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2	Impact of miscanthus lignin and arabinoxylan on Portland cement
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#### 22 Abstract

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

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

46 Miscanthus

#### 47 **1 Introduction**

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

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

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

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

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

Major abbreviations: dioxane lignin (DL); arabinoxylan (AX); kraft lignin (KL); guaiacyl (G);
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 stored in closed containers to avoid any moisture adsorption. M. sinensis rhizomes from 108 nursery Chombart (France) were planted in spring 2007 at the experimental field of INRAE 109 Estrée-Mons (France). The aboveground biomass was harvested in February 2015 and dried at 110 ambient temperature. The sample was ground to about 1 mm before extraction of DL or AX 111 fractions. The determination of the lignin content of the miscanthus sample was performed 112 using the Klason procedure as previously described (Méchin et al., 2014). A commercial kraft 113 lignin KL from softwood was purchased from Sigma Aldrich. 114 115 2.2 Extraction and characterization of dioxane lignin DL fraction from miscanthus biomass 116 117 The isolation of a purified DL fraction from miscanthus stems was performed from 18 g of 118 sample refluxed in 150 ml dioxane/aqueous HCl 2 M (9/1, v/v) for 30 min and under N<sub>2</sub>. The 119 cooled reaction mixture was vacuum-filtrated (porcelain Buchner funnel equipped with a 120 Whatman filter paper N°4) and the residue on the filter was washed with 4 x 30 ml of 121

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 NaHCO <sub>3</sub> 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 <i>p</i> -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 $\mu$ mole/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 $\beta$ -O-4
140	bonds, with the assumption that 1 g of native miscanthus lignins contains 5000 $\mu$ moles 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 and hemicelluloses) by a procedure adapted from (Kumar et al., 2013). The ground 148 miscanthus sample was delignified at 70 °C (water bath) under the hood as follows. In a large 149 Erlenmeyer flask, about 30 g of sample were suspended in 960 ml of deionized water, before 150 addition of 18 ml of glacial acetic acid and 18 g of NaClO<sub>2</sub>. A 50 ml Erlenmeyer flask was 151 inverted in the neck of the reaction flask. The slurry was occasionally and gently mixed and 152 fresh charges of acetic acid and sodium chlorite were added after 2 h. After 4 h of reaction, 153 the slurry was cooled and vacuum-filtered through a porcelain Buchner funnel. The 154 holocellulose fraction recovered on the funnel was then exhaustively washed with about 201 155 of deionized water before drying at 45°C overnight. The whole procedure was performed 4 156 times to recover about 83 g of holocellulose (recovery yield: 76.3% of the initial mass). The 157 lignin content of holocellulose, as measured by the Klason procedure (Méchin et al., 2014), 158 was found to be  $3.50 \pm 0.02$  % by weight (mean  $\pm$  standard deviation (SD) from triplicates). 159 The extraction of hemicelluloses from the holocellulose fraction was performed with aqueous 160 KOH solution (10 % by weight) and at room temperature, as described in (Li et al., 2016). As 161 the major hemicelluloses of grass secondary cell walls are arabinoxylans (AX), the purified 162 hemicellulosic fraction will be referred to as AX fraction in the following. This purification 163 was carried out after acidification of the alkaline extract to pH 5.5, followed by the ethanol-164 induced precipitation of polysaccharides (Li et al., 2016). The AX precipitate was recovered 165 by centrifugation, washed with 70% EtOH and finally freeze-dried. 166 The quality grade of the AX fraction was evaluated by measuring the yield and composition 167 of neutral monosaccharides recovered after 2.5 M trifluoroacetic acid hydrolysis and as 168 compared to that of the initial miscanthus sample. This hydrolysis and the following high 169

- performance anion exchange chromatography of the released neutral monosaccharides were
- performed as previously described (Chupin et al., 2020; Harhold et al., 2005).

173	2.4 Evaluation o	f the kinetics	of cement hydration	by electrical	conductivity
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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 $25 \pm 2^{\circ}$ 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 204 obtained with an 85% yield. The CA amount ester-linked to the miscanthus cell wall lignins 205 was  $89.67 \pm 0.92$  mg/g (mean  $\pm$  SD from triplicates), as calculated from the lignin and CA 206 levels of the miscanthus sample and on the rationale that most CA units acylate lignins 207 (Ralph, 2010). The CA amount ester-linked to the purified DL fraction was  $86.92 \pm 1.79$ 208 mg/g, a value very close to that of the corresponding cell wall lignins. The evaluation of DL 209 structure by thioacidolysis revealed that the molar percentage of lignin units only involved in 210  $\beta$ -O-4 bonds was 18 ± 1% while that of the corresponding cell wall ligning was 22 ± 1%. In 211 addition, and similar to the cell wall ligning of the miscanthus sample, the DL fraction mainly 212 comprised a mixture of G and S units together with low amounts of H units. From its high 213 recovery yield and from its structural similarity to miscanthus cell wall lignins, we could 214 ascertain that the DL fraction was a valuable model to study the impact of miscanthus lignins 215 on cement hydration. 216

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

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

230

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

233

The purified miscanthus DL fraction was added to cement/water mixture to simulate the 234 release of cell wall ligning when miscanthus fibers are suspended in the alkaline cement/water 235 mixture. The DL amount added to 10 g of cement mixed with 200 ml of water varied in the 236 150 to 500 mg range, which corresponds to 1.5 to 5 % by weight of cement. We selected these 237 amounts on the following rationale. A commonly employed cement to miscanthus ratio in 238 vegetal concrete is 2.5 (by weight) (Jury et al, 2022). If 2.5 g of miscanthus fibers containing 239 about 200 mg/g of lignin were subjected to a prolonged contact with the alkaline pore solution 240 of cement/water mixture, it is most likely that about half (or more) of the lignin polymers 241 would be solubilized, which represents 250 mg (or more) of lignins. In other words, the DL 242 range (150-500 mg) added to 10 g of cement encompassed the lignin amount that might be 243 solubilized when 2.5 g of miscanthus fibers are added to the cement water-mixture. 244 Monitoring cement hydration in presence of various DL amounts was performed by electrical 245 conductivity measurements, as compared to the control (cement without lignin addition) 246

(Figure 1). When the DL weight percentage relative to cement was lower than about 3%, the 247 conductivity curves were quite similar to that of the control assay. By contrast, when this 248 percentage was close to 3% or more, a conductivity plateau appeared with a time end varying 249 from about 25 to 55 h (Figure 1). This phenomenon expressed the lignin-induced retardation 250 effect of the nucleation of calcium silicate hydrates (C-S-H) on cement grains. This retarding 251 effect might be induced by the adsorption of lignins under their water-soluble phenolate ions 252 on cement surface. The efficiency of such a barrier effect would require a minimum lignin-to-253 cement ratio, consistently with the observation that low DL amounts do not affect C-S-H 254 nucleation to a large extent. As a further support to this hypothesis, the two conductivity 255 assays run with DL/cement ratios of 222 mg/5 g and of 402 mg/10 g gave very similar curves, 256 which suggests that the kinetics of cement hydration is controlled mainly by the lignin-to-257 cement ratio and not by the DL concentration in the reaction medium. 258 The growth of hydrates, which is reflected by the slope of the curves associated with the 259 conductivity raise (Table 1S), was not affected by DL addition, except for the highest one 260 (about 500 mg in 10 g of cement). 261 262 Figure 1: Conductivity measurements performed to monitor the hydration kinetics of Portland 263 cement in water. 264 Control: 10 g cement mixed in 200 ml water; 149 mg DL: 149 mg of DL added to 10 g 265 cement mixed in 200 ml water; 201 mg DL: 201 mg of DL added to 10 g cement mixed in 266 200 ml water; 256 mg DL: 256 mg of DL added to 10 g cement mixed in 200 ml water; 297 267 mg DL: 297 mg of DL added to 10 g cement mixed in 200 ml water; 402 mg DL: 402 mg of 268

DL added to 10 g cement mixed in 200 ml water; 502 mg DL: 502 mg of DL added to 10 g

cement mixed in 200 ml water; 222 mg DL\*: 222 mg of DL added to 5 g cement mixed in

271 200 ml water.

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 <sup>2+</sup> . 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 <i>p</i> -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

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

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

recondensation reactions during kraft cooking (Marton, 1971; Gellerstedt and Henriksson, 347 2008), may efficiently bind the calcium ions of the alkaline pore solution. Indeed, it has been 348 established that up to 30 Ca<sup>2+</sup> ions can be bound to 100 lignin units of softwood KL (Sundin, 349 2000) and that this fixation can induce the precipitation of the KL polymers in alkaline 350 medium (Sundin and Hartler, 2000). In addition to lignin polymers, commercial kraft lignins 351 may be contaminated by a wealth of aliphatic and organic low-molecular weight compounds, 352 including many carboxylic acids (Niemelä and Sjöström, 1986). Such compounds may also 353 capture calcium ions in the pore solution and then slow down cement hydration. Taken 354 together, the present results, together with the well-established specific features of kraft 355 lignin, strongly support the hypothesis that modelling the effect of cell wall lignins on cement 356 hydration and via the use of severely degraded industrial lignins is not appropriate. 357 358 Figure 2: Conductivity measurements performed to monitor the hydration kinetics of Portland 359 cement in water. 360 Control: 10 g cement mixed in 200 ml water; 100 mg KL: 100 mg of KL added to 10 g 361 cement mixed in 200 ml water; 200 mg KL: 200 mg of KL added to 10 g cement mixed in 362 200 ml water; 250 mg KL: 250 mg of KL added to 10 g cement mixed in 200 ml water; 300 363 mg KL: 300 mg of KL added to 10 g cement mixed in 200 ml water. 364 365 3.4 Comparative impact of miscanthus dioxane lignin fraction and/or of miscanthus 366 arabinoxylan fraction on cement hydration 367 368 Various amounts of DL and of AX samples were added to the cement/water mixture with the 369 objective to compare their impact on cement hydration by electrical conductivity 370 measurements (Figure 3). It is worthy to remind that the weight percentages of DL or AX 371

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

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

408

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.

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

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

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

#### 423 **4. Conclusions**

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To the best of our knowledge, the current study about the impact of lignins and of 425 hemicelluloses on cement hydration is the first one involving polymers extracted from a plant 426 species and by a mild procedure which preserves as much as possible the structural 427 specificities of cell wall polymers. By contrast, past studies about the impact of lignins on 428 cement hydration systematically involved lignin samples obtained from industrial 429 delignification processes which severely degrade the structure of cell wall lignins. 430 Comparative assays allowed us to establish that softwood kraft lignin fraction, a frequently 431 432 lignin model employed in such studies, does not adequately represent the lignin polymers leached out from miscanthus cell walls immersed in alkaline cement/water mixtures. The 433 cement hydration delay induced by the miscanthus dioxane lignin fraction was obtained when 434 its wt% in cement was 3 % or more while lower values had no impact. This threshold-435 dependent action of miscanthus DL fraction suggests that lignin polymers act on the 436 formation of C-S-H nuclei and by forming a lignin barrier on cement grain, which limits the 437 access of water to non-hydrated grains. 438 Suspending miscanthus fibers in alkaline cement/water mixtures is prone to induce the release 439 of both lignins and arabinoxylans. Accordingly, we comparatively evaluated the impact of 440 these two polymers on cement hydration. Electrical conductivity measurements suggested that 441 the AX-induced retardation of cement hydration occurred for lower wt% relative to cement 442 than the DL-induced one. The AX polymers might slow down not only the formation, but also 443 the growth of C-S-H nuclei. Remarkably enough, the co-addition of miscanthus DL and AX 444 fractions (1.6 wt% each, relative to cement) induced a retardation effect more pronounced 445

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 complexe barrier on
451	the cement grains.
452	
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633 <u>Figure 1</u>: 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

mixed in 200 ml water; 201 mg DL: 201 mg of DL added to 10 g cement mixed in 200 ml
 water; 256 mg DL: 256 mg of DL 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; 402 mg DL: 402 mg of DL added

to 10 g cement mixed in 200 ml water; 502 mg DL: 502 mg of DL added to 10 g cement

mixed in 200 ml water; 222 mg DL\*: 222 mg of DL added to 5 g cement mixed in 200 ml

641 water.



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

Control: 10 g cement mixed in 200 ml water; 100 mg KL: 100 mg of KL added to 10 g cement mixed in 200 ml water; 200 mg KL: 200 mg of KL added to 10 g cement mixed in 200 ml 

water; 250 mg KL: 250 mg of KL added to 10 g cement mixed in 200 ml water; 300 mg KL: 

300 mg of KL added to 10 g cement mixed in 200 ml water. 



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661 Figure 3: Conductivity measurements performed to monitor the hydration kinetics of

662 Portland cement in water without or with various amounts of dioxane lignin (DL) fraction 663 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.

665 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.
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681	SUPPLEMENTARY MATERIAL
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683	Impact of miscanthus lignin and arabinoxylan on the hydration kinetics of Portland
684	cement
685	
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Table 1S. Impact of miscanthus dioxane lignin (DL) and of softwood kraft lignin (KL) on the

- <sup>701</sup> hydration of cement, as revealed by electrical conductivity. Data are mean values (and SD) of
- 702 triplicate assays.

Lignin concentration relative	Time end of the induction	Time of the maximum
to cement (% by weight)	period (h)	conductivity peak (h)
DL fract	ion isolated from miscanthus ce	ll walls
0 (control)	0	$5.5\pm0.4$
1.5	0	$6.2\pm0.9$
2.0	0	$7.8\pm0.1$
2.6	$1.2\pm0.1$	$8.5\pm0.8$
3.0	$21.8\pm0.1$	$32.2 \pm 13$
4.0	33.1	46.8
5.0	$54.3 \pm 12.9$	$68.8 \pm 13$
Commercial softwood KL fraction		
1.0	$3.6 \pm 2.6$	$9.9 \pm 3.4$
2.0	$13.2 \pm 2.7$	$21.0 \pm 3.0$
2.5	16.0	24.7
3.0	$27.9\pm4.6$	$38.6 \pm 3.0$