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1 **ON THE EFFECT OF CALCIUM LIGNOSULFONATE ON**
2 **THE RHEOLOGY AND SETTING TIME OF CEMENT PASTE**

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10 **ABSTRACT**

11
12 The effect of softwood calcium lignosulfonate, LSs, on the rheology and setting time of cement paste
13 has been investigated. Two Portland cements with different surface area and C₃A content were used.
14 The lignosulfonate was added either immediately with the mixing water or delayed after 10 minutes of
15 hydration. The cement pastes were characterized in terms of specific surface, rheology and heat of
16 hydration. Extracted pore solutions were analysed for free lignosulfonate concentration and for
17 changes in elemental composition. Immediate addition of LSs increased the specific surface, but not
18 delayed addition. Correlations were found between rheology and surface coverage by LSs, as
19 determined by adsorption isotherms, and between the setting time and the amount of free LSs in the
20 pore solution. An increased setting retardation upon delayed addition related to an increased
21 concentration of Al in the pore solution.

22 **KEYWORDS**

23
24 Lignosulfonate; admixture; rheology; setting retardation; adsorption

25 1 INTRODUCTION

26

27 Water-reducers, or plasticizers, are commonly used admixtures for concrete. Their addition to fresh
28 concrete allows obtaining highly fluid concrete at low water-binder ratios, improving the mechanical
29 properties and the durability of the hardened concrete [1, 2]. The plasticizer used in this paper is a low-
30 sugar softwood calcium lignosulfonate (LSs), commonly used in concrete in dosages 0.25-0.40 mass
31 % of binder. Lignosulfonates are polyelectrolytes derived from lignins in the pulping industry. Lignin
32 can be derived from various sources of biomass, and lignosulfonates of different molecular weight and
33 amount of functional groups (carboxyl groups, phenolic-OH, sulfonic groups) can be produced.

34 The dispersing effectiveness of plasticizers on cementitious materials is, amongst others, a function of
35 the degree of adsorption on the surface of the cement grains and hydrates. There are two main
36 dispersing mechanisms: electrostatic repulsion and steric hindrance. Which of the mechanisms is
37 dominant depends on the plasticizer type. During electrostatic repulsion the adsorbed plasticizer layer
38 renders the particle surface negatively charged, i.e. with a negative zeta potential. As negatively
39 charged particles approach each other, electrostatic repulsion prevents them from forming
40 agglomerates. Additionally, when two surfaces approach close enough for their adsorbed layers to
41 overlap, a steric force develops. This will contribute in hindering particles to get close enough to form
42 agglomerates. The key parameters that govern the steric repulsion are the adsorption layer thickness
43 and its conformation at the solid liquid interface [3]. Lignosulfonate can disperse cement particles by
44 both electrostatic repulsion and steric hindrance, as reported by Vikan [4], amongst others.

45 In addition to dispersion, the interaction between cement and plasticizer can potentially lead to
46 retardation of the setting time of the cement paste. Several mechanisms of retardation are hypothesized
47 in the literature, the main ones being: calcium complexation, nucleation poisoning of hydrates, surface
48 adsorption on anhydrous cement particles, and presence of sugars in the plasticizer [5-8]. Calcium
49 complexation involves the interaction between plasticizing polymers and calcium ions in the pore
50 solution. This would slow down the build-up of calcium supersaturation needed for hydrates
51 nucleation. However, according to Bishop et al. [5], and Marchon and Flatt [7], amongst others, the

52 low dosages of plasticizers generally used limit the amount of calcium potentially complexed. Thus,
53 calcium complexation does not appear likely as a main mechanism of setting retardation of cement. As
54 stated by Thomas and Birchall [9] and Marchon and Flatt [7] amongst others, retardation by nucleation
55 poisoning of hydrates is where the plasticizer poisons the nuclei of CH, preventing its growth. By
56 suppressing CH precipitation, C_3S dissolution is delayed, as the degree of calcium saturation in the
57 pore solution is unaltered. Hence, C-S-H precipitation is hindered, which leads to prolongation of the
58 induction period of the cement paste [7]. Surface adsorption of the plasticizer on unhydrated cement
59 grains might reduce the dissolution of the clinker phases and cause retardation. This, in turn, retards
60 the formation of hydrates, prolonging the induction period of the cement paste [7]. Finally, the sugars
61 contained in the plasticizers generally delay the onset of the acceleration period, by adsorbing on
62 anhydrous phases like C_3S , but also on cement hydrates, especially CH [10]. In conclusion, the
63 mechanisms that most likely retard the cement setting appear to be related to (1) the plasticizers
64 poisoning the nuclei of CH, retarding C_3S dissolution and C-S-H precipitation, (2) the reduced
65 dissolution of clinker phases, and (3) the possible presence of sugars in the plasticizer.

66 Lignosulfonates are known to have a retarding effect on cement hydration [11-13]. The sugars
67 naturally contained in lignin contribute to longer setting times of cement, in particular the hexoses.
68 The sugars can be almost completely removed, however also sugar-reduced LS can cause retardation
69 [14]. Several studies concluded that the addition of calcium lignosulfonate changes the hydration of
70 C_3S and C_3A [13, 15-19]. According to Ramachandran [18], a strongly surface-bound calcium
71 lignosulfonate complex could be detected for both C_3A and C_3S , which could cause retardation of C_3A
72 and C_3S hydration. In another paper [15], Ramachandran stated that the retardation effect of calcium
73 lignosulfonate depends on its concentration in solution and not on its proportion with respect to C_3S .
74 C_3S hydration was delayed in proportion to the concentration, and it practically stopped for
75 concentrations above 3 g/l of water. On the contrary, C_3S hydration was found to speed up for
76 lignosulfonate concentrations under 1 g/l of water. Monosi et al. [16] found that, in a C_3A - C_3S system,
77 the addition of calcium lignosulfonate led to a strong retardation in C_3S hydration, while C_3A
78 hydration was slightly accelerated. The retardation in the C_3A - C_3S system was lower than that in pure

79 C₃S systems. In fact, the lignosulfonate adsorption by C₃A decreases the concentration of polymer
80 available to retard the C₃S hydration. Moreover, the arrest in C₃S hydration is partially
81 counterbalanced by the increase in rate of hydration of C₃A, as stated by Collepari et al. [17]. In
82 conclusion, lignosulfonate was found to retard C₃S hydration [13, 18] depending on its concentration
83 in the pore solution [15]. C₃A hydration was found to be retarded by lignosulfonate by some authors
84 [13, 18, 19], while not retarded [20] or slightly accelerated [16, 17] by other authors.

85 As described by e.g. Flatt and Houst [21], the addition time of the plasticizer to the cement paste
86 greatly affects the amount of plasticizer consumed by the cement paste and the extent of retardation. It
87 has to be noted that the influence of the addition time was found to be lower for admixtures like
88 polycarboxylic superplasticizers [22, 23]. Several studies, amongst others Uchikawa et al. [24],
89 Chiocchio and Paolini [25], Aiad et al. [26], found that, at equal plasticizer dosage, the flow of cement
90 paste prepared by delayed addition is higher than that of cement paste prepared by immediate addition.
91 Moreover, the setting is further retarded in case of DA. Chiocchio and Paolini [25] found that the
92 optimum addition time of plasticizer to achieve the maximum workability corresponds to the
93 beginning of the dormant period of the cement hydration without admixture. Hot [27], Hsu et al. [28],
94 and Aiad [29] found that the optimum addition time was between 10 and 15 minutes after water
95 addition.

96 The rheological behavior of fresh cementitious materials is generally characterized by yield stress (τ)
97 and viscosity (μ). As described by e.g. Roussel et al., the yield stress corresponds to the energy needed
98 to break down a network of interaction between particles in a cementitious system. Its origin lays in
99 colloidal and contact interactions between particles. Viscosity results from hydrodynamic, colloidal
100 and contact forces involved in the motion of the suspended cement grains. The yield stress is often
101 considered as the most relevant parameter to describe workability and the ability of a material to
102 properly fill a mold under its own weight. However, the viscosity also seems to be a very relevant
103 parameter to describe cement or concrete workability, especially for systems with low water-binder
104 ratio [30, 31]. Plasticizing admixtures can change both yield stress and viscosity by adsorbing on
105 cement particles and changing the flocculation state of cement paste [31].

106 The subject of this paper is to investigate the effect of LSs on the rheological properties and setting
107 time of two Portland cements with different physical and chemical properties (e.g. surface area, C₃A
108 content). The samples were studied both by adding the lignosulfonate immediately with the mixing
109 water (IA) and by adding it after 10 minutes hydration (DA). The results were compared to the
110 adsorption isotherms presented in a previous paper by the same authors [32]. The amount of polymer
111 consumed by the cement paste was related to the changes in rheological properties and hydration
112 kinetics of the cement pastes due to LSs addition. Changes in the surface area of the hydrated cement
113 particles were investigated by BET. The elemental composition of the pore solution extracted from the
114 cement paste samples was analysed with ICP-MS. The results of this paper will contribute to a deeper
115 understanding on the physical and chemical mechanisms behind the changes in rheological properties
116 and setting time of cement paste with lignosulfonate.

117 **2 EXPERIMENTAL**

118

119 **2.1 Materials**

120

121 The experiments were performed on two different cements: a CEM I 52.5 N (ANL) and a CEM I 52.5
122 R (CX), as defined in the European standard EN197-1. The content of the main clinker phases of the
123 cements quantified by XRD Rietveld, according to the technique described in [33], are given in Table
124 1. The chemical composition of the cements determined by XRF and the loss of ignition at 950 °C are
125 reported in Table 2. The particle size distribution (d_{10} , d_{50} , d_{90}), Blaine and BET surface area, and
126 density are given in Table 3.

127 A sugar-reduced softwood calcium lignosulfonate (LSs) was used as plasticizer. Its mass weighted
128 molecular weight (M_w), as measured with gel permeation chromatography (GPC), was 29000 g/mol
129 and the number weighted molecular weight (M_n) was 2100 g/mol, giving broad molar-mass dispersity
130 (D_M) equal to 13.8. The molar-mass dispersity, also called polydispersity index, is defined as the ratio
131 between M_w and M_n [34]. Additional physical and chemical properties of the lignosulfonate are listed
132 in Table 4. For the lignosulfonate used in the present investigation, the sugars were removed from the

133 polymer molecule by fermentation and resulting alcohol by distillation. The LSs was dissolved in
134 deionised water to concentrations varying from 1 to 45 % to ease dosing, and the water content was
135 included in the calculation of the water-to-binder ratio (w/b).

136 **2.2 Sample preparation**

137

138 About 300 g cement was mixed with deionised water and/or lignosulfonate solution in a high-shear
139 MR530 by Braun mixer at intensity 6 obtaining a paste with w/b = 0.4. A cement paste volume of
140 about 200 ml was mixed for all the cement pastes. In order to investigate the effect of the time of
141 addition of lignosulfonate, two different mixing procedures were applied: immediate addition of LSs
142 with the mixing water (IA) and delayed addition of LSs after 10 minutes of hydration (DA).

143 For IA, the binder was mixed with deionised water (and/or lignosulfonate diluted in deionised water)
144 according to the procedure used by Vikan : 30 seconds mixing, scraping the mixer walls to
145 homogenize the mix, 5 minutes resting and 1 minute mixing.

146 For DA, the binder and 85% of the water were mixed according to the following mixing procedure: 30
147 seconds mixing, scraping the mixer walls to homogenize the mix, 10 minutes resting (delay time
148 chosen according to several studies in literature [25, 27-29]). LSs diluted in the remaining 15% of the
149 needed water were then added to the mix, which was mixed for 1 minute.

150 **2.3 Methods**

151

152 **2.3.1 Rheological measurements**

153

154 The rheological properties were measured with a Physica MCR 300 rheometer using parallel plates
155 with serrated surfaces of 150 μm depth. The radius of the plates was 30 mm and the gap between the
156 plates was set to 1 mm. The bottom plate or stator was kept at a constant temperature of 20 °C. Some
157 drops of deionized water were put in the water trap located on the upper plate or rotor and an enclosure
158 was used to limit evaporation of water from the paste sample during the measurement.

159 After the mixing sequence (as described in paragraph 2.2), about 2.5 ml of cement paste was placed on
160 the bottom plate of the rheometer, and the rheological measurement was started 10 minutes after water
161 addition. Up-down flow curves were measured at 10, 20 and 30 minutes of hydration. For the samples
162 to which the plasticizer was added at 10 minutes hydration (DA), the first flow curve was measured at
163 12 minutes of hydration instead of 10 minutes. Before every measuring cycle, the paste was stirred for
164 30 seconds at the constant shear rate of 60 s^{-1} . The measuring sequence, described in Table 5, allowed
165 measuring the shear stress of cement paste as the shear rate increased from 0 to 60 s^{-1} (up flow curve)
166 or decreased from 60 to 0 s^{-1} (down flow curve).

167 The flow curves generally showed a pronounced shear-thinning behavior. The Bingham model was
168 applied to the second part of the down flow curve, obtained for shear rate between 26 and 60 s^{-1} . The
169 linear fitting of this flow-curve segment allowed the calculation of the dynamic yield stress, τ_0 , as the
170 extrapolated intercept with the ordinate, and of the plastic viscosity, μ_p , as the slope of the linear fit.

171 In addition, the results from the rheological measurements are also presented in terms of flow
172 resistance, as defined by Vikan et al. in [35]. This value is calculated as the area under the entire flow
173 curve (shear rate from 1 to 60 s^{-1}), and it represents the power necessary to make a certain volume of
174 sample flow at a chosen shear rate range (W/m^3 or Pa/s).

175 **2.3.1 Isothermal calorimetry**

176
177 Isothermal calorimetry was carried out at 20°C in a TAM Air eight-channel isothermal calorimeter
178 produced by Thermometric AB. The evolution in time of the heat of hydration of ANL and CX
179 cements was measured for different dosages of LSs and both for IA and DA of plasticizer. The
180 samples were prepared as described in paragraph 2.2. After mixing, about 6 g cement paste was placed
181 in a 20 ml glass ampoule, which was sealed and placed in the calorimeter. The heat of hydration was
182 recorded for 60 hours.

183 **2.3.2 UV-spectroscopy**

184

185 UV-spectroscopy allowed measuring the LSs concentration in the extracted pore solution from the
186 cement paste samples.

187 After mixing according to section 2.2, about 35 ml paste was poured in 50 ml plastic centrifuge tubes
188 and let to rest until the chosen analysis time. The pore solution was extracted from the cement paste by
189 centrifuging the samples in a Heraeus Megafuge 8 centrifuge by Thermo Scientific for 3 minutes at the
190 speed of 4500 rpm. The supernatant pore solution was extracted and filtered with 0.45 μm syringe
191 filters. The pore solution was analysed with a Genesys 10S UV-spectrophotometer by Thermo
192 Scientific. Wavelengths in the range 280-284 nm had been reported in literature to study the
193 adsorption of lignosulfonate on cement particles [3, 4, 24, 36, 37]. When scanning the absorbance of
194 an LSs solution for the wavelengths in the range of 190 to 350 nm, a clear absorbance peak was
195 observed with a maximum at approximately 281 nm. The maximum intensity of the absorbance peak
196 at 281 nm increased linearly with increasing LSs dosage. The absorbance at this wavelength, 281 nm,
197 was therefore used to determine the LSs concentration in solution.

198 With the help of a calibration curve, obtained measuring the absorbance of solutions of different
199 concentrations of LSs in deionised water, the amount of free plasticizer (g LS/100 g solution) could be
200 determined. This amount was related to the amount of binder in the sample (g LS/100 g binder). The
201 LSs consumed by the investigated systems was then calculated by subtracting the amount of free LSs
202 from the total amount of LSs added to the sample, as displayed in equation 1:

$$203 \text{LSs}_{\text{consumed}} = \text{LSs}_{\text{total}} - \text{LSs}_{\text{free}} \quad (1)$$

204 Polymer adsorption by a solid is usually described using isotherms, in which the amount of polymer
205 adsorbed is plotted against the total amount of polymer added to the system [38]. The shape of an
206 isotherm is largely determined by the adsorption mechanism. In this study, the isotherms were drawn
207 relating the amount of LSs consumed by the cement paste to the amount of total LSs added to the
208 sample.

209 Initially, the free plasticizer in the pore solution extracted from the cement paste was measured by UV-
210 spectroscopy at increasing hydration time (from 5 to 120 minutes hydration). It was found that at 10

211 minutes hydration the LSs uptake reached an equilibrium value. All the samples were then analysed at
212 30 minutes hydration.

213

214 **2.3.3 Solvent exchange**

215

216 A solvent exchange procedure with isopropanol was used to stop the hydration of the cement paste
217 after 30 minutes of hydration.

218 About 5 ml of cement paste was transferred in a 50 ml centrifuge tube and centrifuged for 1 minute at
219 2000 rpm. The supernatant was removed. About 40 ml of isopropanol was poured in the centrifuge
220 tube. The tube was shaken for 30 seconds and let to rest for 5 minutes. The sample was centrifuged
221 again for 1 minute at 2000 rpm and the supernatant liquid was removed. The solvent exchange
222 procedure with isopropanol was repeated once, followed by a final solvent exchange with 10 ml of
223 petroleum ether. The resulting paste was let to dry for 2 days in a desiccator over silica gel, and soda
224 lime to minimize carbonation. After drying, the samples were ground to powder and homogenized in a
225 porcelain mortar and stored in sealed containers in a desiccator over silica gel and soda lime until
226 analysis.

227 **2.3.4 BET of hydrated cement pastes**

228

229 The BET measurements were performed using a Tristar II Plus by Micromeritics on cement paste
230 samples of which the hydration was stopped with the solvent exchange procedure. The measurements
231 were performed purging the samples with nitrogen. The samples were degassed in vacuum before the
232 measurement, and the measurement was performed at 20 °C.

233 **2.3.5 ICP-MS of pore solution**

234

235 ICP-MS (inductively-coupled plasma mass spectrometry) was used to determine the elemental
236 concentration of Al, Ca, Fe, K, Na, S and Si in the pore solution extracted from the cement paste. The

237 pore solution was extracted from ANL and CX cement pastes with 0, 0.8, 1.5 mass % LSs mixed both
238 with IA and DA. The solution was filtered with the same procedure used for UV-spectroscopy
239 (paragraph 2.3.2) and acidified prior to analysis by adding 1:1 by volume of 1:10 diluted HNO₃.

240 **3 RESULTS**

241

242 **3.1 Rheological properties**

243

244 The rheology of ANL and CX cement pastes was measured at 10 (12), 20 and 30 minutes of hydration
245 with increasing dosages of LSs (0/0.4/0.8/1.5 mass % binder LSs for IA and 0/0.1/0.2/0.4 mass %
246 binder for DA). The results at 10 (12 for DA) and 30 minutes hydration are shown in Figure 1 and in
247 Figure 2, respectively, displaying the variation of normalized yield stress and plastic viscosity as the
248 dosage of LSs increases, both for IA and DA. The normalized yield stress was obtained by dividing
249 the yield stress of samples with increasing LSs dosage by the yield stress of the reference sample
250 without LSs. The normalized viscosity was calculated according to the same principle. Table 7 gives
251 the dynamic yield stress and plastic viscosity of the reference samples without LSs.

252 Increasing LSs dosage reduced both the yield stress and the viscosity of both cements both at 10 and
253 30 minutes of hydration, except for CX cement for IA after 30 minutes of hydration. The reduction
254 was achieved for considerably lower LSs dosages for DA compared to IA. Less than one third LSs
255 dosage was needed to reach the same drop in yield stress and viscosity for DA compared to IA.
256 Regarding CX cement, a nearly constant yield stress and a remarkable increase in viscosity were
257 measured for IA after 30 minutes of hydration with increasing LSs dosages.

258 Generally, a drop in yield stress would indicate LSs saturation in the cementitious system. In this
259 study, a clear drop in yield stress was detected for DA for a LSs dosage between 0.10 and 0.25 mass %
260 for ANL cement, and between 0.25 and 0.50 mass % for CX cement. No clear drop in yield stress was
261 measured for IA. After 10 minutes of hydration, the yield stress decreased gradually for both cements.
262 After 30 minutes of hydration, the yield stress showed a gradual decrease for ANL cement, while it
263 remained nearly constant for CX cement.

264 The results expressed in terms of flow resistance are shown in Figure 3. The smaller the flow
265 resistance, the less power is required to make the sample flow. The results presented in Figure 3 seem
266 to agree with the ones presented in Figure 1 and in Figure 2, considering that slightly different regions
267 of the flow curves were used to calculate the parameters.

268 Surprisingly, the yield stress of CX cement with 0.25 mass % LSs mixed with DA was higher than in
269 the sample without LSs. However, with the same LSs dosage, the viscosity was found to decrease, and
270 all the other conditions in the cement paste system were similar. The reason for the increase in yield
271 stress upon 0.25 mass % DA of LSs for CX is currently not known. To understand the underlying
272 mechanism further research is required.

273 **3.2 Setting time**

274

275 The effect of the LSs dosage and of its addition time on the rate of hydration and setting time of ANL
276 and CX cement pastes can be observed in the calorimetric curves in Figure 4 for IA, and in Figure 5
277 for DA. Based on the definition given by the ASTM standard C1679-14 , the setting time was
278 identified as the time to reach half of the average maximum power of the main hydration peak in the
279 calorimetric curve. The silicates and aluminates peaks are marked with different symbols in
280 corresponding grey shade of the respective calorimetric curve.

281 In the reference samples without LSs, after the initial peak of hydration, which takes place almost
282 immediately after the contact of cement with water, two peaks could be observed: first, the peak
283 corresponding to hydration reaction of the silicate phases (mainly C_3S), followed by a peak related to
284 sulfate depletion and hydration reactions of the aluminate phases. Both the silicates and the aluminates
285 peak were delayed by LSs addition in both cement pastes both when mixed with IA and with DA. In
286 general, increasing LSs dosages caused a larger retardation of the silicates peak compared to the
287 aluminates one. The two peaks even merged in most samples with the higher LSs dosages analyzed.

288 Moreover, for the same LSs dosage, DA resulted in a larger retardation of both peaks compared to IA.
289 CX cement paste showed a lower retardation than ANL cement paste both for IA and DA. The

290 doubling of the LSs dosage led to a setting retardation between 1.5 and 2.5 times higher for CX
291 cement, and between 4 and 5 times higher for ANL cement.

292 **3.3 Concentration of aluminum ions in the pore solution**

293

294 The elemental concentration of Al, Ca, Fe, Si and S in the pore solution extracted from ANL and CX
295 cement pastes after 30 minutes of hydration was determined with ICP-MS. The LSs dosages tested
296 were 0.8 and 1.5 mass % LSs both for IA and DA. Additionally, a reference sample without LSs was
297 measured. Moreover, the content in Al, Ca, Fe, Si and S was also measured for two LSs solutions in
298 artificial pore solution. The two solutions, containing 2.0 and 3.7 mass % LSs, were the ones used in
299 the cement samples with 0.8 and 1.5 mass % LSs, respectively. The artificial pore solution was a
300 solution of NaOH and KOH with K/Na molar ratio equal to 2 and measured pH of 12.9. The results
301 from ICP-MS are shown in Figure 6 and reported in Table 8.

302 The samples mixed with DA showed an increase in Al, Fe and Si concentration in the pore solution as
303 the LSs dosage increased. The increase was considerably larger for ANL cement than for CX cement.
304 On the contrary, only a minor increase was measured for the samples mixed with IA.

305 **3.4 Adsorption isotherms**

306

307 The adsorption isotherms obtained for ANL and CX cement pastes were achieved by plotting the
308 amount of consumed LSs after 30 minutes of hydration versus the total amount of LSs added. The
309 tested dosages are given in Table 6. For CX cement it was not possible to extract pore solution at LSs
310 dosages over 1.0 mass % due to paste hardening after 30 minutes hydration. The LSs was added to the
311 cement paste either immediately together with the mixing water (IA), or after 10 minutes hydration
312 (DA). The results per mass % binder and their fitting according to the Langmuir model [38] are
313 presented in Figure 7.

314 Figure 7 shows that the cement pastes displayed similar LSs consumption at low LSs dosage (up to
315 about 0.25 mass % LSs) independent of the time of LSs addition. At higher dosage, the curves
316 obtained for IA differ from those obtained for DA.

317 For IA, no adsorption plateau could be detected within the tested range, neither for ANL nor for CX
318 cement. The isotherms' shape indicated an increasing LSs consumption as more LSs was added to the
319 mix.

320 For DA, an adsorption plateau was found for both cements. The DA isotherms displayed a
321 considerably lower amount of LSs consumed by the cement pastes compared to the IA isotherms. The
322 adsorption plateau was reached for a total LSs amount between 0.8 and 1.2 mass % for ANL cement,
323 and between 1.2 and 1.5 mass % for CX cement. The authors assume the plateau to be due to the
324 achievement of full monolayer surface coverage [32].

325 **3.5 BET of hydrated cement pastes**

326

327 The BET surface area was measured on ANL and CX cement pastes with varying LSs amounts after
328 30 minutes of hydration. The hydration was stopped by solvent exchange, as described in paragraph
329 2.3.3. The results are shown in Figure 8.

330 For both cements the surface area was found to increase as the dosage of plasticizer added to the
331 cement paste increased. The increase in surface area was remarkably larger for IA compared to DA,
332 and, for IA, for CX cement compared to ANL cement.

333 **4 DISCUSSION**

334

335 **4.1 LSs consumption and changes in surface area**

336

337 The adsorption isotherms shown in Figure 7 display a higher LSs consumption for IA than for DA.

338 In a previous article [32], the authors investigated the interactions between LSs and two Portland
339 cements (the same as those used in the present paper). It was found that the LSs consumption
340 mechanisms were different for the two cements used and for the two addition methods.

341 For DA, both cements' adsorption isotherms showed a plateau. According to the theory reported in
342 [38], the achievement of a plateau in an adsorption isotherm corresponds to saturation of the available

343 surface for adsorption. Therefore, the LSs consumption was considered to be mainly due to monolayer
344 surface adsorption on the surface of cement particles and hydrates.

345 For IA, an increase in LSs dosage was found to cause additional ettringite formation and consequently
346 an increase in surface area of both cements after 30 minutes of hydration, to a larger extent for CX
347 cement compared to ANL cement. This was not observed when the cements were mixed with DA
348 [32].

349 A possible explanation of the difference between IA and DA is that when LS is added in the mixing
350 water the dissolution of C_3A is enhanced leading to the formation of additional ettringite. Whereas
351 when no LSs is present in the mixing water the C_3A reaction is limited, potentially by a protective
352 hydrate layer. The delayed addition of LSs is not able to disrupt this potential protective layer initially
353 formed, hence no additional ettringite is observed for DA.

354 The two cements displayed different LSs consumption mechanisms for IA. For CX cement, a large
355 increase in ettringite formation and surface area (see Figure 8) led to a high LSs consumption [32]. No
356 surface saturation plateau was reached, which was explained by the continuous increase in surface
357 available for adsorption for the LSs dosages investigated. Monolayer surface adsorption on the surface
358 of cement particles and hydrates was identified as the dominating LSs consumption mechanism for
359 CX cement [32]. For ANL cement, the adsorption isotherm also showed a high LSs consumption
360 without reaching an adsorption plateau. Since the amount of formed ettringite and the surface area
361 increased only moderately compared to CX cement (see Figure 8), other polymer consumption
362 mechanisms might have played a role for ANL cement in addition to surface adsorption.

363 Finally, in the same paper [32], no AFm could be detected by TGA for the investigated materials.
364 Therefore, intercalation in AFm, as proposed, amongst others, by Flatt and Houst [21], does not appear
365 as a feasible LSs consumption mechanism for the investigated materials and dosages.

366 **4.2 Rheological properties**

367

368 The obtained rheological results indicate that the addition of lignosulfonate generally improved the
369 workability of cement paste after 10, 20 and 30 minutes of hydration, decreasing both the yield stress
370 and the viscosity. As an exception to this general trend, after 30 minutes of hydration, CX cement
371 mixed with IA did not show changes in the yield stress with increasing LSs dosage, while its viscosity
372 increased about 50 %. In general, the improvement in workability was remarkably larger when the
373 samples were mixed with DA compared to IA.

374 When evaluating the rheological results in light of the adsorption isotherms shown in Figure 7, it
375 appears that a clear drop in yield stress was observed solely for the samples which reached an
376 adsorption plateau. The samples that did not reach an adsorption plateau showed a more gradual
377 decrease in yield stress, as for ANL cement, or no decrease at all, as for CX cement. A correlation
378 between the achievement of surface coverage and a drop in yield stress seems to exist. Indeed, as
379 shown in Figure 7, the isotherms obtained for DA started differing from those obtained for IA, and
380 showing the tendency to reach an adsorption plateau, for LSs dosages over about 0.25 mass %. As
381 shown in Figure 1 and in Figure 2, for DA, a drop in yield stress was measured for LSs dosages
382 between 0.10 and 0.25 mass % LSs for ANL cement, and between 0.25 and 0.40 mass % LSs for CX
383 cement. Thus, the rheological behavior seems to relate to the degree of LSs coverage of the available
384 surface.

385 As shown in [32, 39], the TGA measurements performed on ANL and CX cements displayed that 1.5
386 mass % LSs added with IA led to an increase in the amount of bound water after 30 minutes of
387 hydration, compared to the respective samples without LSs. This was explained by an increased
388 amount of ettringite, which also is reflected in a higher surface area, as measured with BET (see
389 Figure 8). For CX cement, the unexpected lack of any decrease in yield stress and the increase in
390 viscosity at 30 minutes of hydration, as displayed in Figure 2 b, are therefore most likely due to the
391 high amount of ettringite formed. A production of large amounts of ettringite was found to cause
392 slump loss by, amongst others, Hanehara and Yamada [40]. The increase in amount of ettringite was
393 larger for CX than for ANL cement. Accordingly, CX cement displayed a larger reduction in
394 workability compared to ANL cement.

395 Moreover, the initial yield stress (without LSs) was remarkably higher for CX than for ANL cement
396 paste. This is most likely due both to the higher content of C_3A in CX cement and to the smaller
397 particle size of the CX cement, leading to higher surface area available to interact with water and
398 plasticizer, and thus higher reactivity.

399 **4.3 Setting time**

400

401 The setting retardation was calculated as the setting time measured with calorimetry, from which the
402 setting time of the sample without LSs was subtracted. In Figure 9 a and b the setting retardation is
403 related to the amount of total and free LSs, respectively.

404 It should be noted that it is unclear which of the different components of LSs cause the effects
405 discussed in the following e.g. sugars or the lignosulphonate molecules. The LSs is considered as a
406 whole. To distinguish the contributions of the different constituents further research is required. For
407 DA, total LSs dosages higher than about 0.25 mass % led to a major setting retardation (see Figure
408 9a). For IA, a more gradual increase in setting time was measured as the LSs added increased. Both
409 for IA and for DA, the setting retardation was higher for ANL than for CX cement.

410 The results shown in Figure 9b indicate correlations between the setting retardation and the amount of
411 free LSs in the pore solution. For LSs dosages over about 0.25 mass %, any increase in free LSs
412 corresponded to a large increase in setting retardation, especially for samples mixed with DA. Over
413 this dosage, the samples mixed with DA also displayed a drop in yield stress, as discussed in
414 paragraph 4.2 and showed in Figure 1 and in Figure 2. These results seem to agree with the
415 conclusions of Yamada et al. [41], who stated a progressive increase in setting time with a higher
416 concentration of free sulfonic and carboxylic groups in the aqueous phase.

417 At equal amount of free LSs in the pore solution, a higher setting retardation was measured for ANL
418 cement than for CX cement. The setting retardation was higher for DA than for IA. This might be due
419 to several reasons:

420 First, in a previous paper [32, 39], increasing LSs dosages added with IA were found to increase the
421 amount of ettringite formed in cement paste. The increase as measured with TGA was larger for CX
422 cement compared to ANL cement, and for IA compared to DA. An increased initial ettringite
423 formation due to LSs addition with IA was also reported by Danner et al. [42]. In another paper,
424 Danner et al. [43] found that Ca-LSs added with IA to a C₃A-gypsum system led to changes in the
425 ettringite morphology, which appeared as wider, shorter and more rounded crystals. According to
426 Zingg et al. [44], the smaller cubic ettringite crystals can be finely dispersed by the plasticizer,
427 providing additional nucleation surface. In the present paper, the possible formation of a larger amount
428 of smaller and more compact ettringite crystals could lead to the lower setting retardation measured for
429 CX cement compared to ANL cement, and for IA compared to DA because of the additional
430 nucleation surface.

431 As shown in Figure 4 and Figure 5, increasing LSs dosages led to larger retardation of the silicate peak
432 compared to the aluminate one, causing the two peaks to merge in most samples with the higher LSs
433 dosages analyzed. Similar observations were made in several studies [45-48], in which it was even
434 observed that the aluminate peak could occur earlier than the silicate one upon high plasticizer
435 dosages. This might lead to poisoning of the C₃S hydration and uncontrolled delay of setting. This is a
436 commonly known phenomenon leading to incompatibility issues between plasticizer and cement. In
437 light of the results reported in the present article, the smaller retardation of the C₃A peak compared to
438 the C₃S one, or even the occurrence of the aluminate peak before the silicate one, might be partially
439 explained by the enhanced precipitation of ettringite within the first 30 minutes of hydration, which
440 could lead to a faster consumption of sulfates, thus to an earlier sulfate depletion point.

441 Regarding the difference in setting retardation between the two cements, Pourchet et al. [49] found
442 that the sulfate type used modified the early C₃A-CaSO₄ hydrates and their rate of formation. The
443 substitution of gypsum with hemihydrate increased the rate of ettringite formation during the first five
444 hours of hydration. The difference in sulfate type between ANL and CX cements (gypsum and
445 hemihydrate for ANL cement, hemihydrate and anhydrite for CX cement) could then be one of the
446 reasons why more ettringite was formed in CX cement than in ANL cement. Moreover, the higher

447 content in C_3A of CX cement and its smaller particle size could allow a higher amount of C_3A to enter
448 in contact with water, favouring the production of ettringite compared to ANL cement.

449 Finally, aluminum ions dissolved in the pore solution appeared to negatively impact the C_3S hydration,
450 both by increasing its induction period [50, 51], and by reducing the extent of its hydration [52]. The
451 results from ICP-MS, displayed in Figure 6, showed that an increased concentration of Al was
452 measured in the pore solution of both cements solely when mixed with DA. The Al concentration was
453 higher for ANL than for CX cement. One of the hypothesized explanations for the retarding effect of
454 Al on C_3S reaction is the substitution of some silicates by the Al ions with consequent formation of C-
455 A-S-H instead of C-S-H. Since the first C-A-S-H nuclei do not grow nor support hydrates nucleation
456 as C-S-H does, the C_3S induction period is extended [53]. Another possible explanation was given by
457 Nicoleau et al. [54], who found that Al ions covalently bind to the silicates on the C_3S surface,
458 strongly inhibiting C_3S dissolution. The poisoning of C_3S by Al ions, with consequent delay in C_3S
459 hydration, appears then to be a feasible explanation for the increased setting retardation measured for
460 DA compared to IA.

461 **5 CONCLUSIONS**

462

463 The aim of this paper was to obtain a better understanding of the effects of calcium lignosulfonate
464 (LSs) on the rheology and setting time of Portland cement pastes. Two Portland cements mainly
465 differing in surface area and C_3A content were used. The LSs was either added immediately with the
466 mixing water (IA), or delayed after 10 minutes of hydration (DA). The following conclusions were
467 drawn:

- 468 - The rheological behavior relates to the degree of LSs coverage of the available surface for
469 adsorption. A drop in yield stress and viscosity was measured for the cement pastes that
470 reached an adsorption plateau, as observed for DA. Samples which did not reach surface
471 saturation showed a more gradual improvement in workability, as observed for IA.

- 472 - An increased formation of ettringite, which was observed with elevated LSs dosages for IA,
473 might lead to early hardening of the cement paste.
- 474 - The setting behavior appears to relate to the amount of free LSs in the pore solution.
- 475 - The difference in setting retardation between IA and DA might be related to the amount of
476 ettringite formed in the system. Indeed:
- 477 ○ The ettringite might supply additional surface area, which increase the amount of LSs
478 consumed by monolayer adsorption. The consequent reduced amount of free LSs in
479 the pore solution was reflected in a lower setting retardation.
 - 480 ○ Enhanced ettringite formation might supply additional nucleation surface, thus
481 reducing the setting retardation when compared to a reference sample without LSs.
 - 482 ○ Increased ettringite precipitation could lead to a faster consumption of sulfates, thus to
483 an earlier sulfate depletion.
 - 484 ○ Increased ettringite formation resulted in less Al dissolved in the pore solution and
485 available to interact and retard the C₃S hydration.

486 **6 FUTURE RESEARCH**

487

488 In a follow-up study, the effect of LSs on the amount and morphology of ettringite and other early
489 cement hydrates produced both for IA and DA will be investigated. The effect of LSs on the hydrates
490 formed in the hardened cement paste will also be considered for future research.

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492

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626

627 Notation

628

629	ANL	Anlegg cement (CEM I 52.5 N)
630	CX	Cemex cement (CEM I 52.5 R)
631	DA	delayed addition of plasticizer (10 min)
632	IA	immediate addition of plasticizer
633	LSs	softwood low-sugar Ca-lignosulfonate
634	OPC	ordinary Portland cement
635	w/b	water-binder ratio
636	$\dot{\gamma}$	shear rate
637	τ	shear stress
638	μ	viscosity

639	-COOH	carboxyl group	
640	ϕ -OH	phenolic OH-group	
641			
642	List of tables		
643			
644	Table 1 – <i>Main phases in cement ANL and CX from XRD-Rietveld analysis ^a: results obtained with</i>		
645	<i>TGA analysis</i>		24
646	Table 2 – <i>Chemical composition of the cements given by the producers</i>		25
647	Table 3 - <i>Physical properties of ANL and CX cements</i>		27
648	Table 4 - <i>Chemical and physical properties of LSs</i>		27
649	Table 5 – <i>Sequence for rheology measurements</i>		28
650	Table 6 – <i>Analysed samples to obtain adsorption isotherms</i>		29
651	Table 7 – <i>The dynamic yield stress and plastic viscosity of the reference mixes ANL and CX without</i>		
652	<i>LSs addition, 10 and 30 min after water addition</i>		29
653	Table 8 – <i>Elemental concentration of Al, Fe, Ca, Si, and S in ANL and CX cements with 0, 0.8 or 1.5</i>		
654	<i>mass % LSs after 30 minutes hydration, and in two LSs solutions (mmol/L): the 2.0 and 3.7 % LSs</i>		
655	<i>solutions were used for the cement samples with 0.8 and 1.5 mass % LSs respectively</i>		30
656			
657	List of figures		
658			
659	Figure 1 – <i>a) Normalized yield stress and b) normalized viscosity vs. total LSs (mass % binder) of ANL</i>		
660	<i>and CX cements mixed with IA or DA of LSs at 10 min of hydration (12 min of hydration for samples</i>		
661	<i>prepared with DA)</i>		31
662	Figure 2– <i>a) Normalized yield stress and b) normalized viscosity vs. total LSs (mass % binder) of ANL</i>		
663	<i>and CX cements mixed with IA or DA of LSs at 30 min of hydration</i>		31
664	Figure 3 - <i>Flow resistance at 10 min. of hydration (12 min of hydration for samples prepared with DA)</i>		
665	<i>in fig. a and at 30 min. of hydration in fig. b vs. total LSs(mass % binder) of ANL and CX cements with</i>		
666	<i>IA or DA of LSs</i>		32
667	Figure 4 – <i>Rate of heat of hydration in time for a) ANL and b) CX cement pastes with increasing</i>		
668	<i>dosage of LSs mixed with IA (0, 0.2, 0.4, 0.8 mass % LSs). The silicates and aluminates peaks are</i>		
669	<i>marked with different symbols in corresponding colour of the respective calorimetric curve.</i>		32
670	Figure 5 - <i>Rate of heat of hydration vs. time for a) ANL and b) CX cement pastes with increasing</i>		
671	<i>dosage of LSs mixed with DA (0, 0.1, 0.2, 0.4 mass % LSs). The silicates and aluminates peaks are</i>		
672	<i>marked with different symbols in corresponding colour of the respective calorimetric curve.</i>		33
673	Figure 6 – <i>Concentration of Al, Fe, Ca, Si, and S ions in the pore solution (mmol/L) expressed in</i>		
674	<i>logarithmic scale vs. total LSs added (mass % binder) to a) ANL and b) CX cement pastes at 30 min of</i>		
675	<i>hydration both for IA and DA</i>		33

676 Figure 7 - Amount of a) consumed LSs and of b) free LSs at 30 min of hydration vs. amount of LSs
677 added to ANL and CX cements for IA and DA, after [33]. The results are calculated per mass % of
678 binder34
679 Figure 8 - Surface area of ANL and CX cement particles hydrated for 30 min vs. total dosage of LSs
680 added (mass % binder) both for IA and DA, after [33]34
681 Figure 9 – Setting time retardation vs. amount of a) total LSs and b) free LSs for ANL and CX cement
682 pastes containing increasing dosage of LSs both for IA and DA. NB. The figures' scales are different
68335
684

685 Table 1 – Main phases in cement ANL and CX from XRD-Rietveld analysis ^a: results obtained with
686 TGA analysis

Phase composition (mass %)	ANL	CX
Alite	60.5	54.3
Belite	14.2	18.8
Aluminate cubic	1.3	4.7
Aluminate orthorhombic	0.9	2.4
Ferrite	14.0	6.5
Periclase	0.4	1.1
Quartz	0.3	-
Calcite	3.2/ 3.8 ^a	3.6/ 3.7 ^a
Portlandite	1.1/ 1.4 ^a	2.6/ 2.5 ^a
Anhydrite	-	2.1
Hemihydrate	2.6	1.8
Gypsum	1.0	-
Arcanite		0.6
Aphthitalite	0.4	0.7

Thenardite	-	0.8
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688

689 Table 2 – *Chemical composition of the cements given by the producers*

Chemical compound (mass %)	ANL	CX
CaO	62.7	64.0
SiO₂	20.6	20.0
Al₂O₃	4.4	4.6
Fe₂O₃	3.5	2.6
SO₃	3.3	3.6
MgO	1.6	2.4
K₂O	0.4	1.0
Na₂O	0.3	0.2
TiO₂	0.2	0.2
P₂O₅	0.2	0.2
LOI (%) 1000 °C	1.6	1.7
Sum	97.2	98.9

690

691

692 Table 3 - *Physical properties of ANL and CX cements*

	ANL	CX
Surface area (BET) (m²/kg)	890	1330
Blaine surface (m²/kg)	360	540
Density (g/cm³)	3.1	3.1
d₁₀ (μm)	2.0	2.0
d₅₀ (μm)	12.0	10.0
d₉₀ (μm)	34.0	26.0

693

694 Table 4 - *Chemical and physical properties of LSs*

Mw	g/mol	29000
Mn	g/mol	2100
Organic S (∞ SO₃)	mass %	4.6
SO₄²⁻	mass %	0.9
Ca²⁺	mass %	4.6
Na⁺	mass %	0.9
-COOH	mass %	7.1
φ-OH	mass %	1.4
Total sugar	mass %	8.3

695

696

697 Table 5 – *Sequence for rheology measurements*

		Duration	Cumulative duration
		(s)	(min)
1	Stir up at $\dot{\gamma} = 60$ 1/s	30	0.5
2	Rest	30	1.0
3	Flow curve up, linear sweep $\dot{\gamma}$ from 0 to 60 1/s in 20 steps lasting 5 sec. each	100	2.7
4	Flow curve down, linear sweep $\dot{\gamma}$ from 60 to 0 1/s in 20 steps lasting 5 sec. each	100	4.3
5	Rest	340	10.0
6	Stir up at $\dot{\gamma} = 60$ 1/s	30	10.5
7	Rest	30	11.0
8	Flow curve up, linear sweep $\dot{\gamma}$ from 0 to 60 1/s in 20 steps lasting 5 sec. each	100	12.7
9	Flow curve down, linear sweep $\dot{\gamma}$ from 60 to 0 1/s in 20 steps lasting 5 sec. each	100	14.3
10	Rest	340	20.0
11	Stir up at $\dot{\gamma} = 60$ 1/s	30	20.5
12	rest	30	21.0
13	Flow curve up, linear sweep $\dot{\gamma}$ from 0 to 60 1/s in 20 steps lasting 5 sec. each	100	22.7
14	Flow curve down, linear sweep $\dot{\gamma}$ from 60 to 0 1/s in 20 steps lasting 5 sec. each	100	24.3

698

699

700 Table 6 – *Analysed samples to obtain adsorption isotherms*

Material	LSs addition procedure	LSs dosage (mass % binder)
ANL cement	IA	0.1; 0.2; 0.4; 0.6; 0.8; 1.2; 1.5
	DA	0.05; 0.1; 0.25; 0.4; 0.8; 1.2; 1.5
CX cement	IA	0.1; 0.2; 0.4; 0.6; 0.8; 1.0
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2; 1.5

701

702

703 Table 7 – *The dynamic yield stress and plastic viscosity of the reference mixes ANL and CX without*

704 *LSs addition, 10 and 30 min after water addition*

		ANL	CX
Yield stress (Pa)	10 min	67	121
	30 min	81	145
Viscosity (Pa.s)	10 min	0.58	1.7
	30 min	0.75	2.2

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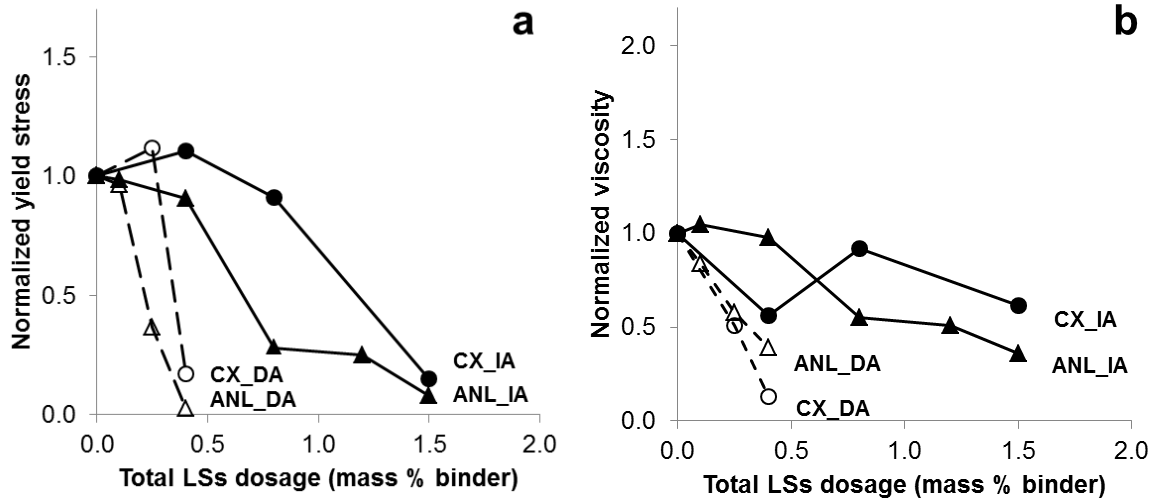
707

708 Table 8 – *Elemental concentration of Al, Fe, Ca, Si, and S in ANL and CX cements with 0, 0.8 or 1.5*
 709 *mass % LSs after 30 minutes hydration, and in two LSs solutions (mmol/L): the 2.0 and 3.7 % LSs*
 710 *solutions were used for the cement samples with 0.8 and 1.5 mass % LSs respectively*

Sample	LSs dosage	Al	Ca	Fe	S	Si
	Mass % binder			Mass %		
ANL IA	0	0.05	236	0.03	767	0.86
	0.8	0.07	260	0.09	963	1.1
	1.5	0.15	445	0.69	1390	1.2
ANL DA	0.8	11.2	375	5.5	1003	8.5
	1.5	35.7	523	14.3	715	26.0
CX IA	0	0.05	239	0.02	1759	0.90
	0.8	0.06	103	0.2	1691	3.0
	1.5	0.11	53.7	1.1	1414	3.6
CX DA	0.8	0.96	282	1.1	1762	2.3
	1.5	7.9	499	4.5	1929	5.6
2.0 % LSs sol.		0.18	183	0.19	370	3.1
3.7 % LSs sol.		0.26	324	0.31	659	2.7

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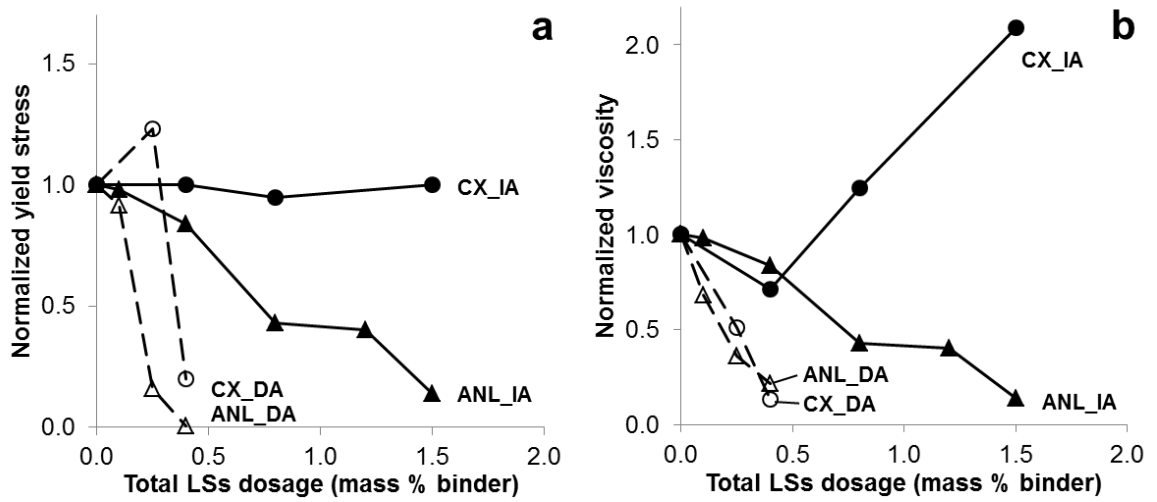
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713

714 Figure 1 – a) Normalized yield stress and b) normalized viscosity vs. total LSs (mass % binder) of ANL
 715 and CX cements mixed with IA or DA of LSs at 10 min of hydration (12 min of hydration for samples
 716 prepared with DA)

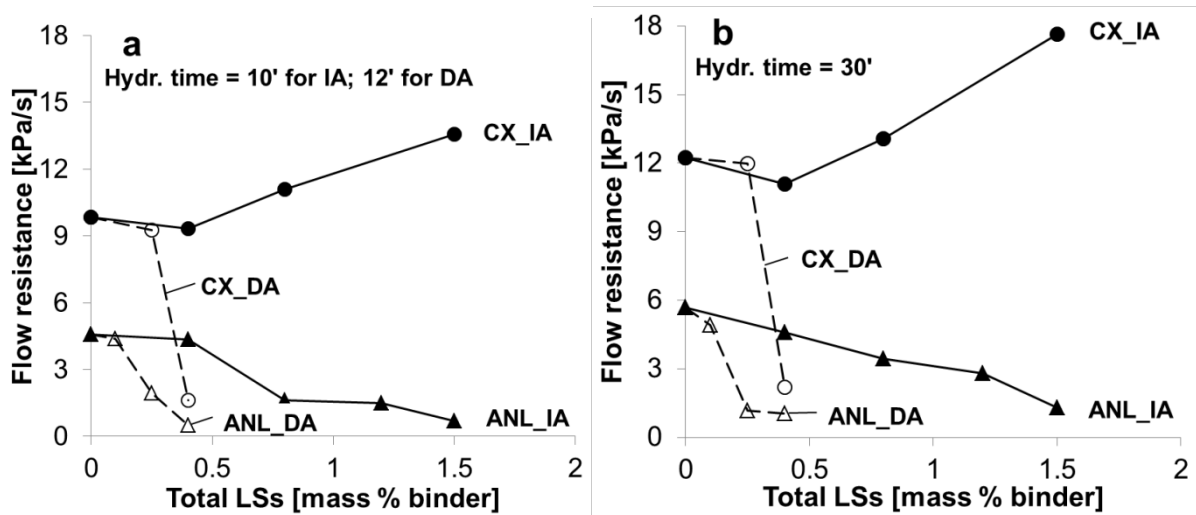
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718

719 Figure 2– a) Normalized yield stress and b) normalized viscosity vs. total LSs (mass % binder) of ANL
 720 and CX cements mixed with IA or DA of LSs at 30 min of hydration

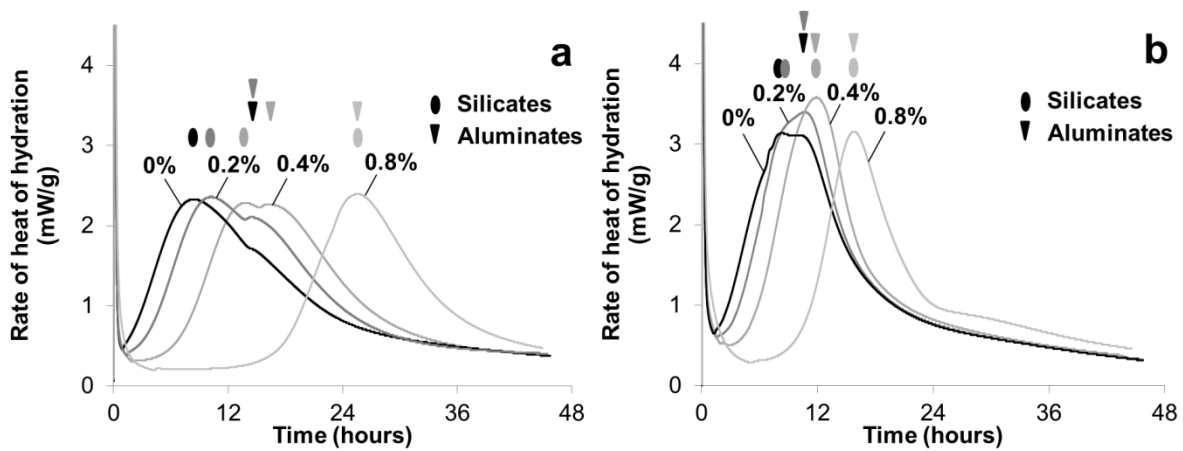
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722

723 Figure 3 - Flow resistance at 10 min. of hydration (12 min of hydration for samples prepared with DA)
 724 in fig. a and at 30 min. of hydration in fig. b vs. total LSs(mass % binder) of ANL and CX cements with
 725 IA or DA of LSs

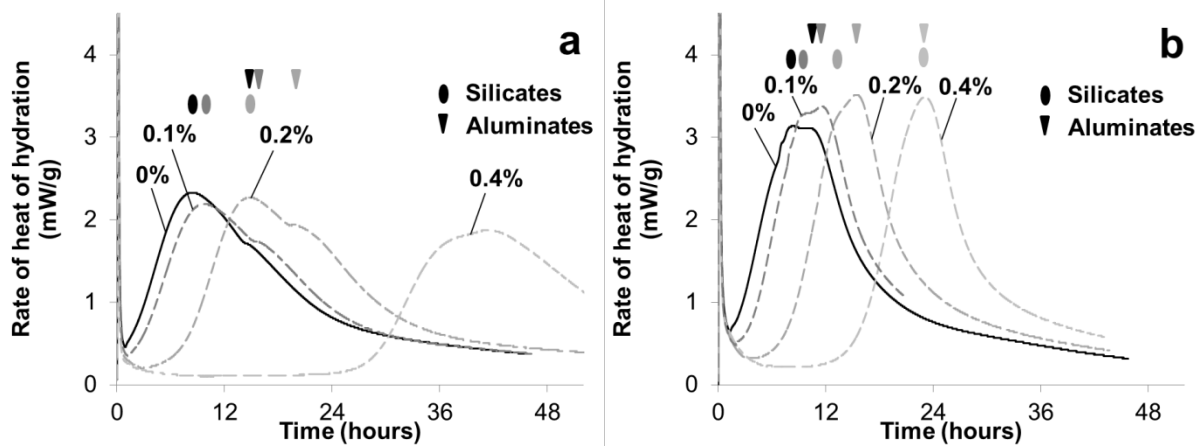
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727

728 Figure 4 – Rate of heat of hydration in time for a) ANL and b) CX cement pastes with increasing
 729 dosage of LSs mixed with IA (0, 0.2, 0.4, 0.8 mass % LSs). The silicates and aluminates peaks are
 730 marked with different symbols in corresponding colour of the respective calorimetric curve.

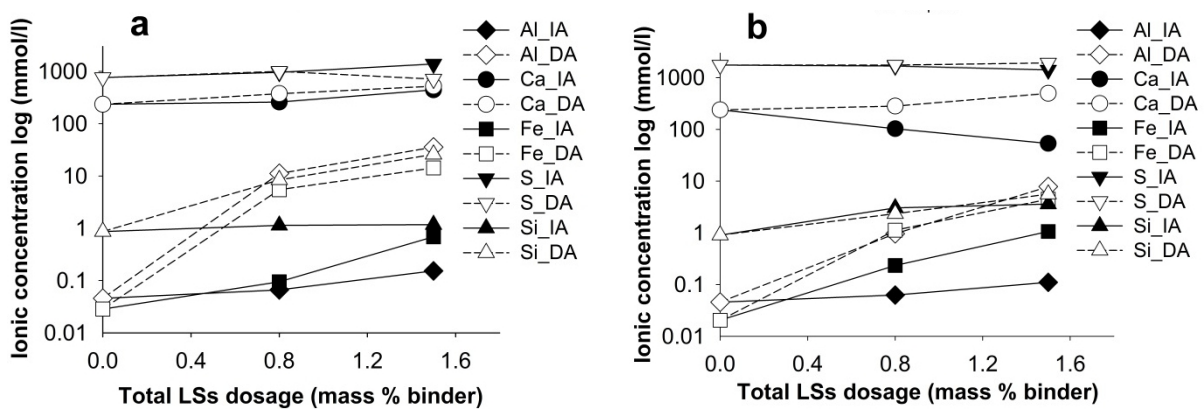
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732

733 Figure 5 - Rate of heat of hydration vs. time for a) ANL and b) CX cement pastes with increasing
 734 dosage of LSs mixed with DA (0, 0.1, 0.2, 0.4 mass % LSs). The silicates and aluminates peaks are
 735 marked with different symbols in corresponding color of the respective calorimetric curve.

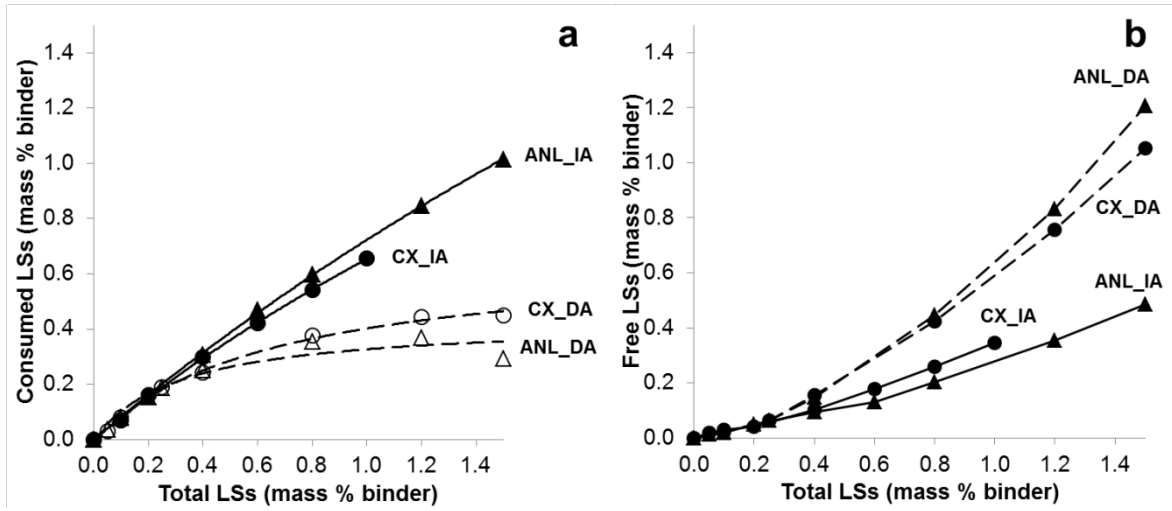
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737

738 Figure 6 – Concentration of Al, Fe, Ca, Si, and S ions in the pore solution (mmol/L) expressed in
 739 logarithmic scale vs. total LSs added (mass % binder) to a) ANL and b) CX cement pastes at 30 min of
 740 hydration both for IA and DA

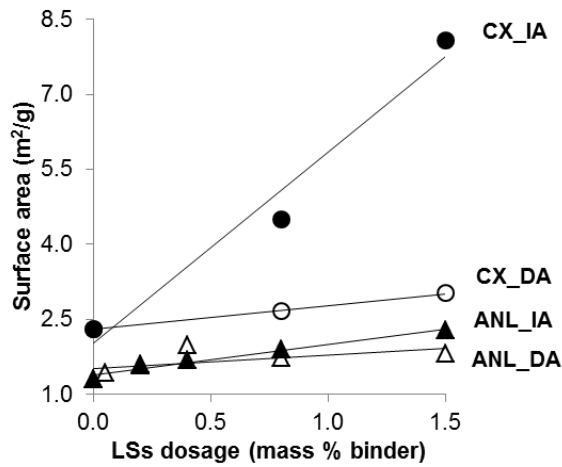
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742

743 Figure 7 - Amount of a) consumed LSs and of b) free LSs at 30 min of hydration vs. amount of LSs
 744 added to ANL and CX cements for IA and DA, after [32]. The results are calculated per mass % of
 745 binder

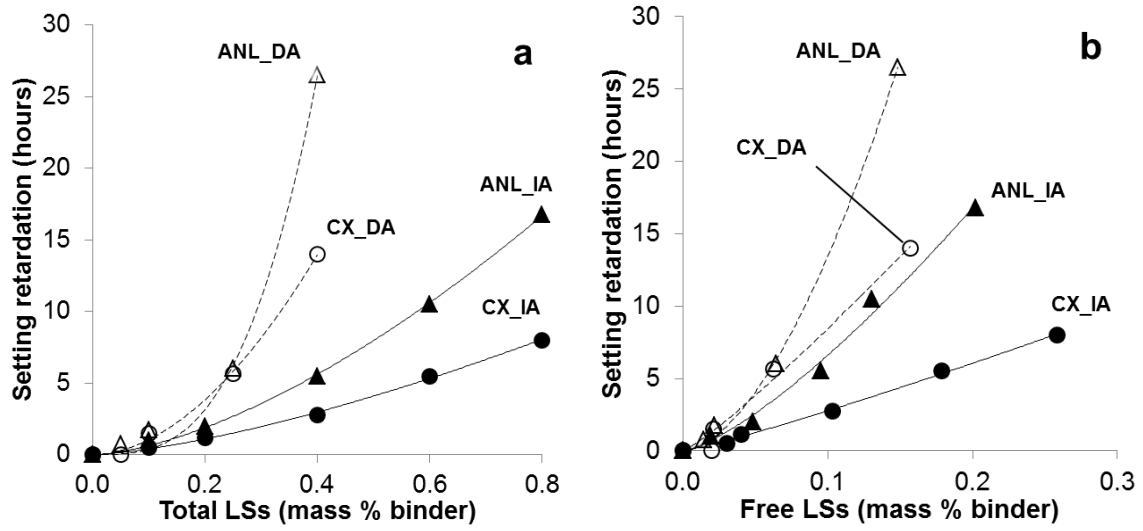
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748 Figure 8 - Surface area of ANL and CX cement particles hydrated for 30 min vs. total dosage of LSs
 749 added (mass % binder) both for IA and DA, after [32]

750



751

752 Figure 9 – Setting time retardation vs. amount of a) total LSs and b) free LSs for ANL and CX cement

753 pastes containing increasing dosage of LSs both for IA and DA. NB. The figures' scales are different.