

Setting behavior of ultra-low cement refractory castables in the presence of citrate and polymethacrylate salts

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Abstract

The effect of citrate and polymethacrylate salts on the setting behavior of ultra-low cement (ULC) refractory castables was addressed in this paper, with special attention to the interactions of such chemical additives with the cement particles in the aqueous medium. Rheological experiments, electrical conductivimetry, temperature measurements, SEM, X-ray diffractometry and mechanical tests were performed to characterize the cement-based compositions prepared in this work. In spite of its strong inhibiting effect on the precipitation of cement hydrated phases, sodium citrate was found to induce the earlier setting of ULC refractory castables, due most likely to the formation of a gelled phase between the citrate anions and the ions originated from the dissolution of cement particles. The most probable reasons for the formation of this unexpected gelled phase are discussed in this paper.

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1. Introduction

Refractory castables used in steel making industries and other high-temperature applications are typically constituted by a mixture of coarse (5 mm–100 µm) and fine (100–0.1 µm) raw materials, a binding agent (e.g., calcium aluminate cement) and chemical additives in water. The chemical additives may be added to the castables for different purposes, as for example: to disperse fine particles through electrostatic/electrosteric mechanisms (dispersants),^{1–6} to improve the wetting ability of some raw materials in water (wetting agents),^{5,7} to induce stiffening reactions (setting, coagulating or gelling agents),^{8–11} to incorporate air-bubbles into the castable (foaming agents) and to control the hydration process of cement particles (retarders/accelerators).^{7,12} As a result, chemical additives have a major impact on several processing characteristics of castables,

including the dispersion state of particles, homogeneity, rheological properties, setting behavior and water consumption.^{1–7} Nevertheless, one must bear in mind that a specific additive may impart more than one of the above mentioned effects. Therefore, a systemic approach is often required to understand the influence of such chemicals on the processing features of refractory castables.

The effect of some chemical additives (dispersants) on the dispersion state and rheological behaviour of zero-cement refractory castables of varying chemical compositions has been recently reported by the authors.^{1–6} However, in the presence of cement particles, the rheological properties are governed not only by the dispersion state of particles, but also by the cement hydration process. The mutable and dynamic nature of cement particles in aqueous medium makes more complex the understanding of the effect of chemical additives on the rheological properties of cement-containing castables, which may be the reason for the few studies found in literature that have systematically addressed this topic. Most investigations have focused on the effect of accelerators/retarders on the development of hydrated products in the consolidated cement-containing materials. Nonetheless, refractory castables usually lose flowability

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and become excessively stiff for placement much earlier than most the precipitation of hydrated phases occurs.

Therefore, a comprehensive study focused on the interactions of chemical additives with cement particles and their impact on the setting behavior of castables is required. In this context, the aim of the present study is to evaluate the influence of two carboxylate salts, namely sodium citrate and a commercially-grade sodium polymethacrylate, on the rheological and setting properties of an ultra-low cement (ULC) refractory castable. Particular attention is given to the effect of these additives on the dissolution of cement particles and the formation of hydrated phases, as well as the interactions between non-adsorbed additives and cementitious ions in the liquid medium. Sodium citrate and polymethacrylate are known to be efficient dispersants for alumina-based suspensions. These additives were chosen in this study due to the apparently contradictory effects they impart in zero-cement and ULC refractory compositions. Although citrate molecules were found to be efficient dispersants for zero-cement castables and are known to retard the precipitation of hydrated cementitious phases, excessively short working times has been obtained with this additive in ultra-low cement compositions.⁷ Sodium polymethacrylate, on the other hand, is not able to appropriately disperse zero-cement castables, due most likely to the viscosity-increasing effects usually associated to long-chain non-adsorbed molecules. However, cement-containing castables displaying high flowability levels and adequate working time have been successfully obtained using this additive.⁷ Al_2O_3 – SiC – SiO_2 – C ULC compositions commonly applied in blast furnace runners, their matrix suspensions and cement aqueous slurries were used to evaluate the influence of citrate and polymethacrylate salts on the setting behavior of cement-containing refractory castables.

A brief summary describing the hydration process of cement particles in water and the possible interactions with chemical additives is presented in the following section in order to aid the interpretation of the results obtained in this study.

2. Cement hydration process

To comprehend the effect of chemical additives on the setting behavior of ULC castables, it is important to first understand the hydration process of cement particles in water. Calcium aluminate cements are known to readily dissociate in water, releasing increasing amounts of Ca^{2+} and $\text{Al}(\text{OH})_4^-$ ions in the liquid medium.^{12–15} The dissolution process takes place until the concentration of these ions in the aqueous solution reaches a certain saturation level, at which point the ions tend to precipitate through a nucleation and growth mechanism

to form hydrated phases. The precipitation of the first hydrated products decreases the concentration of ions in solution to levels below the saturation condition, favoring the further dissolution of cement particles. This leads to a cyclic process of ion dissolution-precipitation that proceeds until most of the anhydrous cement phase has reacted. Some of the possible interactions that may take place between the chemical additives and cement particles in an aqueous medium are:^{1,16} (a) the adsorption of additive molecules on the surface of particles, leading to electrostatic/steric mechanisms of dispersion, (b) the selective adsorption of molecules on reactive surface sites, locally blocking the dissolution of the anhydrous phase, (c) the complexation of dissociating ions by the nonadsorbed additive molecules, which may either retard the precipitation of new hydrated phases or further aid the dissolution process, (d) the inhibition of hydrate growth on the particle surface due to additive adsorption, and/or (e) the formation of hydrated phases that incorporate the additive molecules into its structure, leading to the so-called intercalation phenomenon. These possible interactions were taken as guidelines for the analysis of the experimental results presented herein.

3. Experimental procedure

3.1. Materials

ULC refractory compositions used in blast furnace runners⁷ were prepared to evaluate the influence of chemical additives on the setting behavior of cement-containing refractory castables. White fused and calcined aluminas, silicon carbide, coke, microsilica and high-alumina cement (Table 1) were the raw materials used for the preparation of these compositions, as shown in Table 2.

In addition to the refractory castables, two types of fine aqueous suspensions were also prepared (Table 2) to investigate the effect of additives on the setting process: (a) aqueous suspensions containing only cement and varying contents of the chemical additives and (b)

Table 1

Typical chemical composition of the CA 270 calcium aluminate cement (density = 3.15 g/cm³, Alcoa Chemicals, USA) used in this study

| Oxides | Content (wt. %) ^a |
|-------------------------|------------------------------|
| Al_2O_3 | 70 |
| CaO | 28 |
| Na_2O | 0.25 |
| SiO_2 | 0.30 |
| Fe_2O_3 | 0.20 |
| MgO | 0.20 |

^a Values taken from the product data sheet supplied by Alcoa.

Table 2

Content of raw materials used for the preparation of the ULC refractory castables, matrix representative suspensions and cement slurries evaluated in this study

| Raw materials (wt.%) | | Refractory castable | Matrix suspension | Cement suspension | |
|---|--|------------------------|-------------------|-------------------|-------|
| Aggregates | White fused alumina EK 8R ^a | 57 | – | – | |
| | Tyler # range: 5/16 - 200 | | | | |
| Matrix | Silicon carbide EC 6R ^a | 20 | – | – | |
| | Tyler # range: 6–200 | | | | |
| | Calcined aluminas | A-3000 FL ^a | 10 | 47.6 | – |
| | | A2-G ^a | 3 | 14.3 | – |
| | Coke Unicarbo 50 ^b | | 2 | – | – |
| Distilled water (wt.% based on dry solids) | Microsilica 971-D ^c | | 5 | 23.8 | – |
| | Cement CA-270 ^a | | 3 | 14.3 | 100 |
| | | | 5 | 23.9 | 166.7 |

^a Alcoa Alumínio—Brazil.

^b Unimetal—Brazil.

^c Elkem Refractories—Norway.

matrix representative suspensions containing all the finely-ground raw materials of the refractory castables except coke. This raw material was not introduced into the matrix suspensions in order to avoid the addition of a wetting agent into the system, which could have interfered on the interactions between the chemical additives and cement particles. Both suspensions were prepared using the same weight-ratio water/(fine particles) employed in the refractory castables, resulting in solid loadings of 37.5 and 80.7 wt.% for the cement slurries and the matrix representative suspensions, respectively.

Darvan 7S (Vanderbilt, Norwalk, CT, USA) and trisodium citrate (Mercocitrato, São Paulo, Brazil) were the main chemical additives evaluated in this study. According to the supplier, Darvan 7S is a sodium-neutralized polymethacrylic acid with an average molecular weight (M_w) of 2500 g/mol. An optimum content (0.20 mg/m²) of polyoxyethylene cetyl ether (C₁₆H₃₃(OCH₂-CH₂)₂₀OH, 1120 g/mol, Sigma-Aldrich, St. Louis, MO, USA) was used to promote wetting of coke particles in the refractory compositions.^{5,7} The content of all additives employed in this paper is expressed in terms of wt.% based on dry cement.

3.2. Particle size analysis

Particle size measurements were performed in 2.3 vol.% cement aqueous slurries to estimate the degree of agglomeration of cement particles in the absence or presence of chemical additives (10 wt.%). The test was carried out approximately 10 min after the addition of the cement powder into water (or additive-containing aqueous solution), using a particle-size analyzer based on the Stokes-sedimentation method (Sedigraph 5000 D, Micromeritics, Norcross, GA). All cement suspensions were ultrasonicated for 3 min prior to the analysis.

3.3. Rheological tests

Rheological tests were conducted to evaluate the setting behavior of castables in the presence of different contents of sodium citrate and polymethacrylate. In these experiments the wet castable was submitted to a constant rotation speed in the rheometer (28 rpm) and the torque applied to the material was recorded as a function of time.^{7,10}

The rheological behavior of the matrix representative suspensions was also investigated in this study using a strain-controlled viscometer (model LVDV-III, Brookfield, Middleboro, MA, USA) equipped with a co-axial cylindrical device. The apparent viscosity of these suspensions was determined at the shear rate of 50 s⁻¹ at fixed intervals of 5 min after the addition of the cement powder into the slurry.

3.4. Conductivity measurements

The effect of chemical additives on the dissolution behavior of cement particles in water was evaluated through electrical conductivity measurements of cement aqueous suspensions as a function of time (Micronal, model B 330, São Paulo, Brazil). During the measurements, the suspensions were maintained in a thermbath at a constant temperature of 25 °C. Data acquisition started as soon as the cement powder was introduced into the additive-containing water and lasted until a high viscosity suspension was obtained.

3.5. Preparation of filtrate solutions

The dissolution kinetics of cement particles was also investigated by extracting the liquid medium of cement suspensions using a vacuum filtration apparatus. The filtrations were performed 10 min after the addition of

the cement powder into water and were afterwards chemically analyzed in an Inductively Coupled Plasma emission spectrophotometer (ICP). The aluminum and calcium ions determined through this analysis were assumed to constitute the $\text{Al}(\text{OH})_4^-$ and Ca^{2+} ions, respectively, of the filtrate solutions. The carbon content of these filtrate solutions was also determined with the help of a Total Organic Carbon analyzer (TOC-5000A, Shimadzu Inc., Tokyo, Japan), employing the platinum-catalyzed combustion technique. The sodium and carbon elements found through these analyses were considered to be an indication of the presence of non-adsorbed additives in the suspension liquid medium.

3.6. Formation of hydrated phases

The development of hydrated phases in the cement suspensions was subsequently investigated with the help of scanning electron microscopy (SEM, Leica, model Stereoscan 440, Bannockburn, IL, USA), X-ray diffraction (Siemens AG, model D-5000, Munich, Germany) and temperature measurements as a function of time. Samples for the SEM and X-ray diffraction analyses were obtained from cement slurries maintained at room temperature (26–27 °C) for periods varying from 5 min to 12 days. The cement samples were prepared by rinsing (for at least three times) the cement slurry with ethanol in a filter paper, in order to interrupt the hydration process. After drying, the obtained powder was crushed and afterwards kept in a dessicator until the SEM analysis and the X-ray diffractometry were performed.

The temperature measurements were carried out by inserting a T-type thermocouple into the cement suspension, which was connected to a data acquisition system. During the experiment, the cement suspension was kept inside a sealed vessel submerged in a thermobath at a fixed temperature of 25 °C. A temperature rise in this experiment was associated to the precipitation of hydrated phases in the suspension.

3.7. Mechanical strength tests

The wet mechanical strength of refractory castables was also determined as a function of time through compressive measurements in a universal testing machine (MTS Systems Corp., model 810, Eden Prairie, MN, USA). For this purpose, refractory compositions were cast in cylindrical molds (40 mm high and 40 mm in diameter) and kept under humid environment for different periods of time at room temperature (26–27 °C). The compressive tests were performed using a constant crosshead speed of 2 mm/min in at least four samples for each composition. The mechanical strength of the wet bodies was considered to be the maximum stress value obtained from these compressive tests.

4. Results and discussion

4.1. Setting behavior of castables

The setting behavior of castables was estimated with the help of the torque curves obtained as a function of time shown in Fig. 1. The torque increase observed in these curves indicates the initiation of the setting process and, therefore, can give an idea of the working time of castables. It can be noted that the addition of different contents of sodium polymethacrylate resulted in working time windows ranging from 20 up to 100 min. This enables one to adjust the content of this additive so as to obtain castables displaying a working time long enough for appropriate placement (usually 60–100 min).

The setting rate of castables prepared with sodium citrate, on the other hand, was observed to be markedly higher than that obtained with the polymethacrylate salt, resulting in working times lower than approximately 40 min. It is interesting to note that the increase of the additive content, in this case, increased the setting

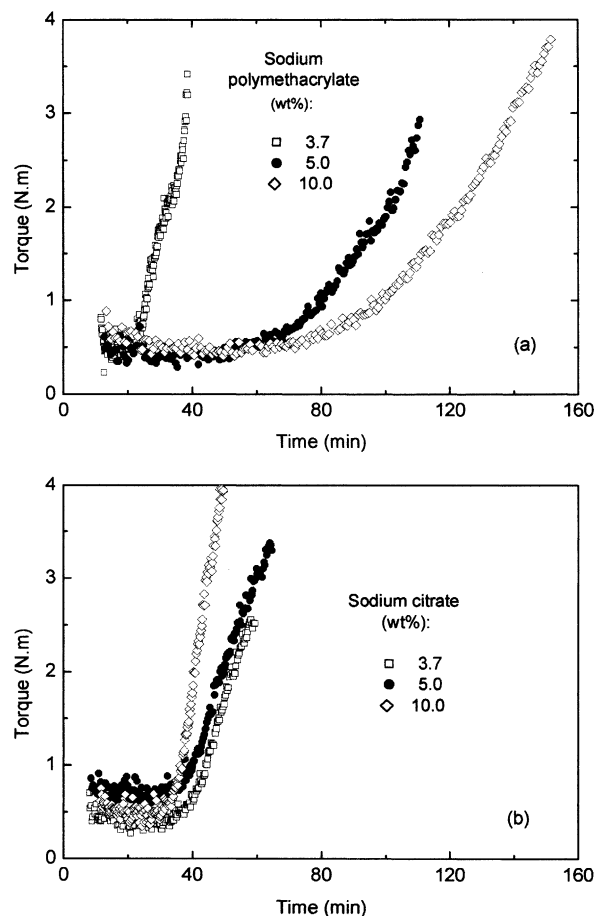


Fig. 1. Torque applied as a function of time to the ULC refractory castables containing varying contents of (a) sodium polymethacrylate and (b) sodium citrate. The additive content is presented as a weight percentage of the cement.

rate, suggesting that the addition of sodium citrate might be contributing to speed up the setting process.

Viscosity measurements as a function of time performed in matrix representative suspensions have also confirmed the higher setting rate observed in the presence of sodium citrate in comparison to that obtained in the case of the polymethacrylate salt (Fig. 2).

These observations seem to be in conflict with the general idea that citrate salts may retard the setting process of cement-based castables. In the next sections, the probable interactions between the additives and cement particles were explored in an attempt to understand the reasons for such unexpected behavior and to determine some of the factors controlling the early setting properties of ULC refractory castables.

4.2. Surface adsorption

Although adsorption tests were not performed in this work, particle size measurements and the chemical analysis of filtrate solutions have indirectly indicated that the citrate and polymethacrylate molecules are probably able to adsorb on the surface of cement particles.

The particle size analysis revealed that the addition of citrate and polymethacrylate salts to the cement slurries resulted in an average particle diameter (D_{50}) of approximately 7 μm , whereas in the absence of additives a D_{50} value of nearly 24 μm was measured. This suggests that the additives have indeed adsorbed on the surface of particles and dispersed the cement suspensions. Additional rheological tests have shown that concentrated cement slurries (74 wt.%) exhibit a significant viscosity decrease in the presence of the citrate and polymethacrylate salts (1–5 wt.%).

Likewise, the chemical analysis presented in Table 3 revealed that not all the amount of additive initially added to the cement suspensions remained in the filtrate solution, indicating that part of the molecules were able to adsorb on the surface of particles. However, the

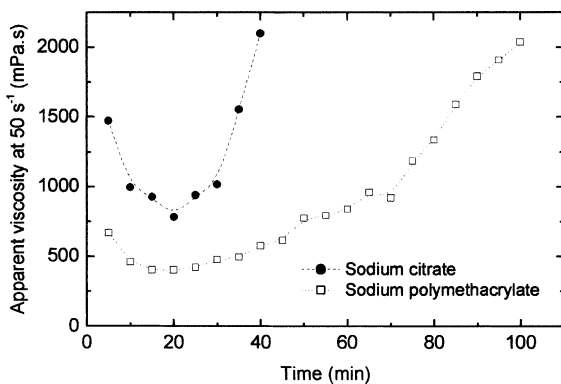


Fig. 2. Apparent viscosity as a function of time of matrix representative suspensions containing 5 wt.% of sodium citrate or sodium polymethacrylate.

amount of citrate and polymethacrylate molecules adsorbed corresponds to only 7 and 16.7% of the initial additive content. Therefore, one can expect that, for the range of additive content used in this study, a small amount is attached to the surface of cement particles, whereas a significant fraction of molecules remain non-adsorbed in the liquid medium during the early stage of the hydration process.

4.3. Dissolution of cement particles

The dissolution of Ca^{2+} and $\text{Al}(\text{OH})_4^-$ ions from cement particles in water is known to cause an increase in the electrical conductivity of cement aqueous suspensions in the early stages of the hydration process,^{12,17} as shown in Fig. 3. Due to the distinct nature (valence and mobility) of the ionic species resulting from the dissociation of chemical additives, one cannot directly compare the absolute electrical conductivity values of suspensions containing distinct additives. However, the initial slope of the conductivity curves depicted in Fig. 3 was still considered to be an indication of the dissolution rate of cement particles. The results therefore reveal that the presence of sodium citrate in the suspension seems to aid the dissolution of cement particles in water, whereas the addition of sodium polymethacrylate tends to retard this process in comparison to the reference

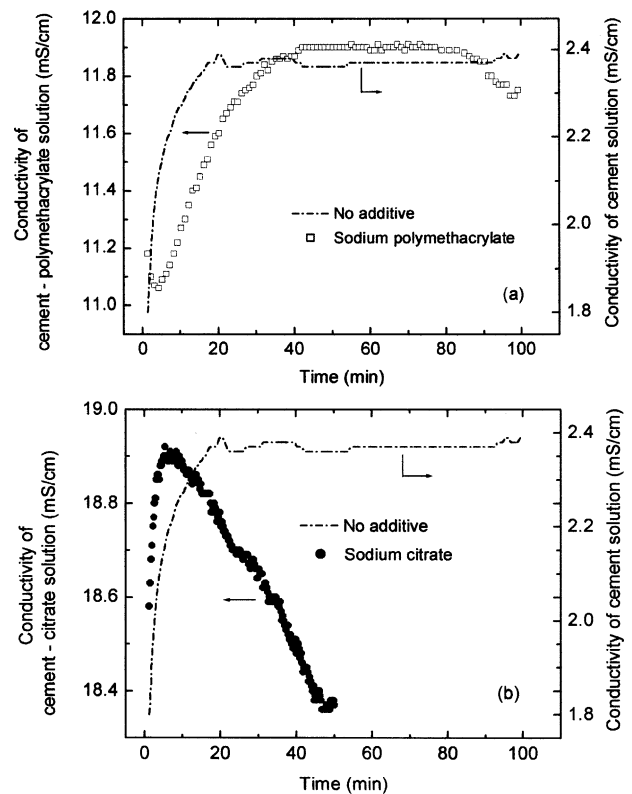


Fig. 3. Electrical conductivity of cement aqueous suspensions prepared with 10 wt.% of (a) sodium polymethacrylate or (b) sodium citrate, in comparison to the reference cement slurry (with no additive).

slurry where the chemical additives were absent. These observations were confirmed by the chemical analysis of the filtrate solutions containing the citrate and the polymethacrylate salts (Table 3). It is interesting to note that the amount of ions dissociated in the presence of chemical additives was significantly higher than in the case of the reference cement slurry. This may be attributed to the fact that the cement particles were not appropriately dispersed in the reference suspension, decreasing the solid–liquid interface area and therefore the dissolution rate of the anhydrous phase.

Taking into account the possible interactions among cement and chemical additives (section 2), the enhanced dissolution rate observed in the presence of sodium citrate may be related to the high affinity of citrate molecules for Ca^{2+} ions, which has most likely favored the dissolution process through the formation of stable complexes among these ionic species. Another factor that might have contributed to such behavior is the relatively thin steric layer (~ 0.5 nm) and lower zeta potential typically obtained for citrate molecules adsorbed on the surface of particles in comparison to that observed in the case of sodium polymethacrylate.⁴ Although this has not been fully investigated yet, a thicker steric layer and higher zeta potential on the surface of cement particles may constitute an electrosteric barrier against the dissolution of ions into the liquid medium, as suggested in Section 2. This effect might have contributed to the lower dissolution rate of cement particles in the presence of sodium polymethacrylate.

In view of the faster dissolution kinetics of cement suspensions containing sodium citrate, one may suppose that the shorter setting time of castables prepared with this additive was caused by the higher ionic strength generated in this case during the early stage of hydration. However, the conductivity curve obtained for the citrate-containing cement suspension (Fig. 3b) exhibits a steep decay after the first 10 min of the dissolution process, suggesting that the Ca^{2+} and $\text{Al}(\text{OH})_4^-$ ions released from the cement particles are most likely forming precipitates or complexes in the solution rather than increasing the ionic strength of the liquid medium.

The following sections are therefore focused on the possible precipitation/complexation reactions that may occur in the liquid medium during the first minutes of hydration, in order to find out the reasons for the shorter setting time of ULC castables prepared with sodium citrate.

4.4. Development of hydrated phases

The most straightforward hypothesis for the sudden conductivity decrease observed in Fig. 3b is that calcium aluminate hydrates precipitated earlier in the presence of sodium citrate, as a result of the higher initial dissolution rate induced by this additive. However, this effect would be in complete disagreement with studies from literature^{18,19} that have reported citrate ions as being efficient retarders of the development of hydrated phases in cement-based systems. Several analyses were therefore conducted to evaluate the precipitation kinetics of hydrated phases in cement slurries containing distinct additives.

Fig. 4 presents results obtained for the temperature measurements as a function of time. A strong temperature peak was detected after approximately 11–12 h in

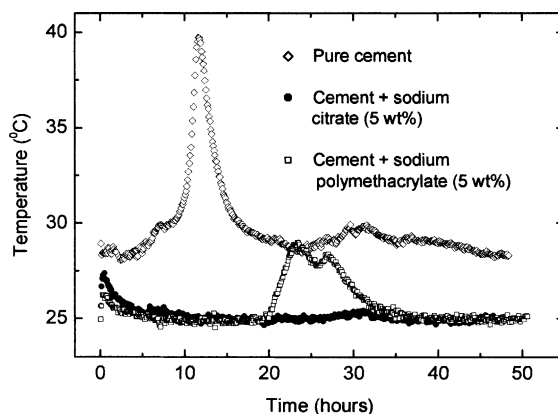


Fig. 4. Temperature measurements as a function of time obtained for cement aqueous suspensions containing sodium citrate or sodium polymethacrylate in comparison to that observed for the reference slurry (with no additive).

Table 3

Chemical analysis of the filtrate solutions obtained from cement suspensions containing distinct chemical additives (10 wt.%)

| Ion concentration (mol/l) | Filtrate solutions obtained from cement suspensions containing | | |
|-------------------------------|--|------------------|---------|
| | No additive | Polymethacrylate | Citrate |
| Ca^{2+} | 0.012 | 0.12 | 0.21 |
| $\text{Al}(\text{OH})_4^-$ | 0.022 | 0.24 | 0.41 |
| Na^+ | 0.007 | 0.45 | 0.57 |
| Citrate ^a | – | – | 0.212 |
| Polymethacrylate ^a | – | 0.020 | – |

^a Amount of citrate and polymethacrylate anions initially added to the cement suspensions: 0.228 and 0.024 mol/l, respectively. In order to evaluate the additive content in the filtrate suspensions, the amount of carbon detected was converted to the equivalent concentration of citrate and polymethacrylate.

the reference cement suspension (no additives), which is typically associated to the precipitation of hydrated phases. This temperature peak was observed after a longer period of time (20–30 h) and in a less pronounced manner when sodium polymethacrylate was added to the cement suspension (Fig. 4). In the presence of sodium citrate, on the other hand, no significant temperature increase was verified within the duration time of the experiment (~50 h). These results reveal that sodium polymethacrylate has retarded the development of hydrated phases in comparison to the reference composition, whereas no detectable precipitation of hydrates occurred in the presence of sodium citrate up to 50 h.

As stated earlier, such inhibiting effect of citrate ions on the precipitation of hydrated phases has been reported in literature^{18,19} and were confirmed by X-ray dif-

fraction and SEM analyses of cement samples cured for varying periods of time.

The X-ray diffractometry results presented in Fig. 5 indicate for comparison with the records JCPDS that the initial anhydrous cement powder consists of a mixture of Al_2O_3 (46-1212), $\text{Al}(\text{OH})_3$ (70-2038), $\text{CaO}\cdot\text{Al}_2\text{O}_3$ (70-0134) and $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ (72-0767) phases. When in contact with polymethacrylate-containing aqueous solutions, this powder was found to originate $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ (11-0205), $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ (72-1109), $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O}$ (02-0083) and $\text{Al}(\text{OH})_3$ phases as main reaction products. However, no clear hydrated phases were observed in specimens prepared with sodium citrate cured for up to 12 days (Fig. 5). Even more surprising was the fact that the X-ray patterns of such samples are quite similar to that obtained for the anhydrous cement particles, suggesting that the

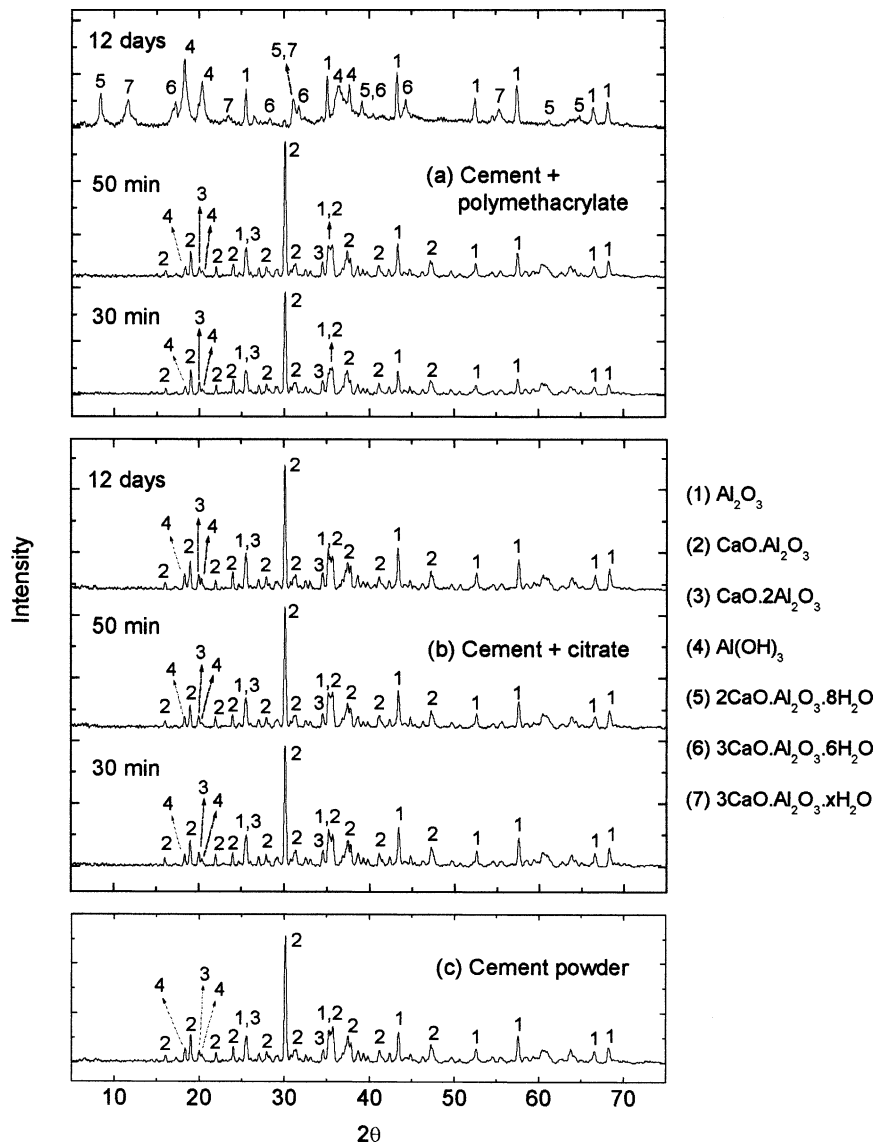


Fig. 5. X-ray diffraction patterns of powders obtained from the cement suspensions containing (a) sodium polymethacrylate (5 wt.%) and (b) sodium citrate (5 wt.%) for different “ageing times”, in comparison to that of the cement dried powder (c).

citrate molecules and cementitious ions (Ca^{2+} and $\text{Al}(\text{OH})_4^-$) might have reacted to form a dense layer on the surface of cement particles that probably prevented the contact of the anhydrous phases with the aqueous medium. Additional X-ray diffraction analyses carried out in the cement-containing matrix suspensions have also indicated the presence of anhydrous phases even after 2 days of curing.

The SEM images presented in Fig. 6 support the X-ray diffraction results discussed above. Plate-like hydrated crystals of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ ^{18,20} were observed in samples obtained from polymethacrylate-containing suspensions, whereas no evidence of hydrate formation was found in the powder derived from slurries containing the citrate salt.

Based on these observations, it can be concluded that the presence of citrate ions does indeed inhibit the precipitation of hydrated phases in cement-containing refractory castables. However, this does not imply that the castables exhibit a prolonged working time, as can be seen in Figs. 1 and 2. These results reveal that methods that rely on the precipitation of hydrated phases to

predict the setting behavior of cement-based compositions (e.g., calorimetry, temperature and X-ray diffraction analyses) would not be appropriate in this case to estimate the working time of castables.

4.5. Possible reactions in the liquid medium

In order to understand the reactions that may occur in the liquid medium of the cement-containing suspensions, one must consider the following ions as the main constituents of the aqueous interparticle solution: Ca^{2+} , $\text{Al}(\text{OH})_4^-$, Na^+ and either the citrate or polymethacrylate anions (Table 3). Besides the precipitation of hydrated calcium aluminate phases, another possible reaction that can take place among these ions is the formation of calcium citrate or calcium polymethacrylate salts. The ability of citrate and polymethacrylate anions to react with Ca^{2+} was evaluated by preparing aqueous solutions containing a fixed amount of these additives and varying contents of CaCl_2 as a source of Ca^{2+} ions. In this test, the concentration of sodium citrate and sodium polymethacrylate initially added to the aqueous solutions was fixed at 0.092 and 0.012 mol/l, respectively, in order to keep the same concentration of carboxylate groups in the liquid medium (0.28 mol/l). Fig. 7 shows that citrate and calcium ions have indeed precipitated in the aqueous solution for initial concentrations of Ca^{2+} (0.1 and 0.2 mol/l) similar to that encountered in the cement suspensions (Table 3), while no significant modifications were observed in the polymethacrylate-containing solutions.

In principle, the precipitation of calcium citrate in the castable liquid medium could increase the matrix solid loading and therefore contribute to the shorter working time of citrate-containing compositions. However, one should expect that the other ions present in the liquid medium may interfere on the precipitation of calcium

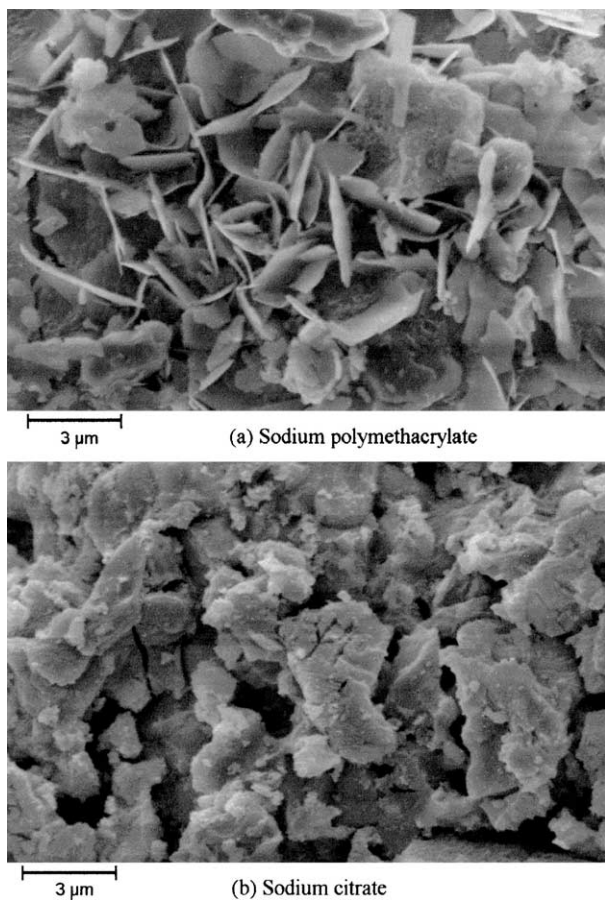


Fig. 6. SEM images of powders obtained from the cement suspensions prepared with 5 wt.% of (a) sodium polymethacrylate (after an elapsed time of 12 days) and (b) sodium citrate (after an elapsed time of 50 min). The powder extracted from the citrate-containing slurries (b) is representative for all the other “ageing” periods (5 min–12 days).

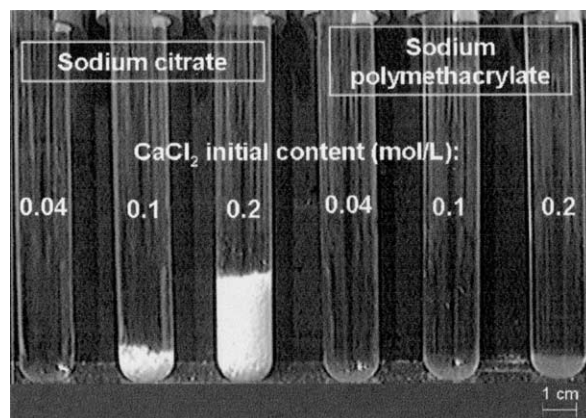


Fig. 7. Aqueous solutions containing sodium citrate (0.092 mol/l, left) and sodium polymethacrylate (0.012 mol/l, right) mixed with varying initial contents of CaCl_2 . The picture illustrates the precipitation of salt (calcium citrate) in the citrate-containing aqueous solutions.

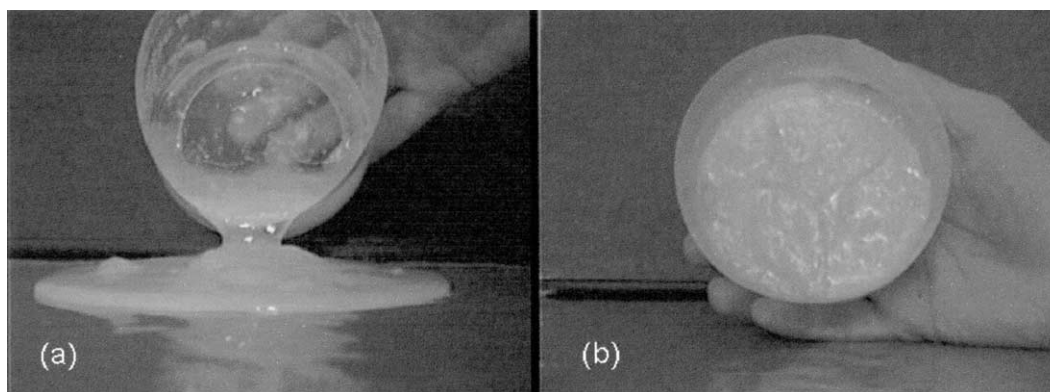


Fig. 8. Gel obtained from the cement filtrate solutions prepared with sodium citrate (5 wt.%), after drying for (a) 4 and (b) 7 days in air at room temperature (26–27 °C).

citrate through competing reactions with the calcium and citrate ions. Therefore, filtrate solutions were prepared from the cement suspensions as described in Section 3.5 (5 wt.% additive) and observed with regard to calcium citrate formation. No salt was found to precipitate in the filtrate solutions obtained from the cement suspensions mixed for 10 min. However, when these filtrate solutions were gently dried in air (26–27 °C) for a period longer than 3 days, a transparent gel was built up through the whole aqueous solution, as shown in Fig. 8. Drying has favored the formation of the gel due most likely to the increase of the ionic concentration of the filtrate solutions. Such gel was also obtained after drying the filtrate solutions in N₂ inert atmosphere, excluding the hypothesis that calcite formation (with atmospheric CO₂) could play a role in the gelling effect observed. Filtrate solutions extracted from suspensions containing a different calcium aluminate cement (CA 14, Alcoa Chemicals, USA) were also found to generate this gelled phase after drying. The gel was found to become more viscous and stiff as a function of drying time, resulting finally in a translucent solid material. In filtrate solutions extracted from polymethacrylate-containing suspensions, no gel formation was verified in the aqueous medium and prolonged drying led to the precipitation of a very small content of white powder, which was concluded to be calcium aluminate hydrated phases.

These observations on the filtrate solutions suggested that the addition of sodium citrate may have induced the early formation of a gelled stiffening phase in the liquid medium that markedly decreased the setting time of castables. The gelled phase was also observed in the cement suspensions, when the initial slurry was cast into plastic molds and rest for a couple of hours without drying. Cement particles settled down during the resting period, leaving a clear supernatant on the upper part of the mold and forming a dense packed body in the bottom. In cement suspensions prepared with sodium citrate, a relatively thick (3–5 mm) layer of a translucent

gelled phase was observed in the upper part of the dense cement bodies, which resembled very much the gel obtained after drying the filtrate solutions.

The major constituents and the actual structure of the gelled phase are still unknown, since NMR and IR tests carried out were not conclusive. The X-ray diffraction analysis of a fully dried gel obtained from the filtrate solutions (Fig. 9) illustrates the low crystalline order nature of this material. Based on the fact that neither calcium citrate nor calcium aluminate hydrates seemed to be formed in the cement suspensions containing citrate salt, one may suppose that the gelled material obtained could be a result of the competition between citrate and aluminate anions for the calcium cations present in the liquid medium. According to this supposition, the similar affinity of citrate and aluminate ions for the Ca²⁺ cation led to the formation of an amorphous structure containing these three ions as major components. The validity of this hypothesis was checked by simulating the formation of the gel in an aqueous solution containing sodium aluminate, calcium chloride and sodium citrate as sources of Al(OH)₄⁻, Ca²⁺ and citrate ions, respectively. These simulating tests showed that a gel is indeed formed when the

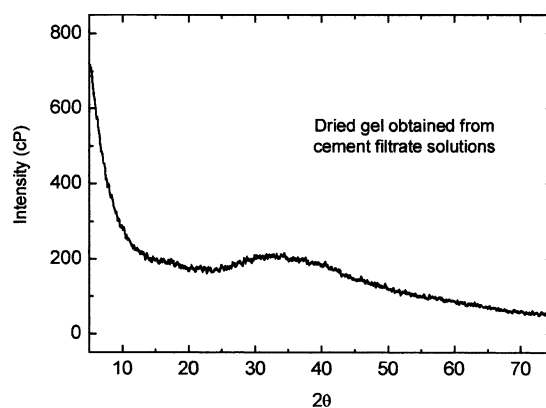


Fig. 9. X-ray diffraction pattern of the gelled phase shown in Fig. 8 after prolonged drying.

sodium aluminate and sodium citrate salts are simultaneously added to the calcium chloride solution, giving support to the assumption formulated above. Among the possible interactions between chemical additives and cement particles depicted in Section 2, the intercalation phenomenon seems to be the one that most resembles the gelling effect observed. However, in the latter case one can assume that the additive has a more pronounced effect over the hydration process, since it does not only locally interrupt the crystal structure of the calcium aluminate hydrates, but prevents the precipitation of the hydrated phase.

4.6. Mechanical strength

Fig. 10 displays the results obtained from the mechanical characterization of refractory wet bodies prepared with sodium citrate and sodium polymethacrylate. This figure shows that samples containing the citrate salt exhibited wet mechanical strength markedly higher than those prepared with sodium polymethacrylate, regardless of the “ageing time” (time elapsed after casting). It is interesting to note that the wet strength of citrate-containing bodies was found to be higher even after the pre-

cipitation of hydrated phases in specimens prepared with the polymethacrylate salt (2–12 days).

Also worth mentioning is the distinguished profile of the stress vs. strain curve obtained for the citrate-containing samples tested only 2 h after casting (Fig. 10b). At this condition, bodies prepared with sodium citrate were quite rigid (high initial slope in the stress vs. strain curve) in comparison to the weak plastic-like samples obtained with the polymethacrylate salt. Specimens prepared with sodium polymethacrylate exhibited in this case a yield-point typical of bodies coagulated through the increase of the liquid ionic strength.^{21,22} The absence of a yield-point in the citrate-containing samples suggests that the ionic strength increase that occurs during cement dissolution plays a minor role on the high mechanical strength of these bodies. Such results support the idea that a gelled phase might have formed in the citrate-containing compositions, leading to the earlier setting effect observed and to enhanced wet mechanical strength levels.

5. Conclusions

The chemical additives sodium citrate and polymethacrylate usually employed in ULC refractory castables were shown to significantly affect several features of the hydration process of calcium aluminate cement, including the dissolution rate of particles, the precipitation of hydrated phases and the reactions between cement ions and non-adsorbed molecules in the liquid medium. The experimental results obtained suggested that the reactions among Ca^{2+} , $\text{Al}(\text{OH})_4^-$ and citrate non-adsorbed ions in the liquid medium play a major role on the setting behavior of the ULC refractory castables evaluated in this work. A gelled phase seems to be formed from the interaction of such ions during the earlier minutes of the hydration process, markedly reducing the working time of the refractory compositions prepared with sodium citrate. The precipitation of this gelled phase have probably prevented the further dissolution of the cement particles in water, since anhydrous calcium aluminate phases were detected in citrate-containing samples even after prolonged periods of time. The absence of hydrated products in specimens prepared with sodium citrate indicates that the experimental methods that rely on the exothermic reaction of hydration would not be suitable in this case to predict the setting time of castables. This reveals the importance of investigations that address in details the actual interactions that take place among chemical additives and cement particles in the liquid medium. The authors expect that this work will motivate further studies on this field so as to improve the current knowledge on the effect of chemical additives on the setting properties of cement-based refractory castables.

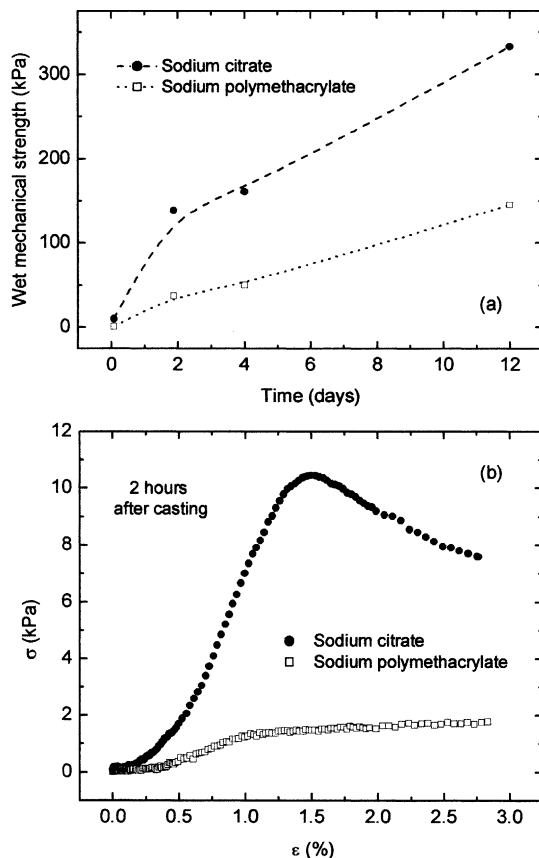


Fig. 10. (a) Wet mechanical strength as a function of “ageing” time of refractory castables containing citrate and polymethacrylate salt (5 wt.% additive), and (b) the stress vs. strain profiles obtained for bodies tested 2 h after casting.

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