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Impact of hydroxypropylguars on the early age hydration of portland cement

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ABSTRACT

Hydroxypropylguars (HPG) are used as admixtures in factory-made mortars. These molecules present water retention properties comparable to those obtained with commonly used cellulosic water-retaining agent.

The influence of HPG on cement hydration was investigated in order to improve understanding on the delayed effect induced by polysaccharides. Hydration kinetics were characterized by means of conductivity and isothermal calorimetry measurements. The influence of polymer concentration and predissolution was studied. A weak influence of HPG on the germination of hydrates was observed. In contrast, HPG induced a significant decrease in the hydrates growth rate. Strong effects of the polymer concentration and predissolution were noticed too. From these results, we supported the hypothesis that HPG adsorption on hydrated phases via polar interactions should be responsible for the delayed effect observed.

KEYWORDS: polysaccharide (D), hydroxypropylguars (D), retardation (A), hydration (A), water retention (C)

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1 Introduction

Traditionally, mortars are based on a mixture of sand, a binder such as cement or lime, and water. Nowadays, modern factory-made mortars are complex materials, in which are added some kinds of admixtures used to exhibit various properties, from the fresh state to the hardened material.

Polysaccharides are one of these admixtures. They are frequently introduced into mortar formulations in order to improve water retention capacity of the freshly-mixed materials, which enhances cement hydration and adhesion to the substrate [1–4]. These products are also expected to act as viscosity-enhancing admixtures to prevent segregation and thus improve the homogeneity and workability of the mortar [5–8].

Among all polysaccharides, **C**ellulose **E**thers (CE) are the most widely used when high water retention capacity is expected. Nevertheless, **H**ydroxy**P**ropyl**G**uars (HPG) were recently presented as a promising new class of water-retaining agent [9]. HPG are already used in various industrial fields, such as textile printing, oil production or paper manufacturing, due to their thickening effect [10]. HPG were also the subject of some patents as admixture for mortars.

The effect of saccharides has been largely studied these fifty last years, in particular from a cement hydration delay point of view. In the first time, the delayed effect of monosaccharides was investigated [11–19]. It appears that sugars could be adsorbed to cement phases by a chelation process. It can thereby form a temporary barrier to further hydration. In broad agreement with Young [11], Thomas and Birchall [12] proposed that sugars would be able to poison the surfaces of the CH and CSH by complexation onto these phases, which inhibit their growth and therefore would be responsible for the delay observed. According to Taplin

[13], sugars could bind to the cement phases if they have a HO-C=O group, or it could be formed in alkaline media, such as cement paste, by hydrolyze [14].

Then, due to the use of polysaccharides in modern factory-made mortars, interactions between polysaccharides and cement have been reported recently. It is established that polysaccharides induce a more or less important delay of Portland cement hydration [20–25], which depends on the nature of the polysaccharide [26]. Pourchez et al. [27, 28] have established a mechanism of interaction between CE and cement.

However, HPG have received scant attention by the academic community although they are already used industrially. As far as we know, only Izaguirre et al. [29] was interested on the impact of HPG, but in lime-based mortars. Thus, the aim of this work is to study the influence of HPG on the Portland cement hydration kinetics at early age.

Firstly, the water-retaining effect induced by the HPG in Portland cement-based mortars will be checked. Secondly, cement hydration kinetics in the presence of HPG will be presented. Hydration kinetics have been monitored by conductivity and isothermal calorimetry measurements. Finally, a special focus on the influence of the polymer predissolution has been performed.

2 Materials

2.1 Mineral product

The investigated ordinary Portland cement (OPC) was a CEM I 52.5 R CE CP2 NF type cement according to the EN 197-1 standard. Its chemical and phase compositions are given in Table 1. Oxide composition was determined by X-ray fluorescence spectroscopy (SRS3400, Bruker-AXS). XRD analysis (D5000, Siemens) also allowed quantifying the phase composition of the given cement by means of Rietveld refinement method (Siroquant V2.5

software).

Table 1: Chemical and phase compositions of the investigated cement.

Chemical composition (% wt)				Phase composition (% wt)	
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)
CaO	66.1 ± 1.2	TiO_2	0.24 ± 0.01	C_3S	73.0 ± 0.53
SiO_2	20.2 ± 0.4	P_2O_5	0.05 ± 0.01	C_2S	12.7 ± 0.50
Al_2O_3	4.8 ± 0.1	MnO	0.04 ± 0.00	C_3A	4.2 ± 0.18
SO_3	3.5 ± 0.2	K_2O	0.01 ± 0.01	C_4AF	6.1 ± 0.22
Fe_2O_3	2.9 ± 0.1	LOI	2.2 ± 0.2	Gypsum	1.7 ± 0.15
MgO	1.11 ± 0.02			Anhydrite	2.3 ± 0.28

2.2 Organic admixtures

Guar gum is a polysaccharide extracted from the seed endosperm of *Cyamopsis tetragonolobus*, a native plant from India. This is a galactomannan consisting of a (1-4)-linked β-D-mannopyranose backbone, with random branchpoints of galactose via an α-(1-6) linkage [30] (Fig. 1a). The ratio of mannose to galactose is about 1.8. Unlike the manufacturing of cellulose, the extraction does not require chemical process, but a thermo-mechanical one. So, guar gum is produced without producing any effluent. Moreover, because of the presence of hydroxyl groups in its structure, guar gum exhibits a high chemical reactivity and is soluble in cold water. Thus, the chemical modification of this polysaccharide does not require hard reaction conditions of temperature and pressure, does not generate large quantity of by-products and needs weak purification procedure [31].

HPG are obtained from the native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Fig. 1b). Table 2 gives a qualitative description of the six HPG samples from *Lamberti S.p.A* which were studied. All the samples have similar molecular weight. The only difference between HPG 1, 2 and 3 is

the Degree of Substitution (DS). The only difference between HPG 4, 5 and 6 is the presence of additional substitution (short or long alkyl chains).

In order to compare with classical polysaccharide admixtures, three CE were also tested (Table 2): two HydroxyPropylMethyl Cellulose (HPMC) named HPMC1 and HPMC2, and one HydroxyEthyl Cellulose (HEC).

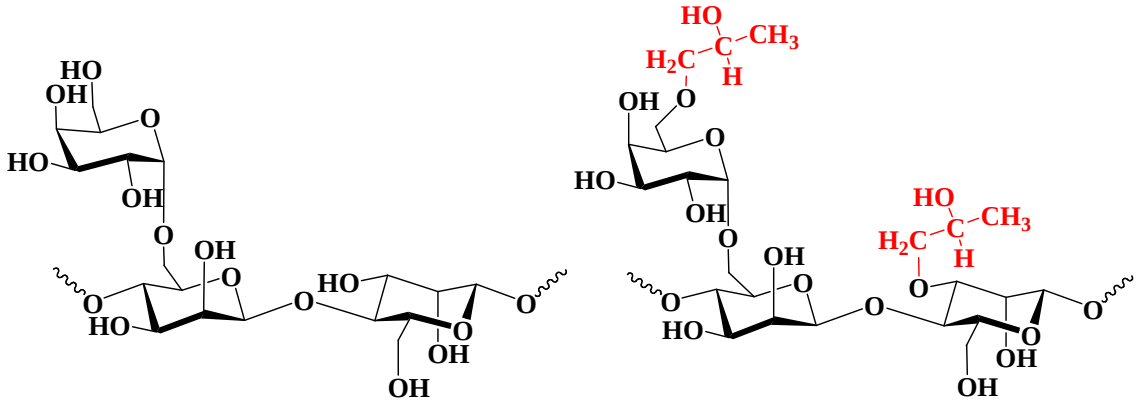

Fig. 1: Molecular structure of native guar gum (a) and hydroxypropylguar (b).

Table 2: Qualitative description of the admixtures used.

Admixtures	DS	Viscosity	Additional substitution
HPG 1	Low	High	-
HPG 2	Medium	Medium	-
HPG 3	High	Medium	-
HPG 4	High	Low	-
HPG 5	High	Medium	Shorter alkyl chain
HPG 6	High	Medium	Longer alkyl chain
HPMC 1	High	Very low	-
HPMC 2	High	Very high	-
HEC	High	Very low	-

3 Experimental methods of investigation

3.1 Water retention measurements

Water retention capacity of mortars was characterized according to ASTM C1506-09 standard [32]. This test is based on a measurement of the removed water after depression and was previously described by Patural et al. [3]. Water retention, noted WR, was calculated using the following equation:

$$WR(\%) = \frac{W_0 - W_1}{W_0} \times 100 \qquad (1)$$

W_0 represents the initial mass of mixing water; W_1 is the loss of water mass after aspiration. Mortars were prepared according to the following mixture proportions: 30% of cement, 65% of sand and 5% of limestone filler (by weight). This mixture design was adapted from the CEReM (european consortium for study and research on mortars) mortars formulation [3]. Admixture amount (0.3 wt%) was in addition to the total dry mixture (*i.e.* cement, sand and filler). Dry mixture was blended in a shaker (Turbula, Wab) for 15 min. Deionized water was added in order to obtain a water to cement ratio W/C = 1. Mixing procedure was in accordance with EN 196-1 [33]. All tests were carried out in triplicate and at controlled temperature of 23°C because water retention is temperature-dependent. A control test was performed with a mortar without admixture.

3.2 Characterization of the cement hydration delay

3.2.1 Conductivity measurements on diluted suspensions

Characterization of the delay induced by the studied polymers on the cement hydration was performed by conductivity measurements. This method appears as a powerful and reproducible tool to monitor the hydration kinetics [34,35].

Conductivity measurements could be achieved in lime suspension. This allows obtaining hydration kinetics close to that observed in cement pastes, in spite of a high liquid to solid weight ratio (noted L/S). Nevertheless, monitoring hydration kinetics in an artificial system of lime water is complicated because the dissolution rate of calcium from the cement could be modified due to the initial high concentration of calcium ions in solution. Thus, conductivity curves were interpreted according to the explanation proposed by Comparet et al. [36]. As soon as cement was put in contact with liquid, the electrical conductivity increased as a consequence of the dissolution of the anhydrous phases. Then, germination of hydrates on the grain surface leads to a period, called “low conductivity increasing period”, where the conductivity evolves weakly. Conductivity then accelerated more quickly. The conductimetric slope is related to the growth rate of the hydration products. Meanwhile, cement dissolution still continued. The conductivity increased to the critical supersaturation point with respect to portlandite and decreased rapidly due to its precipitation. Thus, an electrical conductivity drop is caused by the portlandite precipitation. This phenomenon was used to determine the hydration delay. Therefore, in this study, the portlandite precipitation time (noted t_{CH}) is a benchmark to classify and to quantify the relative retardation ability of admixtures on cement hydration.

Experiments were performed in diluted suspensions, thermostated at 25°C and continuously stirred. Each experiment was carried out in triplicate. The liquid to solid weight ratio (L/S) used was equal to 20. Polymer to cement weight ratios (P/C) equal to 0.5, 1.0, 1.5 and 2.0 %

were studied. Cement and admixture powders were blended in a shaker (Turbula, Wab) for 10 min before contact with the liquid phase. The liquid used was a 20 mM lime solution or deionized water. The control used was the neat cement.

3.2.2 Isothermal calorimetry on cement pastes

Calorimetry is another technique useful to characterize the exothermic hydration process of cement. The hydration process can be followed continuously at realistic water/cement ratios (W/C) in situ and aims at giving an indication of the overall rate of reaction. Thus, calorimetry can be used as a complementary method to conductivity in order to monitor the kinetics of cement hydration and to observe hydration delay induced by retarders [37].

The tests were performed with an isothermal calorimeter (C80, Setaram) at 25°C. The weight ratios used were W/C = 0.4, with deionized water, and P/C = 0.3 %. Ex-situ mixing was preferred to in-situ mixing to improve the homogeneity of the sample, and thus reproducibility. Mixing procedure, with 100g of cement, was in accordance with standard EN 196-1 [33]. 10 min after the beginning of the batch, about 2g of paste are introduced in the calorimeter. The control used was the neat cement.

3.2.3 Predissolution of the admixture

The influence of the polymer predissolution was studied by means of conductivity and isothermal calorimetry measurements. Admixtures were previously dissolved in the liquid phase, deionized water or 20 mM lime solution, for 24h by magnetic stirring. Then, cement was added.

In case of conductivity experiments, the effect of the predissolution has been highlighted by calculating the increase percentage in the portlandite precipitation time t_{CH} as followed (in gray in Fig. 10):

$$Increase\ of\ t_{CH}\ (\%) = \frac{t_{CH}(with\ \ prediss) - t_{CH}(without\ \ prediss)}{t_{CH}(without\ \ prediss)} \times 100 \qquad (2)$$

3.3 Calcium binding capacity

The ability of HPG and also sugars (sucrose which is known to complex calcium ions, galactose and mannose which constitute HPG's molecule) to form complexes with calcium ions was studied. Sugars are valuable insights in order to compare the behavior of HPG and to validate the relevance of this protocol, developed by Thomas and Birchall [12].

Each sample (2 g per liter) was introduced into a volume of water (1L) containing a large excess of solid lime (6 g per liter). After 48 hours of stirring at a controlled temperature of 23°C, the suspension was filtered through a 0.7 µm glass fiber filter. The filtrates were diluted and acidified. Then, a quantification of the calcium ion content by ionic chromatography was performed on a Dionex apparatus composed of a GP 50 gradient pump, a CS 12A cation-exchange column and a CD 20 conductometric detector. The eluent was a solution of metasulfonic acid at 20 mM with isocratic mode. The flow was fixed at 1 mL/min. The results correspond to an average of 3 experiments.

As the solid calcium hydroxide is in large excess, calcium ions consumed by complexation do not affect the "stock" of calcium ions in solution, which thus remains equal to 23 mM during the experiment. However, once the filtrate diluted and acidified, the complexes are destroyed, thus freeing the complexed calcium ions. So, if the calcium concentration is about 23 mM (solubility of lime), no significant complexation has taken place. Instead, a calcium concentration above 23 mM indicates a significant complexation of calcium ions.

3.4 Kinetic of dissolution

HPG absorb in the ultraviolet as evidenced by the absorption spectra (Fig. 2a), and the concentration of HPG in solution is proportional to the absorbance at the maximum of the band (266 nm) as shown in Fig. 2b.

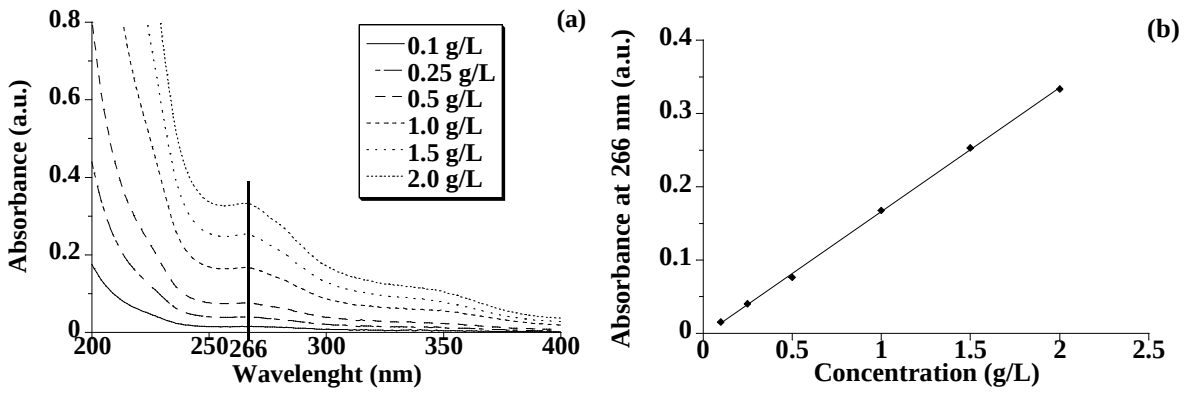

Fig. 2: UV absorption spectra (a) and absorption at 266 nm vs. concentration (b) for HPG in water

The dissolution process was monitored by acquisition of UV-Vis absorption spectra. The procedure was the following: a dispersion of HPG (final concentration: $2 g.L^{-1}$) in deionized water or 20 mM lime solution was prepared in a sealed reactor (1L of solution) thermostated at 25°C. HPG was introduced through a sieve in order to have a good dispersion of the sample into the vortex created by the mechanic stirrer. Thus, the aggregation of particles was minimized and a homogeneous polymer solution was produced. The experiment was done under continuous flow of nitrogen to avoid carbonation of lime. At different times, an aliquot of approximately 5 mL was taken from the batch solution and centrifuged by means of a micro-centrifuge (Eppendorf MiniSpin Plus, 14500 rpm) for 5 min in order to remove undissolved particles. The supernatant was collected and homogenized by vortex-stirring. The absorbance of this solution was measured between 200 and 400 nm using an UV/Visible spectrophotometer (Cary 300 Scan, Varian). A degree of progress of the dissolution reaction $\lambda(t)$ was used, which is equal to the absorption at time t divided by the absorption at the end

of the dissolution reaction (*i.e.* 24 h). This number is adimensional and its value is between 0 and 1.

4 Results and discussions

4.1 Impact of HPG on water retention in fresh mortar

Water retention is a very sensitive mortar property. Indeed, it must be important enough to not disturb the hydration of the cement. It also limits the absorption of the mixing water by the substrate and thus provides good mechanical and adhesive properties to the mortar.

DTU 26.1 [38] specifies three classes of water retention of a fresh mortar. The first one represents mortars which water retention is lower than 86%; they belong to the low water retention category. The second class (intermediate water retention) corresponds to values ranging from 86% to 94%. The last one is defined by water retention higher than 94%. This class is related to strong water retention mortar and is desired by formulators of industrial mortars.

Water retention capacity of the studied mortars according to the admixture used is shown in Fig. 3. With this formulation, mortars containing HPG 2 to 6 and HPMC 2 could be considered as high WR capacity according to the DTU 26.1. Mortars containing HPG 1, HPMC 1 and HEC are in the intermediate category.

Thus, HPG improve considerably the water retention capacity of the mortar compared to the control without water-retention admixture, as announced by Plank [9]. In addition, the results are quite comparable to those obtained with the CE of reference.

Therefore, HPG can be considered as promising water-retention agents for dry-mix Portland cement-based mortars.

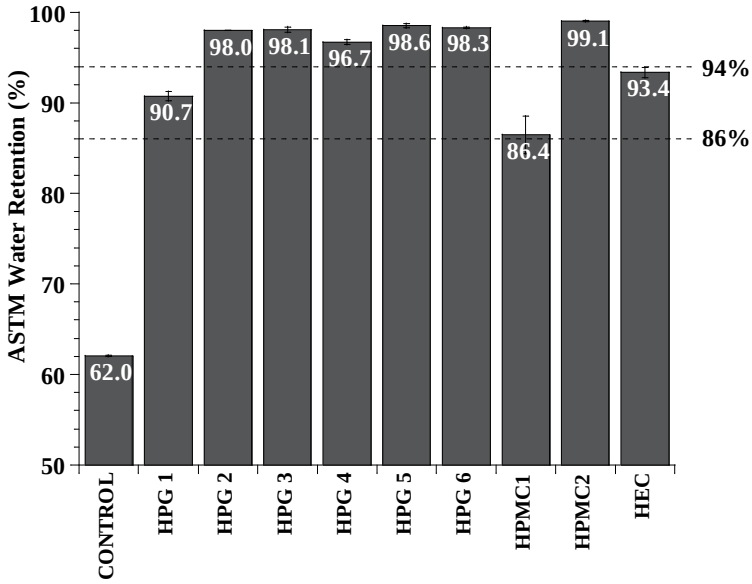

Fig. 3: Water retention capacity of studied mortars with 0.3 %w.t. of admixture.

4.2 Impact of HPG on hydration kinetics of cement

4.2.1 Delayed effect

The delayed effect of HPG on cement hydration kinetics was monitored by conductivity in a 20 mM lime solution, for ratios L/S = 20 and P/C = 2%. To have a clear and readable analysis, all the conductimetric curves will not be presented on the same figure. Thus, Table 3 regroups the conductimetric data obtained (i.e. portlandite precipitation times, delays compared to the control and conductimetric slopes). Fig. 4 presents the influence of the DS on the conductimetric curves by studying HPG 1, 2 and 3 which are the same molecules, except the DS (DSHPG1>DSHPG2>DSHPG3). The influence of the alkyl substitution was studied by comparison of HPG 4, 5 and 6 (see Table 2). The conductimetric curves obtained are shown in Fig. 5.

Table 3: Comparison of conductimetric data according to the admixtures studied

Admixture	Without	HPG 1	HPG 2	HPG 3	HPG 4	HPG 5	HPG 6	HPMC 1	HPMC 2	HEC
Portlandite precipitation time (min)	252 ± 0	1083 ± 13	786 ± 27	611 ± 16	478 ± 9	432 ± 7	420 ± 9	366 ± 3	354 ± 9	1273 ± 15
Delay compared to the control (%)	/	329	212	142	89	71	66	45	40	405
Conductimetric slope ($\mu S.cm^{-1}.min^{-1}$)	19.6 ± 1.5	3.3 ± 0.4	5.0 ± 0.5	7.0 ± 0.5	9.6 ± 0.8	11.4 ± 0.9	11.4 ± 0.9	13.5 ± 1.0	13.5 ± 1.7	3.3 ± 0.0

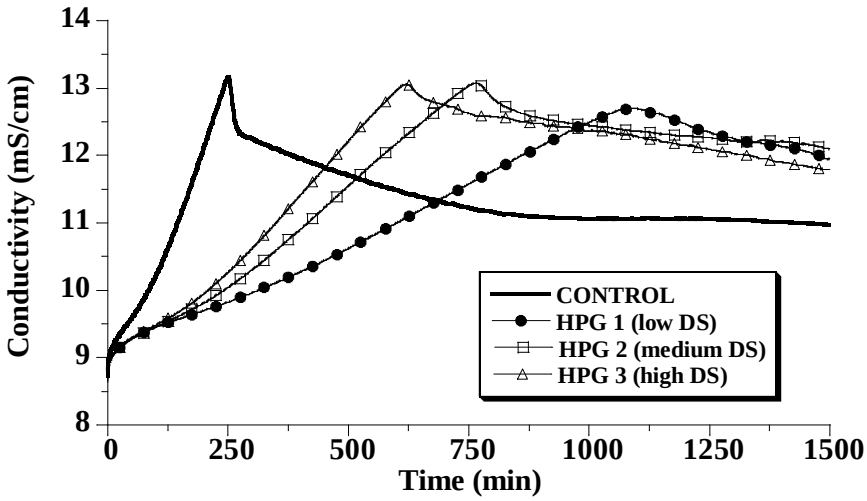

Fig. 4: Influence of the DS on conductimetric curves ([$Ca(OH)_2$]=20 mM, L/S=20, P/C=2%).

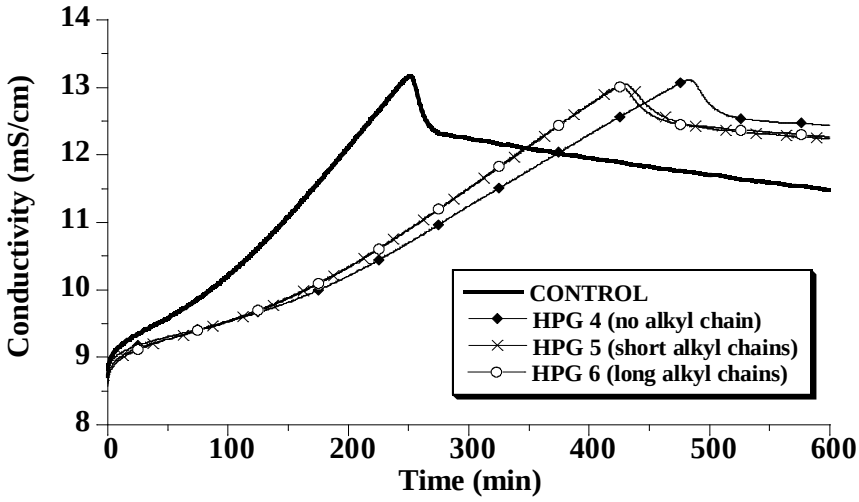

Fig. 5: Influence of alkyl substitution on conductimetric curves ([$Ca(OH)_2$]=20 mM, L/S=20, P/C=2%).

The conductimetric data (Table 3) highlights the impact of HPG on the kinetics of hydration. By focusing on the portlandite precipitation time (conductivity drop) and delays, it appears a wide range of delays induced by the admixtures studied. HPG 5 and 6 exhibit superposed conductimetric curves and the weaker delay (+71% and +66% respectively). The most important delay is observed for HPG 1 (+329%). It also appears that delays induced by HPG are between those obtained for the CE studied (+40% to +405%).

Some polysaccharides (dextrines for example [26]) or other admixtures (setting retarding admixtures such as sugars [19], sodium gluconate [39] or some superplasticizers [36]) induce a blocking effect or an inhibition of the hydration. Here, from the shape of the conductimetric curves obtained, HPG involve a small increase in the duration of the “low conductivity increasing period”. Therefore, this indicates a weak influence of the HPG on the germination of cement hydrates. The delay of portlandite precipitation time seems to be mainly due to a slope decrease (Table 3). Indeed, the slope obtained with the control is almost six times higher than that obtained for HPG 1. The slope of the conductimetric curve is linked to the growth rate of the hydrated cement phases. HPG seem to act preferentially on the growth of hydrates phases, rather than on their germination. This could explain the delays observed and is in agreement with results obtained with CE [40].

In addition, delay increases when DS decreases (Fig. 4). Nevertheless, the alkyl substitution seems to have a slight effect (Fig. 5) because the delay slightly decreases in the presence of alkyl chains. The effect of the chain length is negligible.

4.2.2 Calcium binding capacity

The calcium complexation is often advanced as assumption to explain the effect of retarders [41]. It seemed important to check if HPG complex with calcium ions. The calcium binding capacity at alkaline pH of the 6 HPG and 3 sugars were conducted and the results are

presented in Fig. 6. It appears clearly that the complexation of calcium ions by HPG is null or very weak, like with CE [42]. Indeed, the value of calcium ions concentration found for the HPG samples was close to the reference sample and is only due to the lime solubility. Instead, sugars studied present higher calcium ion concentration due to a greater binding capacity, which is coherent according to the data of the literature [12,42]. Therefore, calcium ion complexation is clearly not responsible for the delay of cement hydration induced by HPG.

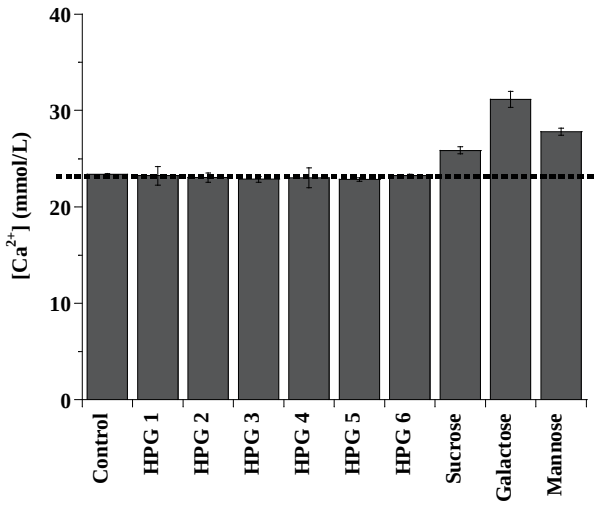

Fig. 6: Calcium binding capacity of HPG and monosaccharides.

4.2.3 Influence of polymer concentration

The influence of the amount of polymer is studied by conductivity in 20mM lime solution by varying P/C ratio with a constant L/S ratio (equal to 20) for each HPG. The effect of polymer concentration is considerable and results in a drastic decrease in the slope (Fig. 7). Thus, a small increase in the amount of polymer leads to a huge increase in the portlandite precipitation time, and so in the delay of hydration. Fig. 8 presents the portlandite precipitation time for each polymer and concentration. The effect of the concentration is similar whatever the molecule. For each polymer, the more the concentration increases, the more the delay increases. As the retarding effect is effective at very low HPG concentrations, it confirms that calcium complexation cannot be responsible for the delay mechanism.

It is generally admitted that cement hydration delay induced by admixtures is due to adsorption of these molecules to surfaces of the hydrating cement particles and/or surfaces of hydration products [41,43]. The concentration dependent behavior of the delay suggests also that HPG delay cement hydration via adsorption on the cement phases.

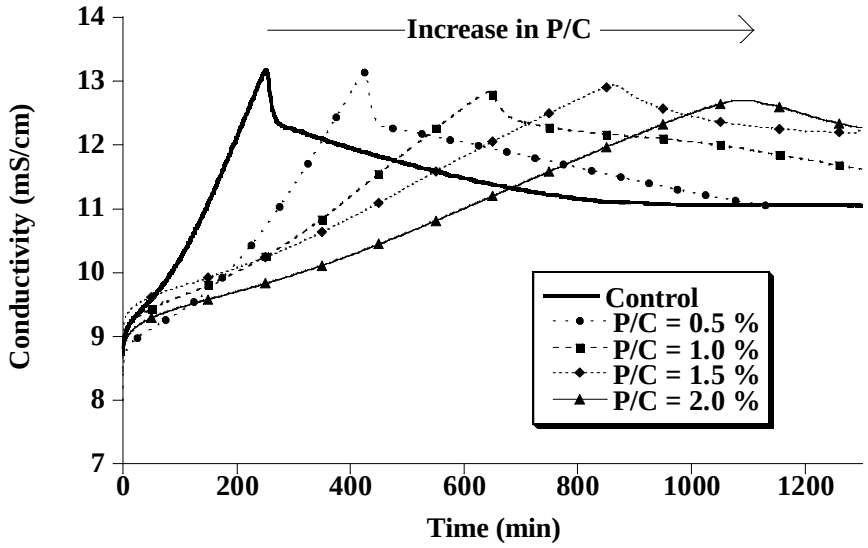

Fig.7: Conductimetric curves of cement admixed with HPG 1 in lime solution according to the P/C ratio ([$Ca(OH)_2$]=20 mM, L/S=20).

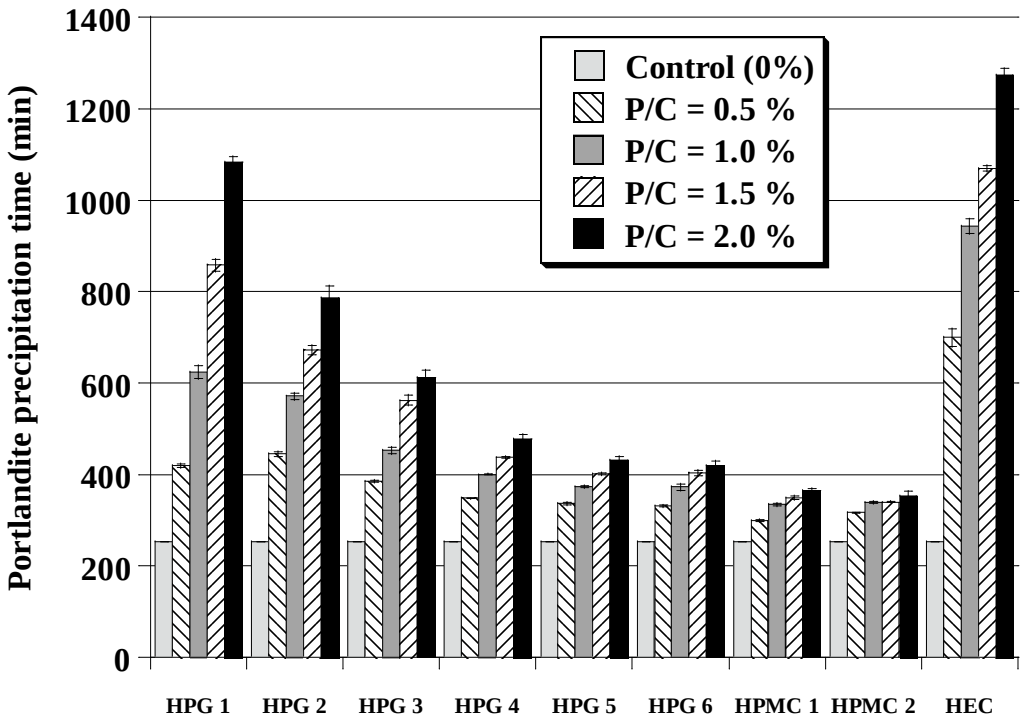

Fig. 8: Influence of admixtures concentrations on portlandite precipitation time.

The mechanism responsible for the delay induced by CE is the adsorption of the molecule on the hydrate cement phases. Indeed, Pourchez et al. have shown evidence of the adsorption of CE on calcium hydroaluminates [44] and CSH/CH [40]. Polysaccharides are molecules which contain a lot of polar functional groups (-OH). Therefore, strong interactions, through electrostatic forces and hydrogen-bonding, can occur between polysaccharides and the highly polar hydrated phases [43]. The relationship between adsorption and retardation was previously shown [25,40]. It results that the higher the substituent content is, the weaker the retardation ability is, because of lower amount of free hydroxyls and so lower adsorption ability.

For HPG, the phenomena could be very close, due to the similarity of the molecules used, in particular the high content of hydroxyl groups. Wang et al. [45,46] have shown that the adsorption mechanism of galactomannose polysaccharides at solid-liquid interfaces involves strong hydrogen bonding. Results obtained are in broad agreement with the relationship between adsorption and retardation described above. Indeed, qualitative data of DS are coherent with the delay observed. For example, the comparison of the HPG with different DS shows that t_{CH}(HPG1) > t_{CH}(HPG2) > t_{CH}(HPG3) with DS(HPG1) < DS(HPG2) < DS(HPG3). Moreover, delay induced by HPG 4 is slightly higher compared to HPG 5 and 6. The only difference between these HPG is the substitution of the alkyl chains which could cause steric hindrance and increase the lipophilic character of the polymer. The presence of alkyl chains could reduce slightly the adsorption and so the delay. Effectively, t_{CH}(HPG4) is higher than t_{CH}(HPG5,6). Nevertheless, the length of the alkyl chains seems to not affect the adsorption because the difference on hydration delay is negligible. Indeed, the portlandite precipitation times for HPG 5 and HPG 6 are very close.

4.2.4 Influence of admixture predissolution

The effect of the admixture predissolution on the cement hydration kinetics has also been observed. Firstly, this effect in concentrated paste was studied by isothermal calorimetry. Heat evolutions within 24h for cement pastes without and with admixtures are presented in Fig. 9. For admixed cement pastes, HPG 1 (a), HPG 2 (b) and HPG 3 (c) were predissolved or not.

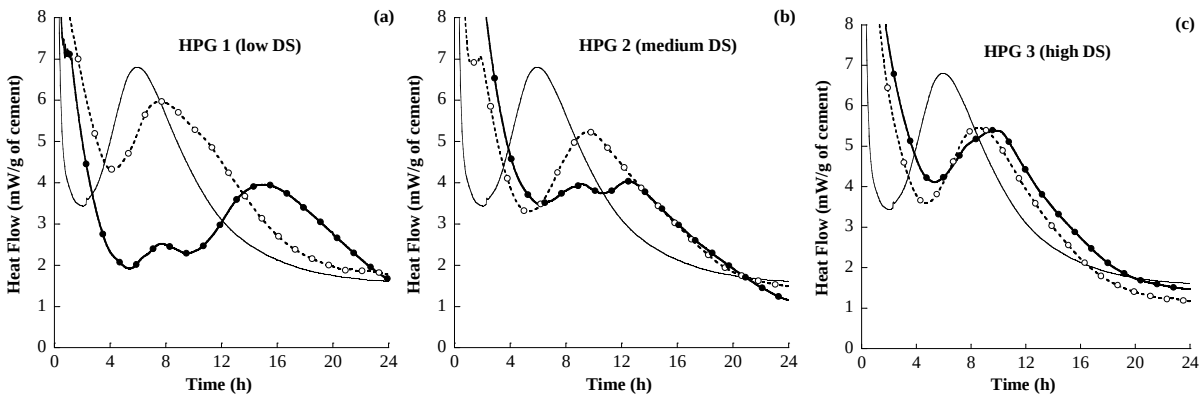

Fig. 9: Isothermal calorimetry curves of cement pastes in presence of HPG 1 (a), HPG 2 (b) and HPG 3 (c) (—— : control; - -○- - : without predissolution; —●— : with admixture predissolution).

Two significant heat flow maxima are observed at early age for the neat cement paste. According to many authors [47-50], the main peak is attributed to the alite hydration reaction. The second peak, only visible as a shoulder, corresponds to renewed dissolution of C_3A once the solid gypsum has been exhausted. For the cement pastes admixed with HPG and without predissolution, the main peak is delayed, whatever the admixture. Thus, HPG retard cement hydration at early age, as well in concentrated cement pastes as in diluted suspensions.

The polymer predissolution seems to allow the separation of the main peak into two peaks. This separation is more easily visible in the case of the HPG 1 (Fig. 9a). For HPG 4, 5 and 6, which have a high DS, the effect is very weak, as for the HPG 3 (Fig. 9c). For HPG 2 (Fig. 9b), which has an intermediate DS, separation of the peak is less pronounced than in the case

of HPG 1, but it is clearly visible. This suggests that the effect is all the more significant since the DS is low. Thus, HPG act preferentially either on the alite hydration or on the exhaustion of the solid gypsum, which is highlighted when HPG are already in the solution.

In diluted suspensions, negligible impact of predissolution is observed in water whatever the admixture considered (Fig. 10a). However, in lime suspension (Fig. 10b), the impact of predissolution is very strong for HPG 1, with a huge increase in portlandite precipitation time of 77%. As observed by isothermal calorimetry, the effect decreases when the DS increases: + 19% for HPG 2 and +10% for HPG 3. The impact of predissolution is negligible for HPG 4 and 5. For CE, no impact of predissolution is observed too, which is coherent with results of Pourchez [51]. For HPG, the delay caused by the polymer is more important after predissolution in 20 mM lime solution than in water (no effect), mainly when DS is low. It is therefore an effect of the alkalinity of the medium.

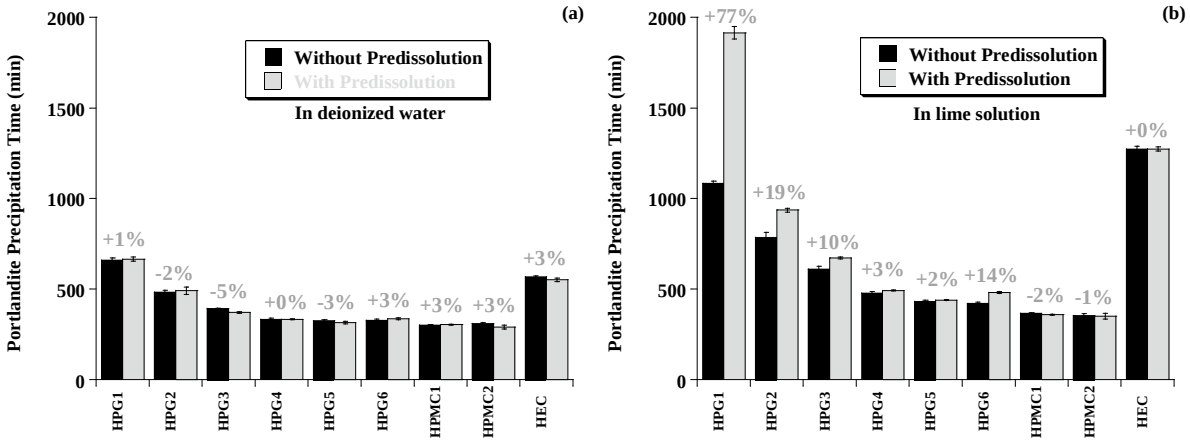

Fig. 10: Effect of predissolution of the polymer on portlandite precipitation time in diluted suspensions with L/S=20 and P/C=2% (a: deionized water; b: 20 mM lime solution).

Different hypotheses can be considered. The polymer could be degraded due to the high alkalinity reached when cement dissolves. This degradation could lead to the formation of carboxylates by peeling reaction, molecules known to have a strong retarding effect [52]. The predissolution in lime would promote this degradation, resulting in an increase in the delay.

Ultra-violet spectroscopy allows highlighting alkaline degradation. Indeed, the alkaline degradation of sugars leads to the formation of a large peak in the UV range, between 250 and 300 nm, due to the formation of saccharinic acids or the enolization of the sugars [12]. To investigate this effect, HPG and sugars (samples tested in calcium binding experiments) were stirred in water and lime solution. UV-Vis absorption spectra were carried out over time. Fig. 11 shows these results in case of HPG 1 and galactose, representing HPG and sugars respectively. In the case of HPG 1, the absorption spectra are different in water and in lime solution. Nevertheless, the difference is almost instantaneous and then remains stable over time. Therefore, it cannot be due to alkaline degradation. The difference in intensity is only due to HPG dissolution. For the other 5 HPG, no difference was observed between UV-Vis absorption spectra of polymer dissolved in water and in lime solution. On the contrary, sugars exhibit actually alkaline degradation. A new peak appears and grows with time when they are dissolved in lime solution.

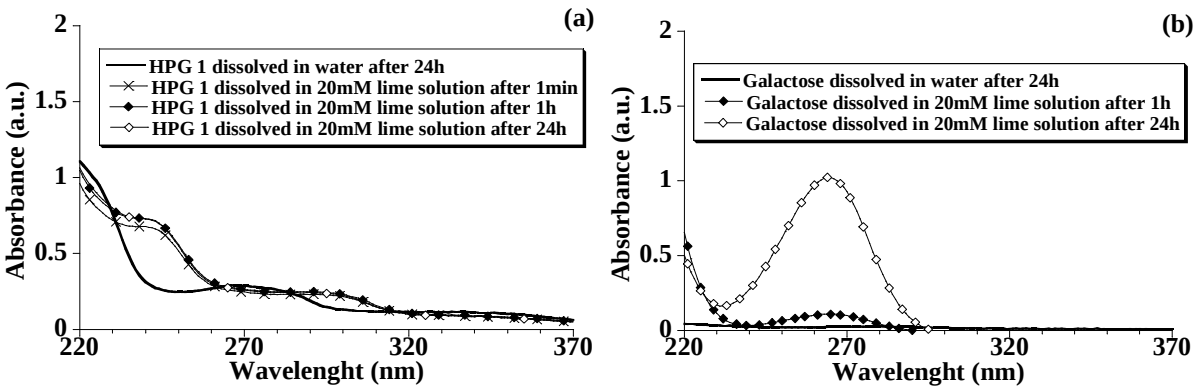

Fig. 11: Effect of dissolution media on UV-Vis absorption spectra of HPG 1 (a) and galactose (b).

Moreover, an infrared investigation was made to determine if carboxylates are formed after dissolution of HPG in alkaline media. As above, HPG were stirred in water and lime solution. After 24h, solutions were neutralized and then placed in an oven until evaporation of the

liquid phase. Solid residues were analyzed by infrared spectrometry. No band at 1590 cm^{-1}, corresponding to carboxylates functions, was observed, neither in water nor in lime solution. Thus, experiments on HPG indicate their alkaline stability. This is consistent with the hypotheses of many authors. A reduction in intrinsic viscosity has been observed for galactomannans under alkaline conditions [53–55]. However, according to these authors, this reduction is not due to degradation by a peeling reaction, but to inhibition of intermolecular interactions (hyperentanglement) because of ionization of hydroxyl groups. Izaguirre et al. reached the same conclusion with HPG [29]. Furthermore, similar results of polysaccharide alkaline stability were observed with CE [42].

A second hypothesis would be slower dissolution kinectis of the polymer in lime solution than in water. In that case, in lime solution, the polymer is not fully active to delay the cement hydration without predissolution because the dissolution would be slowdown. On the contrary, predissolution leads to the complete dissolution of the polymer and therefore a maximum delay. In water, if the dissolution is fast, predissolution could have no effect. Fig. 12 presents the effect of the media on the dissolution kinetics for HPG 1. Dissolution is very fast, both in water and in 20 mM lime solution. The polymer seems to be completely dissolved after 40 min, whatever the dissolution media. Same results are obtained for the other HPG. Thus, dissolution kinetics cannot be responsible for the predissolution effect on cement hydration kinetics. Moreover, guar gum is known to be easily soluble [56].

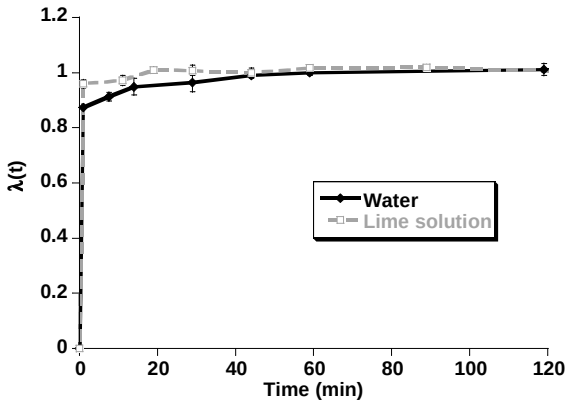

Fig. 12: Dissolution kinetics in water and in 20mM lime solution of HPG 1 at 2 g/L.

According to some authors, hydroxyl groups of galactomannans [53–55] and HPG [29] would ionize in alkaline media. It seems very probable that predissolving the polymer in the lime solution would ionize a maximum of hydroxyl groups and thus enhance the adsorption of polysaccharide on the cement phases. So, the delayed effect is greater after predissolution in lime solution, but there is no change after predissolution in water. That would explain why HPG 1, which is the polymer with the lower DS, thus higher amount of polysaccharidic backbone hydroxyl groups, is the most sensitive to predissolution. Furthermore, this hypothesis is coherent with the adsorption mechanism via the hydroxyl sites proposed to explain hydration delay induced by HPG. This is consistent with the effect of HPG predissolution in water observed by isothermal calorimetry too. Indeed, calorimetry experiments were made in concentrated pastes. The paste is quickly saturated in lime and the pH increases almost instantly. Thus, even if the polymer is predissolved in water, phenomena occurring are closer to what was observed in conductivity experiments after predissolution in lime solution.

5 Conclusions

Based upon this study, it appears that HPG delayed cement hydration with an influence on the growth of the hydrates, rather than on the germination of hydrates. Complexation of calcium ions does not explain this effect. A strong impact of the concentration on the hydration kinetics was observed. The results and the molecular similarity with CE suggest that the delay effect is due to the adsorption of the HPG via the interaction between hydroxyl groups and the highly polar hydrated phases. This hypothesis is coherent with the qualitative data of DS.

An increase in portlandite precipitation time was noticed after predissolution of HPG in lime solution. It was shown that no alkaline degradation of HPG occurs. Moreover, no difference of admixture dissolution kinetics in water or lime solution was observed. Thus, these two phenomena are not responsible for the increase in the delay. We put forward that the ionization of hydroxyl groups in alkaline media enhances the delay. This is consistent with the adsorption theory. In addition, calorimetric investigations on predissolution effect show that the delayed effect induced by HPG would be more specific on silicate or aluminate reaction.

Finally, this paper initiates the study of the interaction between cement and HPG. This polymer, whose study is very scarce in literature, presents very interesting properties. Especially, water retention properties are comparable to those obtained with CE, with the advantage of producing lower pollution during the manufacturing. Therefore, it is very important to improve knowledge of the impact of HPG on cement hydration kinetics.

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