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1 **Impact of hydroxypropylguars on the early age hydration**
2 **of portland cement**

3

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13 *ABSTRACT*

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

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

25

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

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30

31 **1 Introduction**

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

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

41 Among all polysaccharides, Cellulose Ethers (CE) are the most widely used when high water
42 retention capacity is expected. Nevertheless, HydroxyPropylGuars (HPG) were recently
43 presented as a promising new class of water-retaining agent [9]. HPG are already used in
44 various industrial fields, such as textile printing, oil production or paper manufacturing, due to
45 their thickening effect [10]. HPG were also the subject of some patents as admixture for
46 mortars.

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

54 [13], sugars could bind to the cement phases if they have a HO-C=O group, or it could be
55 formed in alkaline media, such as cement paste, by hydrolyze [14].

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

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

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

70 **2 Materials**

71 ***2.1 Mineral product***

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

77 software).

78

79

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

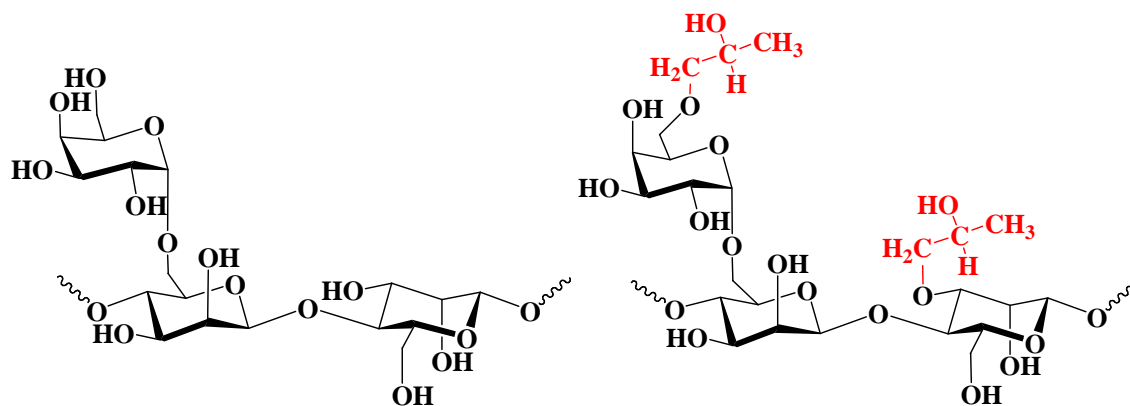
Chemical composition (% wt)				Phase composition (% wt)	
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)
CaO	66.1 ± 1.2	TiO ₂	0.24 ± 0.01	C ₃ S	73.0 ± 0.53
SiO ₂	20.2 ± 0.4	P ₂ O ₅	0.05 ± 0.01	C ₂ S	12.7 ± 0.50
Al ₂ O ₃	4.8 ± 0.1	MnO	0.04 ± 0.00	C ₃ A	4.2 ± 0.18
SO ₃	3.5 ± 0.2	K ₂ O	0.01 ± 0.01	C ₄ AF	6.1 ± 0.22
Fe ₂ O 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

80 2.2 Organic admixtures

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

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

95 the Degree of Substitution (DS). The only difference between HPG 4, 5 and 6 is the presence
 96 of additional substitution (short or long alkyl chains).
 97 In order to compare with classical polysaccharide admixtures, three CE were also tested
 98 (Table 2): two HydroxyPropylMethyl Cellulose (HPMC) named HPMC1 and HPMC2, and
 99 one HydroxyEthyl Cellulose (HEC).



100

101

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

102

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	-

103

104

105 3 Experimental methods of investigation

106 3.1 Water retention measurements

107 Water retention capacity of mortars was characterized according to ASTM C1506-09 standard
108 [32]. This test is based on a measurement of the removed water after depression and was
109 previously described by Patural et al. [3]. Water retention, noted WR, was calculated using
110 the following equation:

$$111 \quad WR(\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

112 W_0 represents the initial mass of mixing water; W_1 is the loss of water mass after aspiration.

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

122 **3.2 *Characterization of the cement hydration delay***

123 *3.2.1 Conductivity measurements on diluted suspensions*

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

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

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

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

150 3.2.2 *Isothermal calorimetry on cement pastes*

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

156 The tests were performed with an isothermal calorimeter (C80, Setaram) at 25°C. The weight
157 ratios used were W/C = 0.4, with deionized water, and P/C = 0.3 %. Ex-situ mixing was
158 preferred to in-situ mixing to improve the homogeneity of the sample, and thus
159 reproducibility. Mixing procedure, with 100g of cement, was in accordance with standard EN
160 196-1 [33]. 10 min after the beginning of the batch, about 2g of paste are introduced in the
161 calorimeter. The control used was the neat cement.

162 3.2.3 *Predissolution of the admixture*

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

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

170
$$\text{Increase of } t_{CH} (\%) = \frac{t_{CH}(\text{with prediss}) - t_{CH}(\text{without prediss})}{t_{CH}(\text{without prediss})} \times 100 \quad (2)$$

171 **3.3 Calcium binding capacity**

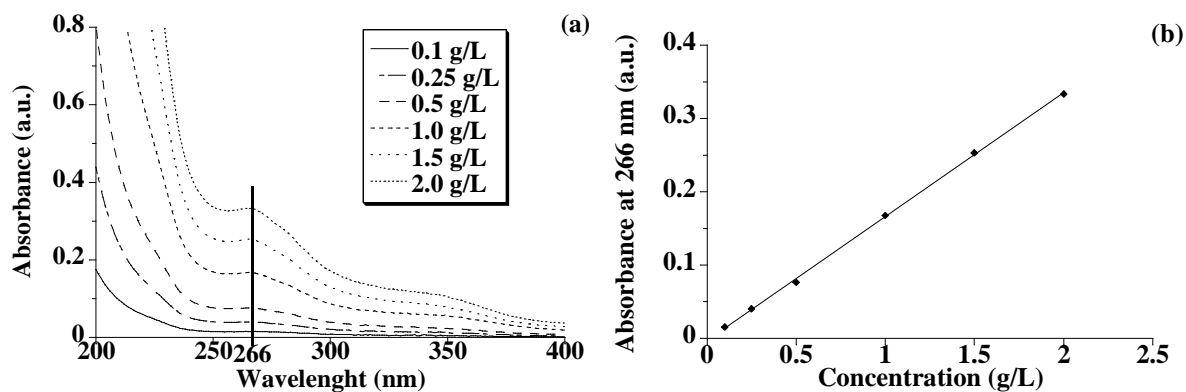
172 The ability of HPG and also sugars (sucrose which is known to complex calcium ions,
173 galactose and mannose which constitute HPG's molecule) to form complexes with calcium
174 ions was studied. Sugars are valuable insights in order to compare the behavior of HPG and to
175 validate the relevance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

176 Each sample (2 g per liter) was introduced into a volume of water (1L) containing a large
177 excess of solid lime (6 g per liter). After 48 hours of stirring at a controlled temperature of
178 23°C, the suspension was filtered through a 0.7 µm glass fiber filter. The filtrates were diluted
179 and acidified. Then, a quantification of the calcium ion content by ionic chromatography was
180 performed on a Dionex apparatus composed of a GP 50 gradient pump, a CS 12A cation-
181 exchange column and a CD 20 conductometric detector. The eluent was a solution of
182 metasulfonic acid at 20 mM with isocratic mode. The flow was fixed at 1 mL/min. The results
183 correspond to an average of 3 experiments.

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

190 **3.4 Kinetic of dissolution**

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



194

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

196 The dissolution process was monitored by acquisition of UV-Vis absorption spectra. The
197 procedure was the following: a dispersion of HPG (final concentration: $2\text{g}\cdot\text{L}^{-1}$) in deionized
198 water or 20 mM lime solution was prepared in a sealed reactor (1L of solution) thermostated
199 at 25°C . HPG was introduced through a sieve in order to have a good dispersion of the sample
200 into the vortex created by the mechanic stirrer. Thus, the aggregation of particles was
201 minimized and a homogeneous polymer solution was produced. The experiment was done
202 under continuous flow of nitrogen to avoid carbonation of lime. At different times, an aliquot
203 of approximately 5 mL was taken from the batch solution and centrifuged by means of a
204 micro-centrifuge (Eppendorf MiniSpin Plus, 14500 rpm) for 5 min in order to remove
205 undissolved particles. The supernatant was collected and homogenized by vortex-stirring. The
206 absorbance of this solution was measured between 200 and 400 nm using an UV/Visible
207 spectrophotometer (Cary 300 Scan, Varian). A degree of progress of the dissolution reaction
208 $\lambda(t)$ was used, which is equal to the absorption at time t divided by the absorption at the end

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

211 **4 Results and discussions**

212 ***4.1 Impact of HPG on water retention in fresh mortar***

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

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

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

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

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

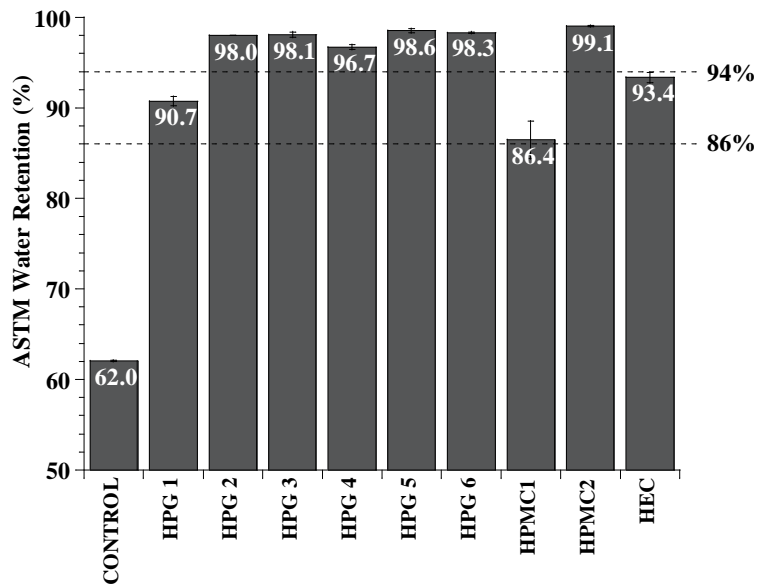


Fig. 3: Water retention capacity of studied mortars with 0.3 %w.t. of admixture.

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 ($DS_{HPG1} > DS_{HPG2} > DS_{HPG3}$). 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.

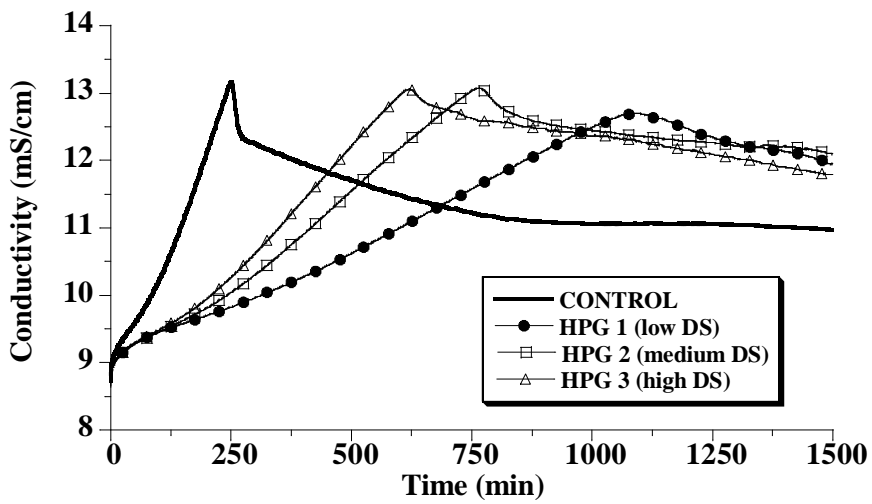
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Table 3: Comparison of conductimetric data according to the admixtures studied

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 ($\mu\text{S}\cdot\text{cm}^{-1}\cdot\text{min}^{-1}$)	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

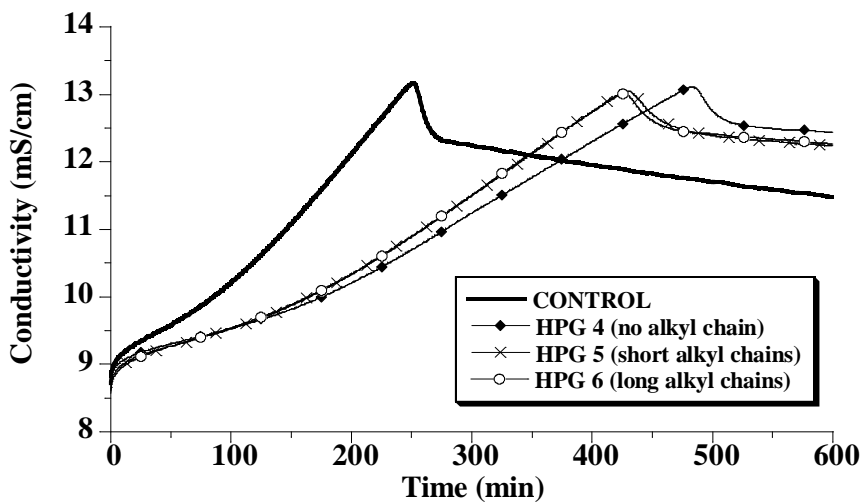
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247

248

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



249

250

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

251

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

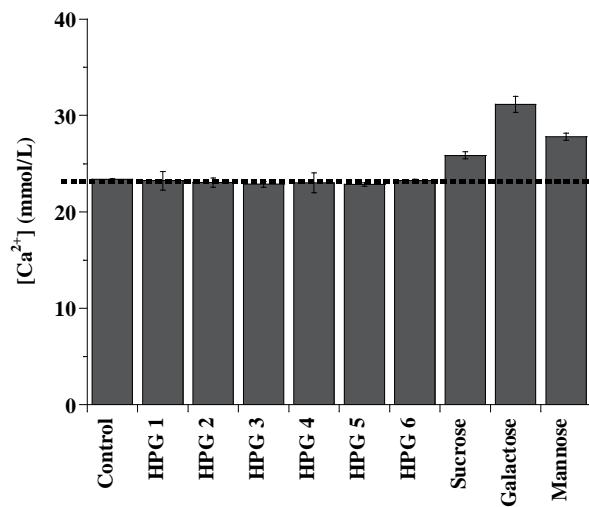
258 Some polysaccharides (dextrines for example [26]) or other admixtures (setting retarding
259 admixtures such as sugars [19], sodium gluconate [39] or some superplasticizers [36]) induce
260 a blocking effect or an inhibition of the hydration. Here, from the shape of the conductimetric
261 curves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

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

272 4.2.2 Calcium binding capacity

273 The calcium complexation is often advanced as assumption to explain the effect of retarders
274 [41]. It seemed important to check if HPG complex with calcium ions. The calcium binding
275 capacity at alkaline pH of the 6 HPG and 3 sugars were conducted and the results are

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



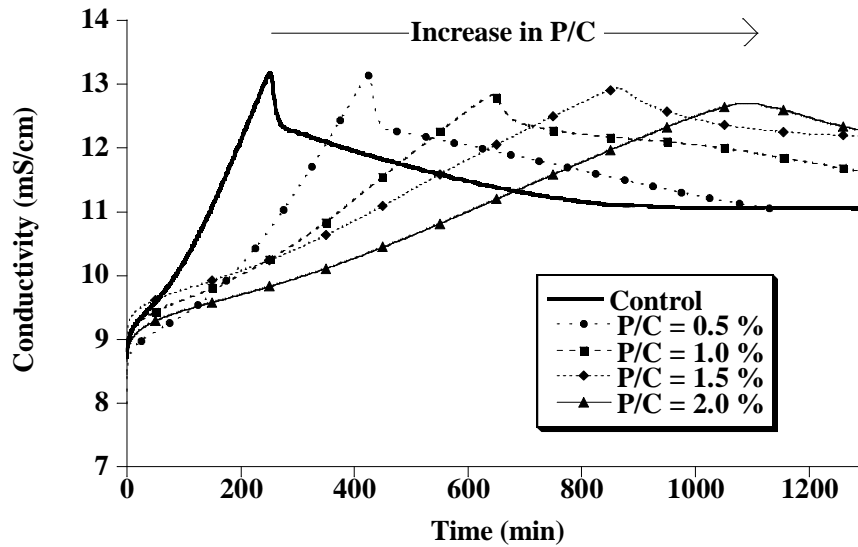
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283 **Fig. 6: Calcium binding capacity of HPG and monosaccharides.**

284 4.2.3 Influence of polymer concentration

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

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

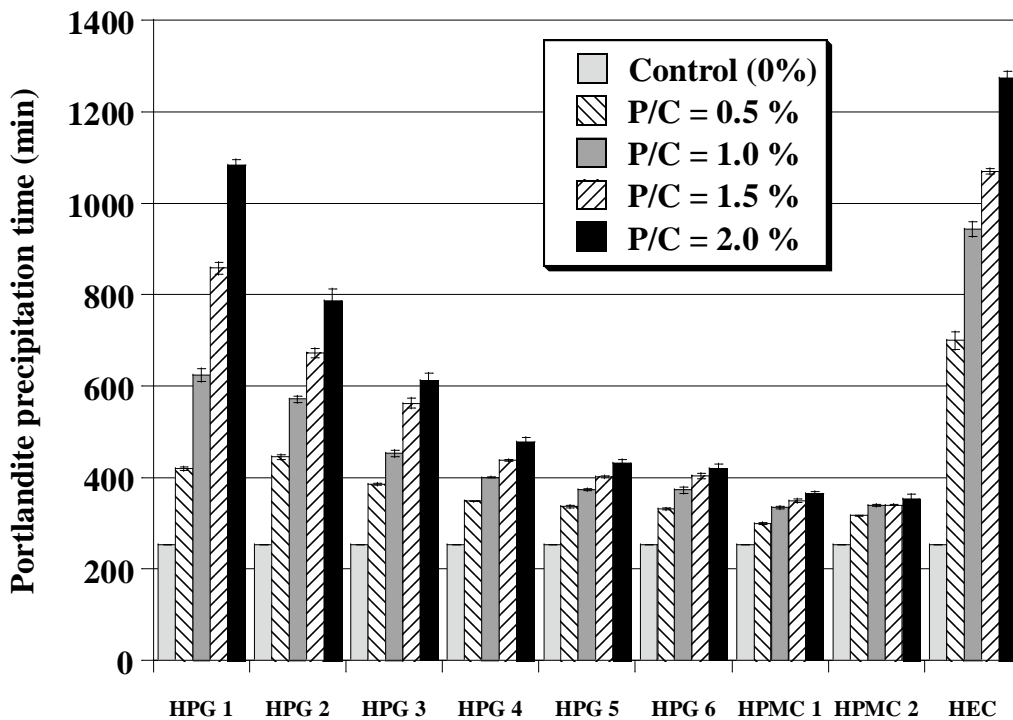


298

299 Fig.7: Conductimetric curves of cement admixed with HPG 1 in lime solution according to the P/C ratio

300

[[Ca(OH)₂]=20 mM, L/S=20).



301
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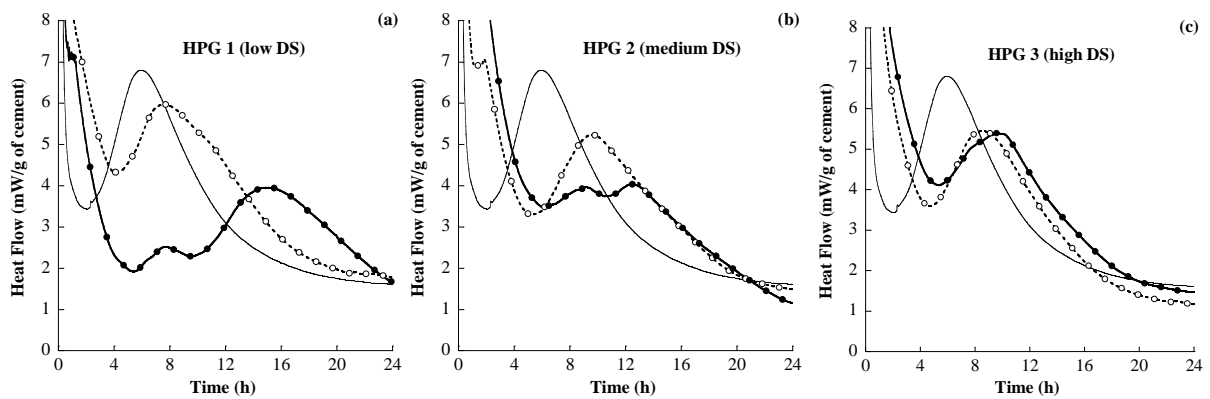
Fig. 8: Influence of admixtures concentrations on portlandite precipitation time.

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

312 For HPG, the phenomena could be very close, due to the similarity of the molecules used, in
313 particular the high content of hydroxyl groups. Wang et al. [45,46] have shown that the
314 adsorption mechanism of galactomannose polysaccharides at solid-liquid interfaces involves
315 strong hydrogen bonding. Results obtained are in broad agreement with the relationship
316 between adsorption and retardation described above. Indeed, qualitative data of DS are
317 coherent with the delay observed. For example, the comparison of the HPG with different DS
318 shows that $t_{CH}(HPG1) > t_{CH}(HPG2) > t_{CH}(HPG3)$ with $DS(HPG1) < DS(HPG2) < DS(HPG3)$.
319 Moreover, delay induced by HPG 4 is slightly higher compared to HPG 5 and 6. The only
320 difference between these HPG is the substitution of the alkyl chains which could cause steric
321 hindrance and increase the lipophilic character of the polymer. The presence of alkyl chains
322 could reduce slightly the adsorption and so the delay. Effectively, $t_{CH}(HPG4)$ is higher than
323 $t_{CH}(HPG5,6)$. Nevertheless, the length of the alkyl chains seems to not affect the adsorption
324 because the difference on hydration delay is negligible. Indeed, the portlandite precipitation
325 times for HPG 5 and HPG 6 are very close.

326 4.2.4 Influence of admixture predissolution

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



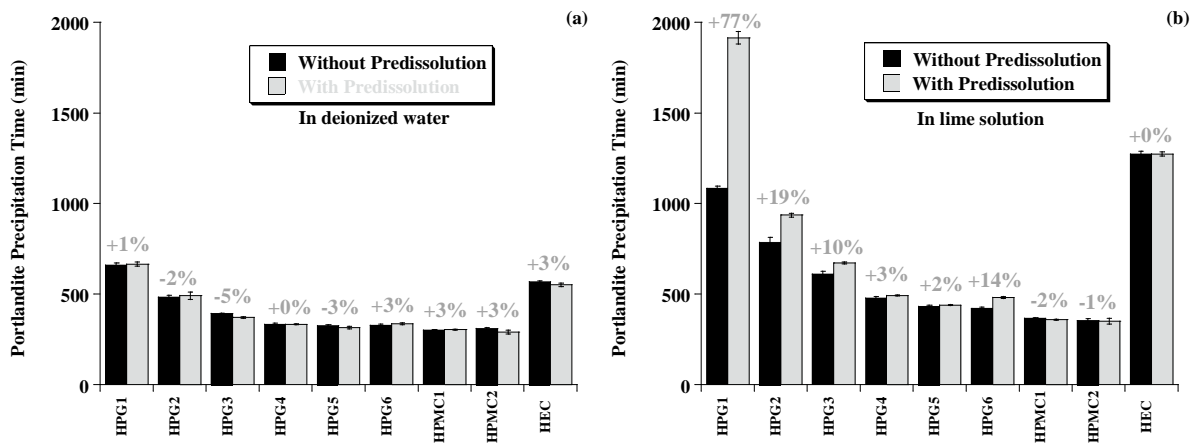
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333 **Fig. 9: Isothermal calorimetry curves of cement pastes in presence of HPG 1 (a), HPG 2 (b) and HPG 3 (c)**
334 **(— : control; --○-- : without predissolution; —●— : with admixture predissolution).**

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

341 The polymer predissolution seems to allow the separation of the main peak into two peaks.
342 This separation is more easily visible in the case of the HPG 1 (Fig. 9a). For HPG 4, 5 and 6,
343 which have a high DS, the effect is very weak, as for the HPG 3 (Fig. 9c). For HPG 2 (Fig.
344 9b), which has an intermediate DS, separation of the peak is less pronounced than in the case

345 of HPG 1, but it is clearly visible. This suggests that the effect is all the more significant since
 346 the DS is low. Thus, HPG act preferentially either on the alite hydration or on the exhaustion
 347 of the solid gypsum, which is highlighted when HPG are already in the solution.
 348 In diluted suspensions, negligible impact of predissolution is observed in water whatever the
 349 admixture considered (Fig. 10a). However, in lime suspension (Fig. 10b), the impact of
 350 predissolution is very strong for HPG 1, with a huge increase in portlandite precipitation time
 351 of 77%. As observed by isothermal calorimetry, the effect decreases when the DS increases: +
 352 19% for HPG 2 and +10% for HPG 3. The impact of predissolution is negligible for HPG 4
 353 and 5. For CE, no impact of predissolution is observed too, which is coherent with results of
 354 Pourchez [51]. For HPG, the delay caused by the polymer is more important after
 355 predissolution in 20 mM lime solution than in water (no effect), mainly when DS is low. It is
 356 therefore an effect of the alkalinity of the medium.

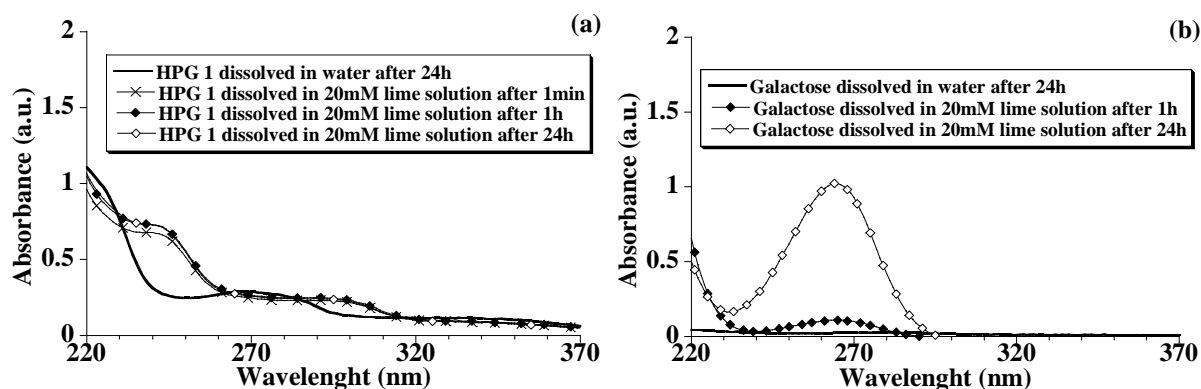


357

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

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

364 Ultra-violet spectroscopy allows highlighting alkaline degradation. Indeed, the alkaline
 365 degradation of sugars leads to the formation of a large peak in the UV range, between 250 and
 366 300 nm, due to the formation of saccharinic acids or the enolization of the sugars [12]. To
 367 investigate this effect, HPG and sugars (samples tested in calcium binding experiments) were
 368 stirred in water and lime solution. UV-Vis absorption spectra were carried out over time. Fig.
 369 11 shows these results in case of HPG 1 and galactose, representing HPG and sugars
 370 respectively. In the case of HPG 1, the absorption spectra are different in water and in lime
 371 solution. Nevertheless, the difference is almost instantaneous and then remains stable over
 372 time. Therefore, it cannot be due to alkaline degradation. The difference in intensity is only
 373 due to HPG dissolution. For the other 5 HPG, no difference was observed between UV-Vis
 374 absorption spectra of polymer dissolved in water and in lime solution. On the contrary, sugars
 375 exhibit actually alkaline degradation. A new peak appears and grows with time when they are
 376 dissolved in lime solution.



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

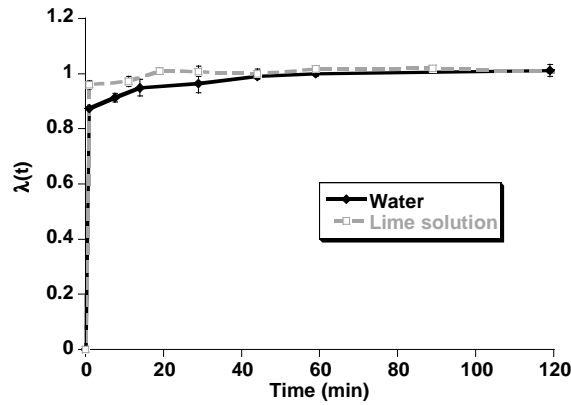
379 Moreover, an infrared investigation was made to determine if carboxylates are formed after
 380 dissolution of HPG in alkaline media. As above, HPG were stirred in water and lime solution.
 381 After 24h, solutions were neutralized and then placed in an oven until evaporation of the

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

391 A second hypothesis would be slower dissolution kinetics of the polymer in lime solution than
392 in water. In that case, in lime solution, the polymer is not fully active to delay the cement
393 hydration without predissolution because the dissolution would be slowdown. On the
394 contrary, predissolution leads to the complete dissolution of the polymer and therefore a
395 maximum delay. In water, if the dissolution is fast, predissolution could have no effect. Fig.
396 12 presents the effect of the media on the dissolution kinetics for HPG 1. Dissolution is very
397 fast, both in water and in 20 mM lime solution. The polymer seems to be completely
398 dissolved after 40 min, whatever the dissolution media. Same results are obtained for the
399 other HPG. Thus, dissolution kinetics cannot be responsible for the predissolution effect on
400 cement hydration kinetics. Moreover, guar gum is known to be easily soluble [56].

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

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According to some authors, hydroxyl groups of galactomannans [53–55] and HPG [29] would

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ionize in alkaline media. It seems very probable that predissolving the polymer in the lime

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solution would ionize a maximum of hydroxyl groups and thus enhance the adsorption of

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polysaccharide on the cement phases. So, the delayed effect is greater after predissolution in

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lime solution, but there is no change after predissolution in water. That would explain why

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HPG 1, which is the polymer with the lower DS, thus higher amount of polysaccharidic

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backbone hydroxyl groups, is the most sensitive to predissolution. Furthermore, this

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hypothesis is coherent with the adsorption mechanism via the hydroxyl sites proposed to

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explain hydration delay induced by HPG. This is consistent with the effect of HPG

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predissolution in water observed by isothermal calorimetry too. Indeed, calorimetry

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experiments were made in concentrated pastes. The paste is quickly saturated in lime and the

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pH increases almost instantly. Thus, even if the polymer is predissolved in water, phenomena

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occurring are closer to what was observed in conductivity experiments after predissolution in

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lime solution.

419 **5 Conclusions**

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

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

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

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