



HAL
open science

Impact of miscanthus lignin and arabinoxylan on Portland cement

Jordi Girones, Loan T.T. Vo, Grégory Mouille, Joan Oñate Narciso, Stéphanie Arnoult, Maryse Brancourt-Hulmel, Patrick Navard, Catherine Lapierre

► **To cite this version:**

Jordi Girones, Loan T.T. Vo, Grégory Mouille, Joan Oñate Narciso, Stéphanie Arnoult, et al.. Impact of miscanthus lignin and arabinoxylan on Portland cement. *Industrial Crops and Products*, 2022, 188, pp.115585. 10.1016/j.indcrop.2022.115585 . hal-04000204

HAL Id: hal-04000204

<https://hal.science/hal-04000204v1>

Submitted on 22 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

Impact of miscanthus lignin and arabinoxylan on Portland cement

Jordi Girones¹, Loan T. T. Vo¹, Grégory Mouille², Joan Oñate Narciso^{2*}, Stéphanie Arnoult³, Maryse Brancourt-Hulmel⁴, Patrick Navard^{1}, Catherine Lapiere²**

*1- MINES ParisTech, PSL Research University, CEMEF*** - Centre de mise en forme des matériaux, CNRS UMR 7635, CS 10207 rue Claude Daunesse 06904 Sophia Antipolis Cedex, France*

2- Institut Jean-Pierre Bourgin, INRAE, AgroParisTech, Université Paris-Saclay, 78000 Versailles, France

3- INRAE, UE GCIE Picardie, Estrées-Mons, 80203 Péronne, France

4 BioEcoAgro Joint Research Unit – INRAE AgroImpact - Université de Liège - Université de Lille - Université de Picardie Jules Verne, Site d'Estrées-Mons CS 50136 80203 Péronne cedex, France

**Present address: ETH Zürich Department of Health Sciences and Technology, Schmelzbergstrasse 9 8092 Zürich Switzerland*

***Corresponding author:*

Patrick Navard: patrick.navard@minesparis.psl.eu

****Member of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu*

22 **Abstract**

23 Miscanthus biomass can be used to produce lightweight concrete. However, cell wall
24 polymers leached in the alkaline cementitious medium can disturb cement setting. This is the
25 case for grass lignin and grass arabinoxylan due to their specific alkali solubility. The main
26 objective of this paper was to study the impact of lignin and of arabinoxylan from miscanthus
27 biomass on the hydration of Portland cement and by electrical conductivity. To this end,
28 dioxan lignin (DL) and arabinoxylan (AX) were extracted from miscanthus by methods
29 preserving the main structural specificities of the native polymers. These DL and AX
30 fractions were added to Portland cement (1-5% w/w in cement) and their impact on the
31 electrical conductivity of cement/water mixtures was time-monitored. The novelty of this
32 study lies in using polymers structurally similar to those of miscanthus fibers rather than
33 commercially available ones, such as kraft lignin (KL). The addition of DL or of KL to
34 cement/water mixture differently affected the electrical conductivity, which is most likely
35 assignable to the severe structural degradation of KL during kraft process. The conductivity
36 curves suggested that cement hydration was substantially delayed when DL % in cement was
37 3% or more while lower values had no impact. The results support the hypothesis that the
38 access of water to cement grains was impeded by the adsorption of ionized lignin entities at
39 their surface. When co-added to the cement (1.6 wt% each), the DL and AX fraction delayed
40 cement hydration more substantially than when the same amounts were separately added. This
41 unexpected synergy suggests that the miscanthus lignin and arabinoxylan polymers form
42 lignin-carbohydrate complexes efficiently adsorbed on cement grains.

43

44

45 **Keywords:** Cement; Dioxane Lignin; Kraft Lignin; Arabinoxylan; Electrical conductivity;

46 Miscanthus

47 **1 Introduction**

48 Concrete is one of the most used materials by human beings. Composed of cement, water,
49 mineral aggregates and various admixtures and reinforcing agents, its mechanical, aesthetical
50 and processing property may vary to a large extent (Neville and Brooks, 2010, Nazar et al.,
51 2020). With the objective to improve the poor environmental performances of concrete, many
52 research efforts have been recently performed to partially replace mineral aggregates by
53 renewable plant fibers (Lilargem Rocha et al., 2022; Amin et al., 2022; Li et al., 2021;
54 Pacheto-Torgal and Jalali, 2011; Vo and Navard, 2016). The addition of plant fibers
55 beneficially reduces the carbon footprint of concrete but may be detrimental to the setting of
56 cement and its mechanical properties to an extent which may vary with the plant material
57 (Amin et al., 2022; Pacheto-Torgal and Jalali, 2011). This effect may be assigned to
58 compounds released from plant fibers into the alkaline cement-water mixture and which
59 interact with cement grains and thereby modify cement hydration and setting (Amin et al.,
60 2022; Bourdot et al., 2019).

61 The objective of this study is to investigate the effect of lignin and of arabinoxylan isolated
62 from miscanthus on the hydration kinetics of Portland cement and by electrical conductivity
63 measurements. Miscanthus, a high biomass yield perennial grass, is considered as a major
64 crop for non-food industrial applications, such as the production of bioenergy and of
65 biomaterials (Ben Fradj et al., 2020; Brosse et al., 2012; Jørgensen, 2011; Moll et al., 2020).
66 Similar to other grass lignins, miscanthus lignins are mainly composed of guaiacyl (G) and
67 syringyl (S) phenylpropane units, together with a low amount of *p*-hydroxyphenyl (H) units.
68 In addition, these grass lignin units are acylated by *p*-coumaric acid (CA) (up to 10% by
69 weight) (Halpin, 2019; Ralph, 2010; Vogel, 2008) These units are interconnected mainly by
70 labile ether bonds, referred to as β -O-4 linkages, together with more resistant carbon-carbon
71 linkages (Gellerstedt et al., 2008; Ralph et al. 2019). By contrast to non grass lignins, grass

72 lignins are substantially solubilized by cold alkali (up to 50-60% of the total lignin amount)
73 (Halpin, 2019; Lapierre, 2010).

74 Since many years, there have been intensive studies about the valorization of industrial
75 lignins, mainly kraft lignins and lignosulfonates, as beneficial additives in cementitious
76 materials (reviewed in Bajwa et al., 2019; Breilly et al., 2021; Jędrzejczak et al., 2021;
77 Klapiszewski et al., 2021; Mullick, 1996). By contrast, the study of cement setting in presence
78 of lignin or of hemicellulose alkali-leached from plant fibers incorporated into cement
79 materials has been studied to a lower extent. These studies were conducted either with plant
80 aqueous leachates containing various compounds (most often carbohydrates) or with various
81 models such as simple sugars, commercially available wood hemicellulose and softwood kraft
82 lignin (Bilba et al., 2003; Delannoy et al., 2020; Govin et al., 2007; Kochova et al., 2017; Xie
83 et al., 2016). A major and overlooked drawback of using commercially available wood
84 polymers as representatives of alkali-leachable miscanthus polymers is the dramatic structural
85 differences between them. Such a structural gap is particularly striking for kraft lignins
86 dramatically degraded during the harsh kraft cooking. To the best of our knowledge, this
87 study is the first one in which the interaction between cement and alkali-soluble wall
88 polymers is performed with purified lignin and arabinoxylan fractions isolated from
89 miscanthus stems by procedures which preserve the structural specificities of the
90 corresponding alkali-leachable polymers. To this end, we purified a dioxane lignin (DL)
91 fraction from miscanthus and added various DL amounts to water/cement mixture. The
92 impact of this miscanthus DL fraction on the hydration kinetics of Portland cement was
93 studied by electrical conductivity measurements and compared to the effect of the commercial
94 kraft lignin (KL) used in previous papers (Bilba et al., 2003; Kochova et al., 2017; Xie et al.,
95 2016). As grass arabinoxylans (AX) are also soluble in cold alkali (Marriott et al., 2016;
96 Scheller and Ulvskov, 2010; Terrett and Dupree, 2019), we purified an AX fraction from

97 miscanthus stems and studied the impact of AX and of (AX+DL) mixture on the hydration
98 kinetics of cement.

99

100 **2 Materials and methods**

101

102 Major abbreviations: dioxane lignin (DL); arabinoxylan (AX); kraft lignin (KL); guaiacyl (G);
103 syringyl (S); *p*-hydroxyphenyl (H); *p*-coumaric acid (CA).

104

105 2.1 Raw materials

106

107 Portland cement (CEM I 52.5R CE CP2 NF) was supplied by Calcia (Guerville, France) and
108 stored in closed containers to avoid any moisture adsorption. *M. sinensis* rhizomes from
109 nursery Chombart (France) were planted in spring 2007 at the experimental field of INRAE
110 Estrée-Mons (France). The aboveground biomass was harvested in February 2015 and dried at
111 ambient temperature. The sample was ground to about 1 mm before extraction of DL or AX
112 fractions. The determination of the lignin content of the miscanthus sample was performed
113 using the Klason procedure as previously described (Méchin et al., 2014). A commercial kraft
114 lignin KL from softwood was purchased from Sigma Aldrich.

115

116 2.2 Extraction and characterization of dioxane lignin DL fraction from miscanthus biomass

117

118 The isolation of a purified DL fraction from miscanthus stems was performed from 18 g of
119 sample refluxed in 150 ml dioxane/aqueous HCl 2 M (9/1, v/v) for 30 min and under N₂. The
120 cooled reaction mixture was vacuum-filtrated (porcelain Buchner funnel equipped with a
121 Whatman filter paper N°4) and the residue on the filter was washed with 4 x 30 ml of

122 dioxane/water mixture (9/1, v/v). The filtrate and the washings were combined and the pH
123 was adjusted to 3-4 with a NaHCO₃ aqueous saturated solution to recover a final volume of
124 about 300 ml of extracted DL solution. All these steps were repeated 6 times, so as to recover
125 a total DL solution of about 2.5 l.

126 The DL solution was concentrated by roto-evaporation under reduced pressure and at 40°C to
127 a final volume of about 300 ml. This concentrated lignin solution was injected (with a 200 ml
128 glass syringe) into 2.5 l cold water and under magnetic stirring, which induces the
129 precipitation of the lignin polymers. The lignin precipitate was recovered by centrifugation
130 (1200 g, 45 min, 4°C), then washed with pure water and then recovered again by
131 centrifugation before freeze-drying.

132 The quality grade of the purified DL fraction isolated from miscanthus was assessed by the
133 determination of *p*-coumaric acid (CA) ester-linked to this fraction and by the evaluation of
134 lignin structures performed by analytical thioacidolysis. The determination of CA esters in DL
135 fraction and in the initial miscanthus sample was carried out by mild alkaline hydrolysis
136 followed by HPLC analysis (Sibout et al, 2016). The analysis of lignin structure by
137 thioacidolysis was performed using a simplified procedure as previously described (Lapierre
138 et al., 2021). When expressed in μmole/g of lignin, the yield of (H+G+S) thioacidolysis
139 monomers allowed us to calculate the molar frequency of lignin units only involved in β-O-4
140 bonds, with the assumption that 1 g of native miscanthus lignins contains 5000 μmoles of
141 lignin units.

142

143 2.3 Extraction and characterization of an arabinoxylan AX fraction from miscanthus biomass

144

145 The extraction and purification of an arabinoxylan fraction from *Miscanthus sinensis* stems
146 was performed using a two-step procedure. The first step consisted in delignification by

147 sodium chlorite/acetic acid mixture to recover a holocellulose fraction (mixture of cellulose
148 and hemicelluloses) by a procedure adapted from (Kumar et al., 2013). The ground
149 miscanthus sample was delignified at 70 °C (water bath) under the hood as follows. In a large
150 Erlenmeyer flask, about 30 g of sample were suspended in 960 ml of deionized water, before
151 addition of 18 ml of glacial acetic acid and 18 g of NaClO₂. A 50 ml Erlenmeyer flask was
152 inverted in the neck of the reaction flask. The slurry was occasionally and gently mixed and
153 fresh charges of acetic acid and sodium chlorite were added after 2 h. After 4 h of reaction,
154 the slurry was cooled and vacuum-filtered through a porcelain Buchner funnel. The
155 holocellulose fraction recovered on the funnel was then exhaustively washed with about 20 l
156 of deionized water before drying at 45°C overnight. The whole procedure was performed 4
157 times to recover about 83 g of holocellulose (recovery yield: 76.3% of the initial mass). The
158 lignin content of holocellulose, as measured by the Klason procedure (Méchin et al., 2014),
159 was found to be 3.50 ± 0.02 % by weight (mean ± standard deviation (SD) from triplicates).
160 The extraction of hemicelluloses from the holocellulose fraction was performed with aqueous
161 KOH solution (10 % by weight) and at room temperature, as described in (Li et al., 2016). As
162 the major hemicelluloses of grass secondary cell walls are arabinoxylans (AX), the purified
163 hemicellulosic fraction will be referred to as AX fraction in the following. This purification
164 was carried out after acidification of the alkaline extract to pH 5.5, followed by the ethanol-
165 induced precipitation of polysaccharides (Li et al., 2016). The AX precipitate was recovered
166 by centrifugation, washed with 70% EtOH and finally freeze-dried.
167 The quality grade of the AX fraction was evaluated by measuring the yield and composition
168 of neutral monosaccharides recovered after 2.5 M trifluoroacetic acid hydrolysis and as
169 compared to that of the initial miscanthus sample. This hydrolysis and the following high
170 performance anion exchange chromatography of the released neutral monosaccharides were
171 performed as previously described (Chupin et al., 2020; Harhold et al., 2005).

172

173 2.4 Evaluation of the kinetics of cement hydration by electrical conductivity

174

175 Electrical conductivity measurements were performed on dilute suspensions with a water-to-
176 cement ratio of 20 (w/w) by using a conductimeter coupled with the sensor probe LF413T-ID
177 (Schott instruments, ProLab 4000, Germany). The constant cell was calibrated with a 0.1M
178 aqueous KCl solution. Fresh cement (10 g) was mixed with 200 ml of distilled water without
179 or with various amounts of DL, KL or AX fraction in a stainless-steel beaker under
180 continuous stirring. Tests were conducted in a temperature-controlled room (at $25 \pm 2^\circ\text{C}$).
181 Various amounts of DL (150 to 500 mg), KL (100 to 300 mg) or AX (100 to 300 mg) were
182 added to the cement/water mixture.

183

184 **3 Results and discussion**

185

186 3.1 Extraction and characterization of purified DL and AX fraction from miscanthus cell 187 walls

188

189 The main objective of this study was to determine whether lignins putatively leached out from
190 miscanthus cell walls into the alkaline cement/water mixture might affect the kinetics of
191 cement hydration. To this end, we extracted a lignin fraction from miscanthus by mild
192 acidolysis which preserves as much as possible the properties of native lignins. This isolation
193 procedure consists of refluxing (30 min under N_2) the cell wall sample in dioxane/0.2M
194 aqueous HCl mixture (9/1, v/v) and then purifying the rough lignin extract by concentration
195 and precipitation. When applied to grass cell walls, this method provides a purified DL
196 fraction with a high yield and few sugar contaminants (about 10% by weight) (Chazal et al.,

2014). In addition, it preserves the structural specificities of grass cell wall lignins, such as their acylation by CA, the relative frequency of G/S/H units or the predominance of β -O-4 interunit bonds. By contrast, published model studies about the lignin impact on cement hydration or on concrete strength have been performed with commercial lignins, mainly kraft lignins or lignosulfonates (Kochova et al., 2017; Klapiszewski et al., 2019; Irekti et al., 2019; Bilba et al., 2003), which are structurally dramatically different from cell wall lignins (Gellerstedt and Henriksson, 2008).

When calculated relative to the lignin content of the miscanthus sample, the DL fraction was obtained with an 85% yield. The CA amount ester-linked to the miscanthus cell wall lignins was 89.67 ± 0.92 mg/g (mean \pm SD from triplicates), as calculated from the lignin and CA levels of the miscanthus sample and on the rationale that most CA units acylate lignins (Ralph, 2010). The CA amount ester-linked to the purified DL fraction was 86.92 ± 1.79 mg/g, a value very close to that of the corresponding cell wall lignins. The evaluation of DL structure by thioacidolysis revealed that the molar percentage of lignin units only involved in β -O-4 bonds was $18 \pm 1\%$ while that of the corresponding cell wall lignins was $22 \pm 1\%$. In addition, and similar to the cell wall lignins of the miscanthus sample, the DL fraction mainly comprised a mixture of G and S units together with low amounts of H units. From its high recovery yield and from its structural similarity to miscanthus cell wall lignins, we could ascertain that the DL fraction was a valuable model to study the impact of miscanthus lignins on cement hydration.

Like grass lignins, grass hemicelluloses, mainly represented by arabinoxylans AX (Scheller and Ulvskov, 2010), can be readily solubilized in cold alkali (Sun and Tomkinson, 2000).

Accordingly, we purified a hemicellulosic fraction, referred to as AX, from the miscanthus sample using a two-step procedure, as recently described (Li et al., 2016). The miscanthus sample was delignified by a mild procedure to yield a holocellulose fraction, mainly

222 comprised of cellulose and hemicelluloses and with a low amount of lignin contaminants (less
223 than 4% by weight). Hemicellulosic polymers were then extracted from holocellulose by
224 solubilization in cold alkali and then purified after acidification followed by ethanol-induced
225 precipitation. The neutral monosaccharides released by trifluoroacetic acid hydrolysis of this
226 purified AX fraction were recovered with an 83% yield while xylose and arabinose
227 respectively accounted for 83.3 and 11.9 % (relative weight %) of these sugars. These yield
228 and sugar composition confirmed that the purified AX fraction was a *bona fide* representative
229 of miscanthus arabinoxylans (Li et al., 2016).

230

231 3.2 Cement hydration in presence of a miscanthus dioxane lignin fraction as a model of
232 miscanthus cell wall lignins

233

234 The purified miscanthus DL fraction was added to cement/water mixture to simulate the
235 release of cell wall lignins when miscanthus fibers are suspended in the alkaline cement/water
236 mixture. The DL amount added to 10 g of cement mixed with 200 ml of water varied in the
237 150 to 500 mg range, which corresponds to 1.5 to 5 % by weight of cement. We selected these
238 amounts on the following rationale. A commonly employed cement to miscanthus ratio in
239 vegetal concrete is 2.5 (by weight) (Jury et al, 2022). If 2.5 g of miscanthus fibers containing
240 about 200 mg/g of lignin were subjected to a prolonged contact with the alkaline pore solution
241 of cement/water mixture, it is most likely that about half (or more) of the lignin polymers
242 would be solubilized, which represents 250 mg (or more) of lignins. In other words, the DL
243 range (150-500 mg) added to 10 g of cement encompassed the lignin amount that might be
244 solubilized when 2.5 g of miscanthus fibers are added to the cement water-mixture.

245 Monitoring cement hydration in presence of various DL amounts was performed by electrical
246 conductivity measurements, as compared to the control (cement without lignin addition)

247 (Figure 1). When the DL weight percentage relative to cement was lower than about 3%, the
248 conductivity curves were quite similar to that of the control assay. By contrast, when this
249 percentage was close to 3% or more, a conductivity plateau appeared with a time end varying
250 from about 25 to 55 h (Figure 1). This phenomenon expressed the lignin-induced retardation
251 effect of the nucleation of calcium silicate hydrates (C-S-H) on cement grains. This retarding
252 effect might be induced by the adsorption of lignins under their water-soluble phenolate ions
253 on cement surface. The efficiency of such a barrier effect would require a minimum lignin-to-
254 cement ratio, consistently with the observation that low DL amounts do not affect C-S-H
255 nucleation to a large extent. As a further support to this hypothesis, the two conductivity
256 assays run with DL/cement ratios of 222 mg/5 g and of 402 mg/10 g gave very similar curves,
257 which suggests that the kinetics of cement hydration is controlled mainly by the lignin-to-
258 cement ratio and not by the DL concentration in the reaction medium.

259 The growth of hydrates, which is reflected by the slope of the curves associated with the
260 conductivity raise (Table 1S), was not affected by DL addition, except for the highest one
261 (about 500 mg in 10 g of cement).

262

263 Figure 1: Conductivity measurements performed to monitor the hydration kinetics of Portland
264 cement in water.

265 Control: 10 g cement mixed in 200 ml water; 149 mg DL: 149 mg of DL added to 10 g
266 cement mixed in 200 ml water; 201 mg DL: 201 mg of DL added to 10 g cement mixed in
267 200 ml water; 256 mg DL: 256 mg of DL added to 10 g cement mixed in 200 ml water; 297
268 mg DL: 297 mg of DL added to 10 g cement mixed in 200 ml water; 402 mg DL: 402 mg of
269 DL added to 10 g cement mixed in 200 ml water; 502 mg DL: 502 mg of DL added to 10 g
270 cement mixed in 200 ml water; 222 mg DL*: 222 mg of DL added to 5 g cement mixed in
271 200 ml water.

272

273 In addition to the adsorption of lignin polymers at the surface of the cement grain, the capture
274 of calcium ions by components of the DL fraction might contribute to the retardation of
275 cement hydration. Such a putative capture cannot be related to the H, G or S lignin units of
276 the DL fraction as these units are devoid of carboxylic or ortho-diphenolic groups capable to
277 efficiently bind Ca^{2+} . However, the S units of DL lignins are acylated by CA and these esters
278 groups are very likely partially hydrolyzed in the alkaline cement/water mixture, thereby
279 generating free carboxylate groups capable to bind calcium ions. As the weight percentages of
280 DL added to cement varied between 1.5 and 5 %, the total hydrolysis of DL-linked CA esters
281 would release a maximum of 0.13 to 0.44 % of CA, relative to cement weight. Accordingly,
282 we may hypothesize that the capture of calcium ions by free *p*-coumarate would not
283 contribute to the DL-induced retardation effect to a large extent.

284

285 3.3 Cement hydration in presence of a commercial Kraft lignin KL fraction

286

287 Most model studies about the impact of lignins released from plant cell walls on cement
288 setting have been performed with commercial lignin samples, such as kraft lignins (Kochova
289 et al., 2017; Klapiszewski et al., 2019; Irekti et al., 2019; Bilba et al., 2003). One of the major
290 uses of Kraft lignin is to modify the setting of the cement in order to improve its final
291 properties. Klapiszewski et al., 2019, added Kraft lignin in cement mortar. This leads to an
292 increase of the compressive strength for some concentrations, without proposing possible
293 mechanisms able to explain this phenomenon. Irekti et al., 2019, prepared black liquor
294 isolated from date palm wood (Kraft process). Replacing water up to 2% in a water-cement
295 mixture increased the workability of concrete. Other studies directly used Kraft lignin to
296 mimic the behavior of plant lignin. Kochova et al., 2017, found that lignin (most probably

297 Kraft lignin) had a small retardation effect on cement hydration, much lower than simple
298 sugars. For example, the addition of 1% of lignin delayed by 63 hours the cement hydration
299 while lower amounts (0.5 and 0.2% of lignin) were slowing down hydration for only 10 and 6
300 hours, respectively. Bilba et al., 2003, added lignin (most probably Kraft lignin) to cement-
301 water mixtures to mimic the behavior of bagasse. They found that Kraft lignin increased the
302 hydration temperature and retarded setting (slower than cellulose). Xie et al., 2016, treated by
303 steam-explosion or chemical bleaching rice straw, and compared these different treated fibers
304 to the pristine rice straw. They deduced that the main compounds of rice straw, hemicellulose
305 and lignin, had a negative impact on the setting and hydration of cement, lignin having less
306 effect than hemicellulose but more than cellulose. The main weakness of the use of Kraft
307 lignin to mimic the behavior of plants is that such lignins are structurally very far from the
308 lignin polymers that can be leached out from cell walls into the cement/water mixture.
309 For instance, the commercially available kraft lignin samples are mainly obtained from
310 softwood samples with guaiacyl-made lignins and are thereby devoid of S units and CA
311 esters. They are obtained from a severe procedure (i.e., cooking wood chips for several hours
312 at 160 to 180°C in a liquor comprising a high sodium hydroxide and sodium sulfide charge)
313 (Gellerstedt and Heriksson, 2008; Marton, 1971; Gierer, 1980; Chakar and Ragauskas, 2004;
314 Fengel and Wegener, 2011; Sjostrom, 1993). In these drastic conditions, cell wall lignins are
315 depolymerized into low molecular weight kraft lignin polymers solubilized in the alkaline
316 medium and then recovered by acid-induced precipitation. Due to many degradation and
317 recondensation reactions, kraft lignins contain functional groups that are absent or very scarce
318 in cell wall lignins, such as stilbene structures, ortho-diphenol rings (referred to as catechols)
319 and carboxylic groups, while the major interunit ether linkages of native lignins, namely the
320 β -O-4 bonds, have been comprehensively destroyed (Gellerstedt and Heriksson, 2008; Gierer,
321 1980; Chakar and Ragauskas, 2004; Fengel and Wegener, 2011; Sjostrom, 1993; Lapierre et

322 al., 1994). In addition, kraft lignins may be contaminated by low-molecular weight
323 compounds (Niemelä and Sjöström, 1986; Niemelä, 1988; Niemelä, 1989). Accordingly,
324 softwood kraft lignins might inadequately represent the lignin polymers which can be
325 solubilized when miscanthus fibers are immersed in cold alkali. To test this hypothesis, we
326 have studied the impact of the SigmaTM-provided softwood kraft lignin on the hydration
327 kinetics of Portland cement and by conductivity measurements (Figure 2). Whereas adding
328 200 mg of the miscanthus DL fraction to the cement/water mixture (10 g in 200 ml) did not
329 affect the conductivity curve to a large extent, a noticeable conductivity plateau appeared with
330 the same KL amount. This result means that the retardation of C-S-H nucleation required less
331 KL amount than DL one. However, 3 % of either DL or KL by weight of cement induced a
332 similar retardation of cement hydration (by about 25 to 30 h). The current retardation effect of
333 KL fraction on cement hydration agrees with a published study reporting that the addition of
334 0.2, 0.5 and 1.0 wt% (based on cement) of SigmaTM-provided kraft lignin to the cement paste
335 delayed cement hydration for about 6, 10 and 63 h, respectively (Kochova et al., 2017). For
336 both DL and KL samples, the curve slopes associated with the large conductivity increase
337 were poorly affected by lignin addition (Table 1S). This result suggests that both KL and DL
338 fractions mainly hindered the nucleation of the C-S-H crystals, rather than their growth. In the
339 case of the miscanthus DL fraction, we hypothetically assigned this retardation effect to the
340 adsorption of DL lignin polymers on cement grains. While this adsorption phenomenon is
341 very likely to occur with the KL lignin polymers, the capture of calcium ions by KL
342 components might substantially contribute to slowing down cement hydration. It is well
343 established that softwood Kraft lignins contain substantial amounts of catechol rings (up to 12
344 catechol groups per 100 C₆C₃ units) (Marton, 1971) and of free carboxylic groups (up to
345 about 2.3 mmol g⁻¹, with a molar mass-dependent level) (Zinovyev et al., 2017). These
346 carboxylic and catechol groups, which are respectively formed from demethylation and

347 recondensation reactions during kraft cooking (Marton, 1971; Gellerstedt and Henriksson,
348 2008), may efficiently bind the calcium ions of the alkaline pore solution. Indeed, it has been
349 established that up to 30 Ca²⁺ ions can be bound to 100 lignin units of softwood KL (Sundin,
350 2000) and that this fixation can induce the precipitation of the KL polymers in alkaline
351 medium (Sundin and Hartler, 2000). In addition to lignin polymers, commercial kraft lignins
352 may be contaminated by a wealth of aliphatic and organic low-molecular weight compounds,
353 including many carboxylic acids (Niemelä and Sjöström, 1986). Such compounds may also
354 capture calcium ions in the pore solution and then slow down cement hydration. Taken
355 together, the present results, together with the well-established specific features of kraft
356 lignin, strongly support the hypothesis that modelling the effect of cell wall lignins on cement
357 hydration and via the use of severely degraded industrial lignins is not appropriate.

358

359 Figure 2: Conductivity measurements performed to monitor the hydration kinetics of Portland
360 cement in water.

361 Control: 10 g cement mixed in 200 ml water; 100 mg KL: 100 mg of KL added to 10 g
362 cement mixed in 200 ml water; 200 mg KL: 200 mg of KL added to 10 g cement mixed in
363 200 ml water; 250 mg KL: 250 mg of KL added to 10 g cement mixed in 200 ml water; 300
364 mg KL: 300 mg of KL added to 10 g cement mixed in 200 ml water.

365

366 3.4 Comparative impact of miscanthus dioxane lignin fraction and/or of miscanthus
367 arabinoxylan fraction on cement hydration

368

369 Various amounts of DL and of AX samples were added to the cement/water mixture with the
370 objective to compare their impact on cement hydration by electrical conductivity
371 measurements (Figure 3). It is worthy to remind that the weight percentages of DL or AX

372 sample relative to cement were chosen to be in the 1 to 3 % range (i.e., 100 to 300 mg in 10 g
373 of cement). This range encompasses the amount of lignin polymers or of arabinoxylan
374 polymers susceptible to be released from 2.5 g of miscanthus fibers co-suspended with 10 g of
375 cement in water. As already shown in Figure 1, the conductivity curve obtained when about 2
376 wt% of DL was added to cement was similar to the control assay. By contrast, the same AX
377 amount noticeably delayed the kinetics of cement hydration (Figure 3). When the total
378 (DL+AX) amount was close to 200 mg (i.e., about 100 mg for each fraction), the conductivity
379 curve was changed to a little extent. This result is not surprising since adding 1 wt% of DL
380 had no impact on cement hydration (Figure 1) and the weak retardation effect can therefore be
381 assigned only to the AX fraction. At this point, we can conclude that hemicellulosic polymers
382 more efficiently affected cement hydration than lignin polymers when the percentage added to
383 the cement was less than 2 wt%. By contrast, this situation was reversed when this percentage
384 was close to 3% by weight of cement. Indeed, with this 3% percentage, the time end of the
385 conductivity plateau was lower for AX (Figure 3) than for DL (Figure 1). In addition, adding
386 3% of AX to cement also reduced the slope of the section associated with the large
387 conductivity raise. This result revealed that 3% of AX delayed not only the nucleation of C-S-
388 H hydrates, but also the further growth of these nuclei. In other words, both DL and AX
389 fractions affected the kinetics of cement hydration, but with some specificities. The analysis
390 of a purified hemicellulose fraction obtained by subjecting a miscanthus sample to the same
391 procedure as the one used in this study revealed that this fraction was made of 81.6 % of
392 xylose, 13.3 % of arabinose, 2.9 % of glucose and 2.2 % of 4-*O*-Me glucuronic acid (mole %)
393 (Li et al., 2016). These 4-*O*-Me glucuronic substituents of the AX xylan chains might capture
394 Ca²⁺ ions of the alkaline pore solution via their ionized carboxylate groups. However and
395 from the 2.2% relative percentage of such acidic sugars in AX, this phenomenon would
396 contribute to the AX-induced retardation effect to a low extent. Strikingly enough, when the

397 total (DL+AX) amount was close to 320 mg (about 160 mg for each), the conductivity curve
398 displayed a substantial plateau indicative of the retardation of C-S-H nucleation (Figure 3)
399 whereas DL fraction alone was ineffective below the 300 mg threshold (Figure 1). This result
400 supports the following hypothetical scenario: (i) when simultaneously added to the
401 cement/water mixture, the lignin and the hemicellulosic polymers would readily form lignin-
402 carbohydrate complexes, a situation similar to the one met in cell walls; (ii) these complexes
403 would be adsorbed on the cement grains and under their ionized forms; (iii) this adsorption
404 would induce the retardation of cement hydration provided that the total (DL+AX) amount is
405 enough to provide an efficient barrier limiting the access of water to non-hydrated grains. In
406 other words, lignin and hemicellulosic polymers would synergistically delay cement
407 hydration.

408

409 Figure 3. Conductivity measurements performed to monitor the hydration kinetics of Portland
410 cement in water without or with various amounts of dioxane lignin (DL) fraction and of
411 arabinoxylan (AX) fraction isolated from miscanthus. The DL and AX fraction were added
412 alone or in combination to 10 g of cement dispersed in 200 ml of water.

413 Control: 10 g cement mixed in 200 ml water.

414 DL or AX added alone: 201 mg DL: 201 mg of KL added to 10 g cement mixed in 200 ml

415 water; 297 mg DL: 297 mg of DL added to 10 g cement mixed in 200 ml water; 201 mg AX:

416 201 mg of AX added to 10 g cement mixed in 200 ml water; 301 mg AX: 301 mg of AX

417 added to 10 g cement mixed in 200 ml water.

418 DL and AX added together: 105 mg DL + 109 mg AX: 105 mg of DL plus 109 mg AX added

419 to 10 g cement mixed in 200 ml water; 165 mg DL + 163 mg AX: 165 mg of DL plus 163 mg

420 AX added to 10 g cement mixed in 200 ml water.

421

422

423 **4. Conclusions**

424

425 To the best of our knowledge, the current study about the impact of lignins and of
426 hemicelluloses on cement hydration is the first one involving polymers extracted from a plant
427 species and by a mild procedure which preserves as much as possible the structural
428 specificities of cell wall polymers. By contrast, past studies about the impact of lignins on
429 cement hydration systematically involved lignin samples obtained from industrial
430 delignification processes which severely degrade the structure of cell wall lignins.

431 Comparative assays allowed us to establish that softwood kraft lignin fraction, a frequently
432 lignin model employed in such studies, does not adequately represent the lignin polymers
433 leached out from miscanthus cell walls immersed in alkaline cement/water mixtures. The
434 cement hydration delay induced by the miscanthus dioxane lignin fraction was obtained when
435 its wt% in cement was 3 % or more while lower values had no impact. This threshold-
436 dependent action of miscanthus DL fraction suggests that lignin polymers act on the
437 formation of C-S-H nuclei and by forming a lignin barrier on cement grain, which limits the
438 access of water to non-hydrated grains.

439 Suspending miscanthus fibers in alkaline cement/water mixtures is prone to induce the release
440 of both lignins and arabinoxylans. Accordingly, we comparatively evaluated the impact of
441 these two polymers on cement hydration. Electrical conductivity measurements suggested that
442 the AX-induced retardation of cement hydration occurred for lower wt% relative to cement
443 than the DL-induced one. The AX polymers might slow down not only the formation, but also
444 the growth of C-S-H nuclei. Remarkably enough, the co-addition of miscanthus DL and AX
445 fractions (1.6 wt% each, relative to cement) induced a retardation effect more pronounced
446 than the one obtained with 3 wt% of AX whereas the addition of only DL had no impact for

447 wt% lower than 3%. Taken together, these unexpected results suggest that the lignin and
448 arabinoxylan polymers leached out from miscanthus fibers immersed in alkaline cement paste
449 are prone to form lignin-carbohydrate complexes capable to synergistically delay the
450 formation of C-S-H nuclei and via the formation of a lignin-carbohydrate complex barrier on
451 the cement grains.

452

453 **5 Acknowledgements**

454

455 This work was supported by the program Investments for the Future (grant ANR-11-BTBR-
456 0006-BFF) managed by the French National Research Agency.

457

458 **6 References**

459

460 Amin, M., Ahmad, W., Khan, K., Ahmad, A., 2022. A Comprehensive Review of Types,
461 Properties, Treatment Methods and Application of Plant Fibers in Construction and Building
462 Materials, *Materials* 15, 4362, <https://doi.org/10.3390/ma15124362>.

463 Bajwa, D.S., Pourhashem, G., Ullah, A.H., Bajwa, S.G., 2019. A concise review of current
464 lignin production, applications, products and their environmental impact, *Industrial Crops and*
465 *Products* 139, 111526, <https://doi.org/10.1016/j.indcrop.2019.111526>.

466 Ben Fradj, N., Rozakis, S., Borzecka, M., Matyka, M., 2020. Miscanthus in the European bio-
467 economy: A network analysis, *Industrial Crops and Products*, 148, 112281,
468 <https://doi.org/10.1016/j.indcrop.2020.112281>.

469 Bilba, K., Arsene, M.A, Ouensanga, A., 2003. Sugar cane bagasse fibre reinforced cement
470 composites. Part I. Influence of the botanical components of bagasse on the setting of
471 bagasse/cement composite, *Cement and Concrete Composites*, 25, 91-96,
472 [https://doi.org/10.1016/S0958-9465\(02\)00003-3](https://doi.org/10.1016/S0958-9465(02)00003-3).

473 Bourdot, A., Magniont, C., Lagouin, M., Niyigena, C., Evon, P., Amziane, S., 2019. Impact
474 of bio-aggregates properties on the chemical interactions with mineral binder, application to
475 vegetal concrete, *Journal of Advanced Concrete Technology*, 17, 542-558,

476 Breilly, D., Fadlallah, S., Froidevaux, V., Colas, A., Allais, F., 2021. Origin and industrial
477 applications of lignosulfonates with a focus on their use as superplasticizers in concrete,
478 *Construction and Building Materials* 301, 124065,
479 <https://doi.org/10.1016/j.conbuildmat.2021.124065>.

480 Brosse, N., Dufour, A., Meng, X., Sun, Q., Ragauskas, A., 2012. Miscanthus: a fast-growing
481 crop for biofuels and chemicals production, *Biofuels Bioproducts & Biorefining-Biofpr*, 6,
482 580-598, <https://doi.org/10.1002/bbb.1353>.

483 Chakar, F.S., Ragauskas, A.J., 2004. Review of current and future softwood kraft lignin
484 process chemistry, *Industrial Crops and Products*, 20 (2004) 131-141,
485 <https://doi.org/10.1016/j.indcrop.2004.04.016>.

486 Chazal, R., Robert, P., Durand, S., Devaux, M.F., Saulnier, L., Lapierre, C., Guillon, F., 2014.
487 Investigating Lignin Key Features in Maize Lignocelluloses Using Infrared Spectroscopy,
488 *Applied Spectroscopy*, 68, 1342-1347, <https://doi.org/10.1366/14-07472>.

489 Chupin, L., Soccalingame, L., de Ridder, D., Gineau, E., Mouille, G., Arnoult, S., Brancourt-
490 Hulmel, M., Lapierre, C., Vincent, L., Mija, A., Corn, S., Le Moigne, N., Navard, P., 2020.
491 Thermal and dynamic mechanical characterization of miscanthus stem fragments: Effects of
492 genotypes, positions along the stem and their relation with biochemical and structural
493 characteristics, *Industrial Crops and Products*, 156, 112863,
494 <https://doi.org/10.1016/j.indcrop.2020.112863>.

495 Delannoy, G., Marceau, S., Glé, P., Gourlay, E., Guéguen-Minerbe, M., Diafia, D., Amziane,
496 S., Farcas, F., 2020. Impact of hemp shiv extractives on hydration of Portland cement,
497 *Construction and Building Materials*, 244, 118300,
498 <https://doi.org/10.1016/j.conbuildmat.2020.118300>

499 Fengel, D., Wegener, G., 2011. *Wood: chemistry, ultrastructure, reactions*, Walter de Gruyter,
500 2011.

501 Gellerstedt, G., Henriksson, G., 2008. Chapter 9 - Lignins: Major Sources, Structure and
502 Properties, in: M.N. Belgacem, A. Gandini (Eds.) Monomers, Polymers and Composites from
503 Renewable Resources, Elsevier, Amsterdam, pp. 201-224, [https://doi.org/10.1016/B978-0-08-](https://doi.org/10.1016/B978-0-08-045316-3.00009-0)
504 [045316-3.00009-0](https://doi.org/10.1016/B978-0-08-045316-3.00009-0).

505 Gierer, J., 1980. Chemical aspects of kraft pulping, *Wood Science and Technology*, 14, 241-
506 266, <https://doi.org/10.1007/BF00383453>.

507 Govin, A., Bartholin, M-C., Schmidt, W., Grosseau, P., 2019. Combination of
508 superplasticizers with hydroxypropyl guar, effect on cement-paste properties, *Construction*
509 *and Building Materials*, 215, 595-604, <https://doi.org/10.1016/j.conbuildmat.2019.04.137>

510 Halpin, C., 2019. Lignin engineering to improve saccharification and digestibility in grasses,
511 *Current opinion in biotechnology* 56, 223-229, <https://doi.org/10.1016/j.copbio.2019.02.013>.

512 Harholt, J., Jensen, J.H.G., Sørensen, S.O., Orfila, C., Pauly, M., Scheller, H.V., 2005.
513 Arabinan deficient 1 is a putative arabinosyltransferase involved in biosynthesis of pectic
514 arabinan in Arabidopsis, *Plant Physiology*, 140, 49-58,
515 <https://doi.org/10.1104/pp.105.072744>.

516 Irekti, A., Oualit, M., Siahmed, H., Buncianu, D., Zibouche, Z., 2019. Effect of black liquor
517 from date palm on the workability and compressive strength of Portland cement and concrete,
518 *Advances in Materials Science*, 19, 5-18, <https://doi.org/10.2478/adms-2019-0013>.

519 Jędrzejczak, P., Collins, M.N., Jesionowski, T., Kłapiszewski, Ł., 2021. The role of lignin and
520 lignin-based materials in sustainable construction – A comprehensive review, *International*
521 *Journal of Biological Macromolecules* 187, 624-650,
522 <https://doi.org/10.1016/j.ijbiomac.2021.07.125>.

523 Jørgensen, U., 2011. Benefits versus risks of growing biofuel crops: the case of Miscanthus,
524 *Current Opinion in Environmental Sustainability*, 3, 24-30,
525 <https://doi.org/10.1016/j.cosust.2010.12.003>.

526 Jury, C., Girones, J., Vo, L.T.T., Di Giuseppe, E., Mouille, G., Gineau, E., Arnoult, S.,
527 Brancourt-Hulmel, M., Lapierre, C., Cézard, L., Navard, P., 2022. One-step preparation
528 procedure, mechanical properties and environmental performances of miscanthus-based

529 concrete blocks, *Mater. Today Commun.*, 31, 103575.
530 <https://doi.org/10.1016/j.mtcomm.2022.103575>

531 Klapiszewski, Ł., Klapiszewska, I., Ślosarczyk, A., Jesionowski, T., 2019. Lignin-based
532 hybrid admixtures and their role in cement composite fabrication, *Molecules*, 24, 3544,
533 <https://doi.org/10.3390/molecules24193544>.

534 Kochova, K., Schollbach, K., Gauvin, F., Brouwers, H.J.H., 2017. Effect of saccharides on
535 the hydration of ordinary Portland cement, *Construction and Building Materials*, 150, 268-
536 275, <https://doi.org/10.1016/j.conbuildmat.2017.05.149>.

537 Kumar, R., Hu, F., Hubbell, C.A, Ragauskas, A.J., Wyman, C.E., 2013. Comparison of
538 laboratory delignification methods, their selectivity, and impacts on physiochemical
539 characteristics of cellulosic biomass, *Bioresource Technology*, 130, 372-381,
540 <https://doi.org/10.1016/j.biortech.2012.12.028>.

541 Lapiere, C. 2010. Determining lignin structure by chemical degradations, in: C.D. Heitner,
542 D., J.A. Schmidt (Eds.) *Lignin and lignans - Advances in Chemistry*, CRC Press/Taylor &
543 Francis Group, Boca Raton (FL, United States), pp. 11-48.

544 Lapiere, C., Monties, B., Meier, D., Faix, O., 1994. Structural investigation of kraft lignins
545 transformed via oxo-ammoniation to potential nitrogenous fertilizers, *Holzforschung*, 48, 63-
546 68, <https://doi.org/10.1515/hfsg.1994.48.s1.63>.

547 Lapiere, C., Sibout, R., Laurans, F., Lesage-Descauses, M-C., Déjardin, A., Pilate, G., 2021.
548 p-Coumaroylation of poplar lignins impacts lignin structure and improves wood
549 saccharification, *Plant Physiology*, <https://doi.org/10.1093/plphys/kiab359>.

550 Li, Q., Ibrahim, L., Zhou, W., Zhang, M., Yuan, Z., 2021. Treatment methods for plant fibers
551 for use as reinforcement in cement-based materials, *Cellulose* 28, 5257-5268,
552 <https://doi.org/10.1007/s10570-021-03903-w>.

553 Li, H., Xue, Y., Wu, J., Wu, H., Qin, G., Li, C., Ding, J., Liu, J., Gan, L., Long, M., 2016.
554 Enzymatic hydrolysis of hemicelluloses from *Miscanthus* to monosaccharides or xylo-
555 oligosaccharides by recombinant hemicellulases, *Industrial Crops and Products*, 79, 170-179,
556 <https://doi.org/10.1016/j.indcrop.2015.11.021>.

557

558 Lilargem Rocha, D., Tambara Júnior, L.U.D., Marvila, M.T., Pereira, E.C., Souza, D., de
559 Azevedo, A.R.G., 2022. A Review of the Use of Natural Fibers in Cement Composites:
560 Concepts, Applications and Brazilian History, *Polymers*, 14, 2043.
561 <https://doi.org/10.3390/polym14102043>

562

563 Marriott, P.E., Gómez, L.D., McQueen-Mason, S.J., 2016. Unlocking the potential of
564 lignocellulosic biomass through plant science, *New Phytologist*, 209, 1366-1381,
565 <https://doi.org/10.1111/nph.13684>.

566 Marton, J., 1971. Reactions in alkaline medium, in: K.V. Sarkanen, C.H. Ludwig (Eds.)
567 *Lignins. Occurrence, formation, Structure and reactions*, John Wiley & Sons, USA, pp. 639-
568 693.

569 Méchin, V., Laluc, A., Legée, F., Cézard, L., Denoue, D., Barrière, Y., Lapierre, C., 2014.
570 Impact of the brown-midrib *bm5* mutation on maize lignins, *Journal of Agricultural and Food*
571 *Chemistry*, 62, 5102-5107, <https://doi.org/10.1021/jf5019998>.

572 Moll, L., Wever, C., Völkerling, G., Pude, R., 2020. Increase of *Miscanthus* Cultivation with
573 New Roles in Materials Production, A Review, *Agronomy* 10, 308,
574 [doi:103390/agronomy10020308](https://doi.org/10.3390/agronomy10020308).

575 Mullick, A.K., 1996. 7 - Use of lignin-based products in concrete, in: Chandra, S. (Ed.),
576 *Waste Materials Used in Concrete Manufacturing*. William Andrew Publishing, Westwood,
577 NJ, pp. 352-429, <https://doi.org/10.1016/B978-081551393-3.50010-7>.

578 Nazar, S., Yang, J., Thomas, J.B.S., Azim, I., Rehman, S.K.U., 2020. Rheological properties
579 of cementitious composites with and without nano-materials: A comprehensive review, *J.*
580 *Clean. Prod.*, 272, 122701, <https://doi.org/10.1016/j.jclepro.2020.122701>

581 Neville, A., Brooks, J., 2010. *Concrete Technology*, Second Edition, Pearson Education
582 Limited, Essex, England.

583 Niemelä, K., 1988. GLC-MS studies on pine kraft black liquors Part I. Identification of
584 monomeric compounds, *Holzforschung*, 42, 169-173, <https://doi:10.1515/hfsg.1988.42.3.169>.

585 Niemelä, K., 1989. GLC-MS studies on pine kraft black liquors Part V. Identification of
586 catechol compounds, *Holzforschung*, 43, 99-103, <https://doi.org/10.1515/hfsg.1989.43.2.99>.

587 Niemelä, K., Sjöström, E., 1986. Simultaneous identification of aromatic and aliphatic low
588 molecular weight compounds from alkaline pulping liquor by capillary gas-liquid
589 chromatography — mass spectrometry, *Holzforschung*, 40, 361-368,
590 <https://doi.org/10.1515/hfsg.1986.40.6.361>.

591 Pacheco-Torgal, F., Jalali, S., 2011. Cementitious building materials reinforced with vegetable
592 fibres: A review, *Construction and Building Materials*, 25, 575-581,
593 <https://doi.org/10.1016/j.conbuildmat.2010.07.024>.

594 Ralph, J. 2010. Hydroxycinnamates in lignification, *Phytochemistry Reviews*, 9, 65-83,
595 <https://doi.org/10.1007/s11101-009-9141-9>.

596 Ralph, J., Lapierre, C., Boerjan, W., 2019. Lignin structure and its engineering. Current
597 opinion in biotechnology, 56, 240-249, <https://doi.org/10.1016/j.copbio.2019.02.019>.

598 Scheller, H.V., Ulvskov, P., 2010. Hemicelluloses, *Annual Review of Plant Biology*, 61, 263-
599 289, <https://doi.org/10.1146/annurev-arplant-042809-112315>.

600 Sibout, R., Le Bris, P., Legee, F., Cezard, L., Renault, H., Lapierre, C., 2016. Structural
601 redesigning Arabidopsis lignins into alkali-soluble lignins through the expression of p-
602 coumaroyl-CoA: monolignol transferase PMT, *Plant Physiology*, 170, 1358-1366,
603 <https://doi.org/10.1104/pp.15.01877>.

604 Sjoström, E., 1993. Wood chemistry: fundamentals and applications, Gulf professional
605 publishing, Academic Press.

606 Sun, R.C., Tomkinson, J., 2000. Essential guides for isolation/purification of polysaccharides,
607 in: I.D. Wilson, E.R. Adlard, M. Cooke, C.F. Poole (Eds.) *Encyclopedia of separation science*,
608 Academic Press, London, pp. 4568-4574.

609 Sundin, J., 2000. Precipitation of kraft lignin under alkaline conditions, in: Ph. D Thesis,
610 Royal Institute of Technology, Stockholm, pp. 82.

611 Sundin, J., Hartler, N., 2000. Precipitation of kraft lignin by metal cations in alkaline
612 solutions, *Nordic Pulp & Paper Research Journal*, 15, 306-312, [https://doi.org/10.3183/npprj-](https://doi.org/10.3183/npprj-2000-15-04-p306-312)
613 [2000-15-04-p306-312](https://doi.org/10.3183/npprj-2000-15-04-p306-312).

614 Terrett, O.M., Paul Dupree, P., 2019. Covalent interactions between lignin and hemicelluloses
615 in plant secondary cell walls, *Curr. Opin. Biotechnol.* 56, 97-104, [https://doi:](https://doi:10.1016/j.copbio.2018.10.010)
616 [10.1016/j.copbio.2018.10.010](https://doi:10.1016/j.copbio.2018.10.010)

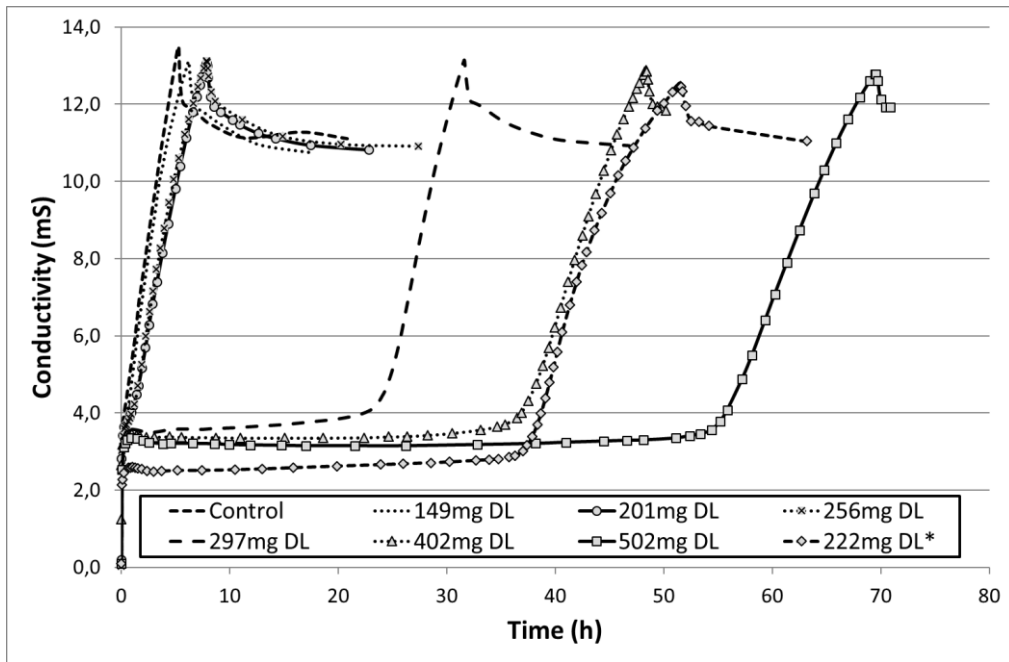
617 Vo, L.T.T., Navard, P., 2016. Treatments of plant biomass for cementitious building materials
618 – A review, *Construction and Building Materials*, 121, 161-176,
619 <https://doi.org/10.1016/j.conbuildmat.2016.05.125>.

620 Vogel, J. 2008. Unique aspects of the grass cell wall, *Current Opinion in Plant Biology*, 11,
621 301-307, <https://doi.org/10.1016/j.pbi.2008.03.002>.

622 Xie, X., Gou, G., Wei, X., Zhou, Z., Jiang, M., Xu, X., Wang, Z., Hui, D., 2016. Influence of
623 pretreatment of rice straw on hydration of straw fiber filled cement based composites, *Constr.*
624 *Build. Mater.*, 113, 449–455, <https://doi:10.1016/j.conbuildmat.2016.03.088>.

625 Zinovyev, G., Sumerskii, I., Korntner, P., Sulaeva, I., Rosenau, T., Potthast, A., 2017. Molar
626 mass-dependent profiles of functional groups and carbohydrates in kraft lignin, *Journal of*
627 *Wood Chemistry and Technology*, 37, 171-183,
628 <https://doi.org/10.1080/02773813.2016.1253103>.

629



630

631

632

633 **Figure 1:** Conductivity measurements performed to monitor the hydration kinetics of
 634 Portland cement in water.

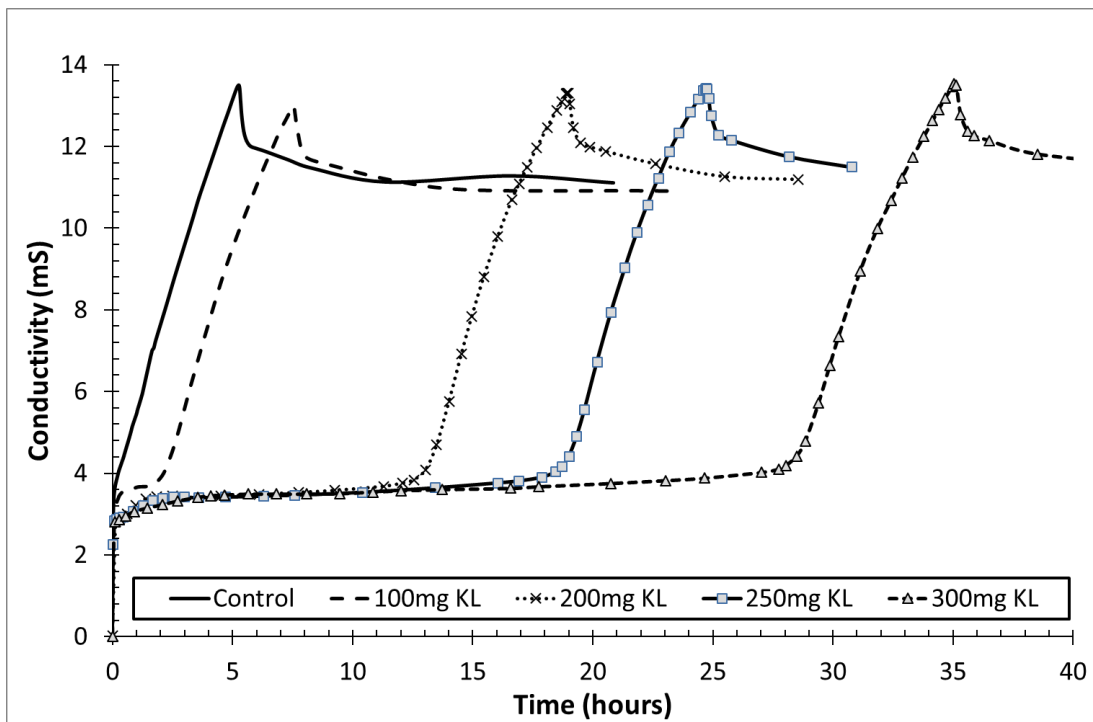
635 Control: 10 g cement mixed in 200 ml water; 149 mg DL: 149 mg of DL added to 10 g cement
 636 mixed in 200 ml water; 201 mg DL: 201 mg of DL added to 10 g cement mixed in 200 ml
 637 water; 256 mg DL: 256 mg of DL added to 10 g cement mixed in 200 ml water; 297 mg DL:
 638 297 mg of DL added to 10 g cement mixed in 200 ml water; 402 mg DL: 402 mg of DL added
 639 to 10 g cement mixed in 200 ml water; 502 mg DL: 502 mg of DL added to 10 g cement
 640 mixed in 200 ml water; 222 mg DL*: 222 mg of DL added to 5 g cement mixed in 200 ml
 641 water.

642

643

644

645



646

647

648

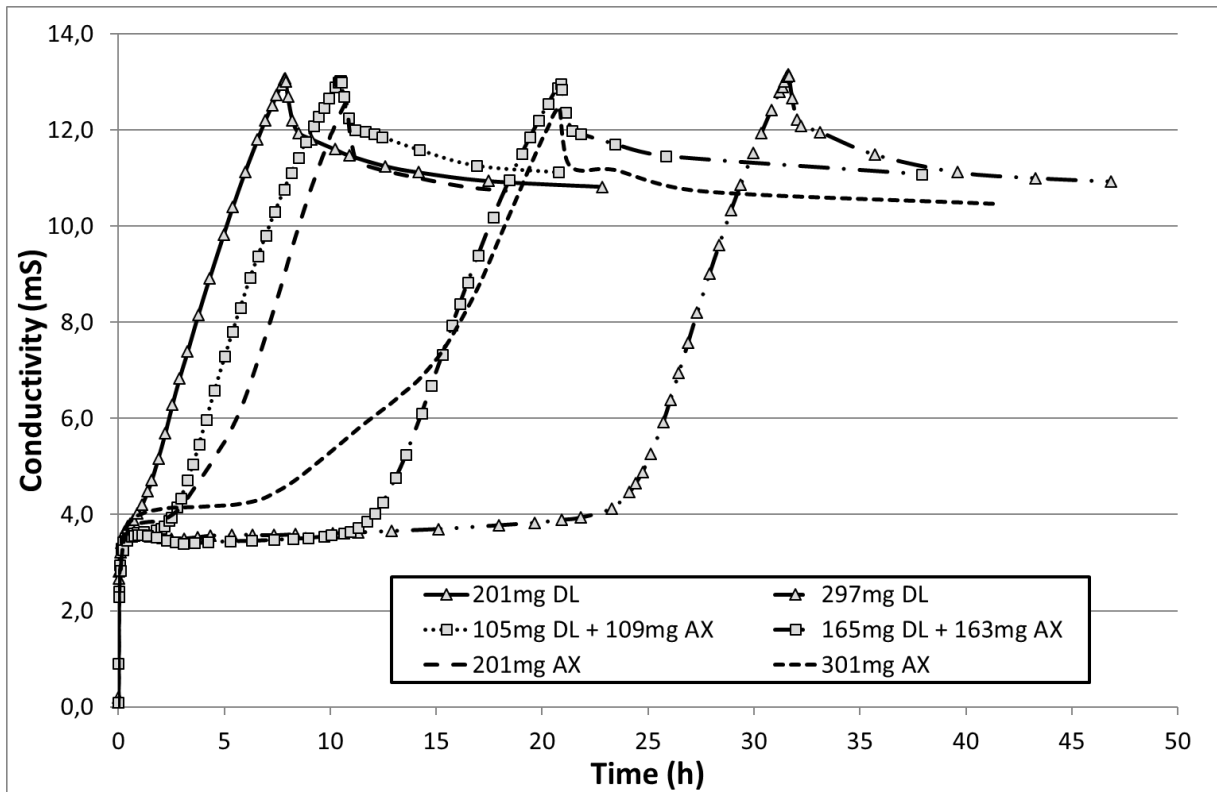
649 **Figure 2:** Conductivity measurements performed to monitor the hydration kinetics of
650 Portland cement in water.

651 Control: 10 g cement mixed in 200 ml water; 100 mg KL: 100 mg of KL added to 10 g cement
652 mixed in 200 ml water; 200 mg KL: 200 mg of KL added to 10 g cement mixed in 200 ml
653 water; 250 mg KL: 250 mg of KL added to 10 g cement mixed in 200 ml water; 300 mg KL:
654 300 mg of KL added to 10 g cement mixed in 200 ml water.

655

656

657



658
 659
 660
 661
 662
 663
 664
 665
 666
 667
 668
 669
 670
 671
 672
 673
 674
 675
 676
 677
 678
 679

Figure 3: Conductivity measurements performed to monitor the hydration kinetics of Portland cement in water without or with various amounts of dioxane lignin (DL) fraction and of arabinoxylan (AX) fraction isolated from miscanthus. The DL and AX fraction were added alone or in combination to 10 g of cement dispersed in 200 ml of water. Control: 10 g cement mixed in 200 ml water. DL or AX added alone: 201 mg DL: 201 mg of KL added to 10 g cement mixed in 200 ml water; 297 mg DL: 297 mg of DL added to 10 g cement mixed in 200 ml water; 201 mg AX: 201 mg of AX added to 10 g cement mixed in 200 ml water; 301 mg AX: 301 mg of AX added to 10 g cement mixed in 200 ml water. DL and AX added together: 105 mg DL + 109 mg AX: 105 mg of DL plus 109 mg AX added to 10 g cement mixed in 200 ml water; 165 mg DL + 163 mg AX: 165 mg of DL plus 163 mg AX added to 10 g cement mixed in 200 ml water.

680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699

SUPPLEMENTARY MATERIAL

Impact of miscanthus lignin and arabinoxylan on the hydration kinetics of Portland cement

Jordi Girones¹, Loan T. T. Vo¹, Grégory Mouille², Joan Onate Narciso², Stéphanie Arnoult³, Maryse Brancourt-Hulmel⁴, Patrick Navard¹, Catherine Lapierre²

*1- MINES ParisTech, PSL Research University, CEMEF** - Centre de mise en forme des matériaux, CNRS UMR 7635, CS 10207 rue Claude Daunesse 06904 Sophia Antipolis Cedex, France*

2- Institut Jean-Pierre Bourgin, INRAE, AgroParisTech, Université Paris-Saclay, 78000 Versailles, France

3- INRAE, UE GCIE Picardie, Estrées-Mons, 80203 Péronne, France

4 BioEcoAgro Joint Research Unit – INRAE AgroImpact - Université de Liège - Université de Lille - Université de Picardie Jules Verne, Site d'Estrées-Mons CS 50136 80203 Péronne cedex, France

700 Table 1S. Impact of miscanthus dioxane lignin (DL) and of softwood kraft lignin (KL) on the
 701 hydration of cement, as revealed by electrical conductivity. Data are mean values (and SD) of
 702 triplicate assays.

703

Lignin concentration relative to cement (% by weight)	Time end of the induction period (h)	Time of the maximum conductivity peak (h)
DL fraction isolated from miscanthus cell walls		
0 (control)	0	5.5 ± 0.4
1.5	0	6.2 ± 0.9
2.0	0	7.8 ± 0.1
2.6	1.2 ± 0.1	8.5 ± 0.8
3.0	21.8 ± 0.1	32.2 ± 13
4.0	33.1	46.8
5.0	54.3 ± 12.9	68.8 ± 13
Commercial softwood KL fraction		
1.0	3.6 ± 2.6	9.9 ± 3.4
2.0	13.2 ± 2.7	21.0 ± 3.0
2.5	16.0	24.7
3.0	27.9 ± 4.6	38.6 ± 3.0

704

705

706