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ScienceDirect
Ceramics International 35 (2009) 1453–1460
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Castable matrix, additives and their role on hydraulic binder hydration

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Received 19 May 2008; received in revised form 9 July 2008; accepted 28 July 2008
Available online 30 September 2008

Abstract

The influence of alumina-based castable matrices, dispersants and Li_2CO_3 on the hydration process of different hydraulic binders was evaluated. The experiments were followed by temperature measurements with the time, the oscillatory rheometry technique and the normal force during the penetration of a blade through the material's surface. By doing these tests, the chemical features of binder hydration, working and demolding time of suspensions could be assessed. The experiments have shown that the alumina-based matrix presented an accelerating effect which is related to its sodium content. Citric acid and ammonium citrate were the dispersants with the highest delaying effect and could be effectively associated with the accelerator (Li_2CO_3) in order to adjust the setting time of the suspensions. Nonetheless, their accelerating and retarding effect varied according to the hydraulic binder.

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

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1. Introduction

Hydraulic binders generally consist of anhydrous oxides that in the presence of water form hydrated phases that impart cohesion to a shaped body. The rheological behavior and strength evolution during the hydration of castables is strongly influenced by the type of hydraulic binder and its hydration kinetics, defining their workability and demolding time, respectively.

Calcium aluminate cements (CAC) may be appointed as the most widely used refractory hydraulic binders [1]. The hydration process of their particles starts when water comes into contact with their surfaces. This step is described by the following chemical equation [2,3]:

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

The $Al(OH)_4{}^-$ ions formed impart a basic character to the suspension, as a small quantity of them dissociate into Al^{3+} and OH^- ions, setting an equilibrium given by the basic constant K_b. As a result, the pH increases, according to Eq. (2) [4]:

$$Al(OH)_4{}^- \Leftrightarrow Al^{3+} + 4OH^- \tag{2a}$$

$$K_b = \frac{[Al^{3+}][OH^-]^4}{[Al(OH)_4^-]} = 1.8 \times 10^{-2} \tag{2b}$$

The dissolution of cement anhydrous phases increases the concentrations of the Ca^{2+} and $Al(OH)_4{}^-$ ions in solution. After a while, the concentration of these ions in water reaches the solubility limit, which is followed by the precipitation of a hydrated calcium aluminate phase, allowing 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 are consumed [4,5]. The cement hydration kinetics decreases at lower temperatures, resulting in longer setting times [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

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doi:10.1016/j.ceramint.2008.07.024

among neighboring particles, which result in the so-called setting phenomenon.

Commercial calcium aluminate cements mainly consist of anhydrous phases: CA ($CaO\cdot Al_2O_3$, 40–70 wt%), CA_2 ($CaO\cdot 2Al_2O_3$, <25 wt%) and $C_{12}A_7$ ($12CaO\cdot 7Al_2O_3$, less than 3 wt%). The CA_2 phase is the most refractory and requires a long time to hydrate completely. Conversely, the $C_{12}A_7$ phase presents low refractoriness and needs a short time for hydration, and can speed up the setting time of the CA [3]. As a consequence, the higher the $C_{12}A_7$ content in the cement, the faster the saturation and precipitation of hydrates is.

The differences in the hydration process of each anhydrous phase is related to the amounts of Ca^{2+} and $Al(OH)_4^-$ they can release in a solution, which defines the hydrated phases that are generated. At 25 °C, if the concentrations of CaO and Al_2O_3 are close, the formation of the CAH_{10} ($CaO\cdot Al_2O_3\cdot 10H_2O$) is favored. The C_2AH_8 ($2CaO\cdot Al_2O_3\cdot 8H_2O$) is induced in solutions with a higher Ca^{2+} concentration, whereas for a higher content of $Al(OH)_4^-$, the formation of AH_3 prevails. However, for temperatures above 35 °C, the precipitation of C_3AH_6 is predominant. These hydrates present the following order of solubility: $C_3AH_6 < C_2AH_8 < CAH_{10} < AH_3$. The formation of less soluble hydrates will imply in an increase of the precipitation, reducing the cement setting time. In contrast, the most soluble hydrate (AH_3) requires a higher induction period [2].

Hydratable alumina is another sort of hydraulic binder, which can be used to substitute CAC cements in calcium-free castables. Such alumina-based binders are produced by the fast calcination of gibbsite, resulting in mainly ρ-alumina, among other alumina transition phases. This reactive alumina presents a high specific surface area, low crystallinity and, in the presence of water, it hydrates according to Eq. (3), setting the castable [6]:

$$\rho\text{-}Al_2O_3 + H_2O \rightarrow Al_2O_3\cdot 3H_2O + Al_2O_3\cdot(1-2)H_2O \qquad (3)$$

In the early stages of hydration, a thick layer of alumina gel is formed, which is partly converted to bohemite ($Al_2O_3\cdot(1-2)H_2O$) and mainly to bayerite ($Al_2O_3\cdot 3H_2O$). The interlinked crystals of bayerite and the gel result in a pre-firing mechanical strength to the castables by filling pores and reducing surface defects. Such crystallization also favors the formation of crystal structures in the surface of aggregates, connecting adjacent grains to the surrounding matrix [7].

The kinetics of a binder's hydration can be significantly affected by the type of hydraulic binder, matrix and additives typically used in castables. Although many papers [8–11] have shown the influence of additives on the binder hydration process, their impact on castable processing, including setting behavior (working time) and demolding time needs to be evaluated.

In this context, the aim of this work was to study the kinetics of the hydration process of different binders in the presence of additives and predict the consequences of the rheological properties and strength evolution of castables, which defines their workability range and demolding time, respectively. Temperature and normal force measurements were associated to oscillatory rheometry in order to investigate these properties in suspensions containing usual castable matrix refractory raw materials.

Table 1
Chemical compositions and physical properties of the binders studied.

Phases (%)	Alphabond 300	CA 270	Secar 71	Secar Plenium
Al_2O_3	88	73	68	82
CaO	0.1	26	31	18
SiO_2	0.3	0.3	0.8	0.3
Na_2O	0.6	0.3	0.5	0.7
25–250 °C[a]	4.5	–	–	–
250–1100 °C[a]	6.5	–	–	–
Density (g/cm^3)	3.20	3.15	2.98	3.25
BET surface area (m^2/g)	194	1.9	1.2	5.8
d_{50} (μm)	3.3	7.8	13	10

[a] Mass loss in the temperature range.

2. Materials and methods

The hydraulic binders evaluated in this work include the hydratable alumina, Alphabond 300 (Almatis, US) and calcium aluminate cements of two different suppliers: CA 270 (Almatis, US), Secar 71 and Secar Plenium (Kerneos, France). The characteristics of these binders are presented in Table 1. Different types of calcined alumina (Esy Pump 1000, A17-NE and A-1000SG, Almatis, US) were also evaluated (Table 2). 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). Lithium carbonate, Li_2CO_3 (Labsynth, Brazil) was selected as an accelerator. Different compounds were evaluated as dispersing agents: sodium polymetacrylate (Darvan-7S, Vanderbilt, 2500 g/mol), citric acid anhydrous (Labsynth, 192 g/mol), diammonium citrate (Sigma Aldrich, 226 g/mol), sodium hexametaphosphate (HMPNa, Labsynth, 612 g/mol) and the family of polyglycol polymers developed by Basf, Germany (FS20, FS30, FS40 and FS60).

A standard laboratory mixer (Ética, Brazil) was used to prepare the suspensions for all experiments. The suspensions were prepared in water heated at 50 °C and mixed for 5 min prior to each measurement.

Table 2
Chemical compositions and physical properties of the aluminas used.

Phases (%)	Esy Pump 1000	A17-NE[a]	A-1000SG[a]
Al_2O_3	99.4	99.8	99.8
CaO	–	0.02	0.02
SiO_2	0.10	0.03	0.03
Na_2O	0.30	0.10	0.07
Density (g/cm^3)	3.99	3.94	3.95
BET surface area (m^2/g)	3.3	2.9	8.4
d_{50} (μm)	2.6	4.0	0.57

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

Table 3
Additive concentrations to evaluate the setting time by means of temperature measurements as a function of time.

Binder	Dispersant (mg/m^2 of powder)	Li_2CO_3 (wt% upon the cement content)
Matrix–binder mixture	0.0	0.01, 0.02 or 0.32[a]
CA 270	0.1 and 0.9	0.01
Secar 71	0.1 and 0.9	0.01
Secar Plenium	0.1 and 0.3	0.02
Alphabond 300	0.1 and 0.3	0.32

[a] According to the binder selection.

The influence of the matrix composition on the setting time was analyzed by means of temperature measurements as a function of time for aqueous suspensions prepared with either a plain binder (16.8 vol.% solids) or with a 50 wt% mixture of binder and the different matrices (26 vol.% solids). This experiment was carried out with and without the addition of Li_2CO_3 and no dispersant was used. The influence of additives was studied for aqueous suspensions of each binder (16.8 vol.%) with different dispersant concentrations containing Li_2CO_3 or not. The additives and Li_2CO_3 concentrations used in this experiment varied according to the binder type and are shown in Table 3.

The temperatures of the suspensions 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 binder and binder–matrix suspensions and the measurements were immediately recorded. With the use of a thermal bath, the suspensions were kept at 50 °C during the heat evolution measurements because the hydration process is faster than at room temperature.

The setting behavior of Esy Pump-binder mixtures (50:50 wt%) in the presence of citric acid (0.1 mg/m^2) and Li_2CO_3 (contents presented in Table 3) was studied by means of oscillatory rheometry and normal force measurements, using a rotational rheometer RS300 (Thermo Haake, Germany) at 50 °C.

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 up to 100 Pa) and frequency (0.01 up to 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, with reduced wall effects and caused minimum disruption of the material structure during the alignment step [12,13].

The normal force tests were carried out using a methodology previously reported [14]. The suspension was split into several equal quantities, which were poured into a bowl and coated with a thin layer of oil to avoid water evaporation. The bowls were kept in an acclimatized chamber (Vötsch, model 20-20) at 50 °C until they were measured at regular time intervals. The test was carried out by inserting a blade-shaped sensor into a sample at a rate of 0.5 mm/s for 20 s, while the normal force was recorded as a function of time. The normal force rate, dF/dt, is plotted as a function of time and, when the suspension reached its maximum deformation resistance, the dF/dt value remained constant.

3. Results and discussion

3.1. Effect of matrix and accelerator on the hydration process of binders

During the hydration of the most reactive phases of calcium aluminate cement, heat is generated increasing the cement paste temperature and promoting the reaction even of the most inert phases [15]. 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 hydration of the transition aluminas is also exothermic [16]. The heating profile during the hydration process shows a first peak, related to the initial wetting of the powder, and a second one associated with the conversion of the anhydrous solid to different aluminum hydroxides [6]. Therefore, in both cases, an assessment of the temperature evolution during the hydration of hydraulic binder pastes is a useful tool to investigate the effects of the matrix and/or additives on the hydration process.

The setting times were determined by the intersection of tangents taken for the maximum slope and at the temperature peak, as depicted in Fig. 1. The results for aqueous suspensions of binders and binder–matrix in the presence of Li_2CO_3 (or not) are presented in Fig. 2.

In the absence of Li_2CO_3 (Fig. 2a), the setting times were clearly shorter for cement–matrix suspensions when compared to the plain ones (CA270 and Secar 71). The presence of the matrix reduced the induction periods because the surface of

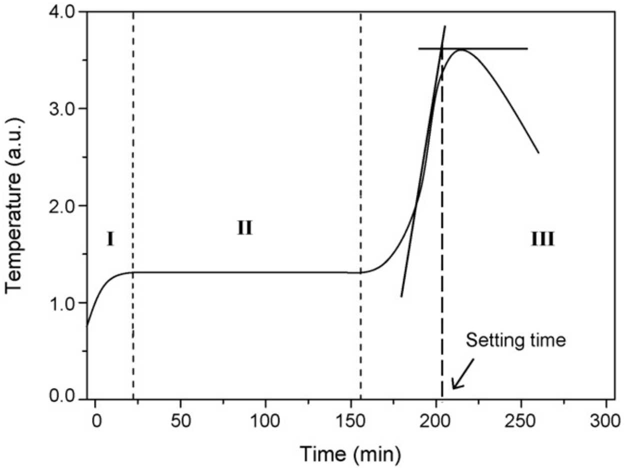

Fig. 1. Schematic representation of temperature profile in arbitrary units (a.u.) as a function of time for a CAC suspension (based on reference [15]).

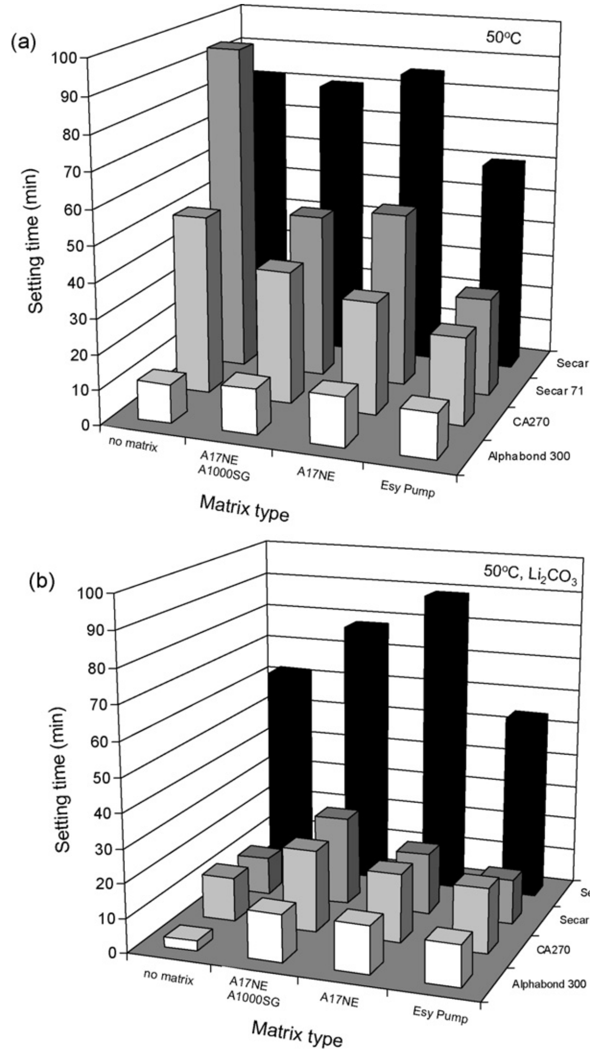

Fig. 2. Setting time evaluated by temperature measurements as a function of time for binders and binder–matrix aqueous suspensions, mixed at 50 °C: (a) no addition of Li_2CO_3 and (b) with Li_2CO_3 (CA270 and Secar 71 = 0.01 wt%, Secar Plenium = 0.02 wt%, Alphabond 300 = 0.32 wt%).

alumina particles works as nucleation sites, lowering the activation energy for hydrate nucleation [17].

Additionally, the presence of Na^+ ions on the particles' surface reduces the induction period [17] because this matrix impurity reacts with $Al(OH)_4^-$ ions and changes the $[Ca^{2+}]$:$[Al(OH)_4^-]$ ions ratio during cement dissolution. The sodium ions form $NaAl(OH)_4$ and because the relative concentration of calcium ions in solution increases, the formation of a less soluble hydrate is favored. In fact, Esy Pump alumina, which presents the highest content of sodium oxide (Table 2), showed the shortest setting time.

Nevertheless, for the suspensions containing Secar Plenium, only the addition of Esy Pump caused some reduction in the setting time, whereas suspensions prepared with Alphabond 300 were not affected by the presence of matrix for those without Li_2CO_3.

Among the calcium aluminate cements, Secar Plenium presents a lower CaO content (Table 1). In this case, AH_3 hydrates might be formed at a higher extent even with the alumina matrix. According to the literature [8,9], having the matrix addition, the formation of the less soluble hydrate (C_3AH_6 at 50 °C) should be favored and the setting time acceleration should be promoted. Nevertheless, the results show that because the concentration of calcium ions for Secar Plenium is lower when compared to the other binders used, only in the presence of Esy pump might have occurred sufficient reaction between Na^+ ions from matrix and the $Al(OH)_4^-$ ones. The formation of $NaAl(OH)_4$ promotes the increase of $[Ca^{2+}]$ in solution, inducing the precipitation of the less soluble hydrate.

The hydration process of Alphabond 300 does not involve the nucleation and growth steps. Instead, it depends strongly on the interaction between the surface area of this binder and water, so that the influence of matrix surface is negligible. Additionally, the high surface area favors its reaction with water, resulting in the shortest setting time.

In the presence of Li_2CO_3 (Fig. 2b), a considerable reduction in the setting time is observed in the presence of this additive. In fact, lithium salts are among the most used setting time additives for the castables. The great interest in these compounds is related to their efficiency, as concentrations as small as 0.01% are sufficient to impart the required accelerating effect on the cement hydration process [8,10].

Accelerating additives generally work at the hydrate precipitation stage by reducing the time required for nucleation. In the case of lithium salts, the Li^+ ions in solution lead to the formation of insoluble hydrates, such as $LiAl(OH)_4$, withdrawing $Al(OH)_4^-$ ions from the solution [8,10]. As a result, the $[Ca^{2+}]$ in solution increases, which favors the formation of calcium aluminate hydrates richer in calcium (less soluble), accelerating the precipitation stage.

The precipitation of low-solubility lithium compounds is faster than the precipitation of the calcium aluminate hydrates. Additionally, these compounds present a crystalline structure that acts as seeds for the nucleation of C_2AH_8 hydrate, at any temperature [8,10]. In other words, they decrease the energy barrier necessary for calcium aluminate hydrate formation. This mechanism also explains why the addition of Li_2CO_3 caused a considerable reduction in the setting time of CA270 and Secar 71 cements, whereas the same effect was less significant for Secar Plenium cement. Because this latter cement presents a lower CaO content (Table 1), the concentration of calcium in the solution was lower, as well as the trend to form the less soluble hydrate (C_2AH_8), as stated in the literature [8,9], when in the presence of Li_2CO_3. Therefore, the seeds that favor the precipitation of low-solubility hydrates have an effect on the setting time acceleration that is again limited by the stoichiometry of ions in solution, as observed in the matrix effect.

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 suspensions, because $Al(OH)_4^-$ ions are supplied by both, alumina and CAC. Moreover, the presence of nucleation sites is observed for both, C_2AH_8

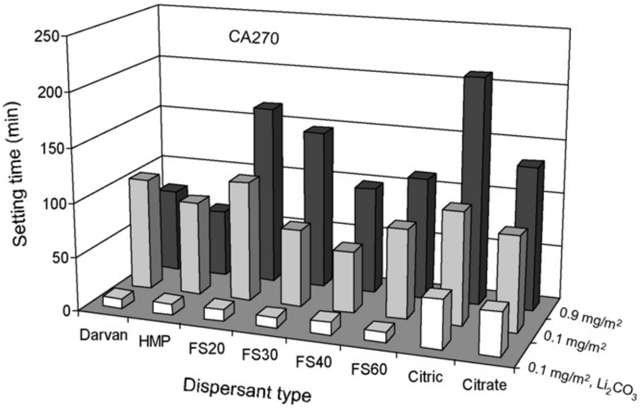

Fig. 3. Setting time at 50 °C evaluated by temperature measurements as a function of time for CA270 cement aqueous suspensions with different dispersants contents (0.1 or 0.9 mg/m^2) and with 0.1 mg/m^2 dispersant in the presence of Li_2CO_3 (0.01 wt%). For the plain CA270 suspension the setting time was 51 min.

[formed by $LiAl(OH)_4$ precipitation] and for AH_3 (due to the matrix).

3.2. The effect of additives on the hydration process of binders

The evaluation of additive effects during the consolidation of binder suspensions has received special attention in order to fit the rheological behavior and setting time of castables.

Fig. 3 presents the influence of different dispersants on the hydration of CA270, based on temperature measurements throughout time for suspensions without a matrix. In general, the addition of dispersants increased the setting time. This effect was enhanced at higher additive concentrations (0.9 mg/m^2, based on the surface of the ceramic matrix).

Chemical compounds may delay the setting time by different mechanisms [10,11]. The anions generated by these compounds in solutions are generally R–COO$^-$ and R–O$^-$ groups, which are strongly attracted by calcium ions. This characteristic has two consequences in the cement hydration process. Firstly, the reaction between these anions and Ca^{2+} generates insoluble salts in alkaline pH (pH of cement-containing media), decreasing the ratio between Ca^{2+} and $Al(OH)_4^-$ ions in solution. As a result, the nucleation and growth of hydrates is slower, because the most soluble phase (AH_3) is favored. The second consequence is related to the precipitation of these insoluble salts on cement particles surface, resulting in a barrier on the solid–liquid interface that hinders further dissolution and delays the saturation stage [10,11].

The retarding effects of citric acid and diammonium citrate were considerably higher than those by other dispersants. Both citric acid and diammonium citrate present ionizable groups which are strongly attracted by calcium ions. Meanwhile, citric acid presents a superior retarding effect that can be explained by its higher number of ionizable hydrogens, when compared to the citrate, as shown in Fig. 4.

Regarding the association of dispersants with the accelerator (Li_2CO_3), Fig. 3 shows that the setting time was slightly affected by the dispersants, except for citric acid and citrate. For these additives, a combination of the retarding (citric acid and citrate) and accelerating (Li_2CO_3) effects was detected, leading to an intermediate setting time.

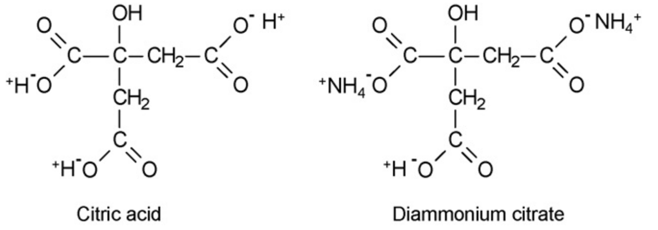

Fig. 4. Chemical structures of main additives used as retarders in the hydration process of binders.

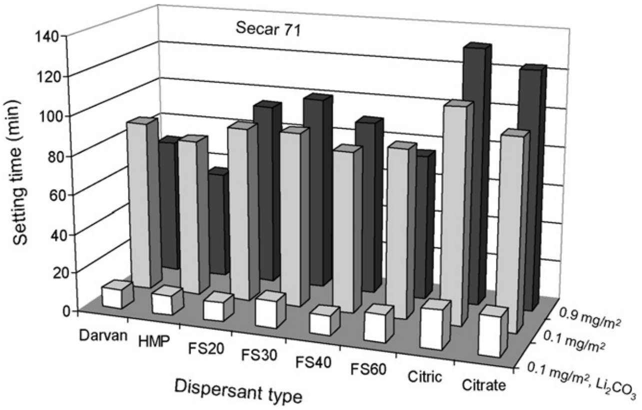

Fig. 5. Setting time at 50 °C evaluated by temperature measurements as a function of time for Secar 71 cement aqueous suspensions with different dispersants contents (0.1 or 0.9 mg/m^2) and with 0.1 mg/m^2 dispersant in the presence of Li_2CO_3 (0.01 wt%). For the plain Secar 71 suspension the setting time was 94 min.

The retarding effect of dispersants in the presence of Secar 71 and Secar Plenium was less significant than that observed for CA270, even for citric acid and citrate (Figs. 5 and 6).

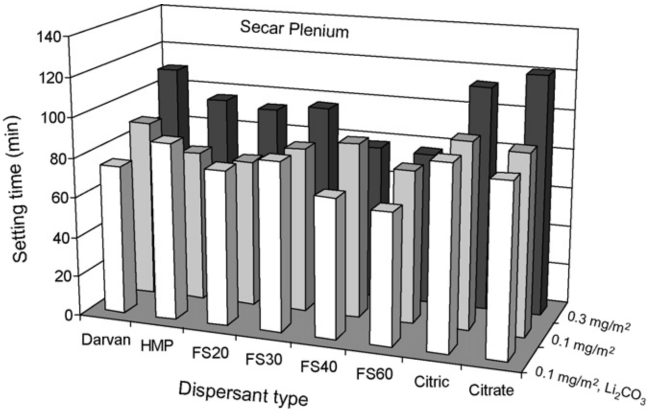

Fig. 6. Setting time at 50 °C evaluated by temperature measurements as a function of the time for Secar Plenium cement aqueous suspensions with different dispersants contents (0.1 or 0.3 mg/m^2) and with 0.1 mg/m^2 dispersant in the presence of Li_2CO_3 (0.02 wt%). For the plain Secar Plenium suspension the setting time was 81 min.

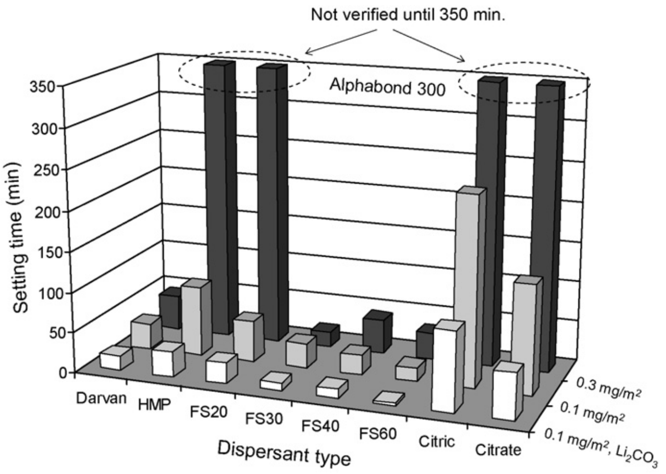

Fig. 7. Setting time at 50 °C evaluated by temperature measurement as a function of the time for Alphabond 300 aqueous suspensions with different dispersants contents (0.1 or 0.3 mg/m^2) and with 0.1 mg/m^2 dispersant in the presence of Li_2CO_3 (0.32 wt%). For the plain Alphabond 300 suspension the setting time was 11 min.

Secar 71 cement has a higher content of CaO than the CA270 one (Table 1). Although part of the Ca^{2+} supplied during the cement dissolution is strongly attracted by dispersants, the concentration of these ions in the solution is still sufficient to form low-solubility hydrates. Therefore, the retarding effect of dispersants is not as effective as for the CA270 cement.

On the other hand, Secar Plenium has a lower CaO content (Table 1), which favors the formation of high-solubility AH_3 hydrates. The fact that the ratio between the concentrations of Ca^{2+} and $Al(OH)_4{}^-$ ions in the solution changes when the dispersants are present, it has a lower influence on the formation of this hydrate than for the low-solubility ones. The accelerating effect of lithium carbonate was also reduced in this case. This behavior is more likely related to the high concentration of $Al(OH)_4{}^-$ ions supplied by this binder. Thus, the formation of insoluble hydrates, such as $LiAl(OH)_4$, only results in a slight change in the relative concentrations of Ca^{2+} and $Al(OH)_4{}^-$ ions, which is not sufficient to favor the formation of the low-solubility C_3AH_6 hydrate.

For the Alphabond 300 binder, the additives HMP-Na, FS20, citric acid and citrate, showed a higher retarding effect (Fig. 7). Nevertheless, only citric acid and citrate showed a significant retarding effect in the presence of Li_2CO_3. The efficient chemisorption of these additives on the particles' surface can explain their superior retarding effect on the hydration process of this binder.

3.3. The effect of additives in the presence of the matrix

The overall effect of additives (dispersant and accelerator) and the matrix was assessed in suspensions prepared with 50:50 wt% mixtures of Esy Pump and binder by means of oscillatory rheometry and normal force measurements.

In the oscillatory test, samples are subjected to stresses or strains applied as a sinusoidal time function [18], while viscosity and elasticity data are recorded. In this technique, samples of viscoelastic fluids and even of soft solids will be mechanically disturbed in a recoverable way and their internal structure will not break during such test [18]. It enables to differentiate between elastic and viscous responses, which are expressed by the elastic modulus (G') and by the viscous modulus (G''). G' indicates that the stress energy is temporally stored during the test, but can be recovered afterwards, whereas G'' indicates that the energy which has been applied to initiate the flow is irreversibly lost and transformed into shear heat [12]. 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 links among the particles still increases, as shown by G', until a constant $G'_{\text{equilibrium}}$ value is attained [19].

The results of oscillatory tests (Fig. 8) have confirmed the accelerating, retarding and intermediate effects of Li_2CO_3,

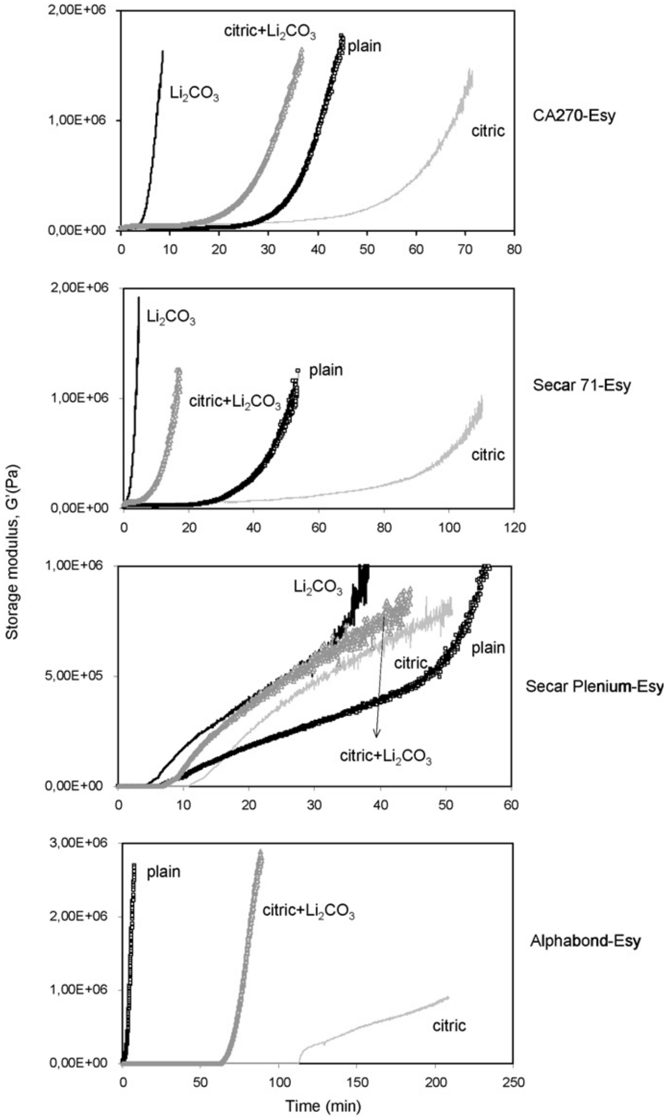

Fig. 8. Storage modulus (G') at 50 °C as a function of time for aqueous suspensions of CA270, Secar 71, Secar Plenium and Alphabond 300 binders in the presence of Esy Pump matrix (50:50 wt%), citric acid (0.1 mg/m^2) and Li_2CO_3 (0.01 or 0.02 wt% for Secar Plenium and 0.32 wt% for Alphabond 300), for plain and combined systems.

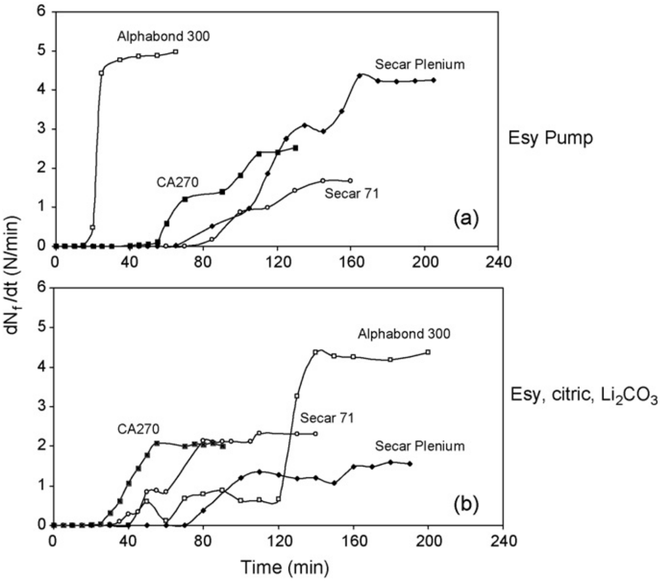

Fig. 9. Normal force rate (dN_f/dt) at 50 °C as a function of the time for CA270, Secar 71, Secar Plenium and Alphabond 300 binders suspensions in the presence of Esy Pump matrix (50:50 wt%) and Esy Pump + citric acid ($0.1\ mg/m^2$) + Li_2CO_3 (0.01 or 0.02 wt% for Secar Plenium and 0.32 wt% for Alphabond 300).

citric acid and the association of citric acid and Li_2CO_3, respectively. Additionally, only slight differences were observed during the setting of suspensions containing Secar Plenium cement and the different additives, as detected from temperature measurements.

It is important to highlight the significant difference in the setting time evaluated by means of oscillatory rheometry and temperature measurements, under the same conditions. The temperature evolution is directly related to chemical aspects of the cement hydration process. On the other hand, oscillatory rheometry points out the kinetics of suspension consolidation, which involves the solid loading and particle size distribution and is related to the workability range of the material.

Nonetheless, during the time interval where the G' value increases, the suspensions are not rigid enough for demolding, which can be observed with the help of a spatula, and after a complete setting of the sample, oscillatory measurements cannot be conducted. Thus, an additional test (normal force measurement) has to be carried out in order to assess the demolding time [14].

The normal force test consists of the measurement of the normal force (N_f) generated as a body's response to a uniaxially imposed deformation. This type of test measures the system's elasticity, as well as the oscillatory test, but not resulting, necessarily, the same sort of information, because the sample is subjected to a stationary flow [12].

This test can be used as an indicative of the deformation resistance of ceramic suspensions. There are various methods to measure this, which generally use the cone–plate or plate–plate geometries. In this work, a novel approach was used [14] 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 displacement represent the resistance to the blade-shaped sensor penetration through the sample's surface.

In this test, the influence of binders and additives on the time span necessary for suspensions to develop the resistance necessary for demolding (Fig. 9) was investigated.

In all cases, the normal force rate (dN_f/dt) increased with time after the dormant period, indicating the beginning of the suspension setting and, eventually, reaching a plateau, which could be associated with the demolding time. The setting behavior observed in this test was similar to that for the suspension consolidation in the absence of additives: Alphabond 300 promoted the setting in the shortest time, whereas for Secar Plenium the dN_f/dt increase was slower (Fig. 9a).

In the presence of additives (Fig. 9b), a predominant accelerating effect for CA 270 and Secar 71 binders was detected. On the other hand, for Alphabond 300, the retarding effect was predominant, whereas for Secar Plenium the demolding time was similar to that in the absence of additives.

Notice that the oscillatory rheometry is sensitive enough to detect the first stages of suspension setting but cannot represent the whole process. Conversely, the normal force test is more suitable when observing the final stages of the setting behavior. A better outlook of the whole process can be seen by the association of both techniques.

4. Conclusions

The experiments have shown that the induction period of cement hydration is shortened in the presence of matrix, which provide sites for the nucleation of cement hydrates and supplies Na^+ cations that most likely form the $NaAl(OH)_4$ compound. This effect is enhanced by adding Li_2CO_3, resulting in $LiAl(OH)_4$. Thus, $Al(OH)_4^-$ ions are withdrawn from the solution, increasing the $[Ca^{2+}]:[Al(OH)_4^-]$ ratio, which favors the formation of less soluble hydrates, accelerating the precipitation stage.

The additives, citric acid and diammonium citrate presented a significant retarding effect for the CA 270 binder. These additives contain $R–COO^-$ and $R–O^-$ groups, which are strongly attracted by calcium ions, decreasing the ratio between Ca^{2+} and $Al(OH)_4^-$ ions in the solution and resulting in a slower nucleation and growth of hydrates. The accelerating and retarding effects of the additives were also combined in order to obtain a balance between workability and the demolding time of the shaped body. The same retarding effects of these additives were observed for the Alphabond 300 binder due to their efficient chemisorption on the particles' surface, inhibiting their contact with water and increasing the setting time.

The temperature measurements were shown to be suitable to study the chemical characteristics of the setting process. The first changes in the suspensions' consistency were satisfactorily detected with oscillatory rheometry, indicating the working time. Finally, the normal force test provided useful information concerning the mechanical strength evolution during the consolidation process.

Acknowledgments

The authors would like to acknowledge Almatis and Kerneos for supplying the raw materials used in this work, as well as FAPESP and CNPq for the financial support and Dr. Fernando dos Santos Ortega for the useful suggestions.

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