



HAL
open science

Influence of chemical treatments of miscanthus stem fragments on polysaccharide release in the presence of cement and on the mechanical properties of bio-based concrete materials

Estefania Boix, Emilie Gineau, Joan Oñate Narciso, Herman Höfte, Gregory Mouille, Patrick Navard

► To cite this version:

Estefania Boix, Emilie Gineau, Joan Oñate Narciso, Herman Höfte, Gregory Mouille, et al.. Influence of chemical treatments of miscanthus stem fragments on polysaccharide release in the presence of cement and on the mechanical properties of bio-based concrete materials. *Cement and Concrete Composites*, 2020, 105, pp.103429. <10.1016/j.cemconcomp.2019.103429>. <hal-02424193>

HAL Id: hal-02424193

<https://minesparis-psl.hal.science/hal-02424193v1>

Submitted on 20 Jul 2022

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.



Distributed under a Creative Commons CC BY-NC 4.0 - Attribution - Non-commercial use - International License

1 **Influence of chemical treatments of miscanthus stem fragments**
2 **on polysaccharide release in the presence of cement and on the**
3 **mechanical properties of bio-based concrete materials**

4
5 **Estefania Boix¹, Emilie Gineau², Joan Oñate Narciso², Herman Höfte², Gregory**
6 **Mouille² and Patrick Navard^{1*}**

7 1- MINES ParisTech, PSL Research University, CEMEF** - Centre de mise en forme des
8 matériaux, CNRS UMR 7635, CS 10207, rue Claude Daunesse, 06904 Sophia Antipolis
9 Cedex, France

10 eboixl@gmail.com; patrick.navard@mines-paristech.fr

11 2- Institut Jean-Pierre Bourgin, INRA, AgroParisTech, CNRS, Université Paris-Saclay,
12 78000, Versailles, France

13 emilie.gineau@inra.fr; JoanOñate.Narciso@inra.fr, hermanus.hofte@inra.fr, gregory.mouille@inra.fr

14

15 ** To whom correspondence must be addressed*

16 *patrick.navard@mines-paristech.fr*

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

18

19

20 **Declarations of interest:** none

21

22 **Abstract**

23 Three types of treatments of miscanthus were performed, alkali, silanization and the
24 combination of both. There is a direct inverse relation between the amount of sugar-
25 containing molecules extracted from miscanthus and the mechanical strength of the concrete

26 blocks. The use of alkali treated stems as fillers increased remarkably the strength of the
27 blocks, and this was even higher when the alkali treated fibers were coated with silica, with a
28 compression strength of 11 MPa compared with an initial 2.2 MPa. The use of alkali-treated
29 stems result in a faster cement hydration, compared to untreated ones suggesting that specific
30 sugars or other components released from the alkali-treated plant may favor cement
31 hydration. A remarkable decrease of the cellulose and xylose content is observed for the
32 miscanthus pieces after being soaked in a cement-water-sand mixture, these two molecules
33 being adsorbed on cement particles.

34

35 **Key-words**

36 Concrete; Fibers; Miscanthus; Chemical treatment; Polysaccharide, Sugar

37

38 **1 Introduction**

39 In the building and construction sector, plant parts can be used as fillers in concrete to reduce
40 the use of non-renewable natural resources such as sand or gravel. In addition, plant-based
41 fillers have a positive CO₂ balance and good thermal and acoustic insulation properties [1] as
42 well as reducing the weight of concrete materials. However, the use of plant-based fillers has
43 several drawbacks. Besides their unfavorable economics [2], such concretes show a lack of
44 affinity between the organic phase (plant) and the inorganic concrete matrix. This results in a
45 non-effective stress transfer at the interface between both materials, weakening the
46 mechanical properties of the concrete composite and leading to a poor compressive strength.
47 Long-term durability is also an open question since plant material may decompose over time.
48 Another difficulty is to limit the amount of water absorbed by the plant material at the
49 expense of the water content needed for cement setting and hardening. Finally, the alkalinity
50 of water in concrete pores has a strong degradation effect on natural fibers [3,4]. This is well
51 known in the pulp and paper industry where soda treatments are used to extract various
52 components from wood or lignocellulosics, in particular hemicelluloses [5]. The extraction of
53 hemicelluloses and their possible degradation in various lower molar mass sugars and sugar
54 derivatives are strongly affecting the setting of concrete. Some sugars, among other
55 components, released from the plants in the presence of water and cement are resulting in a
56 delay of the cement hydration [6] and affecting the setting and hardening process of cement

57 [7]. In the latter study, the authors used three different hemp shiv samples to prepare Portland
58 cement concrete. They concluded that molecules extracted from shiv in contact with the
59 water-cement mixtures had a strong influence on the setting and hardening of cement, acting
60 as strong retarders. They also showed that these extractives are decreasing the amount of
61 Calcium-Silicate-Hydrate (C-S-H) and portlandite in the final product. When extracted in
62 water, the three shivs showed a variation of the total amount of extracted sugar-based
63 molecules, correlated with the retardation and decrease of C-S-H and portlandite in the final
64 products, the highest amount of sugars leading to the strongest effects. The type of sugars
65 could also have an influence in the concrete setting since glucose was not related to any
66 variation of its properties while the shiv having the strongest deleterious effect has a much
67 higher proportion of xylose-based molecules. The effect of sugars on the setting of concrete
68 is a rather complex matter, extensively studied over years, but with very ambiguous and
69 puzzling results. Sugars have been shown to behave as retarders or accelerators, mostly
70 depending on concentration, but in some cases these two effects are observed in an
71 overlapped concentration range or with very small concentration differences [8]. This
72 probably evidences that the mechanisms at stake, adsorption and poisoning, complexation or
73 formation of barriers around cement grains [9–12] are not well understood. Using different
74 types of fibers, it was shown that increasing the percentage of fibers as filler decreased the
75 workability of concrete [13]. One way to overcome some of these difficulties is to treat the
76 lignocellulosic fibers to reduce the water absorption capacity, protect the lignocellulose
77 fraction from the cement alkalinity and improve the affinity between the plant and the
78 inorganic matrix [14]. Another important piece of information is that the behavior of
79 lignocellulosics is different when using cement-water or pure water extracts, rendering the
80 task of understanding the role of these extractives more difficult [15].

81 Lignocellulosic fibers are composed of cellulose, hemicellulose, lignin, pectin, inorganics and
82 waxy components with small amounts of other organic molecules [16]. Cellulose is the main
83 constituent contributing to the strength and stiffness of the biomass, forming intra- and
84 intermolecular hydrogen and Van der Waals bonding between cellulose chains and with
85 hemicellulose constituents. The percentage of each component varies depending on the plant
86 species and tissue types, where fibers with higher cellulose contents are generally stronger
87 [17]. When applying chemical treatments to the plant fibers many different effects can be
88 seen. For example, partial removal of superficial layers of the plant material exposes a
89 rougher surface with many accessible hydroxyl groups, resulting in a better interaction

90 between the fiber and the matrix, as in the case of polymer composites [16,18]. Among the
91 treatments tested, two of them will be examined in more detail in this work: alkali and silane
92 treatments. Treatment with alkali is a very common strategy to remove hemicelluloses,
93 pectins and other minor components [17,19], to change the morphology of the surface of
94 lignocellulosic objects, increasing interface strength [20] and removing surface debris
95 [21,22]. This is expected to lead to an improvement of fiber strength and fiber-matrix
96 adhesion [4,23]. Alkali treatments induce a fibrillation of cell wall cellulose fibers due to the
97 removal of their hemicellulose binder thereby improving matrix-cellulose binding by
98 increasing the biomass - cement contact interface. Many conditions can be applied for alkali
99 treatments such as varying concentrations, usually in the range 0.5-10% as tested with hemp
100 [23], coconut [21,24] and jute [25]. Silane treatment have been shown to reduce the
101 hydrophilic character of natural fillers [4,26–28], to act as compatibilization agents and to
102 increase the mechanical performances of concrete. For example, silanization of bagasse fibers
103 resulted in a decrease in water absorption by the fiber, improved its affinity with the cement
104 matrix and the durability of the fibers within the concrete matrix, and shortened the setting
105 time of the composite [29]. A correlation between the concentration of silane and the strength
106 of Kraft fiber-cement composite was shown [30]. In another study, Eucalyptus Kraft pulp
107 surfaces were modified with several silanes [26] and methacryloxypropyltrimethoxysilane
108 had a positive effect. It reduced the hydrophilicity of the biomass, leading to improved
109 mechanical properties, dimensional stability and durability of the concrete, and decreased the
110 final water/cement ratio, with the cellulose fibers being free from cement hydration products.
111 Aminopropyltriethoxysilane had an adverse effect on concrete properties (increased
112 hydrophilicity, reduced strength and durability, accelerated mineralization and higher
113 embrittlement).

114 The present work is revisiting the use of alkali and silane treatments for improving the
115 properties of plant-based concrete. Its objective is to understand the effect of these treatments
116 on miscanthus stem fragments in the context of the preparation of concrete, in particular
117 considering the effect of polysaccharide release from stems on the compressive mechanical
118 properties of the produced concrete.

119

120 **2 Experimental**

121 2.1 Materials

122 *Miscanthus X giganteus* stems were harvested from Seine-et-Marne region (France) on
123 March 2014 by the Biomass Environment System company and ground by SD Tech (Alès,
124 France). For the preparation of the concrete mixture, Portland cement (CEM I 52.5R
125 Couvrot) was provided by Calcia Ciments (Guerville, France) and sand of grain size 0/4 mm
126 was purchased in Castorama (Sophia Antipolis, France). All experiments were performed
127 with distilled water.

128 The general polysaccharide composition of miscanthus pieces used is given in Chupin *et al.*,
129 2017 [31]. The two major sugars are cellulose and xylose from hemicellulose.

130

131 2.2 Treated miscanthus stem fragments

132 Miscanthus stem fragments were alkali treated and silica coated, as detailed in Boix *et al.*,
133 2016 [32]. Briefly, miscanthus stem fragments of an average length and width of 1.2 ± 0.6
134 mm and 0.2 ± 0.1 mm, respectively, were soaked and stirred in a 5% NaOH solution for 30
135 minutes, then rinsed with diluted acetic acid and abundant water until the rinsing water
136 reached neutral pH. The silane treatment was applied to both the as-received miscanthus stem
137 pieces and to the alkali treated stem pieces using a 2.6 % v/v aqueous tetraethyl orthosilicate
138 (TEOS) emulsions at pH 4, pH 6 and pH 10 during 2 hours. Table 1 summarizes the
139 treatments and properties of miscanthus stem fragments used in this study, including their
140 water absorption and ash content values [32]. These samples were chosen in order to study
141 the effect of silane media conditions in water (noted Sw), acid (noted Sa) and basic (noted
142 Sb) conditions. Samples with only the alkali treatment (no silane) are noted as A and samples
143 with a silica coating in acid conditions on alkali pretreated stem fragments are noted as A-Sa.
144 Untreated stem fragments are noted as U.

145 Table 1. Characteristics of miscanthus samples previously prepared [32] and used in this
146 study. U: untreated miscanthus pieces, A: with only the alkali treatment, Sw: silanization in
147 water, Sa: silanization in acid conditions, Sb: silanization in basic conditions, A-Sa: silica
148 coating in acid conditions on alkali pretreated pieces.

Sample name	Media silane treatment	Alkali pre-treated	Water absorption (Weight %)	Ash content (Weight %)
U	No silane	No	80 ± 3	1.4 ± 0.2
Sw	Aqueous (pH 6)	No	64 ± 5	1.5 ± 0.1
Sa	Acid (pH 4)	No	62 ± 5	4.3 ± 0.1
Sb	Basic (pH 10)	No	62 ± 3	4.9 ± 0.1
A	No silane	Yes	91 ± 3	1.0 ± 0.1
A-Sa	Acid (pH 4)	Yes	84 ± 4	3.2 ± 0.1

149

150 As the size of natural pieces used as fillers for concrete may have a crucial effect on the
151 composite strength, untreated and treated miscanthus fragments were previously sieved at an
152 amplitude of 40 Hz with a Retsch AS200 Digit shaker (Retsch, Germany) operating at 40mm
153 amplitude (2mm/g) in order to use the same length of miscanthus stem fragments for all
154 composites. The sieves applied were 1 mm, 600 µm, 400 µm, 200 µm, 100 µm. However due
155 to their relative abundance, only the most populated and bigger fragments were chosen and
156 population was set as: 26% of ≥ 600 µm, 37% ≥ 400 µm and 37% of ≥200 µm.

157

158 2.3 Concrete blocks preparation and compression test

159 The biomass-based concrete blocks contained a mixture of cement, sand, miscanthus stem
160 fragments and water. The density of untreated miscanthus stem fragments was considered the
161 same for all samples and was measured in ethanol using a 10 ml pycnometer, giving the value
162 of $0.31 \pm 0.01 \text{ g/cm}^3$ obtained from the average of four measurements. The mixture of
163 cement, sand and miscanthus pieces had the following composition: 40% dry weight of
164 cement (density 3.09 g/cm^3), 57% dry weight of sand (density 2.60 g/cm^3) and 3% dry weight
165 of miscanthus (corresponding to 22% miscanthus by volume). The water to cement ratio
166 (w/c) was set to 0.4, which allowed an easy manipulation and a fast demolding of the
167 concrete blocks. The quantity of water was readjusted for each mixture by measuring the
168 moisture contents (Mettler Toledo HX204) of the sand and miscanthus used and subtracting
169 this amount of water from the quantity required for the concrete mixture. A total of 1.5 kg of
170 dry mixture was used per batch, which allowed the production of nine concrete cubes of
171 $5 \times 5 \times 5 \text{ cm}^3$.

172 The wet concrete mixing was performed in a metallic flat-bottom recipient using a trowel.
173 The mixing process was based on the ASTM C192/C192M-07 standard methodology when
174 using a mixing machine. Nonetheless, the manual mixing was found to be more reliable for
175 the preparation of such low quantities. The methodology for the preparation of the bulk
176 mixture was done in six steps: mix sand and miscanthus, add some of the water to wet the
177 stem fragments, add the cement, mix during three minutes, cover the mixture and let it rest
178 for three minutes and mix during two more minutes while adding the remaining water. The
179 wet mixture was then transferred into a metallic mold of 15x15 cm² surface over 5 cm
180 thickness fitted with partitions to obtain cubic structures of 5x5x5 cm³, and then placed on a
181 vibration table (Netter Vibration NV, Germany). After pouring the mixture into the mold, a
182 vibration of 50 Hz during 20s was applied in order to enhance compaction and removal of air
183 bubbles. Concrete samples were then removed from the 15x15 cm mold and kept with the
184 partitions for two days at 21 °C and 99 % relative humidity by covering the specimens with a
185 non-absorbing plastic foil, in a temperature-controlled room. Samples were then removed
186 from the partition mold and kept for a further five days under the same conditions. The
187 compression strength of the concrete cubes (four replicates) were tested after seven days from
188 preparation by a hydraulic Dartec HA 250 (Zwick, Germany) compression test machine. The
189 instrument imposed a displacement of the specimen at a deformation rate of 0.1 mm/sec and a
190 displacement limit of 4 mm. The compression strength was measured before the rupture of
191 the test sample. The density of the concrete blocks was measured from the cube dimensions
192 and weights just prior to the compression test.

193

194 2.4 Chemical analysis

195 Miscanthus-concrete mixture aqueous extracts were obtained after one hour of the
196 preparation of the wet concrete mixture (cement, sand, miscanthus and water), 26 g of the
197 mixture were diluted in 25 ml of water, mixed and filtered (300 µm pore filter) to obtain
198 aqueous extracts for further carbohydrate analysis. Miscanthus-water soak extracts were
199 prepared as follows: miscanthus samples (2 g) were soaked in 400 ml of water for 24 hours.
200 A longer period of soaking was allowed for water extracts (24 h), in comparison to soaks in
201 concrete (1 h), to allow a sufficient amount of sugar to be detected as water extraction was
202 less efficient than the concrete one. The soaking water was then extracted by filtration. 200
203 ml of the soaks were freeze-dried for further carbohydrate analysis. The other 200 ml were

204 used for the cement hydration and setting conductivity studies. The neutral monosaccharide
205 composition was obtained from 100 μL of aqueous extract, which was dried under vacuum
206 and hydrolyzed. This process followed the protocol described by Harholt *et al.*(2006) with
207 slight modifications in the hydrolysis reaction, using 100 μL of 2.5 M trifluoroacetic acid
208 (TFA) for 2 h at 115 $^{\circ}\text{C}$ instead of 2 M TFA for 1 h at 120 $^{\circ}\text{C}$. The hydrolyzed sample was
209 diluted 15 times and the released monosaccharides of hemicellulose were measured using an
210 HPAEC-PAD chromatography [33].

211

212 2.5 Cement hydration and setting studies

213 2.5.1 Conductivity measurements

214 The water soaks of untreated and treated miscanthus samples (1g / 200 ml) were used to
215 hydrate 1 g of cement (cement: water ratio, 1:200). Hydration was followed by an electric
216 conductimeter (SCHOTT instruments, ProLab 4000) during approximately 30 hours at 25 $^{\circ}\text{C}$
217 under stirring. Two independent tests were performed for each case.

218 2.5.2 Attenuated total reflectance-Fourier transform spectroscopy

219 Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR, Bruker
220 Tensor 27) was used to analyze cement setting in concrete samples. Samples were freeze-
221 dried at 7 days in order to stop the hydration/curing process and allow comparison between
222 samples. Dry cementitious samples were ground and filtered through a mesh of 0.1 x 0.1 mm
223 prior to analysis to avoid the presence of most of the lignocellulosic fragments. The
224 instrument was operated from 4000 to 600 cm^{-1} with a 4 cm^{-1} resolution and 32 scans.

225

226 **3 Results and discussion**

227

228 3.1 Influence of chemical treatments on compression properties of concrete

229 The chemically treated miscanthus pieces were used for evaluating their effect on the
230 compression strength of concrete blocks. Figure 1 gives a typical example of the stress-strain
231 curves obtained with samples Sa. As can be seen, there is a clear agreement between the four
232 different test blocks. There is no plastic plateau and rupture is occurring quickly after loading.

233 Figure 2 shows that silica treatments on the untreated stem fragments had a slight positive
234 influence on the compression strength of the composite with no significant differences
235 between treatments at different pH values (Sw, Sa, Sb). The small differences could also be
236 attributed to a variation in the density due to the compaction process. The use of alkali treated
237 stems (Sa) as fillers increased remarkably the strength of the blocks, and this was even higher
238 when the alkali treated fibers were coated with silica (A-Sa). The A-Sa concrete composite
239 had a compression strength of 11 MPa compared with 2.2 MPa for untreated miscanthus stem
240 pieces. The greater compression strength of A-Sa was uniquely attributed to the filler
241 treatment since the densities of the blocks were comparable (see A versus A-Sa specimens in
242 Figure 2). Since the A-Sa treatment (alkali plus silane) showed such a large improvement in
243 mechanical properties, we looked at the influence of the water content for this specific
244 concrete mixture. The amount of water that the A-Sa miscanthus fragments were able to
245 absorb (Table 1) was additionally included in the wet concrete mixture, increasing the w/c
246 ratio from 0.4 to 0.46. Consequently, a higher compression strength (13 MPa) was measured,
247 but the material showed cracks after the compression test. Under compression, the concrete
248 block is compacting until failure, which may or not lead to its disintegration into several
249 pieces. Instabilities were observed for concrete blocks in the absence of miscanthus (blank)
250 even at the low w/c ratio of 0.4 (image not shown). In contrast, miscanthus concrete with w/c
251 ratio of 0.4 had the advantage of keeping its structure after the compression test. There exists
252 thus a range of water/cement ratio for preventing the collapse of the concrete composite
253 under compression by adding flexibility to the material.

254

255 3.2 Sugar-based molecules present in free water of the concrete mixture and cement curing

256 After one hour of contact between cement, sand, miscanthus and water, the available water
257 was collected and the presence of sugar-based molecules was measured. The effect of the
258 plant treatments on the release of sugar-containing molecules when mixed to cement was
259 measured and related to the mechanical properties of the concrete blocks at seven days, as
260 shown on Figure 3.

261 There is a very clear correlation between the presence of sugar-based molecules in the free
262 water of concrete and the compression strength. The higher the amount of sugar-based
263 molecules is, the lower is the compression strength. We conclude that the better performance
264 of the concrete obtained with alkali (A) and alkali-silane (A-Sa)-treated stem fragments may

265 be mainly due to two factors: Firstly, the alkali treatment is eliminating parts of pectin,
266 hemicellulose and waxes leading to a higher roughness of the plant stem surface [32], as well
267 as increasing the number of cellulose molecules exposed to the surface, available to react
268 with the cement matrix [16,34]. Secondly, it is known that polysaccharides and sugars
269 released from the lignocellulosic plants are in most cases delaying cement hydration and
270 setting [35] and in many cases impairing strongly the mechanical properties of concrete [36].
271 The alkali pretreatment (A and A-Sa samples) greatly reduced the amount of sugars in the
272 cement-water mixture and increased the compression strength of the blocks (Figure 3). Thus
273 the presence of extractable sugars could be seen as one of the main factors determining the
274 strength of the composite. Similar observations were reported by Diquélou *et al.*, 2015 [7].
275 By comparing untreated miscanthus to the silane treated samples (Sw, Sa and Sb), one can
276 observe that the silica coating also decreases the amount of sugar present in the water. A
277 similar trend is observed between A and A-Sa samples. The silica coating seems to act as a
278 protection of the lignocellulosic fragments against cement alkalinity. A more detailed
279 analysis of the type of sugars present in concrete water after one hour of contact between the
280 miscanthus stems and cement-water is shown in Figure 4. For both, treated or untreated
281 stems, glucose was the main sugar constituent, followed by xylose for (non-alkali-treated
282 stems) and fucose (for alkali-treated stems).

283 The cement curing can also be evaluated by infrared spectroscopy [7,37]. The hydration
284 process of the concrete samples was stopped at seven days by freeze-drying and then
285 analyzed by FT-IR. The hydrated form of cement is characteristic by the Si-O related peaks
286 for C-S-H at 970 cm^{-1} whereas the 920 cm^{-1} peak is related to the tricalcium silicate (C_3S),
287 which is the non-hydrated phase (see dotted lines in Figure 5). Therefore the hydration of the
288 cement can be estimated from the measurement of the relative abundance of these two Si-
289 related peaks. The lower the $970/920\text{ cm}^{-1}$ ratio, the lower is the amount of hydrates [7]. The
290 970 cm^{-1} peak was not noticed in the untreated and Sw samples. On the contrary, A-Sa had
291 the largest $970/920\text{ cm}^{-1}$ ratio, meaning that this sample had the lowest inhibition of C-S-H
292 formation. This is expected since these samples had the highest mechanical resistance,
293 coming from a more complete C-S-H formation. However, it should be noted that despite the
294 SiO_4^{4-} content within the cement matrix, samples may contain a few additional SiO_2 from the
295 miscanthus coating, although most fibers were filtered out before analysis. These silica bands
296 would appear at a similar wavelength in the infrared spectra. CaCO_3 is one of the components
297 bringing hardness to concrete. It is originally present in cement as well as due to the reaction

298 of portlandite and atmospheric CO₂ and it has associated peaks at 713, 870 and 1421 cm⁻¹
299 [37]. These IR bands are more intense for A, Sa, Sb and specially A-Sa than for U or Sw,
300 which is in full agreement with the mechanical property ranking of these samples.

301

302 3.3 Soaking miscanthus in water and use of soaked water

303 Extracting molecules from lignocellulosic materials by water soaking and using this water to
304 wet cement has been used previously as a way to explore the influence of extractable
305 molecules on the setting and hardening of cement. Results have shown that these extracts are
306 increasing the latency period, increasing the total time for complete setting, decreasing the
307 amount of hydrates and decreasing the mechanical properties compared with pure water
308 [7,15]. It is worth looking if there is a correlation between sugars extracted in water and in
309 cement-water mixtures. Figure 6 is showing the amount and the composition of sugars
310 present in the water from soaking untreated, alkali treated or alkali plus silane-treated stems.
311 There is a factor of five between the amount of sugars extracted by pure water between
312 untreated (158 µg/mL) and alkali-treated stems (32 µg/mL). It shows the expected decrease
313 in the total amount of sugars released in water after a mild alkali treatment of miscanthus (U
314 and A). The relative proportion of sugars is changed before and after an alkali treatment. It
315 shows that while glucose and xylose are the most important released sugars, considering their
316 predominance in miscanthus stems, xylose is the most abundant sugar extracted after an
317 alkali treatment. The difference between A and A-Sa where much less sugars are soluble in
318 water after alkali followed by silanization treatments suggests that the silica coating acts as a
319 barrier protecting miscanthus pieces against water penetration (the relative proportion of
320 sugars between A and A-Sa is considered as similar).

321 A very striking result is that the total amount of sugars extracted from untreated miscanthus
322 in contact with concrete is about 11 µg/mL of fluid (Figure 4), compared to 158 µg/mL of
323 sugars extracted in pure water (Figure 6). The possible explanations are (i) cement is not
324 extracting sugars, a very unlikely result considering the high pH, (ii) these extracted sugars
325 are so degraded that they cannot be detected, not probable considering the sugar detection
326 methods used, or (iii) sugars are extracted and they bind to the cement particles, and are thus
327 not present in the free water present between sand and cement particles. Being the last
328 hypothesis the most probable. There is thus the need to better understand which sugars are
329 released and where they sit.

330

331 3.4 Comparison of sugar composition between miscanthus and the soaks in water and in
332 cement mixture for untreated miscanthus

333 Table 2 gives the composition of untreated miscanthus pieces and of the supernatant after
334 soaking 24 h in water and one hour in cement-sand-water. The results show that water is not
335 extracting cellulose but it does extract a small amount of hemicellulose, which is detected in
336 the supernatant. There is a huge decrease of the cellulose and xylose content of the
337 miscanthus pieces after being soaked in cement-water-sand mixture. The very interesting
338 result is that these two molecules which have been extracted from the miscanthus pieces due
339 to the presence of cement are not found in the water extracts between cement particles and
340 sand grains. They are thus potentially adsorbed on cement particles. This confirms several
341 previous studies in which the effect of extracted molecules on cement is a mechanism
342 associated with the adsorption of sugar-based compounds [9].

343

344 Table 2. Composition of the untreated miscanthus pieces and of the supernatant after soaking
345 24 h in water and one hour in cement-sand-water. The three minor sugars (fucose, rhamnose,
346 mannose) were not measured.

Miscanthus pieces (in µg/mg of used miscanthus)						
Hemicellulose					Cellulose	
	Arabinose	Galactose	Glucose	Xylose	Cellulose	Xylose
24h in water	24.5	5.2	12.5	181.9	418.7	27.3
1 h in cement	22.7	3.9	12.6	140.6	311.3	31.0

347

Supernatant				
Hemicellulose (in µg/mg of used miscanthus)				
	Arabinose	Galactose	Glucose	Xylose
24h in water	0.13	0.4	0.9	0.83
1 h in cement	Nd	nd	0.57	0.13

348

349 3.5 Hydration kinetics

350 The hardness of a cement-based material is tightly related to the physicochemical
351 environment in which the mixture is performed. This is due to hydration and setting being the
352 result of interfacial and solid-state reactions between water and powdered minerals [9]. This
353 includes the degree of hydration, water to cement ratio, the humidity and temperature during
354 curing but also the amount and nature of components released from lignocellulosic
355 fragments. Portland cements are multi-phasic inorganic materials consisting of several oxides
356 with one of the main components being tricalcium silicate (Ca_3SiO_5 or C_3S), which can be
357 used as a tracer to monitor the effect of admixtures in cement hydration by measuring
358 electrical conductivity. During hydration, C_3S is dissolved, followed by the formation of a
359 hydrated mineral (C-S-H) and finally precipitates as portlandite ($\text{Ca}(\text{OH})_2$) [38]. Since the
360 presence of plant sugars is known to have a strong effect on the strength of the concrete
361 blocks, the following analysis aimed to investigate at which stage the plant extracts affected
362 the curing process of the concrete: hydration, setting or hardening, keeping in mind that
363 extraction was conducted by soaking miscanthus in pure water. For this, the cement hydration
364 was monitored by conductimetry measurements with water having been previously soaked in
365 untreated (U), alkali treated (A) and alkali-silane (A-Sa) treated miscanthus fragments. The
366 water to cement ratio (w/c) was set to 200 for all samples. Dilution grades of $0.5 < \text{w/c} < 300$
367 have been previously validated by Nonat *et al.*, 1997 [38], although it should be noted that
368 the higher the w/c ratio is, the longer is the induction period and the later the precipitation of
369 portlandite takes place [38]. As the miscanthus fragments were simply soaked in water, the
370 amount of sugars released is much lower and different in composition than under the alkali
371 conditions to which miscanthus is exposed during the whole concrete formation. However,
372 soaking allows a comparison between the different plant treatments and may bring some
373 clues regarding the effects of miscanthus fillers in concrete formation. To increase the
374 amount of sugars released into the water and allow observing an effect on the cement
375 hydration, the weight ratio of cement over miscanthus was set to 1:1, higher than for the
376 concrete mixture used to prepare the concrete blocks (1: 0.075). The interpretation of the
377 conductivity curves was performed according to previous cement hydration studies by
378 Comparet *et al.*, 2000 and Govin *et al.*, 2005 [6,39]. The curves in Figure 7 show a first fast
379 increase in the conductivity due to the C_3S dissolution and formation of Ca^{2+} ions, followed
380 by a slow increase related to the C-S-H nucleation and a more rapid conductivity rate
381 increase due to the crystal growth. The maximum conductivity peak corresponds to the
382 highest concentration of portlandite before its precipitation, detected by the decrease of the
383 curve due to the conversion of Ca^{2+} ions into $\text{Ca}(\text{OH})_2$.

384 Results show that cement dissolution differs when, instead of pure water, miscanthus soaks
385 were added. In this latter case, a lower conductivity is recorded from the first hours of the
386 measurement (Pure water > Alkali and silane treated (A-Sa) > Alkali (A) > Untreated (U))
387 which suggests a complexation effect of calcium ions by the released polysaccharides, sugars
388 or other released miscanthus organic admixtures [9]. The hydrate nucleation step was delayed
389 for around two hours for the untreated miscanthus soaks compared to pure water, whereas for
390 A and A-Sa, hydration was two hours shorter than the pure water. In previous studies, the
391 delay in the hydrate nucleation was related to a reduced number of hydrate nuclei which are
392 precipitating [39]. This delay in the hydrate nucleation consequently postpones the
393 portlandite precipitation as it is the case for untreated samples relative to the pure water.
394 Therefore, high concentrations of sugar or other extracts released by the untreated plant
395 produce a delay in the hydration of cement. However, the contrary is observed when using
396 soaks from alkali or alkali plus silanization stem fragments which give a faster hydration. It is
397 well known that the effects of sugars are complex and often concentration dependent. For
398 example, adding a small amount sucrose in cement caused a delay in hydration of tricalcium
399 silicate [40] while adding sucrose in large quantities had a positive effect on concrete
400 prepared with flax shaves, increasing the mechanical properties of concrete, decreasing
401 setting time and improving concrete behavior in water. The results found here contradict
402 previous results that suggested that extracts coming from lime or cement-water were
403 detrimental to the setting of cement, concluding that degradation products created in high
404 alkaline environments (mainly carboxylic acids) have a negative effect [6]. The effects of
405 sugars, extracted or added, are not easily predictable. Precipitation of portlandite starts nearly
406 20 h earlier when using alkali treated miscanthus soaks when compared to untreated stem
407 soaks and even sooner than for pure water. This confirms that some sugars or other
408 components released from the alkali-treated plant favors cement hydration. A closer look at
409 Figure 7 shows that despite the similar hydration time for A and A-Sa, the plateau of nuclei
410 growth is longer for A-Sa and precipitation takes place at the same time as the untreated
411 miscanthus composite (U).

412

413 **4 Conclusions**

414 The use of miscanthus stem pieces for preparing concrete is giving blocks with a very
415 moderate compressive strength. Using different treatments, it is shown that there is a relation

416 between the amount of sugar-containing molecules able to be extracted from the miscanthus
417 stem fragments and the mechanical strength of the blocks. The lower the amount of such
418 molecules is extracted, the higher the mechanical strength is obtained. When the miscanthus
419 stem pieces were previously treated with an alkali solution able to extract some of the
420 hemicelluloses present in the cell walls, the extraction of sugar-containing molecules by
421 cement-water-sand mixtures is decreased. Such a treatment is highly efficient for improving
422 the mechanical performances of miscanthus-based concrete. Silanization is moderately
423 efficient as it is also slightly decreasing the sugar-containing molecule released probably due
424 to a barrier effect, and thus improving compression strength. The addition of the two
425 treatments is giving very good results, increasing the compression strength by more than five
426 times compared to untreated miscanthus. The analysis of the sugars present at the beginning
427 of the cement hydration process shows that two sugar-based molecules play a main inhibition
428 role, glucose and xylose. The effect of the amount of sugar released is showing a contrasted
429 image. High amounts of sugar or other extracts released by the untreated plant produce a
430 delay in the hydration of cement. In contrast, a lower concentration of the sugar extracts or a
431 specific composition results in a faster cement hydration, as obtained for the A and A2
432 samples results. Precipitation of portlandite starts nearly 20 h earlier when using alkali treated
433 miscanthus soaks when compared to untreated soaks, even sooner than for pure water. This
434 suggests that some sugars or other components released from the alkali-treated plant may
435 favor cement hydration. When analyzing untreated miscanthus stem pieces and the
436 supernatant after 24 h soaking in water and one hour in cement-sand-water, results show that
437 there is a huge decrease in the cellulose and xylose content of the miscanthus pieces after
438 being soaked in cement-water-sand mixture. These extracted molecules are not sitting in the
439 water present between cement particles and sand grains. They are thus adsorbed on cement
440 particles, probably polluting their surfaces and inhibiting their hydration.

441

442 **5 Acknowledgements**

443 This work was supported by the program Investments for the Future (grant ANR-11-BTBR-
444 0006-BFF) managed by the French National Research Agency. We thank BES and Calcia
445 companies for having provided miscanthus and cement, respectively. The IJPB benefits from
446 the support of the LabEx Saclay Plant Sciences-SPS (ANR-10-LABX-0040-SPS).

447 **6 References**

- 448 [1] C. Niyigena, S. Amziane, A. Chateauneuf, Investigating Hemp Concrete Mechanical
449 Properties Variability Due to Hemp Particles, in: *Mech. Compos. Multi-Functional*
450 *Mater.* Vol. 7, Springer, 2017: pp. 9–17. doi:10.1007/978-3-319-41766-0_2.
- 451 [2] C. Ingrao, A. Lo Giudice, J. Bacenetti, C. Tricase, G. Dotelli, M. Fiala, V. Siracusa, C.
452 Mbohwa, Energy and environmental assessment of industrial hemp for building
453 applications: A review, *Renew. Sustain. Energy Rev.* 51 (2015) 29–42.
454 doi:10.1016/J.RSER.2015.06.002.
- 455 [3] F.C. Jorge, C. Pereira, J.M.F. Ferreira, Wood-cement composites: a review, *Holz Als*
456 *Roh- Und Werkst.* 62 (2004) 370–377. doi:10.1007/s00107-004-0501-2.
- 457 [4] F. Pacheco-Torgal, S. Jalali, Cementitious building materials reinforced with vegetable
458 fibres: A review, *Constr. Build. Mater.* 25 (2011) 575–581.
459 doi:10.1016/J.CONBUILDMAT.2010.07.024.
- 460 [5] H. Sixta, ed., *Handbook of Pulp*, Wiley-VCH Verlag GmbH, Weinheim, Germany,
461 2006. doi:10.1002/9783527619887.
- 462 [6] A. Govin, A. Peschard, E. Fredon, R. Guyonnet, New insights into wood and cement
463 interaction, *Holzforschung.* 59 (2005) 330–335. doi:10.1515/HF.2005.054.
- 464 [7] Y. Diquélou, E. Gourlay, L. Arnaud, B. Kurek, Impact of hemp shiv on cement setting
465 and hardening: Influence of the extracted components from the aggregates and study of
466 the interfaces with the inorganic matrix, *Cem. Concr. Compos.* 55 (2015) 112–121.
467 doi:10.1016/j.cemconcomp.2014.09.004.
- 468 [8] A. Abalaka, Comparative Effects of Cassava Starch and Simple Sugar in Cement
469 Mortar and Concrete, *ATBU J. Environ. Technol.* 4 (2010) 13–22.
- 470 [9] C. Jolicoeur, M.-A. Simard, Chemical admixture-cement interactions: Phenomenology
471 and physico-chemical concepts, *Cem. Concr. Compos.* 20 (1998) 87–101.
472 doi:10.1016/S0958-9465(97)00062-0.
- 473 [10] M.C. Garci Juenger, H.M. Jennings, New insights into the effects of sugar on the
474 hydration and microstructure of cement pastes, *Cem. Concr. Res.* 32 (2002) 393–399.
475 doi:10.1016/S0008-8846(01)00689-5.

- 476 [11] J.F. Young, A review of the mechanisms of set-retardation in portland cement pastes
477 containing organic admixtures, *Cem. Concr. Res.* 2 (1972) 415–433.
478 doi:10.1016/0008-8846(72)90057-9.
- 479 [12] J. Cheung, A. Jeknavorian, L. Roberts, D. Silva, Impact of admixtures on the hydration
480 kinetics of Portland cement, *Cem. Concr. Res.* 41 (2011) 1289–1309.
481 doi:10.1016/J.CEMCONRES.2011.03.005.
- 482 [13] P.K. Mehta, P.J.M. Monteiro, *Concrete: microstructure, properties, and materials.*,
483 McGraw-Hill, New York, 2006.
- 484 [14] L.T.T. Vo, P. Navard, Treatments of plant biomass for cementitious building materials
485 – A review, *Constr. Build. Mater.* 121 (2016) 161–176.
486 doi:10.1016/J.CONBUILDMAT.2016.05.125.
- 487 [15] G. Vaickelionis, R. Vaickelioniene, Cement hydration in the presence of wood
488 extractives and pozzolan mineral additives, *Ceramics-Silikáty.* 50 (2006) 115–122.
- 489 [16] M.M. Kabir, H. Wang, K.T. Lau, F. Cardona, Chemical treatments on plant-based
490 natural fibre reinforced polymer composites: An overview, *Compos. Part B Eng.* 43
491 (2012) 2883–2892. doi:10.1016/j.compositesb.2012.04.053.
- 492 [17] L.Y. Mwaikambo, M.P. Ansell, Chemical modification of hemp, sisal, jute, and kapok
493 fibers by alkalization, *J. Appl. Polym. Sci.* 84 (2002) 2222–2234.
494 doi:10.1002/app.10460.
- 495 [18] B.N. Dash, A.K. Rana, H.K. Mishra, S.K. Nayak, S.C. Mishra, S.S. Tripathy, Novel,
496 low-cost jute-polyester composites. Part 1: Processing, mechanical properties, and
497 SEM analysis, *Polym. Compos.* 20 (1999) 62–71. doi:10.1002/pc.10335.
- 498 [19] R.C. Sun, J. Tomkinson, P.L. Ma, S.F. Liang, Comparative study of hemicelluloses
499 from rice straw by alkali and hydrogen peroxide treatments, *Carbohydr. Polym.* 42
500 (2000) 111–122. doi:10.1016/S0144-8617(99)00136-8.
- 501 [20] A. Valadez-Gonzalez, J.M. Cervantes-Uc, R. Olayo, P.J. Herrera-Franco, Effect of
502 fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced
503 composites, *Compos. Part B Eng.* 30 (1999) 309–320.
- 504 [21] J.M. Ferraz, C.H.S. Del Menezzi, M.R. Souza, E.Y.A. Okino, S.A. Martins,

- 505 Compatibility of Pretreated Coir Fibres (*Cocos nucifera* L.) with Portland Cement to
506 Produce Mineral Composites, Int. J. Polym. Sci. 2012 (2012) 1–7.
507 doi:10.1155/2012/290571.
- 508 [22] G.P. Bowlin, Production of light-weight concrete products, GB1089777(A), 1967.
- 509 [23] D. Sedan, C. Pagnoux, A. Smith, T. Chotard, Mechanical properties of hemp fibre
510 reinforced cement: Influence of the fibre/matrix interaction, J. Eur. Ceram. Soc. 28
511 (2008) 183–192. doi:10.1016/J.JEURCERAMSOC.2007.05.019.
- 512 [24] H. Gu, Tensile behaviours of the coir fibre and related composites after NaOH
513 treatment, Mater. Des. 30 (2009) 3931–3934. doi:10.1016/J.MATDES.2009.01.035.
- 514 [25] S.P. Kundu, S. Chakraborty, A. Roy, B. Adhikari, S.B. Majumder, Chemically
515 modified jute fibre reinforced non-pressure (NP) concrete pipes with improved
516 mechanical properties, Constr. Build. Mater. 37 (2012) 841–850.
517 doi:10.1016/J.CONBUILDMAT.2012.07.082.
- 518 [26] G.H.D. Tonoli, M.N. Belgacem, G. Siqueira, J. Bras, H. Savastano, F.A. Rocco Lahr,
519 Processing and dimensional changes of cement based composites reinforced with
520 surface-treated cellulose fibres, Cem. Concr. Compos. 37 (2013) 68–75.
521 doi:10.1016/J.CEMCONCOMP.2012.12.004.
- 522 [27] P.K. Kushwaha, R. Kumar, Studies on Water Absorption of Bamboo-Polyester
523 Composites: Effect of Silane Treatment of Mercerized Bamboo, Polym. Plast.
524 Technol. Eng. 49 (2009) 45–52. doi:10.1080/03602550903283026.
- 525 [28] P.K. Kushwaha, R. Kumar, Studies on water absorption of bamboo-epoxy composites:
526 Effect of silane treatment of mercerized bamboo, J. Appl. Polym. Sci. 115 (2010)
527 1846–1852. doi:10.1002/app.31317.
- 528 [29] K. Bilba, M.-A. Arsene, Silane treatment of bagasse fiber for reinforcement of
529 cementitious composites, Compos. Part A Appl. Sci. Manuf. 39 (2008) 1488–1495.
530 doi:10.1016/j.compositesa.2008.05.013.
- 531 [30] J.L. Pehanich, P.R. Blankenhorn, M.R. Silsbee, Wood fiber surface treatment level
532 effects on selected mechanical properties of wood fiber–cement composites, Cem.
533 Concr. Res. 34 (2004) 59–65. doi:10.1016/S0008-8846(03)00193-5.

- 534 [31] L. Chupin, D. de Ridder, A. Clément-Vidal, A. Soutiras, E. Gineau, G. Mouille, S.
535 Arnoult, M. Brancourt-Hulmel, C. Lapierre, D. Pot, L. Vincent, A. Mija, P. Navard,
536 Influence of the radial stem composition on the thermal behaviour of miscanthus and
537 sorghum genotypes, *Carbohydr. Polym.* 167 (2017) 12–19.
538 doi:10.1016/j.carbpol.2017.03.002.
- 539 [32] E. Boix, F. Georgi, P. Navard, Influence of alkali and Si-based treatments on the
540 physical and chemical characteristics of miscanthus stem fragments, *Ind. Crops Prod.*
541 91 (2016) 6–14. doi:http://dx.doi.org/10.1016/j.indcrop.2016.06.030.
- 542 [33] J. Harholt, J.K. Jensen, S.O. Sørensen, C. Orfila, M. Pauly, H.V. Scheller,
543 ARABINAN DEFICIENT 1 Is a Putative Arabinosyltransferase Involved in
544 Biosynthesis of Pectic Arabinan in Arabidopsis, *PLANT Physiol.* 140 (2005) 49–58.
545 doi:10.1104/pp.105.072744.
- 546 [34] X. Li, A. Lope, G. Tabil, S. Panigrahi, Chemical Treatments of Natural Fiber for Use
547 in Natural Fiber-Reinforced Composites: A Review, *J. Polym. Environ.* 15 (2007) 25–
548 33. doi:10.1007/s10924-006-0042-3.
- 549 [35] B.W. Jo, S. Chakraborty, H. Kim, Efficacy of alkali-treated jute as fibre reinforcement
550 in enhancing the mechanical properties of cement mortar, *Mater. Struct.* 49 (2016)
551 1093–1104. doi:10.1617/s11527-015-0560-3.
- 552 [36] N. B., W. Z., W. H., L. X., Wood-cement compatibility review, *Wood Res.* 59 (2014)
553 813–825.
- 554 [37] F. Farcas, P. Touze, La spectrométrie infrarouge à transformée de Fourier (IRTF) :
555 Une méthode intéressante pour la caractérisation des ciments, *Bull. des Lab. des ponts*
556 *chaussées.* 230 (2001) 77–88.
- 557 [38] A. Nonat, J.C. Mutin, X. Lecoq, S.P. Jiang, Physico-chemical parameters determining
558 hydration and particle interactions during the setting of silicate cements, *Solid State*
559 *Ionics.* 101–103 (1997) 923–930. doi:10.1016/S0167-2738(97)00386-X.
- 560 [39] C. Comparet, A. Nonat, S. Pourchet, J.P. Guicquero, E. Gartner, M. Mosquet,
561 Chemical Interaction of di-phosphonate terminated monofunctional polyoxyethylene
562 superplasticizer with hydrating tricalcium silicate, in: *Superplast. Other Admixtures*
563 *Concr.*, American Concrete Institute, 2000: pp. 61–74.

564 [40] M. Khazma, N. El Hajj, A. Goullieux, R.M. Dheilily, M. Queneudec, Influence of
565 sucrose addition on the performance of a lignocellulosic composite with a cementious
566 matrix, *Compos. Part A Appl. Sci. Manuf.* 39 (2008) 1901–1908.
567 doi:10.1016/J.COMPOSITESA.2008.09.014.

568

569

570 **7 Caption for the figures**

571 Figure 1. Stress-strain curves for four different tests of sample Sa.

572 Figure 2. Compression strength results and density of the blocks (5x5x5 cm³) prepared with
573 differently treated miscanthus.

574 Figure 3. Crossed data of concrete compression strength versus the total amount of sugar
575 released from miscanthus fragments and present in the free water during the concrete
576 preparation with water and sand, after one hour of contact.

577 Figure 4. Distribution of sugars in the free water from the cement-sand water-miscanthus
578 slurry extract mixture after one hour of the mixing.

579 Figure 5. Infrared spectra of concrete samples after seven days of curing in presence of the
580 miscanthus stems.

581 Figure 6. Sugar content of the extracts used for hydrating cement after a 24 hour soak in
582 water with U: untreated miscanthus stem fragments, A: alkali treated and A-Sa: silica coating
583 on alkali treated.

584 Figure 7. Electric conductimetry monitoring of cement hydration (w/c= 200) in pure water, in
585 water soaks of untreated miscanthus (untreated U), in water soaks of alkali treated miscanthus
586 (A) and of alkali followed by silanization (A-Sa).

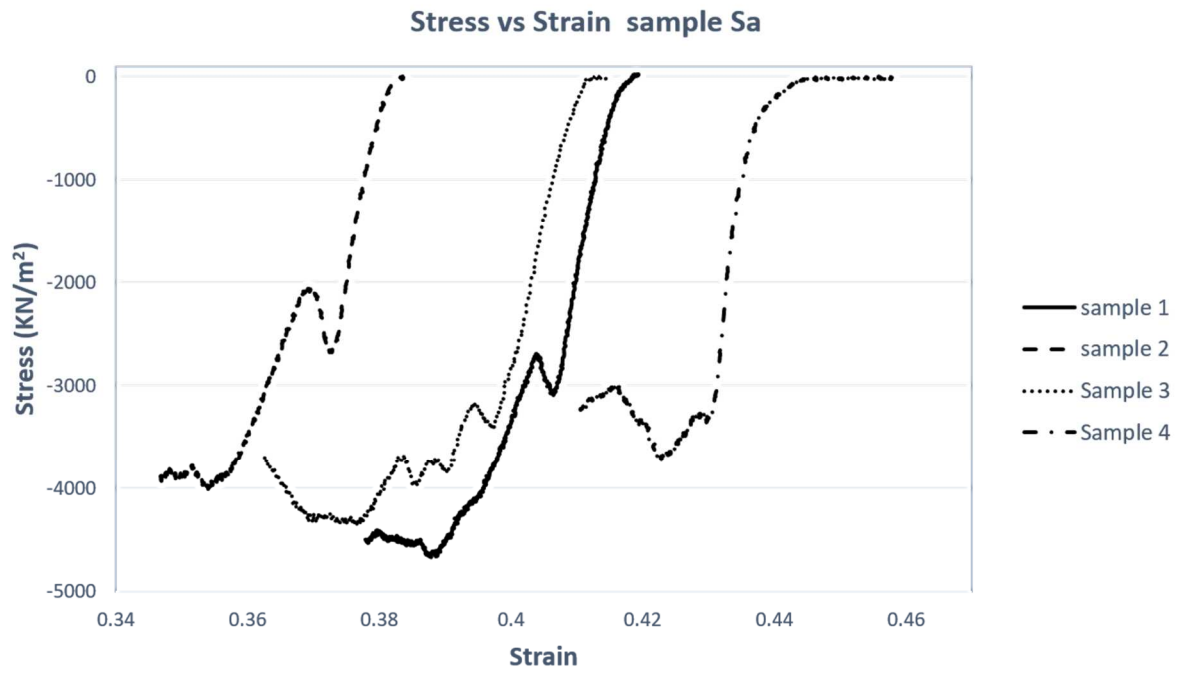


Figure 1. Stress-strain curves for four different tests of sample Sa.

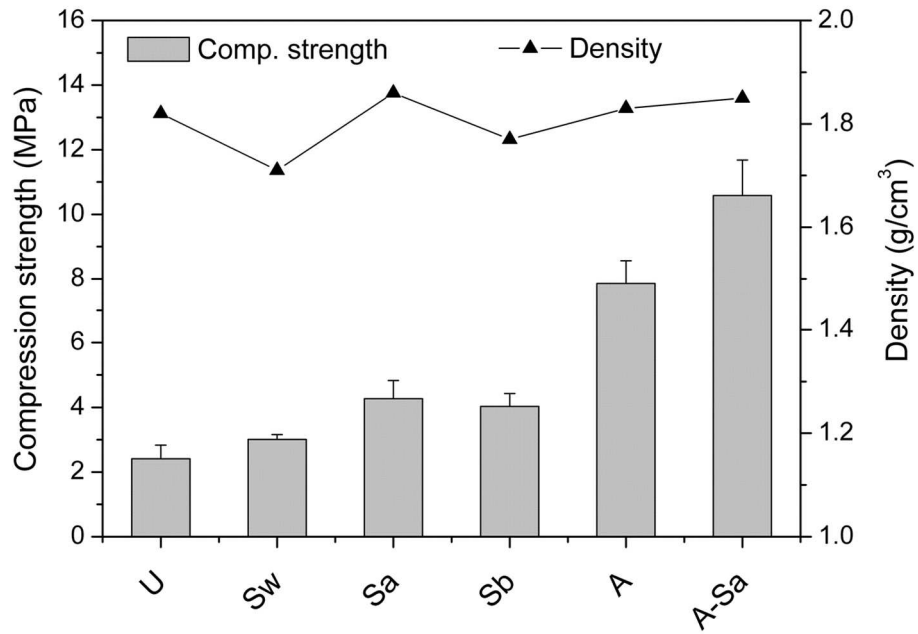


Figure 2. Compression strength results and density of the blocks (5x5x5 cm³) prepared with differently treated miscanthus.

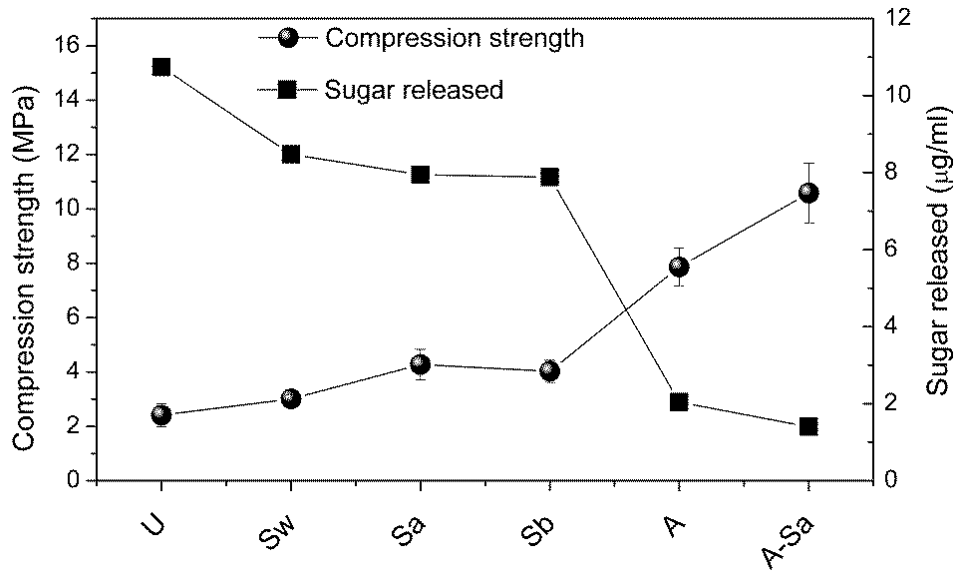


Figure 3. Crossed data of concrete compression strength versus the total amount of sugar released from miscanthus fragments and present in the free water during the concrete preparation with water and sand, after one hour of contact.

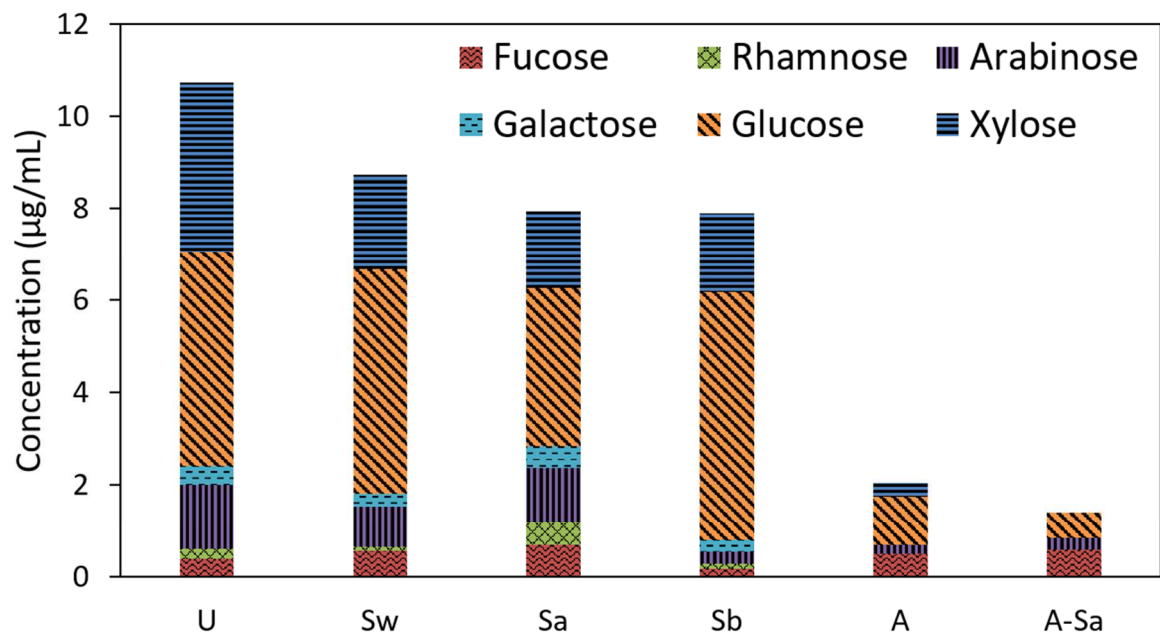


Figure 4. Distribution of sugars in the free water from the cement-sand water-miscanthus slurry extract mixture after one hour of the mixing.

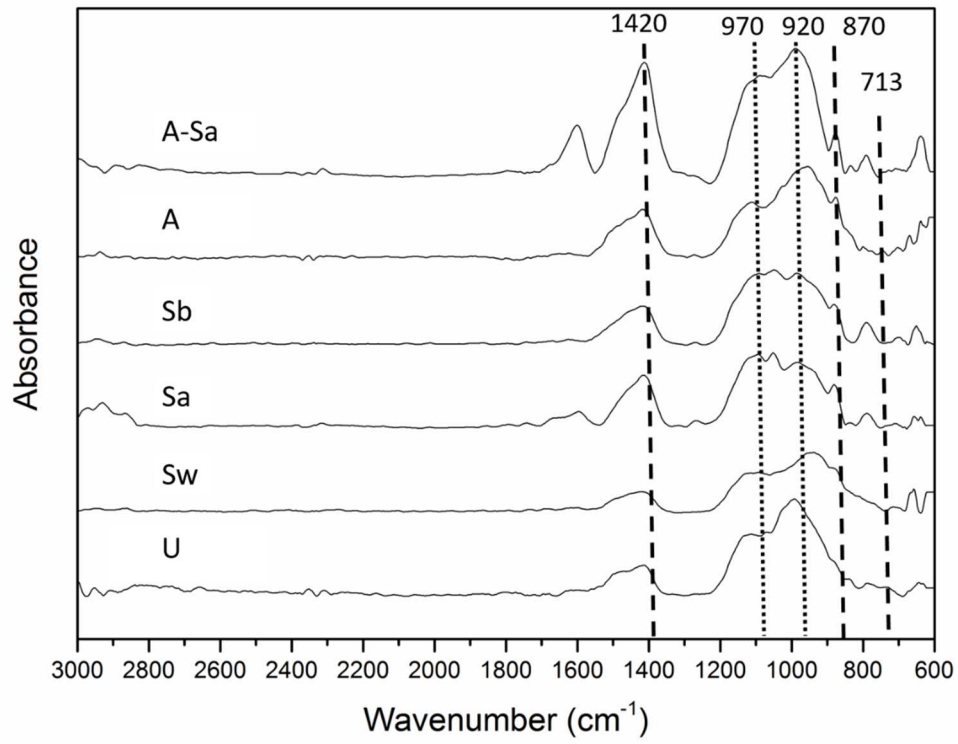


Figure 5. Infrared spectra of concrete samples after seven days of curing in presence of the miscanthus stems.

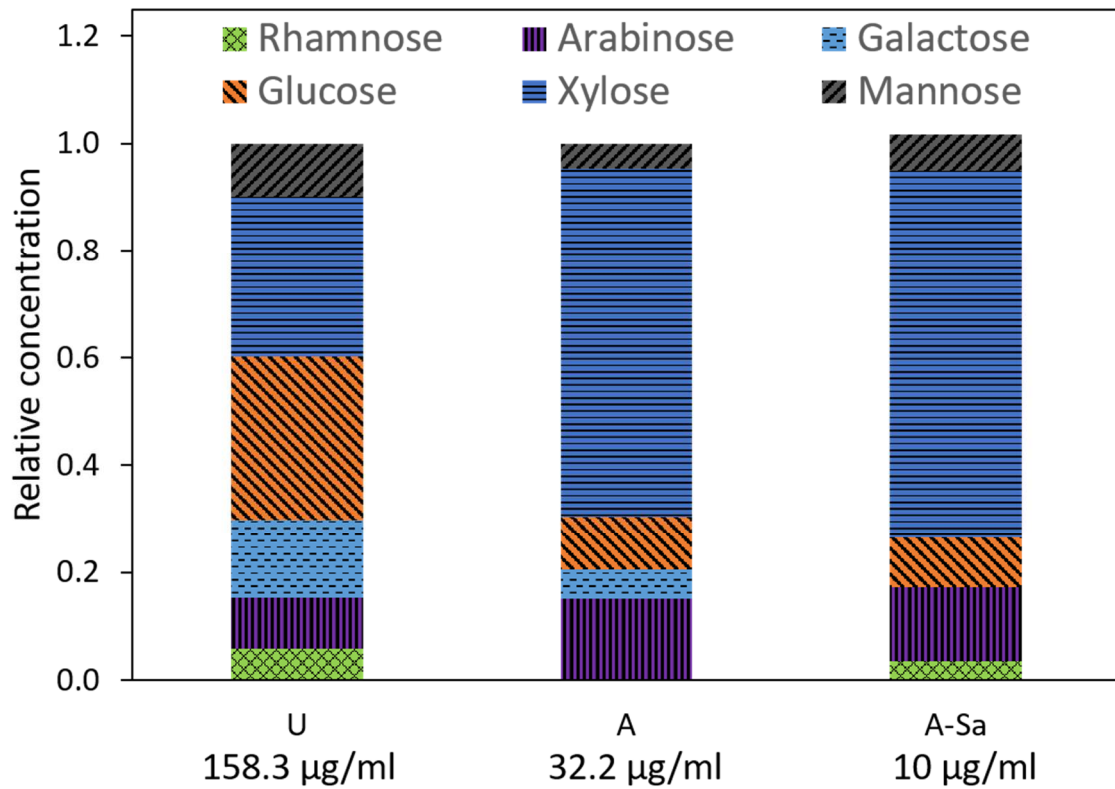


Figure 6. Sugar content of the extracts used for hydrating cement after a 24 hour soak in water with U: untreated miscanthus stem fragments, A: alkali treated and A-Sa: silica coating on alkali treated.

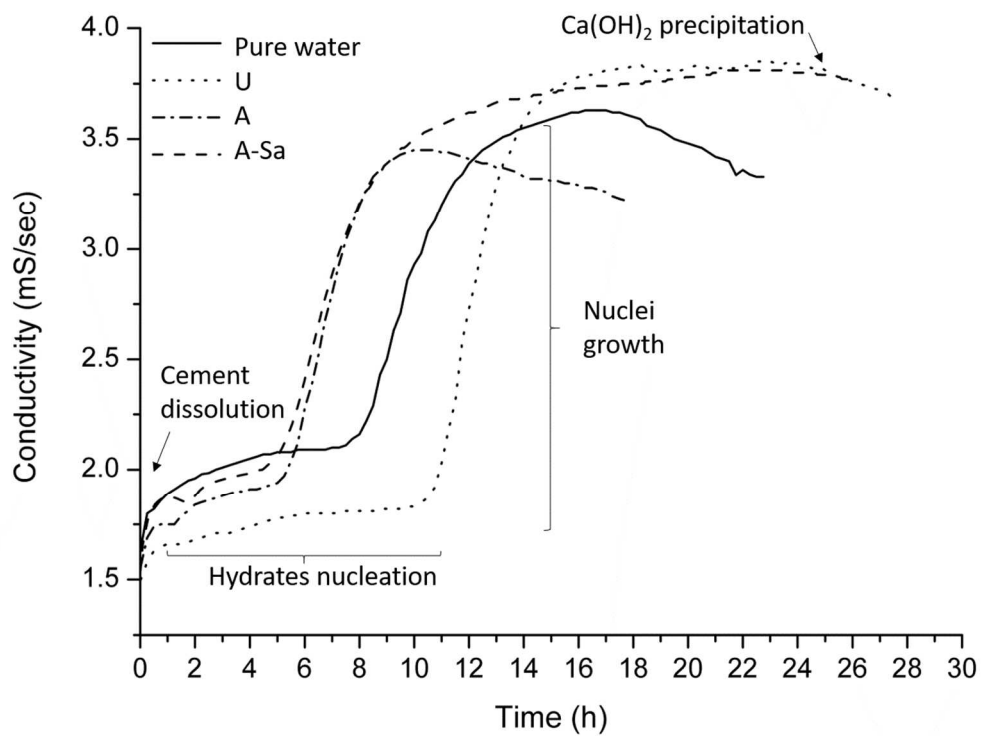


Figure 7. Electric conductimetry monitoring of cement hydration ($w/c=200$) in pure water, in water soaks of untreated miscanthus (untreated U), in water soaks of alkali treated miscanthus (A) and of alkali followed by silanization (A-Sa).