g, 99.5% Al$_2$O$_3$, 0.36% Na$_2$O, Alcoa Alumínio, Salto, Brazil) in a wide range of particle sizes (mesh size # range 4–200) and the calcined Bayer aluminas A-1000 SG (D$_{90}$ = 1.3 μm, D$_{50}$ = 0.4 μm, BET specific surface area = 9.0 m^2/g, 99.8% Al$_2$O$_3$, 0.10% Na$_2$O, Alcoa Chemicals, USA) and A-3000 FL (D$_{90}$ = 7.6 μm, D$_{50}$ = 4.6 μm, BET specific surface area = 3.2 m^2/g, 99.8% Al$_2$O$_3$, 0.07% Na$_2$O, Alcoa Chemicals, USA) were the raw materials used to prepare the concentrated suspensions and high-alumina castables in which the dispersants were tested.

3.2. Preparation of castables and suspensions

Concentrated alumina suspensions were prepared to evaluate the dispersing ability of the distinct short-chain molecules at varying dispersant concentrations and pH conditions. In an attempt to reproduce the matrix (fine particles + water) conditions of typical self-flow zero-cement refractory castables, the suspensions were prepared at a fixed solid loading of 60.5 vol.% using the calcined aluminas A-3000 FL and A-1000 SG at a weight proportion (ratio A-3000 FL:A-1000 SG) of 1.5. To prepare the suspensions, the dry alumina powder was gradually added into distilled water with the help of a laboratory mixer. A fixed amount of dispersant was previously mixed to the dry alumina powder in the case of suspensions prepared with citric acid and gallic acid. In the case of PBTCA-containing suspensions, small aliquots of the 50 wt.% aqueous solution of dispersant were added to the distilled water concurrently to the addition of the alumina powder.

High-alumina castables were subsequently prepared using white fused alumina as aggregates and the calcined aluminas A-3000 FL and A-1000 SG as the matrix constituents (Table 2). The particle size distribution of such castables was adjusted to a theoretical curve based on Andreasen packing model ($q = 0.21$), in order to obtain potentially self-flow compositions.[1–5] Castables were prepared using a fixed water content of 14 vol.% (4.12 wt.% based on dry solids), which resulted in the same ratio (water content)/(calcined alumina content) used to prepare the concentrated suspensions. An optimum mixing procedure recently described by the authors[23,24] was adopted to prepare the zero-cement alumina castables.

3.3. Zeta potential measurement

Electroacoustic measurements (DT-1200, Dispersion technology, Inc., USA) were performed to assess the effect of the distinct short-chain molecules on the zeta potential of alumina particles. The tests were performed in diluted suspensions (2 vol.%) containing the calcined alumina A-1000 SG. A small fixed aliquot of a KOH aqueous solution (1N, Merck, Germany) was first added to the diluted suspension in order to change its initial pH to 11. After ultrasonication for 5 min, zeta potential was measured as a function of pH by titrating the suspension with a HNO$_3$ aqueous solution (1N, Merck, Germany). At least four measurements were accomplished for each dispersant in order to obtain accurate results.

3.4. Rheological tests

The rheological behavior of the matrix representative suspensions was evaluated with the help of a strain-con-

trolled viscometer (model LVDV-III, Brookfield, Middleboro, MA, USA) equipped with a special device (SSA, Brookfield, Middleboro, MA, USA) for small samples (2–16 ml). The rheological analysis was performed in suspensions containing a fixed dispersant content, which had their pH value varied by adding small aliquots of HNO_3 or KOH aqueous solutions. The pH variation to acid and basic values was performed separately in different suspensions for each dispersant concentration. The rheological test was carried out by first applying a constant shear rate of 50 s^{-1} for 30 s, followed by a resting time of additional 30 s and finally a sweep cycle at the shear rates of 2.5, 5.0, 7.5, 10, 20, 30, 40 and 50 s^{-1}. The shear stress data during the sweep cycle were recorded after keeping suspensions at a given shear rate for 20 s. Apparent viscosity data at a shear rate of 50 s^{-1} were considered in the matrix rheological analysis, since it can be directly correlated with castable flowability.[1] Low-viscosity matrixes are expected to render highly fluid castables.

The rheological features of the zero-cement castables were investigated by measuring their free-flow value at different dispersant concentrations, using the flow-table test adapted from the ASTM 860 standard.[1,2,4,5] In this test, castables displaying free-flow values in the range 80–110% are considered to be self-flow compositions.

4. Results and discussion

4.1. Zeta potential evaluation

The effect of the short-chain molecules over the zeta potential of alumina particles in aqueous solution was evaluated in the pH range 2–11 for fixed additions of each dispersant (0.26 mg/m^2). The results presented in Fig. 2 reveal that all molecules were able to effectively
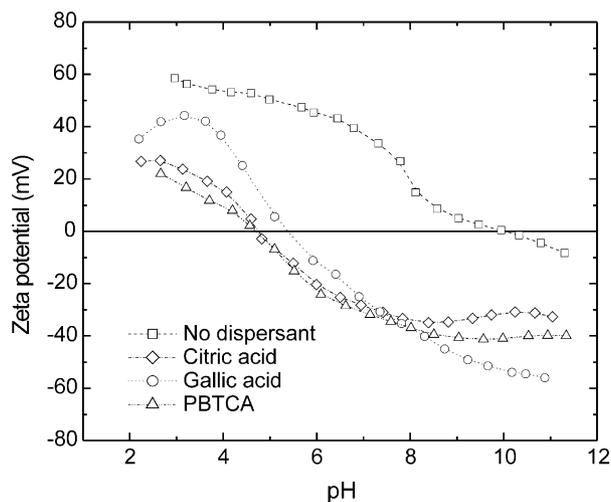
Fig. 2. Zeta potential as a function of pH of calcined aluminas particles without dispersant and in the presence of 0.26 mg/m^2 of citric acid, gallic acid or PBTCA.

shift the isoelectric point (IEP, pH where the net surface charge is null) of alumina particles from approximately 10 to values in the range 4–6, providing high zeta potential values at the usual pH range of zero-cement high-alumina castables (8 < pH < 10).

Fig. 2 also shows that the use of gallic acid and PBTCA rendered higher zeta potential values at the pH range 8–10 in comparison to that obtained with citric acid, indicating that the two dispersion-enhancing approaches investigated in the study could, indeed, increase the alumina surface charge at the pH range of interest.

The slightly higher zeta potential level obtained with PBTCA in comparison to citric acid for pH values superior than 8, agrees with results presented by Liu et al.[21] In the case of gallic acid, the high zeta potential magnitude attained in the pH interval 8–10 could, in principle, be attributed to an efficient adsorption of this molecule on the alumina surface. However, according to the pK_a values of the dissociable groups of gallic acid (Table 1), one would expect that two of the hydroxyl (–OH) groups of this molecule would not be completed dissociated at the pH range 8–10. A similar behavior was observed by Hidber et al.,[6] who found out that the hydroxyl group of the citrate molecule has a significant effect on the zeta potential curve of alumina particles, in spite of its pK_a value higher than 14 (Table 1). This suggests that the pK_a values determined in aqueous solutions (Table 1) may be not representative of the actual dissociation behavior of the dispersant molecules in the ceramic suspensions. Further investigations would be necessary to elucidate this aspect.

The pK_a values of the molecules' functional groups were found to influence also the profile of the zeta potential curves (Fig. 2). In contrast to the plateau observed for citric acid and PBTCA additions, the zeta potential curve obtained with gallic acid exhibited a continuous decay at pH values higher than approximately 8. Such zeta potential decay probably results from the fact that some of the hydroxyl groups of gallic acid can still be dissociated in this pH range and that no significant desorption of this dispersant occurs in such pH interval (Fig. 1). Based on their lower pK_a values (Table 1), most of the functional groups of citric acid and PBTCA would be expected to be already dissociated at these pH conditions. Additionally, a substantial fraction of these dispersants (citric acid and PBTCA) tend to desorb from the particle surface as the pH increases toward alkaline conditions (Fig. 1).[21] These observations are in accordance with the zeta potential curves obtained by Hidber et al.[8] for citric acid and 2,3,4-trihydroxybenzoic acid.

4.2. Stability maps

The rheological behavior of the matrix representative suspensions containing different short-chain molecules

is presented in Fig. 3 as a function of pH and the dispersant content. The results obtained reveal that a specific range of pH values can be identified for each dispersant concentration, where the apparent viscosity of suspensions is minimized. The viscosity increase observed at pH values different from this optimum interval may be attributed to the occurrence of particle coagulation due most likely to: (a) the decrease of zeta potential as the pH value approaches the particle isoelectric point and (b) the increase of ionic strength at alkaline pH conditions due mainly to the increase of the concentration of KOH added to adjust the pH value and the increase of the number of non-adsorbed molecules present in solution (in the case of citric acid and PBTCA).[1]

To facilitate the comparison and interpretation of the viscosity data obtained, stability maps were built up for each of the dispersants evaluated, following the procedure described elsewhere by the authors.[1] The stability maps display the dispersant content and pH conditions necessary to obtain suspensions exhibiting different viscosity levels (represented by the viscosity iso-lines). Therefore, all the combinations of dispersant content and pH values enclosed within a certain iso-line of the stability map are expected to render suspensions displaying viscosity inferior to that associated with the given iso-line.

The stability maps obtained for 60.5 vol.% suspensions containing citric acid, gallic acid and PBTCA as dispersants are shown in Fig. 4. It was observed that the use of PBTCA and gallic acid significantly decreased the suspension minimum viscosity level in comparison to that achieved with citric acid. The most prominent viscosity reduction was verified with the addition of PBTCA, due most likely to the increase of the density of dissociated sites along the molecule (Table 1) combined with the improvement of the dispersant adsorption ability.[21]

However, it must be considered that the adsorption of PBTCA on alumina surface still occurs predominantly at acid pH values,[21] following the same general pH dependence of the adsorption curves with citric acid (Fig. 1). As a result of this similar adsorption behavior, the stability maps obtained for suspensions containing
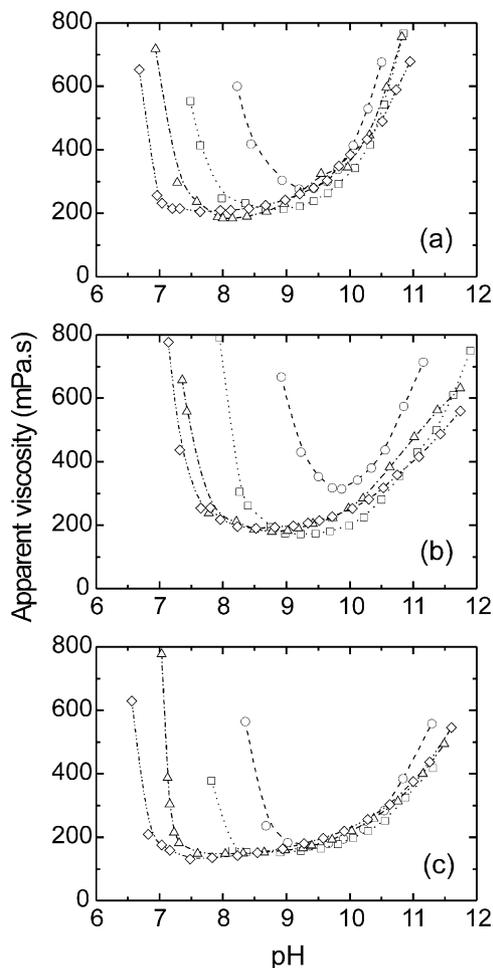

Fig. 3. Apparent viscosity at 50 s^{-1} of 60.5 vol.% alumina suspensions as a function of pH for different (a) citric acid, (b) gallic acid and (c) PBTCA contents (○ 0.140, □ 0.195, △ 0.260 and ◇ 0.320 mg/m²).
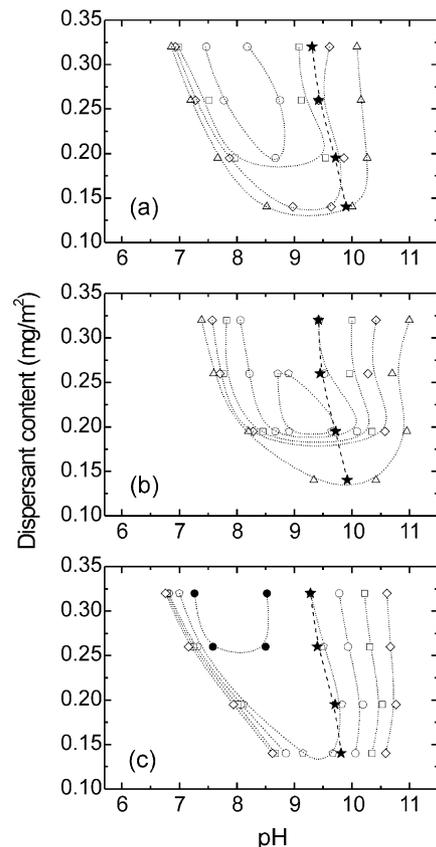

Fig. 4. Stability maps obtained for 60.5 vol% alumina suspensions dispersed with (a) citric acid, (b) gallic acid and (c) PBTCA. The pH values and dispersant contents that result in the same viscosity level were linked together in order to obtain iso-lines indicating distinct dispersing conditions (● 150, ⬡ 180, ○ 210, □ 250, ◇ 300 and △ 400 mPa s). The chart also displays the pH values (★) of castables prepared with different dispersant contents.

citric acid and PBTCA (Fig. 4) exhibit also a very similar pH range for optimum dispersion ($\sim$7.8–8.8 and 7.6–8.5, respectively, for 0.26 mg/m^2 of dispersant). This suggests that the higher density of dissociated sites per molecule is probably the major factor that led to the enhanced dispersing ability of PBTCA in comparison to that of citric acid. The similar profile of the zeta potential curves obtained with these dispersants (Fig. 2) also corroborates to this hypothesis.

In the case of gallic acid, on the other hand, the adsorption efficiency seems to be the main reason for its superior dispersing ability if compared with citric acid. The effective adsorption of gallic acid at basic pH conditions (as suggested by Fig. 1) enabled the reduction of the dispersant content necessary for efficient dispersion ($\sim$0.20 mg/m^2) and also shifted the optimum pH range to higher values (8.9–9.6).

4.3. pH and free-flow values of castables

The effect of the short-chain molecules on the free-flow value of zero-cement high-alumina castables (14 vol.% water) is presented in Fig. 5 as a function of the dispersant content. The results indicate that castables containing gallic acid and PBTCA achieved superior free-flow values than those prepared with citric acid. As in the case of the viscosity results, PBTCA was the most effective dispersant, allowing the preparation of castables with free-flow values of almost 70% using a water content as low as 14 vol.% (4.12 wt.% based on dry solids). Worthy noting is the free-flow values markedly higher obtained with the short-chain molecules even at a lower water content, in comparison to the fluidity level achieved with longer molecules of sodium polyacrylate.[4]

In addition to its benefits to the castable mechanical properties, the reduction of the admixing water content obtained through optimum dispersion may, in principle, speed-up the dewatering process, since a lower amount of liquid would be necessary to be eliminated during drying. However, one should keep in mind that the reduction of the water amount also decreases the permeability of refractory castables.[25] Therefore, a reduction of the water content is only expected to facilitate the refractory dewatering process in case it is associated with the use of other additives (i.e., organic fibers, gas-releasing chemicals) capable of increasing the castable permeability through the formation of a interconnecting network of pores.

The pH value of castables was also monitored as a function of the dispersant content and then introduced into the stability maps in order to evaluate the probable dispersing conditions of the matrix suspension. Taking into account that the addition of bases or acids to shift the castable pH would inevitably increase the liquid ionic strength, the ideal would be that the castable initial pH naturally falls within the optimum pH range
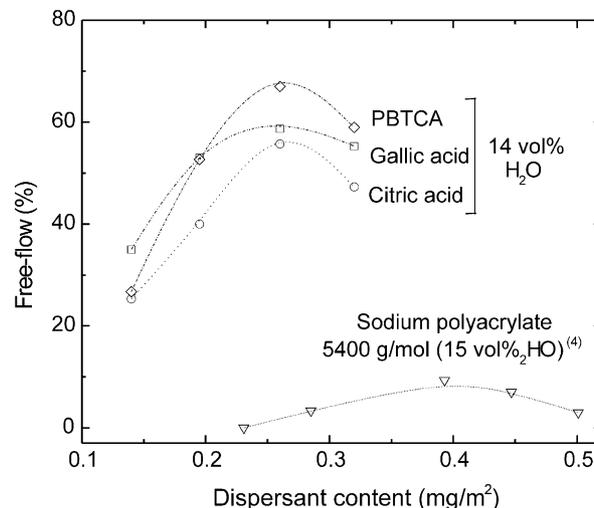

Fig. 5. Free-flow value of castables as a function of the dispersant content for compositions dispersed with citric acid, gallic acid and PBTCA (14 vol.% water). The figure compares the free-flow values obtained in this study with that of castables dispersed with sodium polyacrylate at a higher water content (15 vol.%).[4]

of the stability maps. However, Fig. 4 shows that the pH values of castables containing citric acid and PBTCA were about 1 unit higher than the optimum pH interval. This leads to the conclusion that the higher free-flow values of castables containing PBTCA resulted from the inferior viscosity levels (iso-lines) attained with this dispersant rather than a closer proximity of the initial pH value and the optimum pH interval. In the case of castables containing gallic acid, on the other hand, it was observed that the initial pH was nearer to the ideal pH interval, since the enhanced adsorption ability of this dispersant shifted the optimum range to higher pH values. This suggests that the high free-flow values of castables prepared with gallic acid were predominantly determined by the closer proximity of its initial pH to the optimum pH interval. These observations confirm the superior adsorption efficiency of gallic acid and the higher density of dissociated sites of PBTCA as the main mechanisms that enhanced the dispersing ability of these short-chain molecules.

5. Conclusions

The improvement of the molecule adsorption efficiency on the particle surface and the increase of the density of dissociated sites per molecule were shown to be effective approaches to enhance the dispersion ability of short-chain molecules. The selection of dispersants (gallic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid) following these approaches enabled the production of zero-cement high-alumina castables displaying superior fluidity in comparison to those dispersed with citric acid.

In order to optimize castable dispersion through the improvement of the dispersant adsorption efficiency, it is necessary to select molecules containing functional groups displaying dissociation constants (pK_a values) close to the pH range of interest (usually 8–10). This requisite constitutes an important guideline for the selection of novel short-chain molecules exhibiting enhanced dispersing ability and may give rise to new insights for tailoring the molecular structure of dispersants for zero-cement high-alumina castables (e.g. block and comb-like copolymers with improved adsorption behavior at the castable pH range).

The superior dispersing efficiency of the compounds evaluated in this work enables a reduction of the castable water content for a given flowability level. Therefore, if associated with other mechanisms that improves the castable permeability, such dispersants may also favor the castable dewatering process by decreasing the total amount of liquid to be eliminated in the drying process.

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