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Role of dispersant and humidity on the setting of millimetric films of aluminous cement prepared by tape casting

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Abstract

An aluminous cement (Secar 71 from Lafarge) has been used for preparing millimetre thick films by tape casting. Slurry preparation is described. The effect of several dispersants has been studied. The optimum dispersion, associated with the minimum viscosity, is obtained with minimal amounts of dispersant in the case of acetic and propionic acids. Indeed, the corresponding quantities of dispersant are less than 0.5% by weight relative to cement. In addition to its dispersive role, acetic acid plays a role in the setting. It has a retarding effect below 1% by weight relative to the mass of cement and from this amount, it plays an accelerating role on setting. Tapes prepared with cement, water, acetic acid, PEG 300 have been left to set in different environments at 20 °C (50% or 95% relative humidity, water). The formation of aluminous calcium hydrates is most important when setting is done in water. Lastly, the advantage of setting in water is also discussed with respect to the elimination of the different organic products that have been used for tape casting.

Keywords: Aluminous cement; Dispersant; Rheological behaviour; Tape casting; Films

1. Introduction

Tape casting is a well-known ceramic process for manufacturing ceramic packages[1] and ceramic composites.[2] It has proven its capability for producing high-quality wide and thin ceramic sheets with controlled thickness and smooth surfaces. It basically consists of preparing a stable suspension composed of the ceramic powder in a solvent (aqueous or organic) which contains additives such as dispersant, binders and plasticizers.[3] This suspension is poured into a movable reservoir and deposited onto a stationary sheet of plastic film at a constant speed. The slurry spreads on the substrate to form a thin sheet. In the case of deposition of technical ceramics such as Al_2O_3,[4,5] AlN,[6] $BaTiO_3$,[7] ZrO_2,[8] SiAlON[9] or composite materials,[10] the next stages after deposition are a heat treatment at a moderate temperature to remove organic additives followed by a high temperature treatment to sinter the material. These steps when not well controlled can have detrimental consequences on the quality of the final ceramic tape.[11]

In the present study, we have explored the possibility to apply tape casting for preparing thick films of cements and more specifically aluminous cement.[12,13] These materials show a good durability in aggressive environments and can be used for refractory applications. In this respect, the interest in making tapes with aluminous cements is that it could ultimately be applied to manufacture composite materials with a mineral matrix of low cost and that could be used up to 1000 °C in an oxidizing atmosphere. The first part of the paper is dedicated to a general background about the role of the constituents which are chosen for slurry compositions deposited by tape casting. After a presentation of the raw materials and the different experimental techniques, the second part is devoted to the characterization of different dispersants followed by a presentation of the tested compositions. Lastly, we focus on the consolidation of the cement tapes in different environmental conditions.

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2. Slurry composition

As in the case of other ceramic processes, the microstructure and the performance of the final product are controlled by the physical characteristics of the starting powder,[14] namely particle size and distribution, specific surface area and particle shape. For some specific applications such as electronic components, the chemical composition and in particular the impurity content also plays a role. Usually, the particle size and the specific surface area range between 1 and 4 μm, 2 and 6 $m^2 g^{-1}$, respectively, for films with a thickness of the order a hundred microns. In the case of cement, the average particle size ranges between 1 and 100 μm with an average value around 10 μm. This is suited for the deposition of millimetre thick films.

The role of the solvent is to ensure the solubilization of the different additives. Organic solvents are often mentioned in the literature amongst which we can quote alcohols or ketones. The physical characteristics which are of interest for tape casting are their low viscosity, their low surface tension, which is appropriate for wetting of the grains, or their high vapour pressure. However, these solvents can be toxic and inflammable. In our case, i.e. tape casting of cements, we have a slight economical advantage since we use water as a solvent. On top of its role of solubilization of the different organic products, it will be involved in the hydration reaction. The next important constituent for tape casting is the dispersant. It is necessary to obtain a good de-agglomeration and dispersion of the solid particles in the solvent, to stabilize the suspensions with a high solid over organic additives ratio.[15] A stable dispersion leads to a dense packing and to a homogeneous microstructure. The dispersant usually interacts with the surface of the solid particles and two mechanisms can provide repulsive forces between particles: electrostatic and/or steric stabilization. The choice of the most appropriate dispersant can be accomplished through viscosity measurements and a sedimentation test.[16]

The binder ensures that the green tape has sufficient strength for handling and subsequent processing steps. It consists of polymers that adsorb at the surface of solid particles and ensure bridging between them. The basic requirements are the following: compatibility with the system, efficiency at low concentration, a low glassy transition temperature in order not to increase excessively the viscosity, little or no tendency to adhere strongly to the tape casting support, ease in elimination, usually through pyrolysis. Amongst the frequently used binders in aqueous or organic suspensions, we can quote acrylic polymers such as ammonium polyacrylate and its derivatives. In our case we did not use any organic binder, as water plays this role by hydrate formation with particles of cement. Many studies have been made around the hydration reactions of CA ($CaO{\cdot}Al_2O_3$)[d], the main phase of an aluminous cement.[17–21] The hydration products of CA to short deadlines differ depending on the temperature of the environment. At a relatively low temperature (below 15 °C), CA gives rise mainly to hydrated calcium aluminate hexagonal metastable, CAH_{10}, according to reaction (1):

Table 1
Composition of the aluminous cement, Secar 71.

Constituent	Weight percentages (%)
Mineralogical phases	
CA	56
CA_2	38
$C_{12}A_7$	<1
A	6
Oxide	
C	28
A	72

$$CA + 10H \rightarrow CAH_{10} \quad (1)$$

For medium temperatures (between 15 and 30 °C), the metastable hydrate that forms is C_2AH_8, according to the reaction (2):

$$2CA + 11H \rightarrow C_2AH_8 + AH_3 \quad (2)$$

Above 30 °C, the cubic stable hydrate, C_3AH_6, which is formed according to reaction (3):

$$3CA + 12H \rightarrow C_3AH_6 + 2AH_3 \quad (3)$$

Plasticizers are often used with binders. They are low molecular weight molecules which lower the glassy transition temperature of the binder to room temperature or below, leading to a better plasticity. Glycols like polyethylene glycol (PEG) are commonly used plasticizers.[3,9] Some other constituents such as antifoaming and preservative agents can also be added.

Preparation of slurries is usually carried out in two stages, firstly a de-agglomeration and dispersion stage of the powder in the solvent with the aid of the dispersant, and secondly a homogenization of the slurry with binders and platicizers. In order to have the best effectiveness, the dispersant is introduced first in the slurry thus avoiding any competition with the other components. Several examples of slurry compositions for preparing ceramic components are given in the literature.[22–25] To our knowledge, there is no preparation of slurries for cement tape casting described in the bibliography.

3. Raw materials and experimental procedure

The starting material is an anhydrous aluminous cement (Secar 71 from Lafarge). The principal mineralogical phases are the monocalcium aluminate $CaO{\cdot}Al_2O_3$ (noted CA) and the calcium bialuminate $CaO{\cdot}2Al_2O_3$ (noted CA_2), as shown in Table 1. The initial material has a particle size that ranges between 1 and 100 μm with d_{50} around 10 microns. To reduce the particle size in order to make it suitable for the tape casting process, we studied the effect of attrition milling that we then compared with a simple sieving. In Fig. 1 are represented size distribution curves of aluminous cement Secar 71: (i) initial cement powder (◆); (ii) cement grinded by attrition (▲) and (iii) cement sieved below 40 microns (■). The grinding was

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[d] In the following, CaO, Al_2O_3, and H_2O are noted according to cementitous terminology C, A, and H.

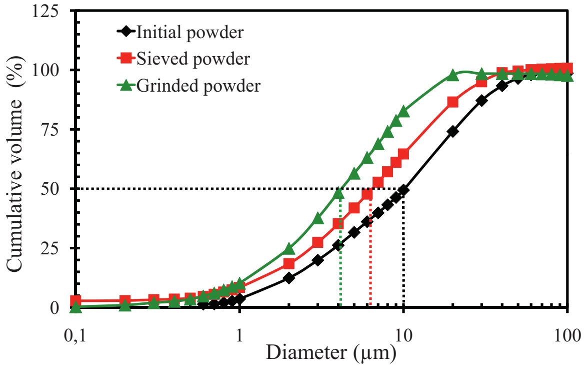


Fig. 1. Particle size distribution of initial powder (♦), cement sieved below 40 microns (■) and cement grinded by attrition (▲).

Table 2
Organic additives tested in the present study with their role.

Constituent	Function	Percentages[a] (%)
Cement (Secar 71)	Powder	–
Water	Solvent/binder	33–35
Bevaloid 35L	Dispersant	0.05–2
PEG 300	Plasticizer	4–8
HOAc	Dispersant	0.3–2

[a] Weight percentages relative to the mass of cement.

carried out in a Teflon jar with 2-propanol as a solvent and in the presence of alumina beads with a size between 0.5 and 1.5 mm (volume distribution: 2/9 balls, 2/9 cement, 2/9 solvent, 1/3 empty). Total time of attrition is 5 h. We find that the value of d_{50} in both cases, of particles sieved at 40 microns and of particles grinded by attrition for 5 h, are respectively equal to 6.4 and 4.1 µm. Moreover, the size distribution curves are slightly different. Only fresh lots are used and once a bag is open, it is kept at 20 °C in a dry atmosphere. It should be noted that the initial powder and the sieved powder tend behave in a similar manner in the presence of an accelerating agent. Table 2 gives the different organic additives that have been tested in this study. The chosen plasticizer is PEG 300, with weight percentages relative to the mass of cement between 4 and 8%; no binder has been added since water itself can play this role. Among the dispersant studied, we chose two: acetic acid, HOAc (PROLABO, France) and Bevaloid 35L (Rhodia, UK). The physical chemistry characterizations of different additives are given in Table 3. The efficiency of a given dispersant has been tested with the sediment volume test.[26] It consists in the observation of the sediment behaviour when the cement is mixed with water containing the dispersant. When the system is flocculated, particles fall rapidly and a loosely packed sediment is observed. On the contrary, when the system is well dispersed, particles settle into a tightly packed sediment. Therefore, the sediment height is inversely related to the dispersiveness of the liquid and the more dispersed the system is, the smaller the sediment volume will be. In the present case, the tested suspensions consist of 3 g of cement, 16 g of deionized water containing increasing quantities of dispersant ($w_{\text{dispersant}}/w_{\text{cement}} = 0, 0.001, 0.005$ and 0.02). Once the powder is poured into the test tube (diameter: 1.5 mm), it is de-agglomerated by ultrasonic treatment for 10 min and left to settle afterwards.

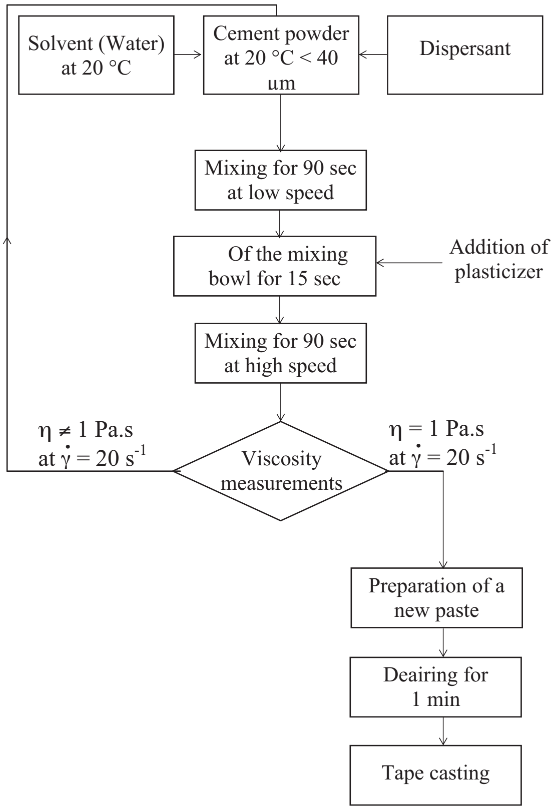


Fig. 2. Description of the preparation of the cement slurry.

Slurries were prepared using a procedure similar to the one described by Chappuis.[27] The procedure is summarized in Fig. 2. Cement pastes are prepared by mixing cement with de-ionized water containing the dispersant at 20 °C for 90 s in a laboratory mixer at a medium speed (Kenwood mixer with a vertical paddle

Table 3
The physical chemistry characteristics of organic products used as additives.

Product	Type of product	Molecular weight ($g\,mol^{-1}$)	Density	pH	Viscosity dynamique (mPa·s)
PEG 300	Polyethylene glycol	300	1.13	–	80–105 (20 °C)
Formic acid 98%	Carboxylic acid	46.03	1.22	–	1.8 (20 °C)
Acetic acid 90%	Carboxylic acid	60.05	1.05	–	–
Propionic acid	Carboxylic acid	74.08	0.99	2.5–100 g/l (20 °C)	1.02 (25 °C)
Bevaloid 35	Sodium salt of a condensed naphthalene sulphonate	–	0.53	–	–
Rhodoline DP 111	Aqueous solution of sodium carboxylate	–	1.05–1.14	9.5–11.5	30–238 (25 °C)
Darvan C	Polyacrylate derivatives	–	1.1–1.2	7.5–9	28–75 (25 °C)

having an eccentric movement). It is stopped for 15 s during which the paste that is stuck on the edges of the mixing bowl is removed and put back with the rest. The addition of organic products is done during this time spell. The paste is mixed again at high speed for 90 s. Then the paste is poured into the viscometer for rheological characterization. Shear stress, τ, versus shear rate, $\dot{\gamma}$, curves are obtained at 20 °C on these slurries using a concentric cylinder rotational viscometer (Haake-Viscotester VT550). The device of the apparatus used is MV2, characterized by a gap of 2.55 mm between the concentric cylinders. The rotor has smooth walls. The apparent viscosity, $\eta_{\exp}$, was determined experimentally at every point of the curve using Eq. (4):

$$\eta_{\exp} = \frac{\tau}{\dot{\gamma}} \quad (4)$$

The measurement cycle consists of increasing $\dot{\gamma}$ from 0.1 up to 100 or 400 s^{-1} during 30 s or 2 min, respectively, and the slurry is left under the maximum shear rate for 30 s. $\dot{\gamma}$ is then decreased to 0.1 s^{-1} during the same duration as for the increase. When the paste presents a rheofluidizing behaviour and has an appropriate apparent viscosity for the tape casting process, i.e. 1–3 Pa·s under a shear rate of 20 s^{-1} a new lot of paste is prepared according to the procedure described in Fig. 1 and de-gazed by a slow rotation on rollers for about 60 s.[13] This is well known for preventing any entrapped bubbles in the green sheet.[28] Then, these paste de-gazed is used for casting tape with thickness of 1 mm and a surface (10 cm wide × 100 cm long).

Lastly, thermal characterizations on set samples have been done with a DTA-TG coupled RIGAKU thermoflex; each experiment has been done on 50 mg of product under dry nitrogen with a heating ramp of 10 °C/min. The reference material is a calcined alumina from PROLABO.

4. Choice of dispersant

Many products have been tested, namely: (i) two polyacrylate derivatives: Darvan C (RT Vanderbilt Company, Inc., USA) and Lomar DLSF (Cognis, France); (ii) two sulphonate: Bevaloid 35 (Rhodia, UK) and Bevaloid 35L (Rhodia, UK); (iii) a solution of sodium carboxylate: Rhodoline DP 111 (Rhodia, UK); (iv) three carboxylic acids namely formic, acetic and propionic (PROLABO, France). The physical chemistry characterizations of different additives are given in Table 3. Concerning the sediment volume test with the dispersants, we notice that just after the ultrasonic treatment, all the suspensions look homogeneous. Differences are noticeable between 10 and 30 min and well marked after 2 h. Fig. 3 presents the sediment height as a function of $w_{\text{dispersant}}/w_{\text{cement}}$ and for the different dispersants. For the reference sample ($w_{\text{dispersant}}/w_{\text{cement}} = 0$), the sediment height is maximum and equal to 3.25 cm and there is almost no change in this value when $w_{\text{dispersant}}/w_{\text{cement}} = 0.001$. For $w_{\text{dispersant}}/w_{\text{cement}} = 0.005$ and 0.02, the five products that reduce significantly the sediment height are the three carboxylic acids (formic acid, acetic acid and propionic acid), Bevaloïd 35L and Darvan C. Acetic acid leads to the smallest height. It can also be mentioned that for these five products it was necessary to wait for 1 h before a distinguishable frontier could be seen between the powder and the liquid. Rheological characterizations of cement pastes prepared with increasing quantities of these dispersants have been carried out. Fig. 4 shows the variations of the apparent viscosity, $\eta_{\exp}$, determined at $\dot{\gamma} = 20\,\mathrm{s}^{-1}$. The best dispersion, which corresponds to a minimum value of viscosity, is obtained with propionic and acetic acids. The corresponding dispersant content is also very low since $w_{\text{dispersant}}/w_{\text{cement}} = 0.005$. An identical quantity of formic acid permits to get a minimum viscosity but with a value that is higher than in the case of the other two acids. With Bevaloïd 35L and Darvan C, the minimum viscosities are reached for $w_{\text{dispersant}}/w_{\text{cement}} = 0.01$ and 0.04, respectively, which is greater than with the carboxylic acids. If we examine the cases of acetic and propionic acids, the first acid permits to maintain a low viscosity level in a larger range of content than the other. Therefore, amongst the different products, acetic acid looks like one of the most efficient dispersing agent. Bevaloïd 35L is also of interest because the sediment height is comparable to that obtained with acetic acid (Fig. 3) and also because the viscosities remain close to the one of acetic acid slurries (Fig. 4).

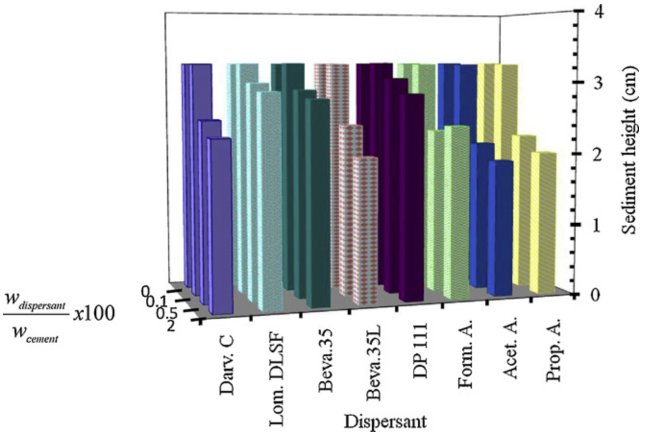


Fig. 3. Variations of sediment height, measured 2 h after ultrasonic treatment, for the different dispersants and for $w_{\text{dispersant}}/w_{\text{cement}} = 0$, 0.001, 0.005 and 0.02.

In a previous paper,[29] we have shown that on top of its dispersing effect, acetic acid can either have a retarding or accelerating effect on cement setting. In fact, the phenomena that occur when

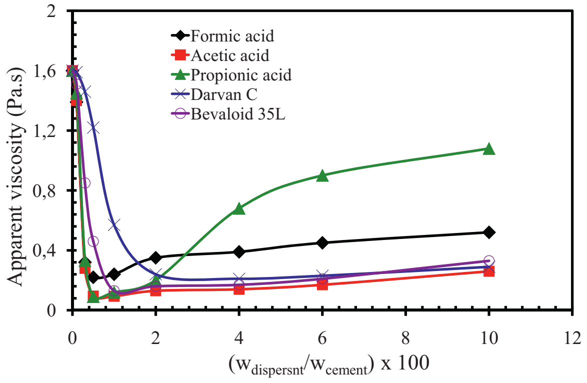
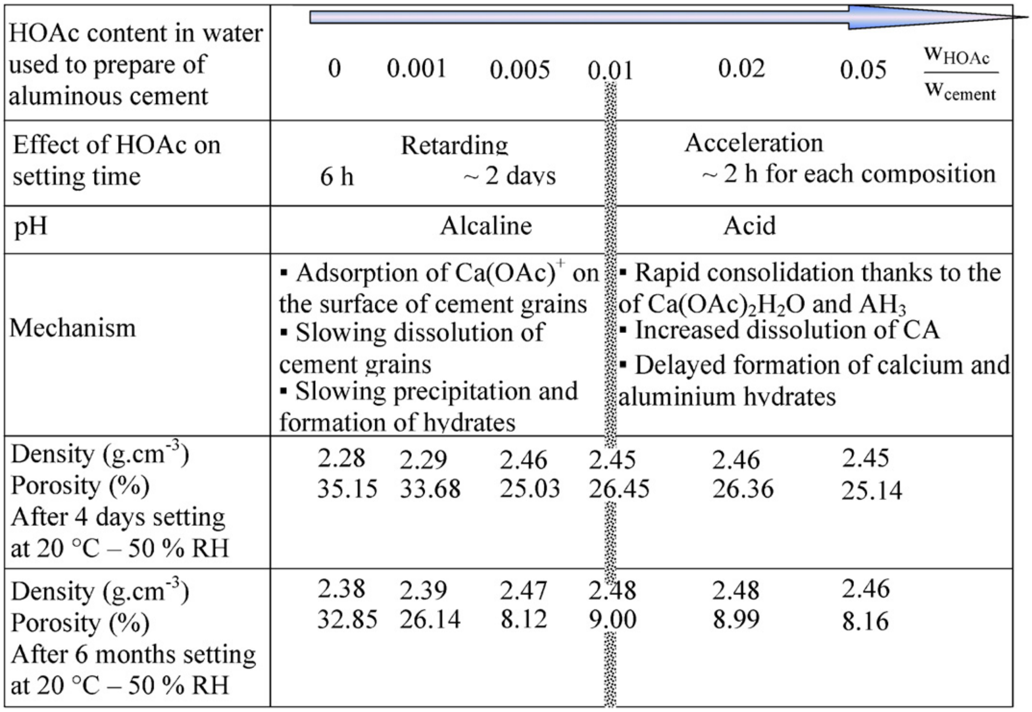


Fig. 4. Apparent viscosity, $\eta_{\exp}$ (in Pa·s), calculated from the $\tau - \dot{\gamma}$ curves for $\dot{\gamma} = 20\ \mathrm{s}^{-1}$. Case cement pastes prepared with a water over cement weight ratio, $w_{\text{water}}/w_{\text{cement}}$, equal to 0.3 and where the water contains increasing quantities of the five tested dispersants.



HOAc content in water used to prepare of aluminous cement	0	0.001	0.005	0.01	0.02	0.05	$\frac{W_{HOAc}}{W_{cement}}$
Effect of HOAc on setting time	Retarding 6 h ~ 2 days			Acceleration ~ 2 h for each composition			
pH	Alcaline			Acid			
Mechanism	▪ Adsorption of $Ca(OAc)^+$ on the surface of cement grains ▪ Slowing dissolution of cement grains ▪ Slowing precipitation and formation of hydrates			▪ Rapid consolidation thanks to the of $Ca(OAc)_2H_2O$ and AH_3 ▪ Increased dissolution of CA ▪ Delayed formation of calcium and aluminium hydrates			
Density ($g.cm^{-3}$) Porosity (%) After 4 days setting at 20 °C – 50 % RH	2.28 35.15	2.29 33.68	2.46 25.03	2.45 26.45	2.46 26.36	2.45 25.14	
Density ($g.cm^{-3}$) Porosity (%) After 6 months setting at 20 °C – 50 % RH	2.38 32.85	2.39 26.14	2.47 8.12	2.48 9.00	2.48 8.99	2.46 8.16	

Fig. 5. Role of HOAc on the setting behaviour of aluminous cement.

HOAc is present have been explained for bulk cement specimens prepared with only water containing increasing quantities of HOAc and left to set at 20 °C and 95% relative humidity and are summarized in Fig. 5. While the beginning of setting for a reference sample, with no HOAc, is equal to 6 h, this time is 43 h when the paste contains 0.1 wt% of HOAc. This delay of the sitting increases and reaches 52 h with a weight percentage of HOAc equal to 0.5%. It then falls sharply to reach 2 h with 1 wt% of HOAc. Beyond this percentage, this time remains fairly unchanged. The retarding effect of HAOc is due to the adsorption of cationic species, especially calcium acetate complex $CaOAc^+$ at the surface of CA particles; this delays the dissolution reaction. The accelerating effect has been interpreted by the rapid consolidation of the cement particles with calcium acetates $Ca(OAc)_2{\cdot}H_2O$ and AH_3. We have also noticed in that case that the addition of HOAc has a densifying effect on the cement.[30]

5. Preparation of slurries for tape casting

Table 4 gives the compositions of the different batches that have been prepared. We have also qualified given the solid and volume loading of the slurries.[13] It is a parameter that is commonly used in the tape casting process.[31] Fig. 6 presents two typical rheological curves that are characteristic of our different compositions. Some show a Newtonian behaviour (Fig. 6a), others are rheofluidizing slurries (Fig. 6b). In order to simulate these curves, we have applied Ostwald's power law:[32]

$$\tau = K\dot{\gamma}^n \tag{5}$$

K is the consistency index and n expresses the deviation from Newtonian behaviour. n is a coefficient equal to 1 or lower than 1 for a Newtonian or a rheofluidizing fluid, respectively. According to this law, the apparent viscosity calculated, η_{calc}, is given by

$$\eta_{calc} = \frac{\tau}{\dot{\gamma}} = \frac{K}{\dot{\gamma}^{(1-n)}} \tag{6}$$

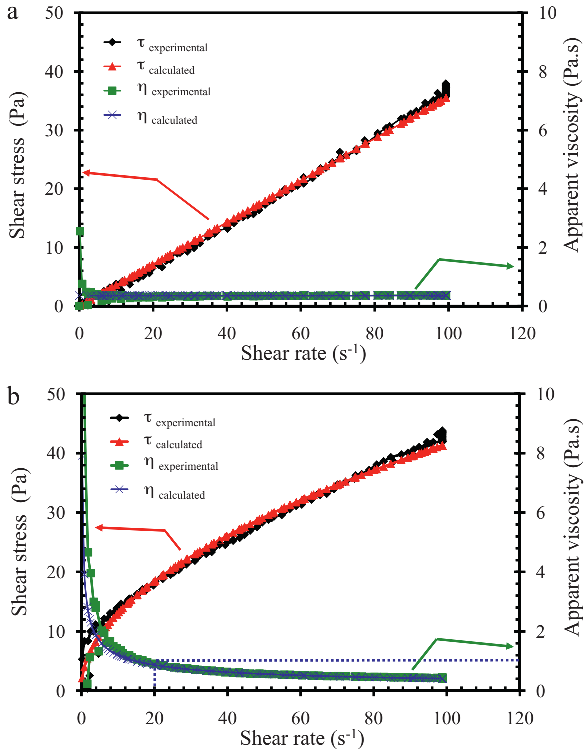


Fig. 6. Typical rheological curves obtained on the tested composition: (a) case of composition 5 and (b) case of composition 1.

Table 4
Weight percentages with respect to cement and with respect to all the constituents for the different batch compositions.

Composition	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6	Comp. 7
% of Water	33	33	35	33	33	33	33
% of Bevaloid 35L	0.1	2	0.1	0.1	–	0.5	0.1
% of PEG 300	4	4	4	8	1	4	8
% of HOAc	2	0.1	2	2	2	0.8	0.3

Table 5
Parameters deduced from Ostwald's power law applied to the experimental rheological curves obtained on the different compositions. η_{exp} and η_{calc} correspond to values at $\dot{\gamma} = 20\ \mathrm{s}^{-1}$.

Composition	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6	Comp. 7
n	0.52	0.51	1	0.74	1	0.56	0.46
K	3.83	3.71	0.29	0.77	0.36	3.24	12.62
$\eta_{experimental}$ (Pa·s)	0.91	0.92	0.28	0.43	0.31	0.93	2.63
$\eta_{calculated}$ (Pa·s)	0.89	0.89	0.29	0.39	0.35	0.90	2.57

It should be noted that the simulated curves fit experimental curve (Fig. 6) except for the lowest shear rates ($<10\,\mathrm{s}^{-1}$). Table 5 summarizes the parameters used for fitting the rheological curves for the different batches. We focus more specifically to the values of viscosity for $\dot{\gamma} = 20\,\mathrm{s}^{-1}$, value used for casting. Since K and η are directly connected, the discussion will focus on n and η.

(i) $n = 1$ *and* $\eta < 1$ *Pa·s (compositions 3 and 5)*

This corresponds to a Newtonian behaviour. Composition 3 is the one which has the highest water content (Table 4). Composition 5 has the lowest plasticizer content and a high quantity of HOAc. It could be the dispersing effect of HOAc that leads to a Newtonian behaviour. In any case, these two compositions are not suited for tape casting since $n = 1$ and η is too low.

(ii) $n < 1$ *and* $\eta < 1$ *Pa·s (composition 4)*

Though this slurry has a rheofluidizing behaviour, its viscosity is too low, probably due to the high content of plasticizer (Table 4). Again, this is not adapted for tape casting.

(iii) $n < 1$ *and* $\eta \approx 1$–2.6 *Pa·s (compositions 1, 2, 6 and 7)*

Composition 1 presents a rheofluidizing behaviour and a viscosity value that is appropriate for tape casting. The permutation between HOAc and Bevaloïd 35L (composition 2) leads to a slurry with similar Ostwald's parameters. In composition 6 where the quantities of HOAc and Bevaloïd 35L have been respectively decreased and increased, there is also a rheofluidizing behaviour. Lastly, composition 7 is the most viscous slurry. Despite its low loading – amount of liquid greater than that of the solid – this slurry presents the highest consistency, that can be explained by a low total content of dispersant (i.e. Bevaloïd 35L and HOAc).

For reference, Fig. 7 shows the rheological curve of a cement paste without organic additives. The paste was prepared with a water over cement weight ratio, w_{water}/w_{cement}, equal to 0.4. There is a thixotropic behaviour, which is not appropriate to tape casting.

6. Consolidation of cement tapes

6.1. Comparison between compositions containing percentages of HOAc having either an accelerating or retarding effect on setting

Only composition 1 containing a high amount of HOAc ($w_{HOAc}/w_{cement} = 0.02$), with an accelerating effect, allows the bands to hydrate and set. The bands containing small amounts of HOAc, with retarding effect, such as $w_{HOAc}/w_{cement} = 0.001$, 0.008 and 0.003 (compositions 2, 6 and 7, respectively), are not setting. For the compositions 3, 4 and 5, because of their low viscosity, tape casting is not possible.

We sought to characterize the difference between a composition that hardens to a composition that does not harden. We studied the compositions 1 and 7. We have also casted a cement paste without any organic additive. Though this batch

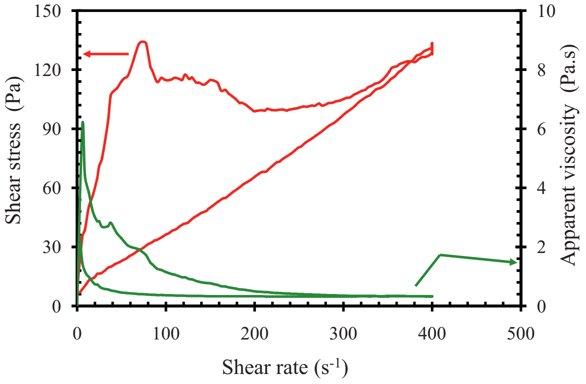


Fig. 7. Variation of the shear stress and apparent viscosity as a function of shear rate for a cement paste prepared with a water over cement weight ratio, w_{water}/w_{cement}, equal to 0.4.

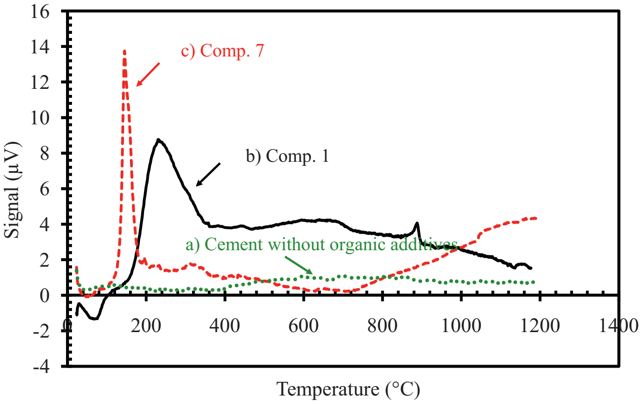


Fig. 8. DTA curves for tapes prepared from: (a) cement alone ($w_{water}/w_{cement} = 0.6$), (b) composition 1 and (c) composition 7.

is not quite suited for tape casting since it has a thixotropic behaviour, the aim of this preparation was to have a cement sample, as reference, with the same thickness (≈1 mm) and surface (10 cm wide × 100 cm long) as the tapes prepared from slurries 1 and 7. Fig. 8 presents the DTA curves obtained on these three compositions after 4 days storage at 20 °C and 50% relative humidity.

The cement tape does not present any event by DTA. Composition 7 is characterized by a narrow exothermal peak between 120 and 180 °C. Composition 1 shows three peaks: one endothermal peak between 40 and 100 °C followed by two exothermal events, a first one that starts at 120 °C and that is relatively broad, and a second one around 900 °C. According to the literature, the first endothermal event is associated to the departure of the free water,[33] the exothermal peak recorded from 120 °C is due to the combustion of organic products that have been used in the tape process, and the one at 900 °C is due to the recrystallization of CA[33] from hydrates. Since this last peak is not present in the cement tape or in composition 7, it means that no hydrates have formed in both cases in these environmental conditions (20 °C – 50% R.H.). In fact, we noticed that water vaporized from the tape before its setting could occur. As we have also shown in another paper,[29] setting of a composition that contains a low percentage of HOAc (as in composition 7) is very long, even if the samples are left to cure in 95% R.H. (Fig. 5). On the contrary, for a composition containing more HOAc (as in composition 1), we have a short setting time, 2 h at 95% relative humidity (Fig. 5).

To verify that the exothermic peak is related to combustion of organic additives, a DTA analysis was performed on a mixture of 2 g of HOAc and 4 g of PEG 300, which represents the essential of the organic additives in the studied compositions. The thermal analysis (Fig. 9) shows that we have an intense exothermic peak between 200 and 350 °C and a less intense peak around 100 °C. The exothermic peak therefore characterized the decomposition of organic products. The endothermic peak is related to the departure of the dilution water of HOAc, since the acetic acid which is used has a concentration of 90%, and thus contains 10% water.

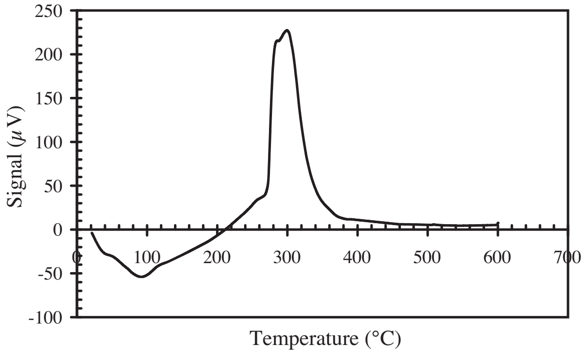


Fig. 9. DTA curves for organic products (liquid mixture of 2 g of HOAc and 4 g of PEG 300).

6.2. Influence of the environment on the hardening of composition 1

Tapes manufactured from composition 1 have been stored in three different environments: (i) 2 h after casting, a tape has been immerged in water at 20 °C (Environment 1: E1), (ii) immediately after casting, a tape has been stored at 20 °C and 95% relative humidity (Environment 2: E2), (iii) a tape is left to set at 20 °C and 50% relative humidity (Environment 3: E3). In each case, the cement tape becomes hard 2 h after mixing the constituents. The same storage conditions have been applied to a cement tape containing no organic additive. The corresponding DTA curves for these two sets of samples are presented in Fig. 10. With respect to the cement tape which has been left to set in water (E1 on Fig. 8a) or at 20 °C – 95% R.H. (E2 on Fig. 10a), there are two endothermal peaks between 40–180 °C and 220–300 °C followed by an exothermal event between 900 and 960 °C. They correspond, respectively, to the decomposition of CAH_{10} and C_2AH_8 (40–180 °C), to the decomposition of gibbsite AH_3 (220–300 °C), and the recrystallization of CA (900–960 °C).[34–37] Consequently, environments E1 and E2 enable hydration to occur, while environment E3 does not as shown earlier.

For composition 1 left in water (E1 on Fig. 10b), we notice two of the peaks mentioned above but with reduced areas. If the environment is 20 °C – 95% R.H. (E2 on Fig. 10b) or air (E3 on Fig. 10b), there is an exothermal peak due to the decomposition of organic additives. This peak does not exist when setting is done in water. Organic matter has been eliminated by a driving force which is the osmotic pressure.[38] In other words, elimination of the organic additives is a much simpler operation than in the case of tapes of technical ceramics since a simple immersion in water is sufficient to get rid at room temperature of all the organic products.

The last interesting information that can be extracted from these different DTA curves is the area of the endothermal peak around 900 °C estimated from a procedure described in Ref.[39] Table 6 presents the areas for the two cases (cement and composition 1) under different storage conditions. If we assume in a first approximation that the area is proportional to the quantity of hydrates, we can tell that for cement alone, these quantities are fairly similar in environment E1 and E2. In the case of

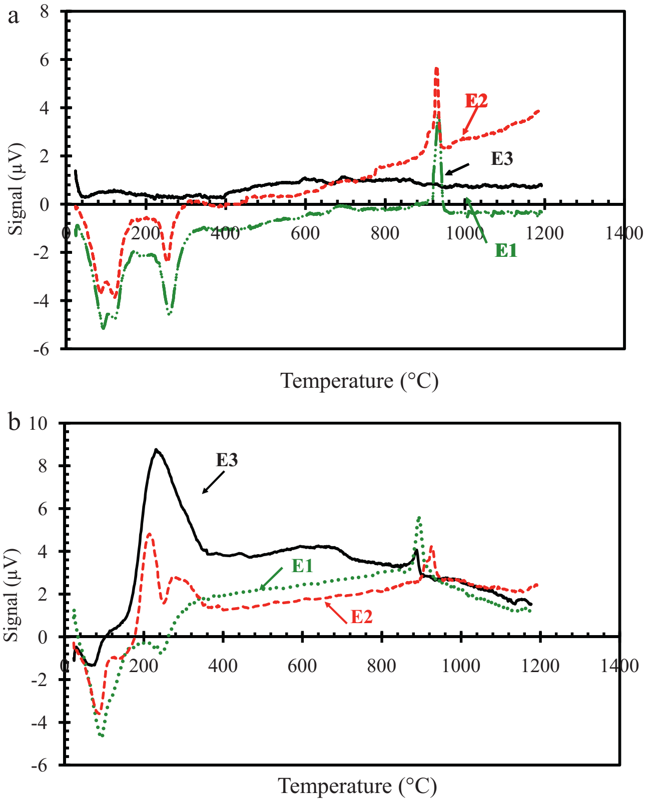


Fig. 10. DTA curves for (a) cement tape and (b) composition 1 stored in different environments: water (E1), 20 °C and 95% relative humidity (E2), 20 °C and 50% relative humidity (E3).

Table 6
Areas of the peak recorded around 900 °C by DTA on the cement tape and on composition 1 that have been left to set in different environments: water (E1), 20 °C and 95% relative humidity (E2), 20 °C and 50% relative humidity (E3).

Environment	Cement tape	Comp. 1
E1	14.0	13.3
E2	13.2	5.9
E3	0	2.6

composition 1, there is always hydration but the quantity of formed hydrates increases with the humidity. When left in environment E3, we notice that less hydrates are formed than in environment E2 and E1.[13]

7. Conclusion

Millimetric thick films of aluminous cement have been deposited by tape casting. The starting cement needs to be fresh and sieved to have particles <40 µm. Different slurries have been prepared. The one that has been selected contains water, Bevaloïd 35L, PEG 300 and acetic acid. The weight percentage with respect to cement is equal to 33, 0.1, 4 and 2%, respectively. Hardening of the tapes has been tested in different environments: water at 20 °C, air at 20 °C and 95 or 50% relative humidity. In each case, hardening starts 2 h after casting. The quantity of formed aluminium and calcium hydrates increases with the surrounding humidity. Lastly, consolidation in water presents a major advantage since it permits to eliminate the organic products used for tape casting by a driving force which is the osmotic pressure. Water also promotes the hydration of the cement.

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