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Effects of flaxseed mucilage and water-to-cement ratio on the characteristics of an OPC mortar

Haris Brevet^{1,2}, Emmanuel Petit-Laiguel², Adeline Goullieux^{1,*}

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Abstract

Biobased mortars are gaining interest because of the opportunity to upgrade agricultural byproducts and to reduce the environmental impact of cementitious materials. However, to overcome the drawbacks linked to the use of flax byproducts, such as mucilage and its hygroscopy, it's necessary to study the impact of the water-to-cement ratio and the addition of mucilage on mortars. The W/C ratios range from 0.5 to 0.8 and the mucilage is added anhydrous with cement or pre-dissolved in the water. High W/C ratios affect both fresh and hardened properties of mortars. A high ratio accelerates the setting process and generates more heat released on unmodified mortars while decreasing the induction period. Conversely, when mucilage is added, the setting time is increased due to a poisoning effect affecting the hydrate growth by a chemisorption mechanism on Ca^{2+} . This delay is higher as the W/C ratio increases and the mucilage is in-solution. Anhydrous mucilage accelerates the setting until the highest water content is reached. The undissolved polysaccharides of the mucilage cannot impact the hydration process at a W/C ratio below 0.8. Increasing the water content is beneficial for the mortar strength but an excessive W/C ratio is harmful for the unmodified mortar. Mucilage polysaccharides generate a lack of strength compared to the standard. This reduction in strengths is lowered in flexural tests due to an elastic behavior conferred by the mucilage. The changes in properties are not correlated to any mineralogical modification as shown by FTIR and TGA analyses.

Keywords: *Portland cement, polysaccharides, flaxseed mucilage, W/C ratio, hydration, mechanical strength*

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1. Introduction

The use of agricultural resources in the cementitious material field is a way to upgrade renewable byproducts or waste and to limit the environmental impact of the concretes and mortars developed. These organic resources impact materials' properties and behavior; so it is important to optimize their formulation. In the literature, the addition of plant mucilages and gums into a cementitious matrix was related to the extraction of *Opuntia Ficus Indica* (OFI) which is of specific interest. Chandra et al. [1] reported that the incorporation of the OFI extract increases the plasticity of the cement paste with a consequent decrease in water absorption by the mortar and an improved freeze-thaw resistance of the mortar. Other authors reported that the use of the OFI extract in mortar formulation decreases the compressive strength as a function of W/C [2], slightly increases the flexural strength [3], and may induce a reduction in porosity [4, 5].

OFI is not available all around the world and France, as the European leader in flaxseed production [6] may have a flaxseed mucilage deposit. The mucilages are composed of water-soluble heteropolysaccharides. Flaxseed mucilage (FM) is a compound rich not only in polysaccharides (50–80%) but also in proteins (4–20%) and minerals (3–9%). These polysaccharides have a high molecular weight and are composed of an acidic fraction

(17%) comprising a mixture of L-rhamnose, L-fucose, L-galactose, and D-galacturonic acid forming the rhamnogalacturonans type I (RG-I) fraction and a neutral fraction (83%) containing L-arabinose, D-xylose, and D-galactose forming the arabinoxylans (AX) [7].

The elaboration of a biobased mortar involves determining how natural polysaccharides are added, as well as carefully balancing the water-to-cement ratio. Poinot et al. [8] studied the addition method of hydroxypropylguar polysaccharides and reported that polysaccharides are more efficient when dissolved in water. Schulze [9] worked on polymer-modified mortars with a 0.4–0.6 range of W/C ratios and stated that increasing the W/C ratio lowers compressing strength, increases shrinkage and water absorption for modified and unmodified mortars, but does not interfere in flexural strength. Regarding the literature, the incorporation of flaxseed mucilage into a cementitious material has never been studied before.

To counterbalance the hygroscopic nature of the flaxseed mucilage, it can be necessary to adjust the W/C ratio of the cementitious materials. For this purpose, this study focuses on the influence of the water/cement ratio, ranging from 0.5 to 0.8, on

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the hydration characteristics and mechanical strengths of an admixed Portland cement mortar in the long-term process. Flaxseed mucilage is used as an admixture in this study (powdered and solubilized in water).

2. Materials and methods

2.1. Raw materials

The cement used in this study was an Ordinary Portland Cement CEM I 52.5 N CE PM-CP2 NF commercialized by Calcia, France. The clinker is the main component (>95% (w/w)) of this cement. Its composition in weight-% is 74.8, 3.7, 8.2, and 8.3 for C₃S, C₂S, C₃A, and C₄AF, respectively. The Bogue approximation gives 66.48, 20.97, 4.84, 2.73, 3.4, and 0.21 % (w/w) for CaO, SiO₂, Al₂O₃, Fe₂O₃, SO₃, and Na₂O, respectively. It exhibits a Blaine fineness of 4360 cm²/g. The different mortars are elaborated with 0/4 mm sand according to the NF EN 12620 standard. With respect to the French standard NF EN 1008, the water used in this study was tap water at a temperature of 20°C ± 2°C. The FM used as an admixture comes from a gold flaxseed cultivar (Eurodor) and is available in lyophilized form after an extraction procedure.

2.2. Extraction of the flaxseed mucilage

Extraction was performed, consistent with the protocol elaborated by Roulard et al. [10], using a seed/distilled water ratio of 1:25 (w/v) in preheated water for 1 hour at 80°C with an adjustable temperature-controlled heater. Mechanical stirring was carried out using a paddle at 140 rpm. The extracts were filtered through a strainer and a 250 µm sieve, and then precipitated using 99% isopropyl alcohol (1:1.5 v/v) under manual stirring. The alcohol/mucilage mixture was left at 4°C for 24 hours. The mucilage precipitate was recovered and rinsed with distilled water before being dispersed in distilled water to undergo freeze drying. The extraction yield was expressed as the percentage of the freeze-dried mucilage mass (g) for 100 g of dried seeds.

2.3. Characterization of the flaxseed mucilage

2.3.1. Fourier Transform Infrared spectroscopy

Fourier Transform Infrared spectroscopy was used to characterize the lyophilized FM but also the different mortars elaborated. FTIR spectra of FM were recorded by using an FTIR spectrophotometer (IR-Prestige 21, Shimadzu). Approximately 1% (w/w) of FM was weighed and crushed on a KBr matrix (200 mg). FTIR spectra were obtained by 200 scans in a transmittance mode, at a resolution of 2.0 where an Happ-Genzel apodization was applied in a 400–4000 cm⁻¹ range.

2.3.2. Protein content

The Kjeldahl method described by AOAC official method 954.01 was used to quantify the protein content of FM. Based on the determination of total nitrogen content in the samples, a conversion factor of 6.25 was used to calculate the crude protein content from the nitrogen content.

2.3.3. Ash content

The AOAC official method 942.05 was used to determine the ash content of FM. Approximately 2 g of raw materials was weighed in porcelain crucibles and then calcined at 600°C for 2 hours in a preheated muffle furnace. The cooling step of the calcined samples was different from the AOAC method. The calcined materials

were cooled in an oven at 70°C for 2 hours to avoid any moisture regain before being weighed.

2.3.4. Molecular weight characterization

The molecular weight of the FM polysaccharides was determined by size-exclusion chromatography (SEC) combined with multi-angle light scattering (MALS). This method allows determining the number average molar mass M_n, the size, and distribution (high, medium, and low molecular weight) of the FM polysaccharide chains. The analysis was performed as described by Guilloux et al. [11].

2.3.5. Monosaccharides composition

High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was used to determine the FM monosaccharide composition and content. Results are expressed in grams of carbohydrates/100 g of FM. The analysis was performed as described by Roulard et al. [10].

2.4. Elaboration of mortars

Mortars are elaborated according to the EN 196-1 standard with a sand/cement ratio of 3 but a water/cement ratio ranging from 0.5 to 0.8 (with a constant step of 0.1). FM was incorporated in two ways: solubilized within water and powdered with anhydrous cement. Samples were molded without a shock table. Six (40 × 40 × 160) mm³ prismatic specimens were made for each mortar. The cure analysis was conducted for 90 days, in a chamber with saturated humidity at room temperature. Mortars were used to carry out thermogravimetric analysis and mechanical measurements. FTIR of 90 days cured mortars was used to determine mineral changes. Before characterization, the samples were dried in an oven at 50°C until obtaining constant mass.

2.5. Choice of the admixture rate

With the aim of incorporating FM in a cementitious matrix, it is necessary to evaluate the in-solution behavior of FM. Warrand [12] studied the viscous behavior of FM and reported that FM shows a shear-thinning behavior where the viscosity, which grows as a function of the polysaccharide concentration, is due to interactions between the two distinct fractions of the FM. The pectic fraction (anionic) has little or no influence in obtaining the physicochemical properties of the solution and almost only the neutral fraction (mainly AX) is responsible for the extreme viscosity of the mucilage. The gelling properties of the AX solution are due to intermolecular hydrogen bonds and a relatively larger Mw compared with the acidic fraction [12, 13].

An important transition point in the apparent viscosity of the mucilage solution is reported by several studies [12, 14]. As many plant extracts [15, 16], the sol-gel transition point corresponds to the concentration or condition in which the solution is no longer considered as a solution but as a gel due to an increasing polymeric chain network entanglement limiting the mobility of the polysaccharide chains which leads to a significant increase in viscosity [12]. From this sol-gel transition point, located in an area around 15–17 g/L of FM [12], and confirmed by viscosity measurements performed on the Eurodor cultivar, the study on mucilage admixture in a cement matrix uses a concentration of 15 g/L in the water corresponding to an addition of 0.75 g FM/100 g cement. The mucilage mass incorporated does not change as the W/C ratio changes.

2.6. Characterization of the FM admixed mortars

2.6.1. Setting time determination

A Calvet calorimeter C80, Setaram, was used to record the hydration heat release of cement pastes (CPs) containing different amounts of FM. This technique is effective for monitoring the hydration process and determining the initial and final setting times of cementitious materials. The CPs were prepared by mixing 100 g of cement with anhydrous and solubilized mucilage with respect to the desired W/C ratio. Each test faithfully repeats the mortar compositions (without sand), with respect to the FM:cement:water ratio. The CPs were homogenized with an electric whisk for 30 seconds. Approximately 3000 mg of the pastes was introduced into a stainless-steel capsule. The heat flow was measured for a minimum of 24 hours in a $25 \pm 0.5^\circ\text{C}$ regulated chamber. Enthalpy was calculated without considering the first hour of the reaction due to the system stabilization. It corresponds to the integration between the first point reaching 0 mW/g to the end of the heat recorded over time.

2.6.2. Hydrate evolution

When the major cement compounds, i.e. tricalcium silicates (C_3S) and dicalcium silicates (C_2S), are in contact with water, the formation in the first few hours of calcium silicate hydrate (also called C–S–H), ettringite, and Portlandite ($\text{Ca}(\text{OH})_2$ also denoted as CH) is observed. Over time, it is possible to form calcium carbonate (CaCO_3) in various forms – calcite, vaterite, and aragonite. These different compounds are dependent on the hydration of the cement grains. To quantify cement hydration, Portlandite and calcium carbonate can be estimated by thermogravimetry.

Thermogravimetry analysis was carried out with a TGA-DSC apparatus (Themys LV, Setaram) on mortars to quantify the hydrates formed and the degree of hydration (DH). Mortars were powdered using a mixer mill (MM400, Retsch). About 130 mg of this powder was introduced into porcelain crucibles. The analysis was started at 25°C and it reached up to 1100°C at a rate of $5^\circ\text{C}/\text{min}$ under helium atmosphere.

2.6.3. Mechanical strength

The strength of the mortars was tested under both bending and compression according to the NF EN 196-1 standard. A multifunctional machine (AG-X, Shimadzu, Japan) with a 10 kN load cell and a machine from Proviteq (France) with a load cell detection limit of 100 kN were used for the bending and compression tests, respectively.

3. Results

3.1. Physicochemical properties of the flaxseed mucilage

3.1.1. Infrared spectroscopy analysis

The FTIR spectrum indicates the presence of the two major mucilage compounds: polysaccharides and proteins. **Table 1** summarizes the elements present in the FM.

3.1.2. Proximate composition of the flaxseed mucilage

The composition of FM is presented in **Table 2**. The FM yield is about 4.97% of the dried weight of the seeds. The protein content of the extracted mucilage is 10.31%. The polysaccharide composition (**Table 2**) shows two distinct fractions. A neutral fraction is composed of xylose (15.6 g/100 g) and arabinose (8.6 g/100 g)

forming arabinoxylans (AX). This fraction represents 71.57% of total polysaccharides. The second fraction, representing 28.42% of the polysaccharide content, is an acidic fraction made up mainly of rhamnose (7.8 g/100 g) and galactose (5.9 g/100 g), forming type I rhamnogalacturonans (RG-I). Moreover, the SEC MALS analysis shows the formation of several peaks corresponding to different polymer sizes. This indicates the presence of a major polymer with a high molar weight (5.1×10^6 g/mol). Smaller molecular weights could correspond to the detachment of the major polymer (1.5×10^6 g/mol and 5.9×10^5 g/mol).

Table 1 • FTIR characteristic peaks of FM

Element	Wavenumber (cm^{-1})	Comment
Proteins	1658	Amide I –NH bending of the proteins contained in FM [17, 18]
	1549	Shoulder characteristic of the bending of the –NH group related to primary amine [19] or to amide II (C–N stretch coupled with N–H bending mode) [17]
	1240	Weak vibration corresponding to the N–H bending, probably due to secondary amide III [17, 20]
Polysaccharides	3392	Elongation of the –OH bond contained in water, sugars, and phenols
	2930	Vibration of the –CH ₂ –CH ₃ of the aliphatic chains of sugars [21–23]
	1414	Scissoring bending of the –CH ₂ of the aliphatic chains of sugars [21–23]
	1321	C–H vibration in a “hairy” zone of polysaccharides [24]
	1075	C–O bond of aliphatic ether or primary alcohols of sugars (Arabinose, Galactose, Glucose, and Xylose) [25]
	1040	Stretching mode of the C–O bond of pyranose [17, 26, 27]
	898–826	Polysaccharide backbone

Table 2 • Proximate composition of flaxseed mucilage

	Eurodor	Literature ^a
Protein (%)	10.31 ± 0.63	7.68–29.2
Ash (%)	3.76 ± 1.75	0.87–11.8
Carbohydrates (g/100g) ^b	45.11 ± 1.79	41–87.7
Mn (g/mol)	$1.291 \times 10^6 \pm 23.238\%$	8.2×10^5 – 3.1×10^6
AX (% molar)	71.57	
RG-I (% molar)	28.46	

^aLiterature review: [7, 10, 14, 28, 29].

^bThe sum of the compounds does not reach 100% due to carbohydrate losses during the HPAEC-PAD hydrolysis [30].

3.2. Characterization of the cement composites

3.2.1. Mineral activity

The hydration mechanisms of the different cement pastes have been studied using isothermal calorimetry. The quantities of energy generated by hydration at each instant were recorded and

the cumulative energies deduced (**Figure 1**). By using the first derivative of the heat flow signal over time, it is possible to determine the initial and final setting times (t_1 and t_2) in an accurate, reliable, and repeatable way. Both t_1 and t_2 are plotted in **Figure 2**.

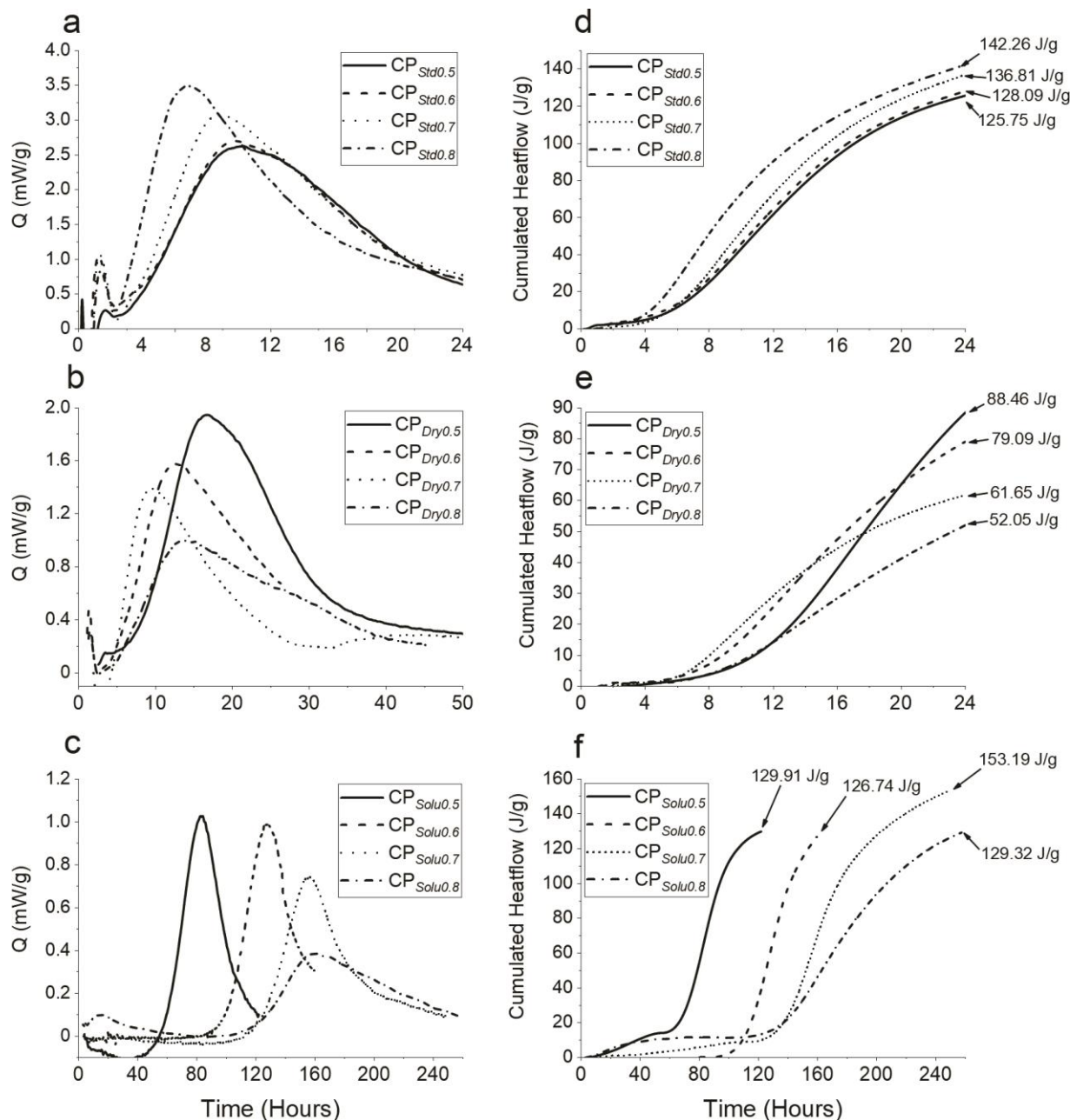


Figure 1 • Calorimetric curves and cumulative heat released of CPs.

Without the FM admixture, **Figure 1a** and **1d** shows that increasing the amount of water for cement hydration accelerates cement setting with an earlier onset and shorter induction period. Moreover, increasing the water content of the CP_{Std} accelerates the setting time and increases mineral activity by reaching a higher mass heat of hydration at 24h (Q_{24h}) (**Figure 1d**). CP_{Std0.5} generates a total of 125.75 J/g within 24 hours, while CP_{Std0.6}, CP_{Std0.7}, and CP_{Std0.8} show a 1.9, 8.8, and 13.1% increase in Q_{24h} . **Figure 2a** confirms that increasing the proportion of water in the cementitious mixture without the FM admixture decreases the initial and final setting times as well as the hardening time (Δt). Δt decreases by 22.8%, 29.4%, and 40% at W/C ratios of 0.6, 0.7, and 0.8, respectively, compared to a W/C ratio of 0.5.

The presence of an organic admixture typically causes a delay in both the initial and final setting times of cement paste as seen in **Figures 1** and **2**. From the moment a mucilaginous material is incorporated into the cement matrix, in anhydrous form, CP_{Dry0.5}, CP_{Dry0.6}, and CP_{Dry0.7} behave like the standard. In other words, increasing the quantity of water in the cement reduces the setting time like CP_{Std}, except for CP_{Dry0.8}, whose setting time and induction period increase. Furthermore, **Figure 1b** clearly indicates a slight and gradual reduction in the heat emitted as W/C increases, at 24 hours, with a reduction of over half from that of the CP_{Std}. In other words, the evolution of the calorimetry results with anhydrous FM is not uniform (**Figures 1b** and **2b**). The initial and final setting times as well as Δt decrease until the W/C ratio value of 0.7 and then increase at the W/C ratio value of 0.8.

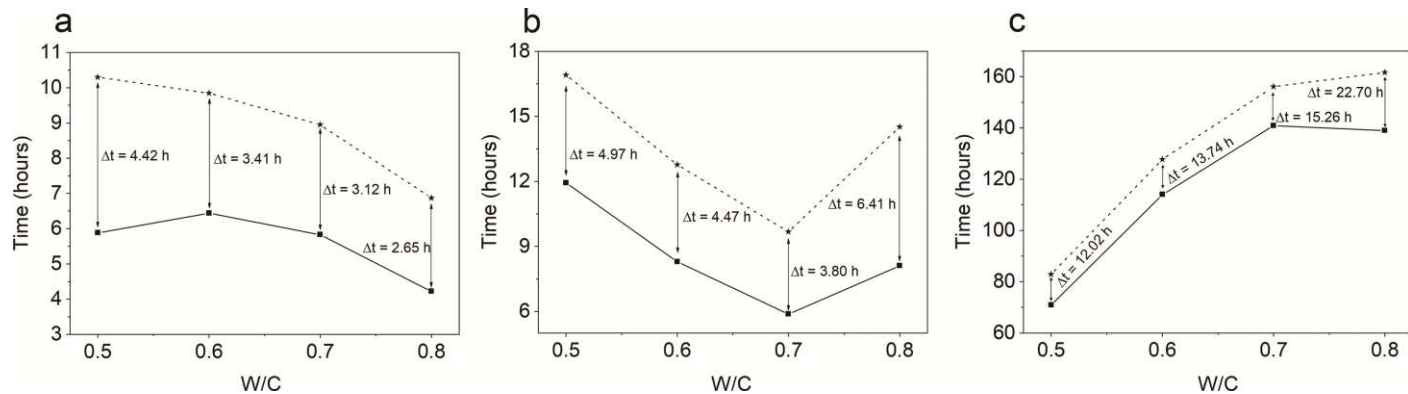


Figure 2 • Influence of the W/C ratios and FM addition ways on initial (t_1) and final (t_2) setting times: (a) M_{Std} ; (b) M_{Dry} ; (c) M_{Solu} — ■ : t_1 ; * : t_2 .

Figure 1c and **1f** demonstrate the highly retardant nature of polysaccharides with a tremendous increase in the setting time. At the end of the hydration process, **Figure 1f** reveals a cumulated heat at the level of the CP_{Std} . It is quite interesting to note that the W/C ratio of 0.8 does not particularly increase the setting time compared to $CP_{Solu,0.7}$ but significantly reduces hydration heat. **Figure 2c** confirms this delaying process induced by FM in-solution addition as $CP_{Solu,0.5}$ induces an increase of 1106% of the delay compared to $CP_{Std,0.5}$. This delay is accentuated as the W/C ratio increases with an increase of 60.8%, 98.7% and 96% for $CP_{Solu,0.6}$, $CP_{Solu,0.7}$, and $CP_{Solu,0.8}$, respectively, compared to $CP_{Solu,0.5}$. The beginning of the setting

is not endlessly delayed. When looking at t_1 and t_2 (**Figure 2c**) of $CP_{Solu,0.7}$ and $CP_{Solu,0.8}$, the initial setting times are equivalent.

3.2.2. Long-term hydration of mortars

Figure 3 shows the FTIR spectra of 90 days cured mortars with different W/C ratios and addition ways. The FTIR spectra of hardened mortars can reveal the presence of the hydrate products (CSH, Portlandite, and carbonate). At 90 days, the W/C ratio and the mode of addition of the flaxseed mucilage do not induce differences in hydration as the characteristic bands of CSH, Portlandite, and calcium carbonate are visible on each spectrum. Major characteristic bonds are spotted in **Figure 3**.

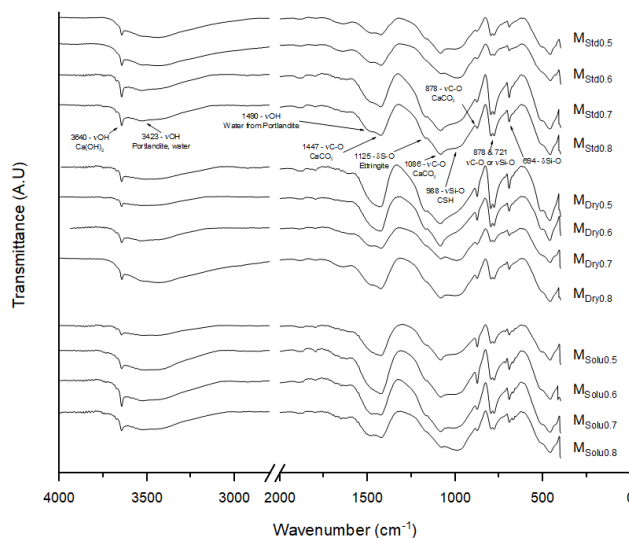


Figure 3 • FTIR spectra of 90 days cured mortars.

3.2.3. Hydrate evolution and DH evaluation

To compare and evaluate if the studied samples differ, a statistical analysis (ANalysis Of VAriance or ANOVA) has been conducted using the Statgraphics® software. The ANOVA analysis reveals that the hydrate evolution results do not show any significant differences whatever the formulation at a 95% confident interval. Neither the W/C ratio nor the addition of FM has a clear influence on the hydrate evolution. This also confirms the results obtained by FTIR on 90 days cured mortars (**Figure 3**). Nonetheless, some trends are observed as the M_{Std} samples have a degree of hydration that increases by 1.1%, 6.2%, and 16.6% at a W/C ratio of 0.6, 0.7, and 0.8, respectively, compared to a W/C ratio of 0.5. The evolution in Portlandite is stable, whatever the W/C ratio, a trend that is equivalent to that for calcium carbonates.

With a FM mucilage intake, DH tends to be higher than the standard when W/C is equal to 0.5 and 0.6. For the M_{Dry} samples at W/C ratios higher than 0.6, this effect seems to be diminished compared to the standard. The amount of Portlandite of the M_{Dry} samples increases by 23.1% and 19.4% compared to $M_{Dry,0.5}$ with W/C = 0.7 and 0.8, respectively. The carbonate content is quite stable except for $M_{Dry,0.6}$ which shows a higher value of 53% compared with $M_{Dry,0.7}$ and $M_{Dry,0.8}$.

Finally, the M_{Solu} samples show a gradual increase of both DH and Portlandite contents as the W/C ratio increases with an evolution of 4.4%, 11.6%, and 16.8% for $M_{Solu,0.6}$, $M_{Solu,0.7}$, and $M_{Solu,0.8}$, respectively, compared to $M_{Solu,0.5}$. This DH value increases with the formation of Portlandite in the material, as confirmed by **Figure 4c**, since the Portlandite values increase

from 9.4%, 25.8%, and 27% for $M_{Solu0.6}$, $M_{Solu0.7}$, and $M_{Solu0.8}$, respectively, compared to $M_{Solu0.5}$.

3.2.4. Mechanical strength

The ANOVA analysis results are visible in **Figure 5**. The significant increase in the amount of water is harmful for the pure cementitious material with a decrease of almost 16.5% for the bending resistance of $M_{Std0.8}$ compared to $M_{Std0.5}$. When mucilage is added to the mortar, whatever the addition way, the compressive strengths collapse, especially for $W/C = 0.5$. However, as soon as the W/C ratio increases, the strengths increase gradually with the bulk density but remain far lower from the M_{Std} values.

This increase is much less significant for compression strengths than for bending strengths, still compared to the M_{Std} . The addition way of the mucilage has a visible impact up to a W/C ratio of 0.6, with an unfavorable point concerning the addition in anhydrous form. Once the W/C ratio value is higher than 0.6, the impact of the addition way is no longer visible on the cementitious matrix. However, the compression and flexural values remain lower than those for the standard, except for $M_{Dry0.8}$ in flexion. In addition, to limit this decrease in the mechanical strength of the admixed mortars, it is necessary to increase the water input at least to $W/C = 0.7$ for anhydrous mucilage and 0.6 for pre-dissolved added mucilage.

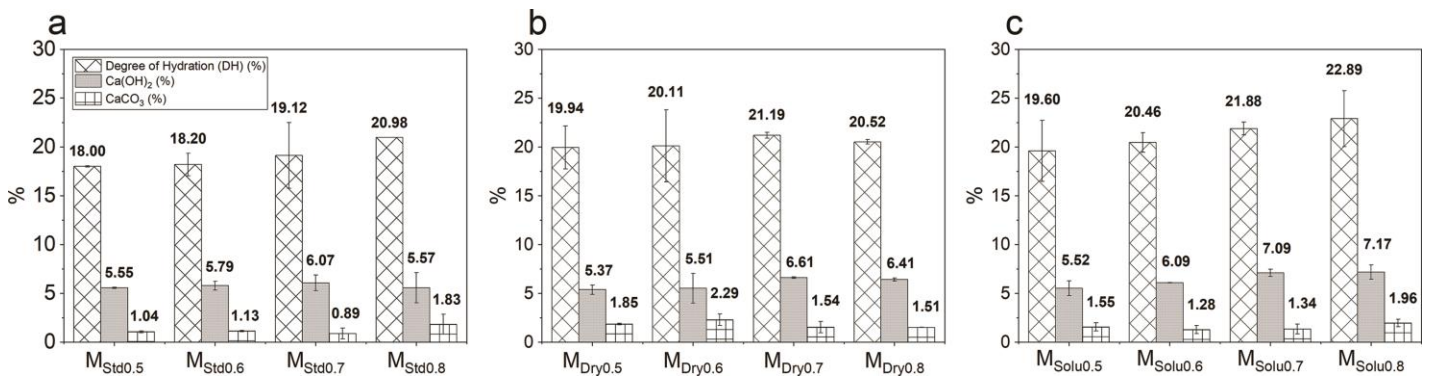


Figure 4 • Hydrate content (%w) and DH of 90 days cured mortars at different W/C ratios: (a) M_{Std} ; (b) M_{Dry} ; (c) M_{Solu} .

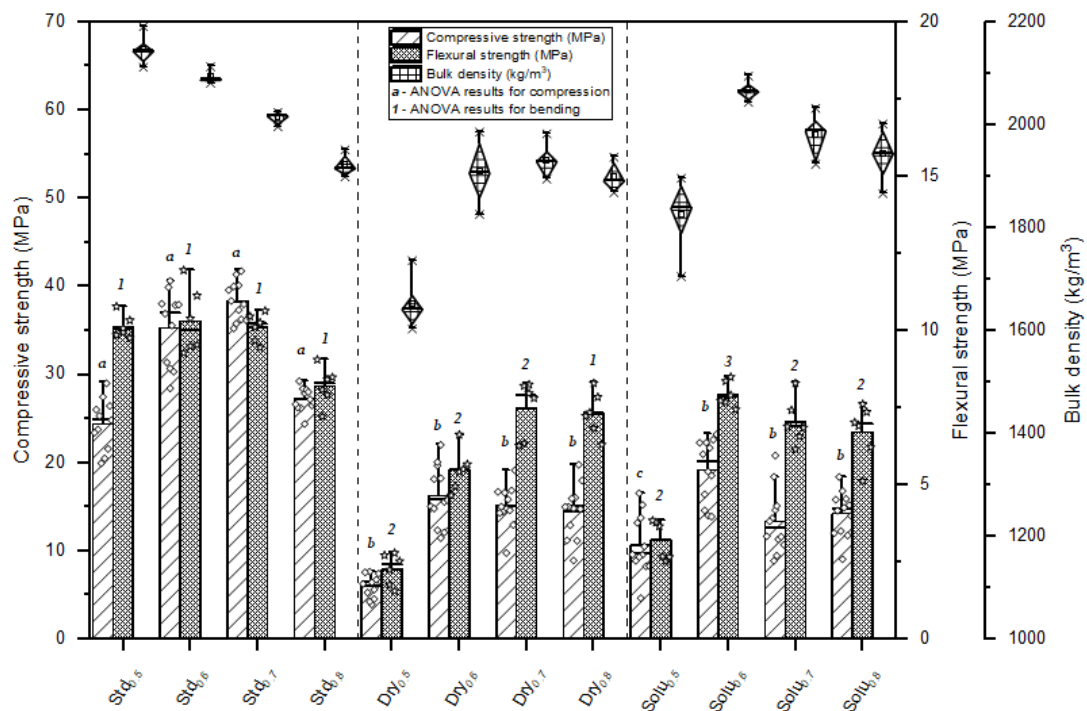


Figure 5 • Flexural and compressive strengths plotted with bulk densities of 90 days admixed mortars with the W/C ratio influence. Different numbers and letters above the bar charts indicate a significant difference ($p < 0.05$) from other formulation with the same W/C ratio.

4. Discussion

The water/cement ratio is a sensitive parameter on which the properties in the fresh and hardened state of mortars depend a lot. **Figures 1a** and **2a** show that increasing the amount of water for cement hydration accelerates cement setting with an earlier onset and shorter induction period. The cement used contains a significant amount of C_3S , a compound that is highly reactive at early ages. Increasing the amount of water in the medium

improves the solubilization and mobility of Ca^{2+} and, to a lesser extent, Si^{4+} . This increase in mobility allows the ions to access the nucleic sites and the hydrates to grow earlier than with a lower quantity of water. These elements are in line with the conclusions made by Larbi and Bijen [31], which are more recently confirmed by Hu et al. [32], who indicate that an increase in the W/C ratio leads to an easily transportation of Ca^{2+} both in and through the aqueous phase and thus produces favorable thermodynamic

conditions for crystallization and growth of the $\text{Ca}(\text{OH})_2$ crystals. These favorable conditions are visible by a more exothermic reaction when the W/C ratio increases (**Figure 1d**). Results for the CP_{Dry} indicate that the anhydrous mucilage does not act regularly probably due to a heterogeneous hydration mechanism (within the cement matrix) caused by an unpredictable presence of undissolved anhydrous mucilage in the paste. Moreover, when the W/C ratio increases (W/C = 0.8) more FM is dissolved. This occurrence can be verified by combining the increasing setting time when W/C = 0.8 (**Figure 2b**) and the gradual reduction in the heat emitted, which are the result of a "poisoning effect" due to the polysaccharides. The fact that the FM, when completely solubilized, generates an extremely significant delay in setting confirms this affirmation (**Figures 1c, 1f and 2c**). This effect has been described in detail by various authors, who indicate that the presence of carboxylic or hydroxyl groups [33], and more precisely $\text{HO}-\text{C}-\text{C}=\text{O}$ [34, 35] groups for sugars, increases the chemisorption of polysaccharide chains on cement grains and especially on metal ions (**Figure 6**) such as Ca^{2+} , Si^{4+} , Al^{2+} , etc. [36, 37]. The major fraction of FM is composed of arabinoxylans containing carboxylic and hydroxyl groups. This fraction is responsible for the setting delay caused by a chemisorption mechanism. Synergistic effects significantly slow down the nucleation of the hydrate products in cement clinkers and their growth rate by prolonging the saturation time of Ca^{2+} in solutions within the pores. Nevertheless, hydration products will slowly

form and grow in the space between the clinkers and the semi-permeable membrane of adsorbed FM as shown by the heat released at the end of the hydration reaction of CP_{Sol} which is equivalent to or even higher than the standard sample (**Figure 1f**). Water molecules pass through the semi-permeable membrane formed by the FM by osmosis. The "barrier" gives way when the quantity of hydration products is sufficient to break the semi-permeable membrane, and then the cement hydration process enters the accelerated period [36–39]. The fact that FM is composed of HMW chains increases the distance between the cement grains by increasing the steric bulk and therefore the semi-permeable layer, further inhibiting the hydration reaction [40]. The higher the W/C ratio, the greater the retarding effect of pre-dissolved mucilage is. This implies the mechanism described by Larbi and Bijen [31] concerning the more important dissolution of reactive ions when the W/C increases, but it also favors the chemisorption of the mucilage since it increases the mobility of the polysaccharide chains of the mucilage and, by the way, the steric hindrance, thus increasing the potential for trapping more Ca^{2+} ions, which conducts to a more delayed hydration process [40]. When looking at $\text{CP}_{\text{Sol}0.7}$ and $\text{CP}_{\text{Sol}0.8}$, the initial setting times are equivalent. This observation probably means that either FM is too diluted to increase the "poisoning effect" on cement or the excess water increases the dilution of Ca^{2+} ions which accelerates the hydration reaction despite the presence of polysaccharides.

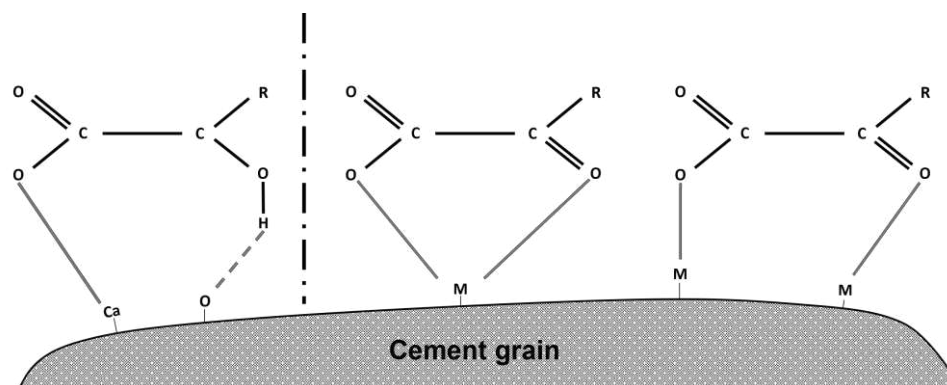


Figure 6 • Absorption mechanism of organic additives on the surface of a cement grain: Left: Chelation of Ca^{2+} and chemisorption of adjacent O^{2-} . Right: Chelation mechanism induced by the loss of hydroxyl groups in an alkaline environment.

The W/C ratio and the FM admixture do not impact the hydrate evolution. The FTIR and TGA analyses confirm that there are no major changes in the mineralogy of the 90 days cured mortars. Obviously, when looking at the calorimetric curves, there may be a slight change in hydration and/or mineralogy during the first few days of the material. The 90 days cured cement mortars do not allow one to spot any differences. However, when a polysaccharide source is added, hydration appears to be slightly higher as seen with the DH in **Figure 4**. It is possible that the addition of FM provides a long-term source of water thanks to its significant hygroscopic properties [2, 5]. Knapen and Van Gemert [41] clearly showed the interaction of polysaccharides with Portlandite in particular. Some organic additives can structure Portlandite and make it durable. Usually, Portlandite is not able to resist the stresses of early cement hydration, but the very visible bonds between Portlandite and polysaccharides create a layer-like structure of the Portlandite platelets increasing the strength of Portlandite. These conclusions may be consistent with our results as CP_{Sol} has a Portlandite content value higher than other samples (**Figure 4c**).

The excessive increase in the amount of water (W/C = 0.8) in the cement mortar diminishes the material strength. Increasing the W/C ratio gradually lowers the bulk density as mentioned by Schulze [9]. FM modified mortars exhibit both flexural and compressive strengths collapsing when the W/C ratio is 0.5. This is explained by a macroscopic effect. Both admixed mortars $\text{M}_{\text{Dry}0.5}$ and $\text{M}_{\text{Sol}0.5}$ have a dry granular-shaped structure, which reduces the cohesive strength of the entire material and, by the way, the strengths. This finding is probably due to a flocculation mechanism of FM on cement grains previously described by Dickinson and Eriksson [42] and confirmed by Negro et al. [43]. This macroscopic structure is representative of the low bulk density of these mortars. However, as the W/C increases, the mechanical strength of the admixed mortars also increases, with a better behavior under mechanical stress in flexion than in compression. The mucilage in the cementitious matrix makes it possible to generate slightly more elastic behavior by "strengthening" the structure. This flexural behavior has been reported by Schulze [9] who worked on polymer modified and unmodified mortars, and stated that increasing the W/C ratio

lowers the compressing strength on unmodified mortars but does not interfere in the flexural strength of the modified mortars. This elastic behavior is of no benefit under compressive loading. For mortars with the mucilage admixture, it is therefore more interesting to increase the quantity of water in the matrix to obtain an appropriate strength, but lower than that of the standard.

Finally, the results show that the lack of strength in the admixed mortars is not due to a poorer hydration or a mineralogical change. However, this needs to be confirmed by a more in-depth mineralogical study.

5. Conclusion

It was seen in this study that FM, whatever its method of incorporation, generates a significant delay in setting and increases the induction period due to the limitation of Ca^{2+} mobility provoked by the polysaccharides (viscosity and chemisorption). These effects are all true as the W/C ratio increases. The delay induced does not generate, in the longer term, any significant change in hydration and hydrates development as shown by TGA and FTIR analyses. However, it should be noted that the FM significantly reduces the mechanical strength of the material regardless of the W/C ratio used. Nevertheless, at a W/C ratio above 0.5, the bending strength increases probably due to an elastic behavior conferred by the mucilage.

The results are contradictory with those reported in the literature using OFI extracts as the admixture. The difference in the behaviors surely originates from the composition of the OFI extracts which contain polysaccharides but also fibers, a high ash content, and a lot of water. The OFI extract contains a low percentage of xylose and a high percentage of glucose and galacturonic acid [44, 45]. Galacturonic acid and glucose are well known to enhance the viscosity of a cement by forming strong intermolecular association among the galacturonan chain by forming calcium bridges [46]. Conversely, FM contains a high xylose and arabinose content. The protein content of the OFI extract is lower than that of FM but the higher ash content and especially calcium [47, 48] could generate a pozzolanic reaction helping the microstructure.

A further study will be conducted to assess the effect of the FM admixture on the macro- and microstructure of the mortar. It will also be interesting to check how harmful the concentration of the mucilage is on the cement.

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Author contributions

HB, EPL, and AG conceptualized the work. HB devised the experiments, collected, analyzed the data, and drafted the manuscript. AG and EPL supervised the study and finalized the manuscript. All authors approved this work and take responsibility for its integrity.

Conflict of interest

The authors declare no conflict of interest.

Data availability statement

Data supporting these findings are available within the article or upon reasonable request from the corresponding author.

Institutional review board statement

Not applicable.

Informed consent statement

Not applicable.

Sample availability

Samples are securely stored at EPROAD/University of Picardie Jules Verne, Amiens, France. Please note that in time sample degradation can occur, which may impact their integrity.

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