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► **To cite this version:**

Thomas Poinot, Alexandre Govin, Philippe Grosseau. Impact of hydroxypropylguars on the early age hydration of Portland cement. *Cement and Concrete Research*, 2013, 44, pp.69-76. 10.1016/j.cemconres.2012.10.010 . hal-00758284v1

HAL Id: hal-00758284

<https://hal.science/hal-00758284v1>

Submitted on 29 Nov 2012 (v1), last revised 15 Feb 2013 (v2)

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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
26
27 *KEYWORDS: polysaccharide (D), hydroxypropylguars (D), retardation (A), hydration (A),*
28 *water retention (C)*

29

30 **1 Introduction**

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

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

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

46 The effect of saccharides has been largely studied these fifty last years, in particular from a
47 cement hydration delay point of view. In the first time, the delayed effect of monosaccharides
48 was investigated [11–19]. It appears that sugars could be adsorbed to cement phases by a
49 chelation process. It can thereby form a temporary barrier to further hydration. In broad
50 agreement with Young [11], Thomas and Birchall [12] proposed that sugars would be able to
51 poison the surfaces of the CH and CSH by complexation onto these phases, which inhibit
52 their growth and therefore would be responsible for the delay observed. According to Taplin
53 [13], sugars could bind to the cement phases if they have a HO-C=O group, or it could be
54 formed in alkaline media, such as cement paste, by hydrolyze [14].

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

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

64 Firstly, the water-retaining effect induced by the HPG in Portland cement-based mortars will
65 be checked. Secondly, cement hydration kinetics in the presence of HPG will be presented.

66 Hydration kinetics have been monitored by conductivity and isothermal calorimetry
67 measurements. Finally, a special focus on the influence of the polymer predissolution has
68 been performed.

69 **2 Materials**

70 ***2.1 Mineral product***

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

77 2.2 *Organic admixtures*

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

88 HPG are obtained from the native guar gum via an irreversible nucleophilic substitution,
89 using propylene oxide in the presence of an alkaline catalyst (Fig. 1b). Table 2 gives a
90 qualitative description of the six HPG samples from *Lamberti S.p.A* which were studied. All
91 the samples have similar molecular weight. The only difference between HPG 1, 2 and 3 is
92 the Degree of Substitution (DS). The only difference between HPG 4, 5 and 6 is the presence
93 of additional substitution (short or long alkyl chains).

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

97 **3 Experimental methods of investigation**

98 **3.1 Water retention measurements**

99 Water retention capacity of mortars was characterized according to ASTM C1506-09 standard
100 [32]. This test is based on a measurement of the removed water after depression and was
101 previously described by Patural et al. [3]. Water retention, noted WR, was calculated using
102 the following equation:

$$103 \quad WR(\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

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

114 **3.2 Characterization of the cement hydration delay**

115 **3.2.1 Conductivity measurements on diluted suspensions**

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

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

136 Experiments were performed in diluted suspensions, thermostated at 25°C and continuously
137 stirred. Each experiment was carried out in triplicate. The liquid to solid weight ratio (L/S)
138 used was equal to 20. Polymer to cement weight ratios (P/C) equal to 0.5, 1.0, 1.5 and 2.0 %
139 were studied. Cement and admixture powders were blended in a shaker (Turbula, Wab) for 10
140 min before contact with the liquid phase. The liquid used was a 20 mM lime solution or
141 deionized water. The control used was the neat cement.

142 3.2.2 *Isothermal calorimetry on cement pastes*

143 Calorimetry is another technique useful to characterize the exothermic hydration process of
144 cement. The hydration process can be followed continuously at realistic water/cement ratios
145 (W/C) in situ and aims at giving an indication of the overall rate of reaction. Thus,
146 calorimetry can be used as a complementary method to conductivity in order to monitor the
147 kinetics of cement hydration and to observe hydration delay induced by retarders [37].
148 The tests were performed with an isothermal calorimeter (C80, Setaram) at 25°C. The weight
149 ratios used were W/C = 0.4, with deionized water, and P/C = 0.3 %. Ex-situ mixing was
150 preferred to in-situ mixing to improve the homogeneity of the sample, and thus
151 reproducibility. Mixing procedure, with 100g of cement, was in accordance with standard EN
152 196-1 [33]. 10 min after the beginning of the batch, about 2g of paste are introduced in the
153 calorimeter. The control used was the neat cement.

154 3.2.3 *Predissolution of the admixture*

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

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

162
$$\text{Increase of } t_{CH} (\%) = \frac{t_{CH}(\text{with prediss}) - t_{CH}(\text{without prediss})}{t_{CH}(\text{without prediss})} \times 100 \quad (2)$$

163 **3.3 *Calcium binding capacity***

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

168 Each sample (2 g per liter) was introduced into a volume of water (1L) containing a large
169 excess of solid lime (6 g per liter). After 48 hours of stirring at a controlled temperature of
170 23°C, the suspension was filtered through a 0.7 µm glass fiber filter. The filtrates were diluted
171 and acidified. Then, a quantification of the calcium ion content by ionic chromatography was
172 performed on a Dionex apparatus composed of a GP 50 gradient pump, a CS 12A cation-
173 exchange column and a CD 20 conductometric detector. The eluent was a solution of
174 metasulfonic acid at 20 mM with isocratic mode. The flow was fixed at 1 mL/min. The results
175 correspond to an average of 3 experiments.

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

182 **3.4 *Kinetic of dissolution***

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

186 The dissolution process was monitored by acquisition of UV-Vis absorption spectra. The
187 procedure was the following: a dispersion of HPG (final concentration: $2\text{g}\cdot\text{L}^{-1}$) in deionized
188 water or 20 mM lime solution was prepared in a sealed reactor (1L of solution) thermostated
189 at 25°C . HPG was introduced through a sieve in order to have a good dispersion of the sample
190 into the vortex created by the mechanic stirrer. Thus, the aggregation of particles was
191 minimized and a homogeneous polymer solution was produced. The experiment was done
192 under continuous flow of nitrogen to avoid carbonation of lime. At different times, an aliquot
193 of approximately 5 mL was taken from the batch solution and centrifuged by means of a
194 micro-centrifuge (Eppendorf MiniSpin Plus, 14500 rpm) for 5 min in order to remove
195 undissolved particles. The supernatant was collected and homogenized by vortex-stirring. The
196 absorbance of this solution was measured between 200 and 400 nm using an UV/Visible
197 spectrophotometer (Cary 300 Scan, Varian). A degree of progress of the dissolution reaction
198 $\lambda(t)$ was used, which is equal to the absorption at time t divided by the absorption at the end
199 of the dissolution reaction (*i.e.* 24 h). This number is adimensional and its value is between 0
200 and 1.

201 **4 Results and discussions**

202 ***4.1 Impact of HPG on water retention in fresh mortar***

203 Water retention is a very sensitive mortar property. Indeed, it must be important enough to not
204 disturb the hydration of the cement. It also limits the absorption of the mixing water by the
205 substrate and thus provides good mechanical and adhesive properties to the mortar.
206 DTU 26.1 [38] specifies three classes of water retention of a fresh mortar. The first one
207 represents mortars which water retention is lower than 86%; they belong to the low water
208 retention category. The second class (intermediate water retention) corresponds to values

209 ranging from 86% to 94%. The last one is defined by water retention higher than 94%. This
210 class is related to strong water retention mortar and is desired by formulators of industrial
211 mortars.
212 Water retention capacity of the studied mortars according to the admixture used is shown in
213 Fig. 3. With this formulation, mortars containing HPG 2 to 6 and HPMC 2 could be
214 considered as high WR capacity according to the DTU 26.1. Mortars containing HPG 1,
215 HPMC 1 and HEC are in the intermediate category.
216 Thus, HPG improve considerably the water retention capacity of the mortar compared to the
217 control without water-retention admixture, as announced by Plank [9]. In addition, the results
218 are quite comparable to those obtained with the CE of reference.
219 Therefore, HPG can be considered as promising water-retention agents for dry-mix Portland
220 cement-based mortars.

221 ***4.2 Impact of HPG on hydration kinetics of cement***

222 ***4.2.1 Delayed effect***

223 The delayed effect of HPG on cement hydration kinetics was monitored by conductivity in a
224 20 mM lime solution, for ratios $L/S = 20$ and $P/C = 2\%$. To have a clear and readable
225 analysis, all the conductimetric curves will not be presented on the same figure. Thus, Table 3
226 regroups the conductimetric data obtained (i.e. portlandite precipitation times, delays
227 compared to the control and conductimetric slopes). Fig. 4 presents the influence of the DS on
228 the conductimetric curves by studying HPG 1, 2 and 3 which are the same molecules, except
229 the DS ($DSHPG1 > DSHPG2 > DSHPG3$). The influence of the alkyl substitution was studied
230 by comparison of HPG 4, 5 and 6 (see Table 2). The conductimetric curves obtained are
231 shown in Fig. 5.

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

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

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

252 4.2.2 *Calcium binding capacity*

253 The calcium complexation is often advanced as assumption to explain the effect of retarders
254 [41]. It seemed important to check if HPG complex with calcium ions. The calcium binding
255 capacity at alkaline pH of the 6 HPG and 3 sugars were conducted and the results are
256 presented in Fig. 6. It appears clearly that the complexation of calcium ions by HPG is null or

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

262 4.2.3 *Influence of polymer concentration*

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

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

276 The mechanism responsible for the delay induced by CE is the adsorption of the molecule on
277 the hydrate cement phases. Indeed, Pourchez et al. have shown evidence of the adsorption of
278 CE on calcium hydroaluminates [44] and CSH/CH [40]. Polysaccharides are molecules which
279 contain a lot of polar functional groups (-OH). Therefore, strong interactions, through
280 electrostatic forces and hydrogen-bonding, can occur between polysaccharides and the highly
281 polar hydrated phases [43]. The relationship between adsorption and retardation was

282 previously shown [25,40]. It results that the higher the substituent content is, the weaker the
283 retardation ability is, because of lower amount of free hydroxyls and so lower adsorption
284 ability.

285 For HPG, the phenomena could be very close, due to the similarity of the molecules used, in
286 particular the high content of hydroxyl groups. Wang et al. [45,46] have shown that the
287 adsorption mechanism of galactomannose polysaccharides at solid-liquid interfaces involves
288 strong hydrogen bonding. Results obtained are in broad agreement with the relationship
289 between adsorption and retardation described above. Indeed, qualitative data of DS are
290 coherent with the delay observed. For example, the comparison of the HPG with different DS
291 shows that $t_{CH}(HPG1) > t_{CH}(HPG2) > t_{CH}(HPG3)$ with $DS(HPG1) < DS(HPG2) < DS(HPG3)$.
292 Moreover, delay induced by HPG 4 is slightly higher compared to HPG 5 and 6. The only
293 difference between these HPG is the substitution of the alkyl chains which could cause steric
294 hindrance and increase the lipophilic character of the polymer. The presence of alkyl chains
295 could reduce slightly the adsorption and so the delay. Effectively, $t_{CH}(HPG4)$ is higher than
296 $t_{CH}(HPG5,6)$. Nevertheless, the length of the alkyl chains seems to not affect the adsorption
297 because the difference on hydration delay is negligible. Indeed, the portlandite precipitation
298 times for HPG 5 and HPG 6 are very close.

299 4.2.4 *Influence of admixture predissolution*

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

305 Two significant heat flow maxima are observed at early age for the neat cement paste.
306 According to many authors [47-50], the main peak is attributed to the alite hydration reaction.

307 The second peak, only visible as a shoulder, corresponds to renewed dissolution of C_3A once
308 the solid gypsum has been exhausted. For the cement pastes admixed with HPG and without
309 predissolution, the main peak is delayed, whatever the admixture. Thus, HPG retard cement
310 hydration at early age, as well in concentrated cement pastes as in diluted suspensions.

311 The polymer predissolution seems to allow the separation of the main peak into two peaks.
312 This separation is more easily visible in the case of the HPG 1 (Fig. 9a). For HPG 4, 5 and 6,
313 which have a high DS, the effect is very weak, as for the HPG 3 (Fig. 9c). For HPG 2 (Fig.
314 9b), which has an intermediate DS, separation of the peak is less pronounced than in the case
315 of HPG 1, but it is clearly visible. This suggests that the effect is all the more significant since
316 the DS is low. Thus, HPG act preferentially either on the alite hydration or on the exhaustion
317 of the solid gypsum, which is highlighted when HPG are already in the solution.

318 In diluted suspensions, negligible impact of predissolution is observed in water whatever the
319 admixture considered (Fig. 10a). However, in lime suspension (Fig. 10b), the impact of
320 predissolution is very strong for HPG 1, with a huge increase in portlandite precipitation time
321 of 77%. As observed by isothermal calorimetry, the effect decreases when the DS increases: +
322 19% for HPG 2 and +10% for HPG 3. The impact of predissolution is negligible for HPG 4
323 and 5. For CE, no impact of predissolution is observed too, which is coherent with results of
324 Pourchez [51]. For HPG, the delay caused by the polymer is more important after
325 predissolution in 20 mM lime solution than in water (no effect), mainly when DS is low. It is
326 therefore an effect of the alkalinity of the medium.

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

331 Ultra-violet spectroscopy allows highlighting alkaline degradation. Indeed, the alkaline
332 degradation of sugars leads to the formation of a large peak in the UV range, between 250 and
333 300 nm, due to the formation of saccharinic acids or the enolization of the sugars [12]. To
334 investigate this effect, HPG and sugars (samples tested in calcium binding experiments) were
335 stirred in water and lime solution. UV-Vis absorption spectra were carried out over time. Fig.
336 11 shows these results in case of HPG 1 and galactose, representing HPG and sugars
337 respectively. In the case of HPG 1, the absorption spectra are different in water and in lime
338 solution. Nevertheless, the difference is almost instantaneous and then remains stable over
339 time. Therefore, it cannot be due to alkaline degradation. The difference in intensity is only
340 due to HPG dissolution. For the other 5 HPG, no difference was observed between UV-Vis
341 absorption spectra of polymer dissolved in water and in lime solution. On the contrary, sugars
342 exhibit actually alkaline degradation. A new peak appears and grows with time when they are
343 dissolved in lime solution.

344 Moreover, an infrared investigation was made to determine if carboxylates are formed after
345 dissolution of HPG in alkaline media. As above, HPG were stirred in water and lime solution.
346 After 24h, solutions were neutralized and then placed in an oven until evaporation of the
347 liquid phase. Solid residues were analyzed by infrared spectrometry. No band at 1590 cm^{-1} ,
348 corresponding to carboxylates functions, was observed, neither in water nor in lime solution.

349 Thus, experiments on HPG indicate their alkaline stability. This is consistent with the
350 hypotheses of many authors. A reduction in intrinsic viscosity has been observed for
351 galactomannans under alkaline conditions [53–55]. However, according to these authors, this
352 reduction is not due to degradation by a peeling reaction, but to inhibition of intermolecular
353 interactions (hyperentanglement) because of ionization of hydroxyl groups. Izaguirre et al.
354 reached the same conclusion with HPG [29]. Furthermore, similar results of polysaccharide
355 alkaline stability were observed with CE [42].

356 A second hypothesis would be slower dissolution kinetics of the polymer in lime solution than
357 in water. In that case, in lime solution, the polymer is not fully active to delay the cement
358 hydration without predissolution because the dissolution would be slowed down. On the
359 contrary, predissolution leads to the complete dissolution of the polymer and therefore a
360 maximum delay. In water, if the dissolution is fast, predissolution could have no effect. Fig.
361 12 presents the effect of the media on the dissolution kinetics for HPG 1. Dissolution is very
362 fast, both in water and in 20 mM lime solution. The polymer seems to be completely
363 dissolved after 40 min, whatever the dissolution media. Same results are obtained for the
364 other HPG. Thus, dissolution kinetics cannot be responsible for the predissolution effect on
365 cement hydration kinetics. Moreover, guar gum is known to be easily soluble [56].
366 According to some authors, hydroxyl groups of galactomannans [53–55] and HPG [29] would
367 ionize in alkaline media. It seems very probable that predissolving the polymer in the lime
368 solution would ionize a maximum of hydroxyl groups and thus enhance the adsorption of
369 polysaccharide on the cement phases. So, the delayed effect is greater after predissolution in
370 lime solution, but there is no change after predissolution in water. That would explain why
371 HPG 1, which is the polymer with the lower DS, thus higher amount of polysaccharidic
372 backbone hydroxyl groups, is the most sensitive to predissolution. Furthermore, this
373 hypothesis is coherent with the adsorption mechanism via the hydroxyl sites proposed to
374 explain hydration delay induced by HPG. This is consistent with the effect of HPG
375 predissolution in water observed by isothermal calorimetry too. Indeed, calorimetry
376 experiments were made in concentrated pastes. The paste is quickly saturated in lime and the
377 pH increases almost instantly. Thus, even if the polymer is predissolved in water, phenomena
378 occurring are closer to what was observed in conductivity experiments after predissolution in
379 lime solution.

380 **5 Conclusions**

381 Based upon this study, it appears that HPG delayed cement hydration with an influence on the
382 growth of the hydrates, rather than on the germination of hydrates. Complexation of calcium
383 ions does not explain this effect. A strong impact of the concentration on the hydration
384 kinetics was observed. The results and the molecular similarity with CE suggest that the delay
385 effect is due to the adsorption of the HPG via the interaction between hydroxyl groups and the
386 highly polar hydrated phases. This hypothesis is coherent with the qualitative data of DS.
387 An increase in portlandite precipitation time was noticed after predissolution of HPG in lime
388 solution. It was shown that no alkaline degradation of HPG occurs. Moreover, no difference
389 of admixture dissolution kinetics in water or lime solution was observed. Thus, these two
390 phenomena are not responsible for the increase in the delay. We put forward that the
391 ionization of hydroxyl groups in alkaline media enhances the delay. This is consistent with
392 the adsorption theory. In addition, calorimetric investigations on predissolution effect show
393 that the delayed effect induced by HPG would be more specific on silicate or aluminate
394 reaction.

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

400 **Acknowledgments**

401 The authors would like to acknowledge Lamberti S.p.A. for the provided products.

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