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Hydration of CAC cement in a castable refractory matrix containing processing additives

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Abstract

A growing demand for refractory castables with a particular behavior has been inducing a continuous technological evolution, where one of the most important aspects, is an in-depth knowledge of hydraulic binders. These materials greatly influence the rheological properties and mechanical strength evolution of castables, defining their workability range and demolding time, respectively. The hydration process of hydraulic binders is influenced by the presence of matrix and additives (dispersants and accelerators), which affect the setting and demolding time of shaped bodies. In this work, the influence of these variables on the hydration process of calcium aluminate cement was studied by means of temperature measurements, oscillatory rheometry and normal force measurement. These techniques were able to evaluate the setting behavior of different binders, either in plain water or in matrix-representative suspensions. In both cases, the dispersants presented a retarding effect on the hydration process, which was more significant for citric acid and diammonium citrate. The combination of these additives with an accelerator (Li_2CO_3) was shown to be an efficient tool to control the setting time of castables.

Keywords: A. Suspensions; D. Al_2O_3; E. Refractories

1. Introduction

The rheological behavior of refractory castables is greatly dependent on the dispersion of matrix components and defines the most suitable methods for placing these materials. The understanding of the factors that affect their rheology has attained increasing importance in order to make the automation easy and improve the reliability and final properties of refractories. For many applications, the rheological behavior of castables should result in high flowability, pumping characteristics and the ability to fill molds with complex shapes without vibration. Because refractory castables may be considered as high solid loading suspensions, this behavior can be attained only with the use of dispersants. Although the use of these additives results in castables with longer workability, they delay the setting, increasing demolding times of shaped bodies [1,2].

The pre-firing strength of castables results from the hydration of a binder (generally calcium aluminate cement) that leads to the formation of a rigid structure connecting matrix and aggregate particles [3]. The demolding time of castables may be reduced by accelerating the hydration process [4].

Commercial calcium aluminate cements mainly consist of the following anhydrous phases: $CaO{\cdot}Al_2O_3$ (CA, 40–70%); $CaO{\cdot}2Al_2O_3$ (CA_2, <25%) and $12CaO{\cdot}7Al_2O_3$ ($C_{12}A_7$, <3%). The CA_2 phase is the most refractory, requiring a long time to be completely hydrated. Conversely, the $C_{12}A_7$ phase presents low refractoriness, but hydrates in a shorter time and it can speed up the setting time of the CA phase [5].

The hydration process begins with the dissolution, when water comes into contact with a cement particle surface. Eq. (1) shows an example of this reaction:

$$Ca(AlO_2)_2 + 4H_2O \Leftrightarrow Ca^{2+} + 2Al(OH)_4^- \qquad (1)$$

A small part of $Al(OH)_4^-$ ions dissociates according to Eq. (2), increasing the pH. The equilibrium in this reaction is

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ruled by the basic constant (K_b):

$$Al(OH)_4^- \Leftrightarrow Al^{3+} + 4OH^- \qquad K_b = 1.8 \times 10^{-2} \qquad (2)$$

The dissolution of cement anhydrous phases increases the concentrations of the Ca^{2+} and $Al(OH)_4^-$ ions in solution. After some time, the concentration of these ions in water reaches the solubility limit, which is followed by the precipitation of a hydrated calcium aluminate phase, favoring further dissolution of the anhydrous phases. As a result, a cyclic process of ion dissolution-precipitation proceeds until most (or all) of the anhydrous cement particles exposed to water have been consumed [4,5]. The kinetics of cement hydration decreases at lower temperatures, resulting in a longer time to set the cement [5].

A slow nucleation process precedes the precipitation of hydrated phases. This period, which is known as the ‘‘induction period’’, remains until the first crystalline hydrate nuclei are formed [5]. After the induction period, precipitation is carried out quickly, as a result of crystal growth. Because heterogeneous nucleation on the particle surface is favored, the precipitated hydrated phases tend to form strong connections among neighboring particles, which results in the so-called setting phenomenon.

The retarding effect of dispersants used in castables may be partially counterbalanced by the presence of the castable matrix, which increases the cement hydration kinetics. Lithium carbonate is well known as an effective accelerating agent for the setting of cements [6–10]. Therefore, it is expected that the combination of these additives may result in suitable workability and reduced demolding time for the shaped body.

Although various techniques are available to study the setting time of refractory castables, flowability as a function of time and green strength measurements are the most frequently used ones. These procedures demand large amounts of material, are time-consuming and result in a limited description of the viscoelastic changes occurring during the setting phenomena. In this work, temperature and normal force measurements were associated to oscillatory rheometry in order to investigate the hydration kinetics of calcium aluminate cement in suspensions containing usual refractory raw materials of a castable matrix.

1.1. Temperature measurements, oscillatory rheometry and normal force tests

During the calcium aluminate hydration of the most reactivate phases, a certain amount of heat is released (exothermic reaction), increasing the cement paste temperature and favoring the reaction of the most inert phases [11]. A small temperature increase is observed when the hydration of calcium aluminate begins (region I, Fig. 1), which is followed by a dormant period (region II). The hydrate precipitation is followed by an increase in the heat released (region III). These temperature changes can easily be recorded by inserting a thermocouple in the cement paste.

The variables that influence the process of cement hydration may also be attained by combining oscillatory rheometry and normal force tests. These tests can be evaluated quantitatively considering the viscoelastic changes occurring in ceramic suspensions during cement hydration. By monitoring these changes, it is possible to detect when demolding conditions were feasible [12].

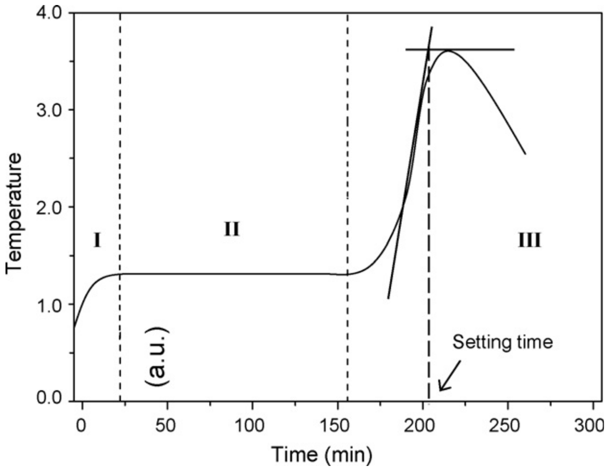

Fig. 1. Schematic representation of temperature profile as a function of time for a CAC suspension (based on Ref. [11]).

In the oscillatory test, a sinusoidal time function is used to apply stresses or strains to the sample [13], while viscosity and elasticity data are recorded. This method is particularly suitable for systems that gradually change from a viscous liquid to an elastic solid as a result of physical or chemical processes, because the sample structure is not disrupted during the test [13].

The material’s response to the applied stress may be expressed in terms of the complex modulus (G^*), which represents the total resistance of a substance to an applied deformation. The complex modulus involves both the storage or elastic (G') and loss or viscous (G'') moduli according to

$$G^* = G' + iG'' \qquad (3)$$

The G' modulus indicates the fraction of mechanical work reversibly stored as elastic energy during the test, whereas G'' indicates the fraction that is irreversibly lost as shear heating in the viscous flow [14]. When $G'' > G'$ for all the frequency spectrum, it implies that the material behaves predominantly as a viscous fluid, whereas if $G' > G''$, the elastic solid behavior prevails [15].

The cement hydration increases both the storage and loss moduli of the suspension, until a transition from a viscous fluid to an elastic solid is observed. Even after this point, the number of connections among particles still increases up to a constant value, named $G'_{\mathrm{equilibrium}}$ [15]. The measurement of both moduli throughout time can be used to assess the setting of suspensions containing calcium aluminate cement.

The normal force test consists of the measurement of the normal force (N_f) as a result of a body response to a uniaxially imposed deformation. This type of test measures the system elasticity, such as in the oscillatory test, but not resulting, necessarily, in the same sort of response, because the sample is subject to a stationary flow [14].

This test can be used as an indicative of the deformation resistance of ceramic suspensions. Various methods are available to perform this measurement, which generally uses the cone–plate or plate–plate devices. However, in this work a novel approach was used [12] which evaluates the sample's response to the penetration of a blade-shaped sensor at a constant deformation rate. The normal force values as a function of the displacement represents the difficulty that the blade-shaped sensor faces to penetrate the sample's surface.

In this work, the influence of lithium carbonate and different dispersants on the setting time of some matrix-representative suspensions was assessed by means of temperature measurements, oscillatory rheometry and normal force test.

2. Materials and methods

Calcium aluminate cement (CA14 M, Almatis-US) and different types of calcined alumina (Esy Pump 1000, A17-NE and A-1000SG, Almatis-US) were used in this study. Their characteristics are presented in Table 1. These aluminas are commonly used in the matrix of refractory castables and were tested either separately (Esy Pump or A17-NE) or combined (A17-NE:A-1000SG = 93:7 wt.% ratio). As dispersing agents, different compounds were evaluated: sodium polymetacrylate (Darvan-7S, Vanderbilt), citric acid anhydrous (Labsynth), diammonium citrate (Sigma Aldrich), sodium hexametaphosphate (HMPNa, Labsynth) and the family of polyglycol polymers developed by Bayer (FS20, FS30 and FS40). Lithium carbonate (Li_2CO_3, Labsynth-Brazil) was used as the accelerating additive.

Aqueous suspensions of the different powders were prepared in order to evaluate their fluidity as a function of dispersant additions. These suspensions had a different solid loading due to the distinct particle size distribution: 35 vol.% (A-1000SG) and 57 vol.% (A17-NE and Esy Pump). Viscosity measurements as a function of dispersant contents were carried out for each suspension at 50 s^{-1} shear rate, in a rotational rheometer (RS300, Thermo Haake, Germany).

The influence of the matrix composition on the setting time was studied for aqueous suspensions containing 26 vol.% solid loading, prepared with plain CA14 M cement and with a 50 wt.% mixture of cement and the different matrices. These formulations were also used to evaluate the influence of Li_2CO_3 (0.01 wt.% on cement mass basis), dispersant content (0.1 and 0.9 mg/m^2 of powder) and the combined effect of Li_2CO_3 (0.01 wt.% on the cement mass) and dispersants (0.1 mg/m^2). The dispersant amount was calculated based on the surface area of the matrix.

The suspensions' temperatures were recorded as a function of time with the help of a thermocouple connected to an automatic acquisition system (ESA 9800, Matec Applied Sciences-UK). This sensor was inserted into the cement-matrix suspensions and the measurements were immediately recorded. The suspensions were kept at 50 °C during the heat evolution

Table 1
Chemical compositions and physical properties of the materials used.

Phases (%)	CA14M	Esy Pump 1000	A17-NE[a]	A-1000SG[a]
Al_2O_3	72.0	99.4	99.8	99.8
CaO	27.0	–	0.02	0.02
SiO_2	0.3	0.10	0.03	0.03
Na_2O	0.3	0.30	0.10	0.07
Density (g/cm^3)	2.96	3.99	3.94	3.95
BET surface area (m^2/g)	1.9	3.3	2.9	8.4
Particle size range (μm), d_{50} (μm)	63–3.3, 9.4	37.8–0.15, 2.6	11.3–0.21, 4.0	53–0.42, 0.57

[a] The A17-NE:A-1000SG (93:7 wt.% ratio) matrix presents a surface area = 3.28 m^2/g and the Na_2O content = 0.098%.

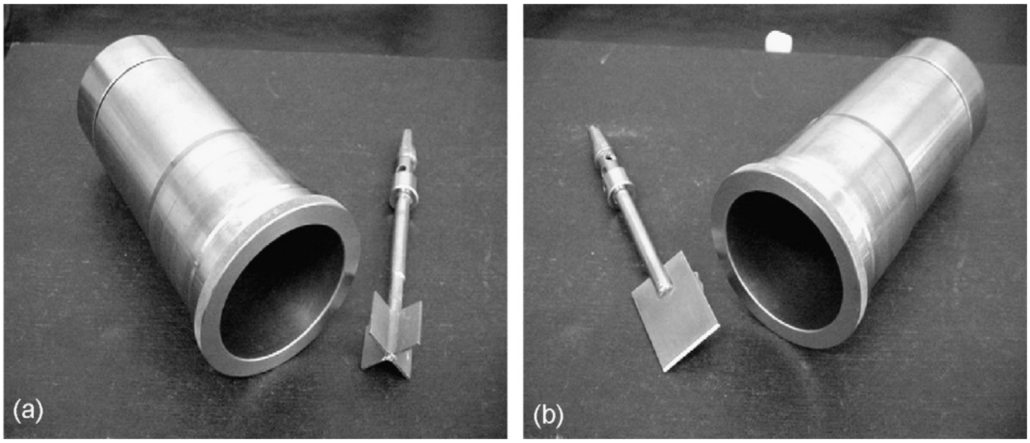

Fig. 2. (a) Vane sensor used in the oscillatory rheometry tests and (b) blade-shaped sensor for the normal force measurements.

measurements, because the hydration process is faster than room temperature.

The oscillatory tests were carried out on a stress-controlled mode. The stress and frequency applied during the tests were previously defined by conducting G' measurements as a function of stress (0.01–100 Pa) and frequency (0.01–10 Hz). A linear viscoelastic behavior, characterized by a constant value of G', was observed for all systems up to 1 Hz and 1 Pa, which were chosen as standard values for the following oscillatory tests.

G' and G'' moduli were measured as a function of time using a vane type sensor, which shows reduced wall effects and causes minimum disruption of the material structure during the alignment procedure [14,16]. The geometry of this tool is shown in Fig. 2a.

The normal force tests were carried out using a methodology previously published [12]. In this technique, the suspension is split into several equal quantities, which are poured into cups and covered with a thin oil layer to avoid water evaporation. The cups were kept in an acclimatized chamber (Vötsch, model 20-20) at 50 °C until the measurement is carried out, at regular time intervals. The test is carried out by inserting a blade-shaped sensor (Fig. 2b) into a sample at a rate of 0.5 mm/s for 20 s, while the normal force is recorded as a function of time. The normal force rate increase, dF/dt, is plotted as a function of time and, when the suspension reaches its maximum deformation resistance, the force is constant [12]. The CA14M-Esy Pump (26 vol.% of solids) suspension was evaluated either without additives or with the addition of Li_2CO_3 (0.01 wt.%), citrate (0.05 wt.%) or both Li_2CO_3-citrate additives. The oscillatory and normal force tests were carried out in a rotational rheometer (RS300, Thermo Haake, Germany) at 50 °C.

Finally, electrical conductivity measurements as a function of time were carried out. A conductivity electrode (ESA 9800, Matec Applied Sciences-UK) was inserted in aqueous suspensions with 16.8 vol.% solids loading to perform the measurements, at 50 °C, for all matrix combinations.

3. Results and discussion

3.1. The effect of matrix and accelerator in the hydration process of CAC

The temperature measurements and viscoelastic constants attained from oscillatory tests as a function of time performed with CA14M and CA14M-matrix suspensions in the absence of additives are shown in Fig. 3. This figure also shows how the setting time was determined for both tests. Except for the plain cement suspension, the determined setting times with the different techniques were not the same for the cement-matrix suspensions. Additionally, the hydrate precipitation and the suspension consolidation were accelerated in the presence of matrix particles, which worked as nucleation sites. This effect will be discussed later.

The viscosities of alumina suspensions with optimum dispersant concentration and in the absence of this additive are

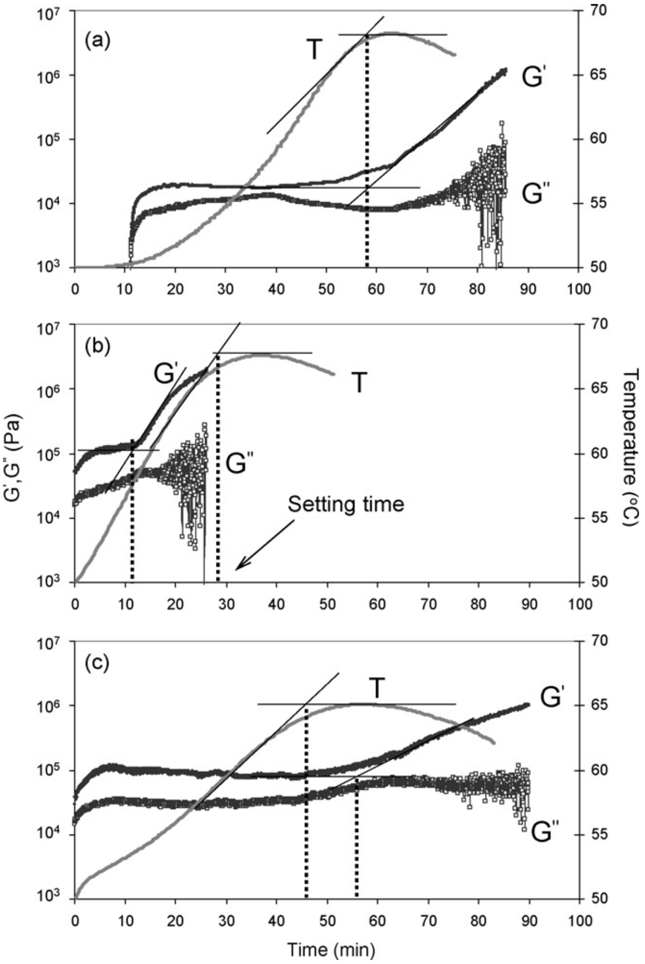

Fig. 3. Oscillatory rheological tests and temperature measurements as a function of time for (a) plain CA14M aqueous suspensions (b) CA14M plus Esy Pump and (c) CA14M plus A17/A1000 matrix, all at 50 °C, in the absence of additives.

Table 2
Viscosity values of Esy Pump (57 vol.%), A17-NE (57 vol.%) and A-1000SG (35 vol.%) alumina suspensions prepared with optimum dispersant content and without additive.

Additives	Optimum content (mg/m^2)	Minimum viscosity at 50 s^{-1} (mPa s)		
		Esy pump	A17-NE	A-1000SG
No additive	0	4270	852	7980
Darvan-7S	0.1	264	412	59
Citric acid	0.1	93	190	95
Diammonium citrate	0.1	93	192	55
HMP-Na	0.1	148	–	34
	0.2	–	190	–
FS20	0.1	107	209	56
FS30	0.1	2626	381	–
	0.2	–	–	130
FS40	0.1	–	211	–
	0.2	162	–	–
	0.3	–	–	59

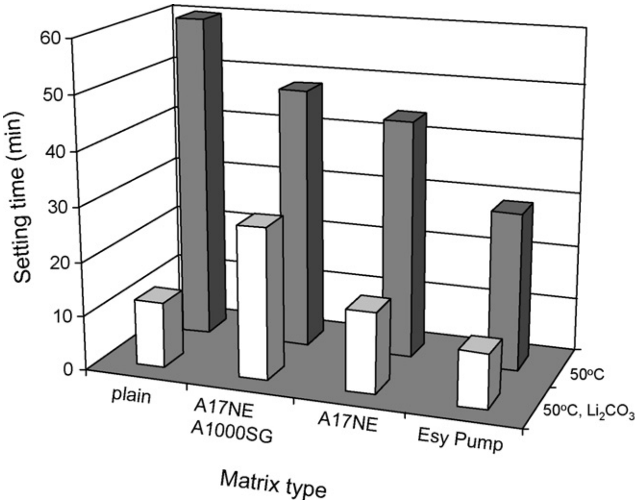

Fig. 4. Setting time evaluated by temperature measurements as a function of time for aqueous suspensions of CA14M cement (26 vol.% solids) and cement-matrix (50:50 wt.%) with or without Li_2CO_3 (0.01 wt.%), at 50 °C.

shown in Table 2. Without dispersants, the Esy Pump suspension presented a superior viscosity value when compared to the A17-NE one, indicating a higher tendency for particle agglomeration. The reduced distance between alumina particles results in extended particle interlacement. Thus, when in the presence of cement, the hydrate crystals begin to precipitate (as depicted by the temperature increase) and grow on the alumina particle surface, resulting in an earlier G′ increase (suspension consolidation). This explains why the setting time attained by the rheological test was shorter than that with the temperature measurements. On the other hand, the growth of crystals in suspensions with larger interparticle distance (lower viscosity) requires a longer time to promote their interlacement, resulting in a delay of the G′ increase.

Because the evaluation of the matrix setting time based on *G*′ changes is affected by the particle size distribution and dispersion state, the influence of matrix and additives on the cement hydration was analyzed considering only the setting times obtained from temperature measurements. Fig. 4 shows the results for CA14M and CA14M-matrix suspensions, either containing Li_2CO_3 or not.

In the absence of Li_2CO_3, the setting times were clearly shorter for all cement-matrix suspensions, when compared with plain CA14M suspension. The induction periods were reduced due to the nucleation sites on the surface of alumina particles, which lower the activation energy for hydrate nucleation [6]. Additionally, the presence of Na_2O reduces the induction period [1,6] because this impurity reacts with $Al(OH)_4^-$ ions, changing the $[Ca^{2+}]$:$[Al(OH)_4^-]$ ions ratio during cement dissolution.

The hydrate precipitation is greatly dependent on the concentration ratio of these ions [17]. At 25 °C and $[Ca^{2+}]$:$[Al(OH)_4^-]$ ratio close to 1, the formation of the CAH_{10} hydrate is induced. In solutions with a higher Ca^{2+} concentration, C_2AH_8 formation is favored and, for higher content of $Al(OH)_4^-$, AH_3 prevails. However, at the temperature used in this work, 50 °C, C_3AH_6 (not C_2AH_8) hydrate is the major formed phase. These hydrates present the following order of solubility: $C_3AH_6 < C_2AH_8 < CAH_{10} < AH_3$. If the formation of the less soluble phase is favored, this means very fast precipitation, reducing the cement setting time. In contrast, the precipitation of the most soluble hydrate (AH_3) leads to a longer induction period [4].

The alumina powders used in this work present a surface area in a narrow range between 2.9 and 3.3 m^2/g (Table 1). On the other hand, Esy Pump presents the highest Na_2O content. As a result of these characteristics, Esy Pump showed the shortest setting time. Fig. 5 shows the suspensions' conductivity with the time increased quickly in the presence of Esy Pump, when compared to other suspensions. This result confirms that this alumina presents a higher Na^+ concentration in the solution.

The setting time was also evaluated for cement and cement-matrix suspensions in the presence of the inorganic additive (Li_2CO_3), Fig. 4. A significant reduction in the setting time was observed in the presence of this additive. Li^+ ions supplied by this salt in a solution favor the formation of insoluble compounds such as $LiAl(OH)_4$, withdrawing $Al(OH)_4^-$ ions from the solution [9,10]. Therefore, the lithium salt also works on the cement hydration by increasing the calcium ions concentration, which favors the formation of less soluble hydrate and accelerates the precipitation stage.

Moreover, the precipitation of these insoluble lithium compounds is faster than the precipitation of the calcium aluminate hydrates. Additionally, they present a crystalline structure that works as nuclei for other hydrates (C_2AH_8), at any temperature, decreasing the energy barrier necessary for the formation of calcium aluminate hydrates.

Nevertheless, the effect of Li_2CO_3 in cement-matrix suspensions was less effective than in plain cement suspensions. When Li^+ is added to the cement-matrix system, the increase in $[Ca^{2+}]$:$[Al(OH)_4^-]$ ratio is smaller than that observed for plain cement, because the $Al(OH)_4^-$ ions are supplied by both alumina and CAC. Furthermore, the presence of nucleation sites was observed for both, C_2AH_8 (formed by $LiAl(OH)_4$ precipitation) and for AH_3 (due to the matrix presence).

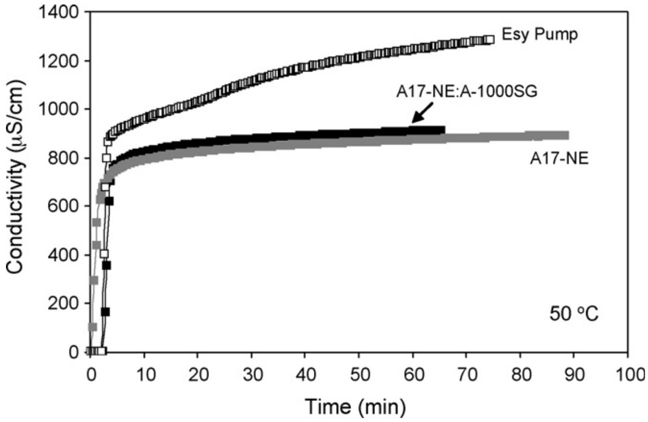

Fig. 5. Electrical conductivity as a function of time for aqueous suspensions of the different matrixes, at 50 °C.

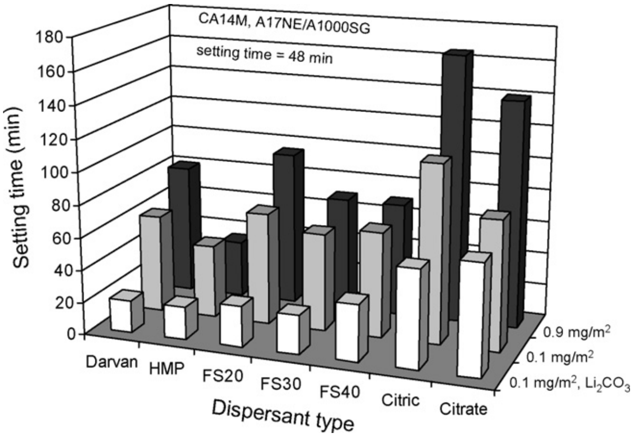

Fig. 6. Setting time evaluated by temperature measurements as a function of time for cement-A17NE/A1000SG (50:50 wt.%) aqueous suspensions with different dispersants (0.1 or 0.9 mg/m^2) and with 0.1 mg/m^2 dispersant in the presence of 0.01 wt.% Li_2CO_3, at 50 °C.

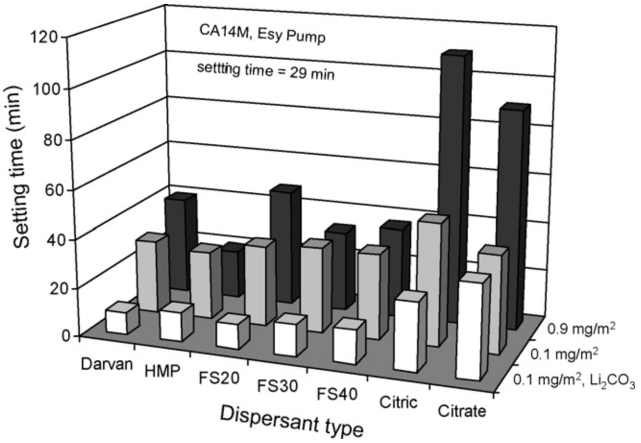

Fig. 8. Setting time evaluated by temperature measurements as a function of time for cement–Esy Pump (50:50 wt.%) aqueous suspensions with different dispersants (0.1 or 0.9 mg/m^2) and with 0.1 mg/m^2 dispersant in the presence of 0.01 wt.% Li_2CO_3, at 50 °C.

3.2. *The effect of additives on the hydration process of CAC-matrix*

The evaluation of additive effects throughout the consolidation of cement-matrix suspensions has been receiving special attention in order to fit the rheological behavior and setting characteristics of castables to the shaping method selected. For short setting times, the pumpability of the material through metal pipes, for instance, is limited, increasing the risk of blockage. On the other hand, an excessive delay in the material consolidation increases the time necessary to resume operation. The type and concentration of additives are crucial to adjust the castable workability as required.

Figs. 6–8 present the influence of different dispersants on the hydration kinetics of CA14M cement in the presence of A17NE/A1000, A17NE and Esy Pump matrices, based on temperature measurements with time. As observed, except for sodium hexametaphosphate (HMP-Na), all additives increased the setting time, noticeably at a higher content (0.9 mg/m^2). On the other hand, HMP-Na showed an accelerating effect when added at a higher amount. The sodium added could decrease the amount of $Al(OH)_4^-$ in solution by forming $NaAl(OH)_4$, resulting in a less soluble hydrate, C_2AH_8.

Citric acid and citrate additives, which were more efficient in the dispersion of matrices (Table 2) presented the higher retarding effect. The higher dispersion of the matrix particles should result in more nucleation sites, inducing the hydrate precipitation and, therefore, shortening the setting time. However, these additives showed a significant retarding effect, which may be explained in terms of the number of ionizable sites. For the same mass of additive used, citric acid and diammonium citrate present a higher number of ionizable sites due to their low molecular mass, which generates a high number of anions such as R–COO$^-$ and R–O$^-$ in the pH range of the tests. The strong attraction between these anions and the Ca^{2+} cations in the solution has two consequences in the cement hydration process [18,19].

The first one is the reaction between the anions and the Ca^{2+} in alkaline pH (pH of the cement-containing media), which withdraws Ca^{2+} cations from the solution. As a result, the ratio between the concentrations of Ca^{2+} and $Al(OH)_4^-$ ions in the solution becomes imbalanced and the formation of the most soluble phase (AH_3) is favored. Thus, the nucleation and growth of hydrates is slowed down. This reaction could also happen for the other anionic additives, but to a lesser extent, which explains their reduced retarding effect.

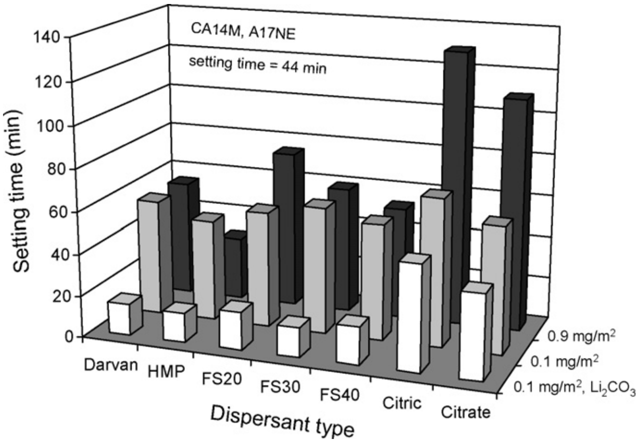

Fig. 7. Setting time evaluated by temperature measurements as a function of time for cement-A17NE (50:50 wt.%) aqueous suspensions with different dispersants (0.1 or 0.9 mg/m^2) and with 0.1 mg/m^2 dispersant in the presence of 0.01 wt.% Li_2CO_3, at 50 °C.

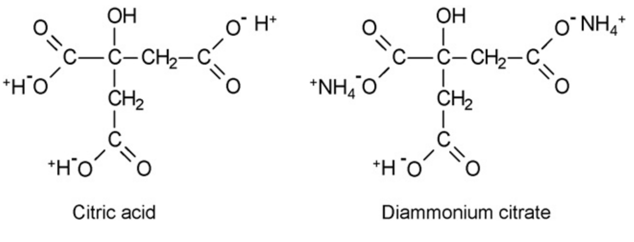

Fig. 9. Chemical structures of additives with retarding effect on the setting time of cement-matrix systems.

The other consequence is related to the formation of insoluble salts as a result of the reaction between those ions. These salts precipitate on cement particles, forming a protective layer that hinders further cement dissolution, delaying the ions saturation of the solution and, eventually, the hydrate precipitation. This mechanism occurs only with citrate anions and is related to its significant retardant effect, comparatively to the other dispersants.

Citric acid presented more retarding effect when compared to diammonium citrate, regardless of the system studied. The nucleation of hydrates involves the connection among OH^- groups of neighboring calcium aluminate hydrate molecules by the overlapping of an isolated pair of electrons of oxygen with an empty orbital of calcium ion [9]. Hydrogen ions supplied by citric acid can hinder the nucleation process, delaying the precipitation step by replacing the Ca^{2+} ions position. The larger number of ionizable hydrogens of citric acid, compared to diammonium citrate, explains its superior delaying effect, as shown in Fig. 9.

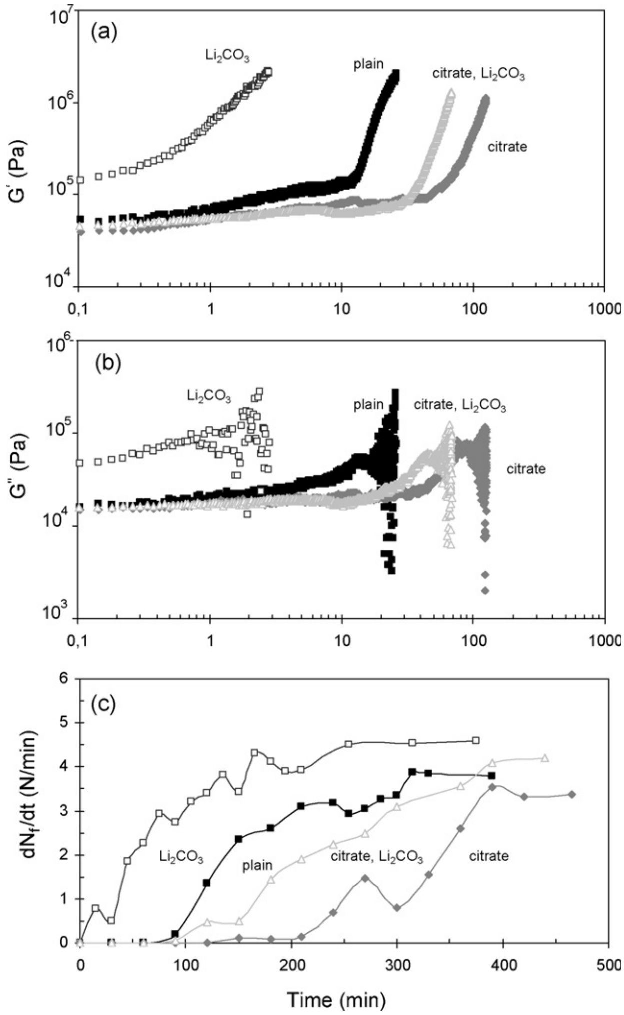

Fig. 10. (a) Storage modulus (G'), (b) loss modulus (G'') and (c) normal force rate (dN_f/dt) as a function of time for plain CA14M–Esy Pump suspension and in the presence of Li_2CO_3 (0.01 wt.%), citrate (0.05 wt.%) and Li_2CO_3-citrate addition, measured at constant 50 °C.

Therefore, the retarding effect of dispersing agents basically results in their action on the ion dissolution and hydrate nucleation, whereas they present minor effects on the hydrate precipitation. Additionally, regardless of the type and content of additives, the presence of castable matrix delayed the setting time of cement in the following order: Esy Pump < A17NE < A17-A1000. This behavior agrees with the results presented previously where, the reduction in the setting time increased with the Na_2O content.

Regarding combining the dispersing agents and accelerator (Li_2CO_3), Figs. 6–8 show that the accelerating effect was not affected by the dispersants, except for citric acid and diammonium citrate, which form a protective layer on the cement particle surface, as discussed previously. For these cases, a combined effect of the retarder (citric acid and citrate) and the accelerator (Li_2CO_3) occurred, leading to an intermediate setting time.

The combined effect of additives on the setting time of cement-matrix suspensions was confirmed by means of oscillatory rheometry and normal force measurements, as presented in Fig. 10, for CA14M-Esy Pump suspension. These techniques are complementary, because oscillatory rheometry gives accurate measurements of the viscoelastic behavior of cement pastes in the early stages of cement hydration, which is related to the castable workability. Conversely, normal force measurements show the rigidity evolution during the first hours of the hydration process, which is related to the demolding time. Both techniques clearly showed the isolated effects of Li_2CO_3 and citrate comparatively to the plain suspension and their combined effect on viscoelastic changes and setting time.

4. Conclusions

The techniques presented in this work were shown to be useful to study the consolidation of ceramic suspensions. Temperature measurements throughout time made it possible to assess the hydration kinetics, differentiating the chemical nature of the process from the dispersion state and particle size distribution. Oscillatory rheometry provided important information regarding the workability of castables in the early stages of hydration and the normal force could indicate if the necessary conditions for castable demolding were attained. These methods required small quantities of material and were not time-consuming, making easier the investigation of variable combinations which influence the consolidation of castables.

The induction period is shortened by the presence of the matrix and addition of inorganic additives due to the formation of compounds such as $NaAl(OH)_4$ and $LiAl(OH)_4$, which withdraws $Al(OH)_4^-$ ions from the solution. It results in the increase of calcium ion concentration which induces the formation of less soluble hydrate and accelerates the precipitation stage. Moreover, the $LiAl(OH)_4$ precipitation is faster than the calcium aluminate hydrate ones and present the required crystalline structure for the nucleation of the C_2AH_8 hydrate, accelerating the cement setting.

Amongst the dispersant additives, the citric acid and diammonium citrate present the largest retarding effect.

Capturing Ca^{2+} ions by their anions decreases the concentration ratio between the Ca^{2+} and $Al(OH)_4^-$ ions, resulting in the precipitation of the most soluble hydrate. These additives were also the most efficient to be combined with the Li_2CO_3 accelerator, making the required match between workability and demolding time of the shaped body possible.

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