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1 **THE EFFECT OF CALCIUM LIGNOSULFONATE ON**  
2 **ETTRINGITE FORMATION IN CEMENT PASTE**

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10 **ABSTRACT**

11 The effect of a softwood calcium lignosulfonate, LSs, on the ettringite formed in cement paste  
12 was investigated. Two Portland cements, mainly differing in surface area and C<sub>3</sub>A content,  
13 were used. The effect of LSs addition time was studied, by adding either the LSs immediately  
14 with the mixing water or after 10 minutes of hydration. After 30 minutes of hydration of both  
15 cement pastes, the immediate addition of LSs caused the formation of numerous small  
16 ettringite crystals. The ettringite crystals had similar shape in pastes with and without LSs  
17 addition: cubic or cuboidal shape with length between 0.1 and 0.4 μm. These small particles  
18 caused an increase in surface area, which in turn increased the LSs adsorption by the cement  
19 paste. This could potentially lead to incompatibility issues between cement and plasticizer.

20 **KEYWORDS**

21 Ettringite; Hydrated surface area; Adsorption; Fresh cement paste; Lignosulfonate

## 22 1. INTRODUCTION

23 Water-reducers, or plasticizers, allow obtaining highly fluid concrete with low water-to-  
24 binder ratios, additionally improving the mechanical properties and the durability of the  
25 hardened concrete.

26 In this paper, a low-sugar softwood calcium lignosulfonate (LSs) is investigated. LSs is  
27 commonly used in concrete in the dosage of 0.25-0.40 mass % of binder. Lignosulfonates are  
28 polyelectrolytes derived from lignins in the pulping industry. Lignin can be derived from  
29 various sources of biomass, which allows producing lignosulfonates with different molecular  
30 weight and amount of functional groups, as explained by Gelardi et al. [1], amongst others.

31 Amongst the clinker phases,  $C_3A$  is the one with the highest hydraulic reactivity, reacting  
32 immediately upon water contact. In the presence of gypsum, the first stable hydration product  
33 from  $C_3A$  is ettringite (AFt). Ettringite forms as long as there are enough sulfate ions in  
34 solution. When gypsum is depleted, ettringite will start further reacting with the residual  $C_3A$ ,  
35 forming monosulfoaluminate hydrate (AFm) [2].

36 The dispersing effectiveness of a superplasticizer on cementitious materials is, amongst  
37 others, a function of its degree of adsorption on the surface of cement grains and hydrates.  
38 The two main dispersing mechanisms are electrostatic repulsion and steric hindrance. The  
39 plasticizer type determines which of the two mechanisms will be dominant. During  
40 electrostatic repulsion the adsorbed plasticizer layer renders the particle surface negatively  
41 charged. As negatively charged particles approach each other, electrostatic repulsion prevents  
42 them from forming agglomerates. Additionally, when two surfaces approach close enough for  
43 their adsorbed layers to overlap, a steric force develops. This will contribute in hindering  
44 particles to get close enough to form agglomerates. The key parameters that govern the steric  
45 repulsion are the adsorption layer thickness and its conformation at the solid liquid interface

46 [3]. Lignosulfonate can disperse cement particles by both electrostatic repulsion and steric  
47 hindrance, as reported by Vikan [4], amongst others.

48 The amount of substrate surface which is covered by adsorbed polymer is referred to as  
49 surface coverage. As both major dispersion mechanisms rely on surface coverage, it will be a  
50 dominating parameter with regard to the dispersing efficiency of plasticizers. In a previous  
51 paper [5], the authors showed that the rheological behavior relates to the degree of polymer  
52 coverage of the available surface for adsorption. In particular, the achievement of high or full  
53 surface coverage was found to correspond to a drop in yield stress and viscosity of the cement  
54 paste.

55 The polymer is not adsorbed equally on the four main cement phases. According to Yoshioka  
56 et al. [6], a much higher adsorption occurs on aluminate and ferrite than on the silicate phases.  
57 According to Zingg et al. [7] and Plank et al. [8], the plasticizer will be adsorbed also on the  
58 cement hydrates, ettringite being the hydrate adsorbing the most.

59 It is known that plasticizers can cause changes in hydrates morphology, especially for  
60 ettringite. Prince et al. [9] studied a system of calcined kaolin, lime and anhydrite and found  
61 that sodium polynaphthalene sulfonate blocks the development of needle-like ettringite  
62 crystals. Instead, ettringite formed in small massive clusters. Hekal and Kishar [10] found that  
63 the size of the ettringite crystals formed in a  $C_3A$ - $CaSO_4$  system decreased as the dosage of a  
64 sodium naphthalene sulfonate-formaldehyde polycondensate increased. Cody et al. [11]  
65 synthesized ettringite in presence of a commercial lignosulfonate. They found that a large  
66 amount of ettringite formed in the form of small spherical crystals. Danner et al. [12]  
67 observed that the addition of calcium and sodium lignosulfonate led to the formation of small  
68 ettringite crystals with rounded oval shape. On the other hand, Kerui et al. [13] investigated a  
69 fly ash cement, reporting that a mixture of calcium lignosulfonate and sodium bicarbonate

70 caused a change in ettringite formation from a large number of tiny crystals into a limited  
71 number of large needle-like crystal particles. In conclusion, generally [9-12] plasticizers have  
72 been reported to cause the ettringite crystals to be smaller in size and to deviate from the  
73 typical needle-shape, taking a spherical or cubic morphology, except for Kerui et al. [13], who  
74 found that ettringite formed in few large needle-like crystals. However, it should be kept in  
75 mind that the results might have been influenced by the fact that lignosulfonate was combined  
76 with  $\text{NaHCO}_3$ .

77 Several studies reported that also the amount of formed hydrates might change upon  
78 plasticizer addition. Zingg [14] found that some polycarboxylate-type superplasticizers (PCE)  
79 had a limited influence on the amount of ettringite formed in Portland cements. This was  
80 confirmed by Dalas et al. [15], who found only a slight decrease in the amount of ettringite  
81 precipitated in a  $\text{C}_3\text{A}$ - $\text{CaSO}_4$  system, though its specific area was strongly increased. Hekal  
82 and Kishar [10] investigated a similar system of  $\text{C}_3\text{A}$  and  $\text{CaSO}_4$  reporting that the ettringite  
83 formation was increasingly retarded in the first 24 hours of hydration as the dosage of a  
84 sodium naphthalene sulfonate-formaldehyde polycondensate increased. Lignosulfonate was,  
85 on the other hand, found to accelerate ettringite formation in cement by Bishop and Barron  
86 [16]. The amount of ettringite formed by a fly ash cement was found to increase in presence  
87 of a mixture of calcium lignosulfonate and sodium bicarbonate by Kerui et al. [13]. Danner et  
88 al. [17] investigated three different cements in combination with a calcium-lignosulfonate and  
89 reported that the initial formation of ettringite was accelerated. In conclusion, the amount of  
90 ettringite formed has both been observed to increase and decrease depending on the  
91 plasticizers used.

92 The aim of this paper is to understand the effect of a calcium lignosulfonate (LSs) on the  
93 formation of ettringite in Portland cement paste. Two Portland cements mainly differing in  
94 surface area and  $\text{C}_3\text{A}$  content were chosen. The effects were studied both by adding the

95 lignosulfonate immediately with the mixing water (IA), and by adding it after 10 minutes of  
96 hydration (DA). Changes in composition and amount of cement hydrates after 30 minutes of  
97 hydration caused by the addition of the LSs were investigated with thermogravimetric  
98 analysis (TGA) and X-ray powder diffraction (XRD). The effect of LSs on the hydrates of  
99 hardened cement was also studied with TGA after 28 days of hydration. The hydrates  
100 morphology was observed with scanning electron microscopy (SEM) after 30 minutes of  
101 hydration, and their chemical composition was analyzed with energy dispersive spectroscopy  
102 (EDS). The elemental composition of the pore solution extracted from the cement paste  
103 samples after 30 minutes of hydration was analysed with inductive coupled plasma – mass  
104 spectroscopy (ICP-MS). In addition, the effect of LSs on the solubility of the different  
105 calcium sulfates, i.e. anhydrite, hemihydrate and gypsum, was investigated by determining the  
106 soluble Ca and S by ICP-MS in calcium sulfate suspensions containing increasing LSs  
107 dosages. The adsorption isotherms and BET measurement presented in a previous paper by  
108 the same authors [18] were combined with the new results reported in the present paper. In the  
109 present paper, the authors succeeded in observing the morphology of ettringite in real cement  
110 paste with and without the LSs, and not as a pure synthesized phase. The results of this paper  
111 are connected to those discussed in a previous paper by the same authors [5], which was more  
112 focused on the effect of LSs on setting time and rheology of cement paste. The results of the  
113 present paper give further insight on the effect of LSs on the formation of cement hydrates,  
114 and thus contribute to a deeper understanding of the mechanisms behind the interactions  
115 between lignosulfonate and cement paste.

## 116 2. EXPERIMENTAL

### 117 2.1 Materials

118 The experiments were performed on two different cements: a CEM I 52.5 N (ANL) produced  
119 by Norcem, and a CEM I 52.5 R (CX), produced by Cemex, as defined by the European  
120 Standard EN197-1. The content of the main clinker phases of the cements quantified by XRD  
121 Rietveld, according to Le Saoût et al. [19], are given in Table 1. The chemical composition of  
122 the cements determined by XRF and the loss of ignition at 950 °C are reported in Table 2. The  
123 particle size distribution ( $d_{10}$ ,  $d_{50}$ ,  $d_{90}$ ), Blaine surface area, density, and BET surface area are  
124 given in Table 3.

125 A sugar-reduced softwood calcium lignosulfonate (LSs), produced by Borregaard, was used  
126 as plasticizer. Fractionated lignosulfonate samples with low polydispersity indices and known  
127 molecular weight were used as calibration standards for determination of molecular weight.  
128 Its weight average molecular weight ( $M_w$ ), as measured with gel permeation chromatography  
129 (GPC), was 29000 g/mol and the number average molecular weight ( $M_n$ ) was 2100 g/mol,  
130 giving broad molar-mass dispersity ( $\mathcal{D}_M$ ) equal to 13.8. The molar-mass dispersity, also called  
131 polydispersity index, is defined as the ratio between  $M_w$  and  $M_n$  [20]. Additional physical and  
132 chemical properties of the lignosulfonate are listed in Table 4. For the lignosulfonate used in  
133 the present investigation, the sugars were removed from the product by fermentation and  
134 resulting alcohol by distillation. The LSs was dissolved in deionised water to concentrations  
135 varying from 1 to 45 % to facilitate dosing, and the water content was included in the  
136 calculation of the water-to-binder ratio (w/b).

137 In order to study the effect of LSs on the solubility of calcium sulfates, anhydrite ( $\text{CaSO}_4$ ),  
138 hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) and dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) were used. The anhydrite,  
139 produced by Thermo Fisher, and the dihydrate, produced by Merck, were analytical grade,

140 while the hemihydrate, produced by VWR Chemicals, was technical grade. In order to mimic  
141 the pH of cement paste, the calcium sulfates samples were mixed with LSs solution diluted in  
142 artificial pore water. The artificial pore water was a solution of 2.1 g/l NaOH and 5.9 g/l KOH  
143 with K/Na, reaching a measured pH of 12.9. A molar ratio of 2 for K/Na is typical for a  
144 Norwegian Portland cement, see [21].

## 145 **2.2 Sample preparation**

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

152 For IA, the binder was mixed with deionised water (and/or lignosulfonate diluted in deionised  
153 water) according to the procedure used by Vikan [4]: 30 seconds mixing, 5 minutes resting  
154 and scraping the mixer walls to homogenize the mix, and 1 minute mixing.

155 For DA, the binder and 85% of the water were mixed according to the following mixing  
156 procedure: 30 seconds mixing, 10 minutes resting and scraping the mixer walls to  
157 homogenize the paste. The delay time of 10 minutes was found to be included in the range of  
158 optimum delay times to obtain the maximum workability increase with a given plasticizer  
159 dosage [22-25]. LSs and the remaining 15% of the needed water were then added to the mix,  
160 which was mixed for 1 additional minute.



## 161 **2.3 Methods**

### 162 **2.3.1 UV-spectroscopy**

163 UV-spectroscopy allowed measuring the LSs concentration in the pore solution of the cement  
164 paste samples, which again allows the determination of the LSs uptake.

165 After mixing according to paragraph 2.2, about 35 ml paste was poured in 50 ml plastic  
166 centrifuge tubes and left to rest until the selected hydration time. The pore solution was  
167 extracted from the cement paste by centrifuging the samples in a Heraeus Megafuge 8  
168 centrifuge by Thermo Scientific for 3 minutes at the speed of 4500 rpm. The supernatant pore  
169 solution was extracted and filtered with 0.45  $\mu\text{m}$  cellulose syringe filters. The pore water was  
170 analysed with a Genesys 10S UV-spectrophotometer by Thermo Scientific. Wavelengths in  
171 the range 280-284 nm had been reported in literature to study the adsorption of lignosulfonate  
172 on cement particles [3, 4, 26-28]. After scanning at several wavelengths, 281 nm was chosen  
173 as the most suitable wavelength to analyse the samples in this study.

174 After centrifugation plasticizer consumed by the cement paste was determined with UV-  
175 spectroscopy at increasing hydration times (from 5 to 120 minutes hydration). It was found  
176 that, after 10 minutes of hydration, the LSs uptake reached a plateau and did not change  
177 considerably with time. 30 minutes hydration was used for determination of the adsorption  
178 isotherms.

179 A calibration curve was obtained measuring the absorbance of pure LSs solutions dissolved in  
180 deionised water in different concentrations. Based on the absorbance value of the pore  
181 solution extracted from the samples of cement paste, the calibration curve allowed the  
182 calculation of the amount of free plasticizer (g LS/100 g solution) in the pore solution. This  
183 amount was then related to the amount of binder in the sample (g LS/100 g binder). The LSs  
184 consumed by the investigated systems was calculated by subtracting the amount of free LSs to

185 the total amount of LSs initially added to the sample (also called depletion method), as  
186 displayed in equation 1:

$$187 \quad \text{LSs}_{\text{consumed}} = \text{LSs}_{\text{total}} - \text{LSs}_{\text{free}} \quad (1)$$

188 Polymer adsorption by a solid is usually described through isotherms, in which the amount of  
189 polymer adsorbed is plotted against the total amount of polymer added to the system [29]. The  
190 shape of an isotherm is largely determined by the adsorption mechanisms. In this study, the  
191 isotherms were drawn relating the amount of LSs consumed by the cement paste to the  
192 amount of total LSs added to the sample. When expressed as mass % of binder, the amount of  
193 LSs consumed was calculated considering the actual available water in the system, i.e. the  
194 mixing water was reduced by the bound water measured with TGA (paragraph 2.3.3).

### 195 **2.3.2 Solvent exchange**

196 A solvent exchange procedure with isopropanol and petroleum ether, similar to the one  
197 suggested by Winnefeld et al. ([30]) and Lotenbach et al. ([31]), was used to stop the  
198 hydration of the cement paste. It should be noted that the method for stopping hydration of the  
199 cement paste and drying might affect the amount and the morphology of the ettringite  
200 observed [30, 31].

201 About 5 ml of cement paste after 30 minutes of hydration was transferred in a 50 ml  
202 centrifuge tube and centrifuged for 1 minute at 2000 rpm. The supernatant water was  
203 removed. About 40 ml of isopropanol was poured in the centrifuge tube. The tube was shaken  
204 for 30 seconds and let to rest for 5 minutes. The sample was centrifuged again for 1 minute at  
205 2000 rpm and the supernatant liquid was removed. The solvent exchange procedure with  
206 isopropanol was repeated once, followed by a final solvent exchange with 10 ml of petroleum  
207 ether. The resulting paste was let to dry in a ventilated oven for 15 minutes at 40 °C, and then  
208 for 2 days in a desiccator over silica gel and soda lime to minimize carbonation. After drying,

209 the samples were pulverized and homogenized in a porcelain mortar and stored in sealed  
210 containers in a desiccator over silica gel and soda lime until analysis.

211 After 6 hours of hydration, a slice of 6 mm was cut from the mid-section of the sample with  
212 an electric saw (the samples were not plastic anymore, but neither fully hardened). For this  
213 reason, the semi-hardened cement paste was crushed in a porcelain mortar and the hydration  
214 was stopped in equal manner as for the samples hydrated for 30 minutes.

215 A different set of samples of cement paste was let to hydrate for 28 days at 20 °C in sealed  
216 conditions. After 28 days, a slice of 6 mm, equivalent to about 5 g of cement, was cut from  
217 the mid-section of the sample with an electric saw. The sample was crushed in a porcelain  
218 mortar until the powder passed through a 1 mm sieve. The powder was then transferred into a  
219 125 ml plastic bottle together with 50 ml isopropanol, which was shaken for 30 seconds and  
220 let to rest for 5 minutes until solids sedimented. The isopropanol was decanted and the  
221 procedure was repeated once more. The isopropanol was then filtered off with a filtration unit  
222 connected to a water pump, using Blauband filters by Schleicher & Schuell. The sample was  
223 then flushed with 10 ml petroleum ether while still in the filtration unit, and let to rest for 5  
224 minutes, before removing the ether by filtration in the water pump. The sample was then  
225 transferred to a watch glass and let to dry in a ventilated oven for 15 minutes at 40 °C. After  
226 drying, the samples were stored in sealed containers in a desiccator over silica gel and soda  
227 lime until analysis. Prior to analysis, the sample was pulverized and homogenized in a  
228 porcelain mortar.

### 229 **2.3.3 TGA**

230 The thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA DSC3+ on  
231 hydrated cement paste after stopping the hydration using solvent exchange. Approximately

232 200 mg of cement paste powder was loaded in 600 µl alumina crucibles. The samples were  
233 heated from 40 to 900 °C at a rate of 10 °C/min while purging with 50 ml/min N<sub>2</sub>.

234 It was decided to present the results in terms of mass loss % of the mass of dry binder in  
235 different temperature intervals (see Figure 7 and Table 6). The intervals selected were:  
236 interval 1, from 50 to ca. 300 °C, interval 2 from ca. 300 to ca. 500 °C, and interval 3 from ca.  
237 500 to 900 °C. The temperature ranges could slightly vary according to the actual peak  
238 boundaries in the derivative of the thermogravimetric curve (DTG). For the samples hydrated  
239 for 28 days, the intervals slightly changed in temperature ranges: interval 1, from 50 to ca.  
240 420 °C, interval 2 from ca. 420 to ca. 540 °C, and interval 3 from ca. 540 to 900 °C.

241 Interval 1 includes the mass loss corresponding to the decomposition of ettringite, calcium  
242 sulfates, and C-S-H; interval 2 consists mainly of the mass loss corresponding to the  
243 decomposition of CH; interval 3 comprises the mass losses corresponding to the  
244 decomposition of carbonates. The sum of the mass loss in the interval 1 and 2 represents the  
245 release of bound water.

246 The mass losses are expressed relative to the dry mass of the sample as the dry weight is  
247 assumed to be constant during the hydration. Commonly the mass at 500 °C is used as the dry  
248 mass of hydrated cement paste containing limestone [21]. However, the addition of LSs to the  
249 cement paste led to an increase in mass loss in the temperature range between 500 and 800 °C  
250 due to the decomposition of LSs. Therefore, the dry weight was calculated as the sum of the  
251 sample weight at 800 °C ( $w_{800}$ ) and the mass loss due to the decomposition of limestone in the  
252 sample without LSs ( $w_{ref,500} - w_{ref,800}$ ). For example, the mass loss in interval 1 was calculated  
253 as in equation 2:

$$254 \text{ Mass loss Int. 1 (mass \%)} = \frac{w_{50} - w_{300}}{w_{800} + (w_{ref,500} - w_{ref,800})} * 100 \quad (2)$$

255 To calculate the amount of bound water in the cement paste, the mass loss in the interval from  
256 50 to 500 °C was considered. The amount of bound water was calculated as:

$$257 \text{ Amount of bound water (mass \% dry weight of cement)} = \frac{w_{50} - w_{500}}{w_{800} + (w_{ref,500} - w_{ref,800})} * 100 \quad (3)$$

258 In order to have an approximate quantification of the maximum amount of ettringite formed  
259 after 30 minutes in the cement pastes in which 1.5 mass % of LSs was added by IA, the whole  
260 mass loss in the interval 1 (50 - ca. 300 °C) was considered. The amount of ettringite (AFt)  
261 was calculated as:

$$262 \text{ Amount of AFt (mass \% dry weight of cement)} = \frac{w_{50} - w_{300}}{w_{800} + (w_{ref,500} - w_{ref,800})} * \frac{M_m(\text{AFt})}{M_m(\text{H})} * 100 \quad (4)$$

263 Where  $M_m(\text{AFt})$  and  $M_m(\text{H})$  is the molecular mass of ettringite and water respectively.

264 It should be noted that in this temperature interval also C-S-H and calcium sulfate  
265 components could lose water. However, the mass loss due to C-S-H decomposition was  
266 expected to be very small as no C-S-H was not observed in these samples using SEM-EDS.  
267 The mass loss due to the release of crystalline water from the remaining calcium sulfate  
268 components present cannot be separated from the mass losses corresponding to ettringite as  
269 the TGA peaks overlap. This might lead to a slight overestimation of the amount of ettringite  
270 formed, however this is acceptable as the aim is to obtain an estimate of the potential  
271 maximum amount of ettringite.

#### 272 **2.3.4 XRD**

273 The X-ray diffraction (XRD) analysis was performed using a Bruker AXS D8 Focus with a  
274 Lynxeye super speed detector operating at 40 kV and 40 mA. A  $\text{CuK}\alpha$  source ( $\lambda_{\text{CuK}\alpha} = 1.54$   
275 Å) with a 0.2 mm slit was used. The scan was performed between 7 and 55° 2θ with an

276 increment of 0.02 and a scanning speed of 0.5 s/step. Front-loading sample holders were used.  
277 The scans are used qualitatively to detect changes in crystalline phases.

### 278 **2.3.5 BET of hydrated particles**

279 The BET measurements were performed using a Flowsorb II 2300 by Micromeritics. The  
280 sample mass was about 2 g. The measurement was performed by purging the samples with  
281 nitrogen at room temperature. The initial flow of gas through the sample was stable, hence the  
282 samples were dry. Therefore, the samples were neither dried nor degassed before the  
283 measurement, in order to preserve the ettringite possibly present in the sample. The sample  
284 preparation applied in this study, similar to the one described in [32], aimed to limit  
285 destruction of hydrates such as gypsum and ettringite. The hydration was stopped with the  
286 solvent exchange procedure described in paragraph 2.3.2.

### 287 **2.3.6 SEM-EDS**

288 An ultra-high-resolution in-lens cold field emission SEM S-5500 by Hitachi was used for the  
289 scanning electron microscopy (SEM). The cement powder was dried for 2 days in a desiccator  
290 over silica gel and soda lime prior to the analysis. The powder sample was placed on a sample  
291 holder with copper tape and the excess powder was removed with a N<sub>2</sub> gun. A voltage of 5 kV  
292 and a current varying between 1 and 7 μA were used to observe the samples with the scanning  
293 electron microscope in secondary electron-mode (SE). The chemical composition of the  
294 samples was analyzed with energy-dispersive X-ray spectroscopy (EDS) using a Bruker  
295 XFlash detector set on a voltage of 5 kV and a current of 20 μA. The samples were coated  
296 with a 4 nm-thick layer of a platinum-palladium alloy to avoid charging of the sample during  
297 the analysis.

### 298 **2.3.7 ICP-MS**

299 Inductively-coupled plasma mass spectrometry (ICP-MS) was used to determine the  
300 elemental concentration of Al, Ca, Fe, K, Na, S and Si in the pore solution extracted from the  
301 cement paste. A triple quad Agilent 8800 by Agilent Technologies was used. The samples  
302 were filtered with the same procedure used for UV-spectroscopy (paragraph 2.3.1) and  
303 acidified by adding 1:1 by volume of 1:10 diluted HNO<sub>3</sub>.

## 304 **3 RESULTS**

### 305 **3.1 TGA after 30 minutes of hydration**

306 The effect of the dosage of LSs on cement hydrates after 30 minutes of hydration was  
307 investigated with TGA. The analysis was performed on ANL and CX cement pastes with  
308 different dosages of LSs both for immediate addition (IA) and for delayed addition (DA). A  
309 maximum LSs dosage of 1.5 mass % of binder was used for the samples prepared with DA  
310 because of the extremely large setting retardation displayed by this sample, as showed in a  
311 previous paper [5]. Reference samples of neat ANL and CX without LSs were also measured.  
312 The hydration of the tested samples was stopped after 30 minutes with the solvent exchange  
313 procedure with isopropanol and petroleum ether, as described in paragraph 2.3.2. The results  
314 are displayed in Figure 1 and in Figure 2 for ANL cement and in Figure 3 and in Figure 4 for  
315 CX cement.

316 Several peaks could be observed: the peak at about 110 °C and the smaller one at 240 °C  
317 indicate the presence of AFt. The peak around 150 °C represents the release of water from  
318 calcium sulfates (anhydrite, hemihydrate or gypsum) (CaSO<sub>4</sub>·xH<sub>2</sub>O). This peak might overlap  
319 with the one representing the decomposition of AFm, but, since no AFm was detected with  
320 XRD (see Figure 5 and Figure 6), it is assumed that this peak is only ascribable to the release  
321 of crystalline water from the calcium sulfates. The peak around 420 °C relates to the release of

322 crystalline water from portlandite (CH); the ones around 610 °C and 780 °C represent the  
323 decomposition of carbonates (C) (release of CO<sub>2</sub>). The peaks over 500 °C can be attributed  
324 both to the decomposition of limestone included in the used cements and, for the samples  
325 containing LSs, to the decomposition of LSs.

326 After 30 minutes of hydration, the TGA data for ANL cement (see Figure 1 and Figure 2)  
327 shows a peak at 150 °C corresponding to the dehydration of gypsum and hemihydrate, which  
328 is in line with the composition of the cement given in Table 1. The TGA data for CX cement  
329 after 30 minutes of hydration (see Figure 3 and Figure 4) only shows a small peak at 150 °C,  
330 most likely associated with the hemihydrate already present in the unreacted cement (Table  
331 1). Changes in the anhydrite content present in the CX cement (Table 1) cannot be monitored  
332 by TGA as it does not contain chemically bound water. One might expect that anhydrite and  
333 hemihydrate present in the unreacted cement would convert to gypsum upon contact with  
334 water, but that does not seem to be the case.

335 The mass loss was quantified with the horizontal step method applied in three temperature  
336 intervals, as described in paragraph 2.3.3. The results are shown in Figure 7 and summarized  
337 in Table 6.

338 From the results showed in Figure 7 and reported in Table 6, it can be observed that, for IA,  
339 the increase in LSs dosage led for both cements to an increase in the intensity of the peak  
340 corresponding to the decomposition of ettringite and a reduction in the one corresponding to  
341 the decomposition of calcium sulfate hydrates up to a LSs dosage of 1.5 mass % of binder.  
342 Similar trends were observed for both cements, even though the ettringite peak was noticeably  
343 more intense and the one of calcium sulfate hydrates less intense for CX cement compared to  
344 ANL cement. For higher LSs dosages, the increase in intensity of the ettringite peak was  
345 lower than that with 1.5 mass % of binder LSs for both cements.



346 The mass loss corresponding to the decomposition of CH did not noticeably change with  
347 increasing LSs amount.

348 The mass loss corresponding to carbonates decomposition was found to increase in intensity  
349 with the increase of the LSs amount, and thereby seems to include a contribution from the  
350 decomposition of consumed LSs.

351 The amount of bound water (calculated according to formula 3) followed a trend similar to the  
352 one of ettringite. The highest increase in amount of bound water is shown by CX cement paste  
353 for IA, which agrees with the observation that, for IA, CX was found to set already after 30  
354 minutes of hydration for LSs dosages over 1.0 mass % of binder.

355 In the sample of CX cement paste with 1.5 mass % of binder LSs (IA), the amount of bound  
356 water resulted to be about 5 mass % of dry weight of cement, which represented the 12 % of  
357 the initial mixing water (40 mass % of dry weight, since  $w/b = 0.4$ ).

358 For DA, no noticeable changes in the ettringite, calcium sulfate hydrates, or CH amount were  
359 observed for any of the cements. Only an increased intensity of the carbonate peak was  
360 measured with increasing LSs amount.

### 361 **3.2 XRD**

362 The increase in the ettringite amount measured with TGA for IA was confirmed by x-ray  
363 diffraction (XRD) on ANL and CX cement pastes containing 0, 0.8, 1.5 mass % of binder LSs  
364 added with IA. The hydration of the cement pastes was stopped after 30 minutes with the  
365 solvent exchange procedure using isopropanol and petroleum ether, as described in paragraph  
366 2.3.2. The results are shown in Figure 5 and Figure 6.

367 The main peaks displayed by the XRD curves are summarized in Table 7. The peak at  $2\theta =$   
368  $9.1^\circ$ , representing ettringite, increases in intensity with the increase of LSs for both cements,

369 supporting the results found with TGA. For the ANL cement samples, clear peaks at  $2\theta = 11.6$   
370  $^\circ$  and  $20.7^\circ$  are observed, representing gypsum. Whereas for CX cement samples, peaks at  $2\theta$   
371  $= 25.7^\circ$  and  $31.2^\circ$  were detected and represent anhydrite. This is in line with the composition  
372 on the unhydrated cements (Table 1), where the sulfate source in CX cement is anhydrite and  
373 hemihydrate, and for ANL cement gypsum and hemihydrate, with the exception that  
374 hemihydrate was not detected in the XRD spectrum, supposedly because it dissolves very  
375 quickly. For ANL and CX cement, the peak intensities of respectively gypsum and anhydrite  
376 noticeably decreased with the LSs dosage, indicating enhanced reaction of the calcium sulfate  
377 phases upon addition of LSs. The peaks at  $2\theta = 12.2^\circ$  and  $2\theta = 24.3^\circ$  indicates  $C_4AF$ , which  
378 appeared to slightly decrease with increasing LSs dosage. The peak at  $2\theta = 14.9^\circ$  represents  
379  $C_3S$  and displayed an approximately constant intensity with increasing LSs dosage in both  
380 cement pastes, which is in line with the fact that the hydration of  $C_3S$  is still very low after  
381 only 30 minutes of hydration. The peak at  $2\theta = 23.0^\circ$  indicates either ettringite or  $CaCO_3$ .  
382 This peak was found to slightly increase with the increase in LSs for both cements.

### 383 **3.3 SEM**

#### 384 **3.3.1 After 30 minutes of hydration**

385 The morphology and size of early hydrates in presence of LSs was investigated with SEM.  
386 Pastes of both cements containing 1.5 mass % of binder LSs both for IA and DA were  
387 studied. The hydrates formed in these samples were compared to those formed in reference  
388 samples without LSs.

389 Figure 8 displays grains of left) ANL and right) CX cement after 30 min hydration without  
390 LSs. Both cements showed large areas of unhydrated surface and few initial hydrates. It was  
391 noted that the presence of hydrates was largest inside cavities and holes on the particles'  
392 surface. It should also be kept in mind that the presence of crystals on the surface of

393 anhydrous cement particles depends on the fact that the crystals, which are initially dispersed  
394 in the pore solution, land on the surface of the anhydrous cement particles when the sample is  
395 dried.

396 Figure 9 and Figure 10 display a typical particle of ANL and CX cement after 30 minutes of  
397 hydration, respectively, with 1.5 mass % of binder LSs mixed with IA. Large portions of the  
398 particles' surface were covered with crystals. The crystals were cubic with size between 0.1  
399 and 0.2  $\mu\text{m}$  for ANL cement, and cuboidal with length between 0.2 and 0.4  $\mu\text{m}$  for CX  
400 cement (aspect-ratio varying between 1.5:1 and 4:1). For CX cement, the crystals appeared to  
401 be larger in amount than in ANL cement, being located densely on top of each other on the  
402 cement grains' surface.

403 When the same LSs amount was added with DA, as shown in Figure 11 and in Figure 12 for  
404 ANL and CX cement, respectively, the surfaces of particles and hydrates appeared rough and  
405 irregular, with fewer well-defined crystals than when the LSs was added with IA (see Figure 9  
406 and Figure 10).

407 SEM-EDS was performed in order to analyse the chemical composition of the crystals present  
408 on the surface of unhydrated cement grains. The results from the SEM-EDS analysis of two  
409 crystals are displayed in Figure 13 and in Figure 14. It has to be noticed that the crystals  
410 turned to more rounded shapes during the scanning due to dehydration.

411 The SEM-EDS line scans allowed a qualitative chemical analysis of a line of points which  
412 included both the crystals and the unhydrated cement grain below them. In both cements, the  
413 results showed that, in comparison to the cement grain on which the crystals lay, the crystals  
414 were richer in Al, S and Ca, while they contained less Si.

415 The chemical composition of the samples was analysed by performing SEM-EDS analysis on  
416 4 points for each object analysed. The objects analysed were both the crystals and the

417 underlying cement grains. The average content in Al, Si, S and Ca of 4 analysis points was  
418 calculated for both cement pastes. Al and S were used to identify the phase composing the  
419 crystals, as the crystals analysed were deposited on C<sub>3</sub>S surfaces. The crystals were found to  
420 contain Al and S in ratio of about 1:3 in ANL cement and 1.8:3 in CX cement. The theoretical  
421 Al to S ratio in ettringite is 2:3. Considering the non-ideal conditions for SEM-EDS analysis  
422 (e.g. relief, small crystals, and charging material) and the limited number of data points, the  
423 crystals were identified as ettringite, even though the observed ratio between Al and S was  
424 lower than the theoretical one for ettringite for both cement pastes.

### 425 **3.3.2 After 6 hours of hydration**

426 The ettringite formed by pastes of the two cements without LSs was observed with SEM at  
427 final setting. The aim was to verify whether the ettringite crystals formed by pastes of the two  
428 cements without the LSs at a later stage of hydration displayed a needle-like shape and to  
429 compare them to those formed after 30 minutes of hydration.

430 The analysis time was after 6 hours of hydration, which corresponded to a time right before  
431 the main hydration peak determined by isothermal calorimetry, as shown in a previous paper  
432 [5]. It was assumed that, at this time of hydration, a minor amount of AFm or no AFm was  
433 present. The results are shown in Figure 15 for ANL cement paste and in Figure 16 for CX  
434 cement paste.

435 The particles of both cement samples without LSs were completely covered by hydrates after  
436 6 hours of hydration. C-S-H appeared as thin needles or fibres about 0.3 µm long and about  
437 0.05 µm wide. The C-S-H fibres embedded some ettringite crystals varying in morphology.  
438 Some ettringite crystals appeared as parallelepipeds with dimensions about 0.10x0.15 µm,  
439 while other crystals appeared more needle-like, with dimensions about 0.4x0.1 µm. Some  
440 clinker grains displayed more ettringite crystals on their surface, others less. In general, there

441 seems to be an indication of more ettringite crystals on the CX clinker grains compared to  
442 ANL ones, in agreement with the difference in cement composition and fineness.

443 The identification of ettringite and C-S-H was based on visual appearance and on the  
444 comparison to references in literature [33] and supported by SEM-EDS. Because of the high  
445 density of hydrates on the surface of unhydrated cement grains, it was difficult to analyse  
446 their chemical composition with SEM-EDS. However, the SEM-EDS analysis of the crystals  
447 visually identified as ettringite indicated that they contained Al and S, while the crystals  
448 identified as C-S-H appeared to be richer in Ca and Si.

### 449 **3.4 BET**

450 The BET surface area was measured for ANL and CX cement pastes with varying LSs  
451 amounts after 30 minutes of hydration. The hydration was stopped by solvent exchange after  
452 30 minutes. The results are shown in Figure 17.

453 For both cements the surface area was found to increase as the dosage of plasticizer added to  
454 the cement paste increased. The increase in surface area was noticeably larger for CX than for  
455 ANL cement, and for IA compared to DA, corresponding to more AFt formed.

### 456 **3.5 Adsorption isotherms**

#### 457 **3.5.1 Cement pastes**

458 The adsorption isotherms obtained for ANL and CX cement pastes were achieved by plotting  
459 the amount of consumed polymer versus the total amount of polymer added after 30 minutes  
460 of hydration. The tested dosages are given in Table 5. The LSs was added to the cement paste  
461 either immediately together with the mixing water (IA), or after 10 minutes of hydration  
462 (DA). Note that the adsorption isotherm obtained for CX cement for IA could only be  
463 measured up to 1.0 mass % of binder LSs. At higher dosages it was not possible to extract  
464 pore water as the paste had hardened after 30 minutes of hydration. The results and their fits

465 according to the Langmuir model [29] are presented as mass % of binder in Figure 18 a, and  
466 relative to the BET hydrated specific surface area (Table 3) available for adsorption in Figure  
467 18 b.

468 Figure 18 a shows that, for DA, an adsorption plateau was found for both cements. At high  
469 LSs dosage the isotherms obtained for DA also displayed a considerably lower amount of LSs  
470 consumed by the cement pastes compared to the isotherms obtained for IA. According to the  
471 theory reported in [29], an adsorption plateau is achieved when full monolayer surface  
472 coverage is reached. Therefore, for DA, the LSs consumption was considered to be mainly  
473 due to monolayer surface adsorption on the cement particles and hydrates, as reported in a  
474 previous paper [18].

475 For IA, no adsorption plateau could be detected within the tested range, neither for ANL nor  
476 for CX cement. The isotherms' shape indicated a continuous LSs uptake as more LSs was  
477 added to the mix.

478 In Figure 18 b the consumed LSs was expressed relative to the available surface after 30  
479 minutes of hydration. The adsorption isotherms of CX cement paste for IA and DA nearly  
480 coincided, both reaching an adsorption plateau. As found in [18], this indicates that the high  
481 LSs consumption by CX cement paste for IA was mainly due to monolayer surface adsorption  
482 on the large specific surface area caused by the additional ettringite formed.

483 For ANL cement, the amount of ettringite formed, and in turn the surface area, increased only  
484 moderately compared to CX cement (see Figure 17). Thus, as concluded in [18], surface  
485 adsorption could not entirely explain the measured LSs consumption. Therefore, for IA, other  
486 polymer consumption mechanisms, still to be determined, might have played a role in  
487 consuming the LSs in ANL cement paste.

### 488 **3.5.2 Calcium sulfates**

489 CX cement paste formed a larger amount of ettringite for IA compared to ANL cement paste.  
490 One of the differences between CX and ANL cement is the calcium sulfate source present, i.e.  
491 CX contains mainly anhydrite whereas ANL contains mainly gypsum (see Table 1). The  
492 difference in the amount of ettringite formed in both cement pastes might be related to the  
493 differences in the dissolution of the calcium sulfates i.e. enhanced dissolution of anhydrite  
494 compared to gypsum in the presence of LSs might have led to a higher amount of ettringite  
495 formed. In order to verify this, the interaction between the LSs and gypsum, hemihydrate and  
496 anhydrite was investigated. Adsorption isotherms were measured for anhydrite ( $\text{CaSO}_4$ ),  
497 hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The samples had water-to-powder  
498 ratio 1.0 and they were analysed 30 minutes after mixing. The results are displayed in Figure  
499 19 with unit a) mass % of solid and b) g LSs /  $\text{m}^2$  unhydrated surface. The isotherms of ANL  
500 for IA are also shown as reference.

501 Figure 19 a shows that the adsorption isotherms of the three different calcium sulfates reached  
502 a plateau, which corresponds to monolayer surface saturation. The influence of the surface  
503 area was eliminated by normalizing the adsorption isotherms obtained by the BET surface  
504 area of each calcium sulfate. The results shown in Figure 19 b display that the higher LSs  
505 consumption of anhydrite was due to its higher surface area. Hemihydrate still showed a LSs  
506 consumption slightly higher than gypsum and anhydrite. Even when taking into account a  
507 hypothetical 30 % error in the BET results, the trends shown in Figure 19 b did not noticeably  
508 change. The amount of LSs consumed by the calcium sulfates was, however, noticeably lower  
509 than the one of ANL cement for IA (which was similar to that of CX cement).

### 510 **3.6 ICP-MS**

511 The elemental concentration of Al, Ca, Fe, Si and S in the pore solutions extracted from ANL  
512 and CX cement pastes after 30 minutes of hydration was determined with ICP-MS. The

513 cement pastes contained 0.8 and 1.5 mass % of binder LSs added either with IA and DA.  
514 Additionally, a reference sample without LSs was measured. Moreover, the content in Al, Ca,  
515 Fe, Si and S was also measured for two LSs solutions dissolved in artificial pore water at  
516 concentrations corresponding to those used in cement pastes (see Table 8). The artificial pore  
517 water composition is described in paragraph 2.1. The results from ICP-MS are shown in  
518 Figure 20 and reported in Table 8.

519 The samples mixed with DA showed an increase in Al, Fe and Si concentration dissolved in  
520 the pore solution as the LSs dosage increased. The increase was considerably larger for ANL  
521 cement than for CX cement. Only minor increases were measured for the samples mixed with  
522 IA. Moreover, except for CX cement for DA, the concentration of S and Ca appeared to be  
523 rather constant with increasing LSs dosage, in spite of the increased amount of these elements  
524 added by the increasing amount of LSs.

525 In order to investigate the effect of increasing LSs dosages on the solubility of the sulfates  
526 present in the cement pastes, the elemental concentration of Ca and S in the pore solution  
527 extracted from anhydrite, hemihydrate, and gypsum slurries after 30 minutes of hydration was  
528 determined with ICP-MS. The LSs dosages tested were 0.2, 0.4, 0.8 and 1.5 mass % of binder  
529 LSs added with IA. Additionally, a reference sample without LSs was measured. Moreover,  
530 the content in Ca and S was also measured for two LSs solutions dissolved in artificial pore  
531 water (see Table 9). The artificial pore water composition is described in paragraph 2.1. The  
532 results from ICP-MS are shown in Figure 21 and reported in Table 9.

533 The results, shown in Figure 21, highlight that, for LSs dosages between 0 and around 0.4  
534 mass % of binder LSs, the trend of the content in Ca and S deviates from the one observed for  
535 higher LSs dosages. As shown by the isotherms in Figure 19, with LSs dosages under about  
536 0.4 mass % of binder, all the samples were in a highly dynamic stage and far from reaching a



537 constant level of surface adsorption. For this reason, the authors decided to focus on the  
538 values of Ca and S concentrations obtained for LSs dosages higher than about 0.4 mass % of  
539 binder. The content in Ca and S was found to be nearly independent of the LSs dosage for  
540 anhydrite and hemihydrate, while for gypsum it increased slightly as the LSs dosage  
541 increased. However, the increase was less than the Ca and S provided by the additional LSs.

### 542 **3.7 TGA after 28 days of hydration**

543 The effect of increasing the LSs dosage on the hydrates formed in hardened cement paste  
544 were investigated with TGA. The analysis was performed on ANL and CX cement pastes  
545 after 28 days of sealed curing at 20 °C containing different dosages of LSs both for IA and  
546 DA. A reference sample of neat ANL and CX without LSs was also measured. The hydration  
547 of the tested samples was stopped after 28 days with the solvent exchange procedure with  
548 isopropanol and petroleum ether, as described in paragraph 2.3.2. The results are displayed in  
549 Figure 22.

550 The peak at about 125 °C and the smaller one at 270 °C indicate the presence of AFt. The  
551 peak around 170 °C in this case represents most likely the decomposition of AFm, since it can  
552 be expected that, after 28 days of hydration, the sulfates are depleted. The peak around 480 °C  
553 shows the decomposition of portlandite (CH). Note that C-S-H loses water over the entire  
554 temperature range from 50 to 600 °C, with a main weight loss coinciding with the first  
555 ettringite peak just above 100 °C. The peaks over 600 °C represent the decomposition of  
556 carbonates (CC). These can be attributed to the decomposition of limestone included in the  
557 used cements and, for the samples containing LSs, to the decomposition of LSs.

558 The peaks corresponding to ettringite and to, most likely, AFm strongly overlapped for most  
559 samples. It was therefore difficult to quantify the amount of these phases. Hence it was  
560 decided to present the results in terms of mass loss % of the mass of dry binder in different

561 temperature intervals, as described in paragraph 2.3.3. The results are shown in Figure 23 and  
562 summarized in Table 10.

563 From the results shown in Figure 23 and reported in Table 10, it can be observed that,  
564 variations in the LSs dosage and time of addition (IA vs. DA), in general, led to little or no  
565 differences in mass loss % in the range comprising the AFt decomposition. For IA, there is an  
566 indication that the increase in LSs dosage for both cements led to a slight increase in the mass  
567 loss measured in interval 1 (AFt, AFm, C-S-H). As expected, the mass loss due to the  
568 decomposition of carbonates increased when more LSs was present in the mix. For ANL  
569 cement, the DA of 1.5 mass % of binder LSs caused the cement not to harden even after 28  
570 days of hydration. For this reason the data of this sample is not showed in Figure 23 and is  
571 reported in brackets in Table 10.

## 572 **4 DISCUSSION**

### 573 **4.1 Effect of LSs on ettringite formation in fresh cement paste**

#### 574 **4.1.1 Ettringite amount**

575 As displayed in Figure 1 and Figure 3, when LSs was added to the cement pastes with IA, a  
576 higher amount of ettringite was formed after 30 minutes in both cements compared to the  
577 sample without LSs, up to a threshold LSs dosage of 1.5 mass % of binder. With equal LSs  
578 dosage, a larger amount of ettringite is observed in CX cement paste compared to ANL  
579 cement paste, which might have been influenced by the larger amount of C<sub>3</sub>A and the higher  
580 fineness of CX cement compared to ANL cement.

581 A higher amount of ettringite crystals in CX cement paste when LSs was added with IA could  
582 also be observed with SEM, as shown in Figure 9 and Figure 10. The ettringite morphology  
583 will be discussed more in detail in paragraph 4.1.2.

584 With 1.5 mass % of binder LSs added with IA, the amount of ettringite calculated according  
585 to Equation 4 was about 8 and 14 mass % of the dry weight of cement for ANL and CX  
586 cement pastes, respectively, after 30 minutes of hydration. These amounts of ettringite appear  
587 feasible when compared to other references in literature [21, 34], taking into account possible  
588 differences due to the different materials used and time of analysis.

589 Theoretically, the maximum amount of ettringite that can form in a cementitious system is  
590 limited either by the amount of  $\text{Al}_2\text{O}_3$  or by the amount of  $\text{SO}_3$  available. The amount of  
591 ettringite that theoretically can form can be calculated with the following formulas, where  $M_m$   
592 is the molar mass:

$$593 \quad \text{Amount of AFt} = \text{Al}_2\text{O}_3 \text{ amount} \cdot \frac{M_m(\text{AFt})}{M_m(\text{Al}_2\text{O}_3)} \quad (5)$$

$$594 \quad \text{Amount of AFt} = \text{SO}_3 \text{ amount} \cdot \frac{M_m(\text{AFt})}{M_m(\text{SO}_3)} \quad (6)$$

595 Knowing the amount of  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$  available, the theoretical amount of ettringite was  
596 calculated. This amount was then compared to the amount of ettringite measured with TGA.

597 The  $\text{Al}_2\text{O}_3$  amount was calculated only considering the aluminates contained in  $\text{C}_3\text{A}$ , since it  
598 was assumed that  $\text{C}_4\text{AF}$  only slightly reacted after 30 minutes of hydration. This resulted in  
599 0.8 and 2.7 mass %  $\text{Al}_2\text{O}_3$  in ANL and CX cement, respectively. The maximum amount of  
600 ettringite that could have formed with this amount of  $\text{Al}_2\text{O}_3$  is 11 and 35 mass % of solid,  
601 respectively. These values are higher than those measured with TGA (8 and 14 mass % of  
602 solid for ANL and CX cement, respectively), therefore the alumina content appears not to be a  
603 limiting factor for the formation of ettringite.

604 The amount of  $\text{SO}_3$  present in the calcium sulphates, as measured with XRD Rietveld, was 2.0  
605 and 3.2 mass % of solid in ANL and CX cements, respectively. The maximum amount of  
606 ettringite that could have formed with this amount of  $\text{SO}_3$  is 11 and 18 mass % of solid,

607 respectively. When these values are compared with the amount of ettringite formed in the  
608 system as measured with TGA (8 and 14 mass % of solid for ANL and CX cement,  
609 respectively), it can be noticed that neither the  $\text{SO}_3$  content appears to be a limiting factor for  
610 the formation of ettringite.

611 Finally, the LSs molecule contains sulfonate groups, which might replace the sulfates and  
612 enter in the ettringite structure. Indeed, the possible replacement of the sulfates coming from  
613 the calcium sulfates with the sulfonate groups contained in the LSs molecule, forming  
614 intercalated calcium aluminate hydrates, was highlighted by Stöber and Pöllmann [35, 36]. In  
615 the present paper, the highest amount of ettringite was formed in CX cement paste with 1.5  
616 mass % of binder LSs for IA. This amount was found to be in the same range as the calculated  
617 amount of ettringite based on the amount of available sulfates considering that not all the  
618 sulfates were consumed after 30 minutes of hydration (14% vs. 20%). In addition, the  
619 inclusion of elements or molecules in the ettringite structure would have most likely caused a  
620 shift in the peaks representing ettringite in the XRD spectrum, which was not observed in the  
621 samples analysed. Therefore, the intercalation of the sulfonate groups of the LSs appeared to  
622 be a minor mechanism, if present at all.

623 In conclusion, the amount of ettringite measured by TGA was large, but feasible when  
624 compared with literature. In the sample where the largest amount of ettringite formed, enough  
625 aluminates and sulfates were available to form the entire amount of ettringite. Therefore,  
626 mechanisms such as intercalation of sulfonate groups from the LSs molecule in the ettringite  
627 structure seemed minor, if present at all.

#### 628 **4.1.2 Ettringite morphology**

629 ANL and CX cement paste with 1.5 mass % of binder LSs added either with IA or with DA  
630 where hydration was stopped after 30 minutes were studied with SEM in order to investigate

631 possible changes in hydrates morphology caused by the addition of LSs. The results were  
632 compared to those obtained for pastes of the two cements without LSs. After 30 minutes of  
633 hydration, ANL and CX cement grains appeared to be partially covered by crystals, identified  
634 as ettringite with EDS (Figure 13 and Figure 14). The degree of coverage and the crystals'  
635 size varied according to the presence of LSs and to its addition method: considerably fewer of  
636 the smaller crystals could be observed in the samples of cement paste where no LSs was  
637 added and in those where LSs was added with DA, compared to those where LSs added with  
638 IA.

639 Several studies in literature found that plasticizers can change the morphology of ettringite  
640 from the typical needle-like structure, to a more round or cubic one [9-12]. In partial  
641 disagreement, Kerui et al. [13] found that the shape of the ettringite crystals was changed  
642 from numerous small needles to few large needle-like crystals. Indeed, as observed by Shi et  
643 al. [37] and hypothesized by Dalas et al. [15], superplasticizers can inhibit ettringite growth  
644 by adsorbing on their surface. The crystal shape will therefore depend on the preferred surface  
645 for adsorption. In the present study, the ettringite is visually observed in a real cement system  
646 and not as a pure synthesized phase. The crystals observed for the two cements appeared of  
647 different size and shape: cubic with size between 0.1 and 0.2  $\mu\text{m}$  for ANL cement (Figure 9),  
648 and with cuboidal shape with length between 0.2 and 0.4  $\mu\text{m}$  for CX cement (aspect-ratio  
649 varying between 1.5:1 and 4:1) (Figure 10).

650 When comparing samples of the same cement containing no LSs or 1.5 mass % of binder LSs  
651 added with IA or with DA after 30 minutes of hydration, it can be noticed that the crystals of  
652 ettringite displayed a similar cubic or cuboidal shape for all samples. It can be therefore  
653 concluded that, after 30 minutes of hydration, the addition of LSs did not lead to changes in  
654 ettringite shape for the cements analysed in this study.

655 Finally, ANL and CX cement paste without LSs were investigated with SEM after 6 hours of  
656 hydration. The aim was to verify whether the ettringite crystals formed by pastes of the two  
657 cements without the LSs at a later stage of hydration displayed a needle-like shape. The time  
658 of analysis corresponded to a time right before the main hydration peak determined by  
659 isothermal calorimetry, as shown in a previous paper [5], when the ettringite crystals were  
660 expected to be fully developed. The results (Figure 15 and Figure 16) displayed no major  
661 difference in ettringite morphology between the samples with 1.5 mass % of binder LSs added  
662 with IA hydrated for 30 minutes and those without LSs hydrated for 6 hours, and between the  
663 two cements. Indeed, in both systems the ettringite crystals appeared with a compact and  
664 cuboidal shape instead of the expected needle-like shape.

665 In conclusion, for the system analysed in this paper, no changes in the morphology of the  
666 ettringite crystals appeared to be caused by the LSs addition. These results do not fully agree  
667 with what found by other studies in literature [9-13]. This might be connected to the analytical  
668 technique used and to potential difference in the behaviour of synthetic ettringite crystals and  
669 ettringite in a hydrating cement paste.

#### 670 **4.2 Effect of LSs on the solubility of cement phases and calcium sulfates**

671 The LSs used for the experiments reported in this paper is particularly rich in Ca and S (see  
672 Table 8).

673 Increasing dosages of LSs led to an increased concentration of Al, Fe, and Si in the pore  
674 solution of ANL and CX cement pastes (Figure 21), as shown from the ICP-MS results (Table  
675 8). The concentration of these elements was particularly pronounced for DA. For DA, the LSs  
676 addition did not change the amount nor the type of hydrates formed by the cement pastes. The  
677 higher concentration of Al, Fe and Si relates to the dissolution of the cement phases and  
678 potentially to complexation of these elements by LSs, as mentioned by Caruso et al. [38].

679 The higher amount of ettringite formed in the CX cement might be due to a higher dissolution  
680 of the anhydrite present in CX compared to the dissolution of gypsum present in ANL. In  
681 order to verify this or rule this out, the content in Ca and S of the pore solution extracted from  
682 gypsum, hemihydrate and anhydrite slurries containing increasing LSs dosages was measured.  
683 For LSs dosages higher than about 0.4 mass % of binder, the LSs adsorption by all the  
684 calcium sulfates was constant and reached a plateau, as shown by Figure 19. Therefore, when  
685 more LSs was added in the solution, one would expect the concentration in Ca and S to  
686 increase, as LSs is rich in both elements. However, as the LSs dosage increased, the calcium  
687 sulfates showed a different behaviour: the content in Ca and S was found to be nearly constant  
688 in the pore solutions extracted from anhydrite and hemihydrate, while it increased in the pore  
689 solution of gypsum. However, the increase in Ca and S content was lower than it would be  
690 expected from the added LSs (Table 9). These results indicate that the LSs might even  
691 suppress the dissolution of gypsum, anhydrite and hemihydrate after 30 minutes of hydration.

692 In conclusion, for IA, the dissolution of gypsum, hemihydrate and anhydrite was found not to  
693 be enhanced upon LSs addition. Therefore, it appears that the large increase in ettringite  
694 formed was not due to an increased dissolution of the calcium sulfates.

695 The only remaining option to explain the enhanced ettringite formation is changes in the  $C_3A$   
696 reaction. When LSs is added with DA, the mixing water interacts with the clinker surface and  
697 slows down the reaction of the clinker phases during the dormant period. The SEM  
698 investigation of the samples where LSs was added with DA showed clinker particles with  
699 many intact surfaces and very few signs of dissolution. One could imagine the formation of a  
700 thin hydrate layer on the clinker surface which prevents further reaction. However when LSs  
701 is added with the mixing water (IA), this hypothetical protective layer is disrupted and the  
702 reaction of the  $C_3A$  is enhanced resulting in additional ettringite formation. Craters after  $C_3A$   
703 parts of the clinker grains were observed by SEM for the samples where the LSs was added

704 with IA, indicating accelerated reaction. In conclusion the enhanced ettringite formation is  
705 due to accelerated  $C_3A$  reaction caused by the LSs in the mixing water.

#### 706 **4.3 On the surface area and LSs consumption by cement paste**

707 In a previous article [18], the increase in the amount of ettringite formed in cement paste after  
708 30 minutes of hydration was found to correspond to an increase in the hydrated surface area,  
709 as shown in Figure 24. The increase in surface area was larger when the LSs was mixed with  
710 IA and for CX cement.

711 As shown in Figure 1 and in Figure 3, a difference in amount of ettringite formed was found  
712 between IA and DA with the same LSs dosage for pastes of both cements. This led to a  
713 difference in surface area between IA and DA, especially for CX cement (Figure 24). This  
714 caused, in turn, a difference in LSs consumption for monolayer adsorption between IA and  
715 DA (Figure 18 a).

716 The amount of LSs that could potentially adsorb in a monolayer on the additional amount of  
717 ettringite formed for IA was calculated. The following assumptions were made:

- 718 - The ettringite is characterized by a density of  $1778 \text{ kg/m}^3$  [39], a cubic shape, and an  
719 average size of  $0.15 \text{ }\mu\text{m}$  for ANL cement and  $0.3 \text{ }\mu\text{m}$  for CX cement;
- 720 - The entire ettringite surface area is available for polymer adsorption;
- 721 - The molecular footprint of LSs is  $27.5 \text{ nm}^2$  for both cements. This value is an average  
722 of the molecular footprints of the two cements, as calculated in a previous paper [18]  
723 based on the amount of LSs adsorbed on the cement surface at the plateau value in the  
724 adsorption isotherms.

725 The calculated amount of consumed LSs was compared to the difference in consumed LSs  
726 amount experimentally measured between the sample mixed with IA and the one mixed with  
727 DA at the LSs dosages of 0.8 and 1.5 mass % of binder (Table 11). The calculated ettringite



728 amounts were found to be lower than the measured ones for all the samples. However, for CX  
729 cement, the calculated amount was relatively close to the measured amount, also taking into  
730 account the error connected to the approximations made.

731 These results confirm that, for CX cement, the difference in LSs consumption between IA and  
732 DA appears to mainly be due to the additional surface available for adsorption given by the  
733 increased ettringite amount formed for IA. On the contrary, for ANL cement, the difference in  
734 LSs consumption between IA and DA cannot be due solely to the additional surface offered  
735 by the increased ettringite formed for IA.

#### 736 **4.4 Impact of the increased amount of ettringite on setting time and rheology of** 737 **cement paste**

738 As investigated in a previous paper [5], the increased formation of ettringite seems to have an  
739 impact on the properties of fresh cement paste, in particular on setting time and rheology. The  
740 following aspects will be separately discussed in the following paragraphs.

##### 741 **4.4.1 On the setting time of cement paste**

742 In a previous paper [5] it was found that the setting retardation was directly correlated to the  
743 amount of free LSs in the pore solution. In the samples which formed the higher amounts of  
744 ettringite (IA), the increased LSs adsorption caused by the additional surface area reduced the  
745 amount of free LSs in the pore solution compared to DA for the same LSs dosage. This was  
746 reflected in a lower setting retardation for IA compared to DA for the same LSs dosage. In  
747 addition, the retardation appeared to be less sensitive to small variations in dosing for IA than  
748 for DA, i.e. the system was more robust for IA. Small variations in the dosing of the LSs with  
749 DA led to large differences in retardation: the same LSs dosage of 0.4 mass % of binder  
750 caused an increase in setting retardation of 21 and 11 hours for ANL and CX cement  
751 respectively, when compared to the setting retardation caused by the same LSs dosage added

752 with IA. This severe delay of setting can be a source of incompatibility between cement and  
753 plasticizer, as described by Marchon and Flatt [40].

#### 754 **4.4.2 On the rheology of cement paste**

755 The presence of numerous ettringite crystals on the surface of unhydrated cement grains, as  
756 observed in the present paper, could change the workability of the cement paste. The  
757 increased formation of ettringite led to early stiffening of the cement paste, reduced  
758 workability until potential rapid set, as measured in a previous paper [5] for CX cement with  
759 1.5 mass % of binder LSs added with IA. This is a form of incompatibility between cement  
760 and plasticizer, as described by Marchon and Flatt [40].

#### 761 **4.5 Effect of LSs on the hydrates of hardened cement paste**

762 In light of the differences in amount of ettringite in fresh cement paste caused by the addition  
763 of LSs, the effect of LSs on the hydrates of 28 days-old cement were also investigated.

764 From the TGA results shown in Figure 23 and reported in Table 10, it can be observed that, in  
765 all intervals, few or no differences in mass loss could be observed; neither between samples  
766 containing different LSs amounts, nor between the samples prepared with IA and those  
767 prepared with DA. The most noticeable change, even though still of limited entity in a general  
768 scale, was observed for IA, where the increase in LSs dosage led for both cements to a slight  
769 increase in the mass loss measured in interval 1 (AFt, AFm, C-S-H). In particular, the  
770 intensity of the peak corresponding to the decomposition of ettringite was found to increase  
771 slightly with the LSs dosage, especially for ANL cement.

772 In conclusion, the addition of LSs and its addition time seemed not to play a major role in  
773 type and amount of hydrates formed in ANL and CX cement pastes after 28 days of  
774 hydration. For DA, the addition of a high LSs dosage (compared to the dosages normally used

775 in practice), was found to cause lack of hardening in ANL cement even after 28 days of  
776 hydration.

## 777 **5 CONCLUSIONS**

778 The aim of this paper was to investigate the effect of varying dosages of a softwood calcium  
779 lignosulfonate (LSs) on the amount and morphology of ettringite formed in Portland cement  
780 paste. Two Portland cements, CX and ANL, mainly differing in surface area and C<sub>3</sub>A content  
781 were chosen; CX had higher surface area and C<sub>3</sub>A content than ANL. The influence of two  
782 different LSs addition methods was investigated. The LSs was either added immediately to  
783 the cement with the mixing water (IA), or after 10 minutes of hydration (DA). The following  
784 conclusions are drawn:

785 Immediate addition (IA) of LSs to the cement pastes led to a considerable increase in the  
786 amount of ettringite formed compared to pastes of the same cements without LSs. Delayed  
787 addition (DA) of LSs did not affect the amount of ettringite formed.

788 For the systems analyzed in this paper, no changes in the morphology of the ettringite crystals  
789 appeared to be caused by LSs addition.

790 SEM imaging allowed observing the finely dispersed ettringite crystals in the cement paste. In  
791 case of immediate addition (IA) of LSs, the ettringite shape was cubic with size between 0.1  
792 and 0.2 μm for ANL cement, and cuboidal with length between 0.2 and 0.4 μm for CX  
793 cement (aspect-ratio varying between 1.5:1 and 4:1).

794 The study of pure calcium sulfate systems indicated that the large amount of ettringite formed  
795 upon LSs addition with IA was not due to an increased dissolution of the calcium sulfates.  
796 The increased amount of ettringite is due to enhanced C<sub>3</sub>A reaction taking place when LSs is  
797 added immediately with the mixing water (IA).

798 The presence of numerous small ettringite crystals on the surface of unhydrated cement grains  
799 upon LSs addition with IA led to an increase in plasticizer adsorption. This renders the system  
800 more robust, i.e. less sensitive to variations in dosing, regarding retardation and slump loss  
801 compared to DA. However, the large amount of crystals might potentially cause  
802 incompatibility problems due to early stiffening.

803 After 28 days of hydration, no noticeable effect of LSs addition and of its addition time on the  
804 amount of hydrates formed was observed, despite the large differences in the amount of  
805 ettringite formed after 30 minutes.

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910

911 Notation

912	ANL	Anlegg cement (CEM I 52.5 N)
913	CX	Cemex cement (CEM I 52.5 R)
914	$\underline{\text{C}}\text{SH}_x$	Calcium sulfate hydrates
915	$\underline{\text{C}}$	Carbonates (contained in $\text{CaCO}_3$ and in the LSs)
916	DA	delayed addition of plasticizer (10 min)
917	IA	immediate addition of plasticizer
918	LSs	softwood low-sugar Ca-lignosulfonate
919	OPC	ordinary Portland cement

920	w/b	water-binder ratio	
921	-COOH	carboxyl group	
922	$\phi$ -OH	phenolic OH-group	
923			
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1008	It has to be noticed that the crystals turned to more rounded shapes during the scanning due	
1009	to dehydration. The curve representing Si was scaled down by multiplying it by 0.5 for better	
1010	graphical representation. ....	57
1011	Figure 15 – SEM images of ANL cement grains without LSs after 6 hours of hydration. Width	
1012	of micrograph: left) 6 $\mu\text{m}$ , and right) 2.5 $\mu\text{m}$ . The identification of the hydrates (right) was	
1013	based on visual appearance and comparison to literature, e.g.[33] . ....	57
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1015	micrograph: left) 4 $\mu\text{m}$ , and right) 1.6 $\mu\text{m}$ . The identification of the hydrates was based on	
1016	visual appearance and comparison to literature, e.g. [33].....	58
1017	Figure 17 - Surface area of pastes of ANL and CX cements after 30 minutes of hydration vs.	
1018	LSs dosage added (mass % of binder) both for IA and DA, after [18]. The specific surface	
1019	area comprehends the surface area of unhydrated cement grains and hydrates.....	58
1020	Figure 18 – Amount of consumed LSs at 30 min. hydration vs. LSs dosage in neat ANL and	
1021	CX cements for IA and DA, after [18]. The results are calculated as a) mass % of binder and	
1022	as b) unit of surface area available for adsorption of hydrated pastes of ANL and CX cements	
1023	.....	59
1024	Figure 19 - Amount of consumed LSs at 30 min. hydration vs. LSs dosage added to calcium	
1025	sulfate anhydrous (anh.), hemihydrate (hem ) and dihydrate (gyp.) for IA. The results are	
1026	calculated as a) mass % of powder, and b) g LSs/m <sup>2</sup> unhydrated surface.....	59
1027	Figure 20 – Concentration of Al, Fe, Ca, Si, and S in the pore solution (mmol/l) expressed in	
1028	logarithmic scale vs. total LSs added (mass % of binder) to a) ANL and b) CX cement pastes	
1029	analysed after 30 minutes of hydration both for IA and DA. The legend in figure b) also	
1030	applies to figure a). ....	60
1031	Figure 21 - Concentration of Ca and S in the pore solution (mmol/l) expressed in logarithmic	
1032	scale vs. total LSs added (mass % of powder) with IA to calcium sulfate anhydrous,	
1033	hemihydrate, and dihydrate, analyzed after 30 minutes of hydration.....	60
1034	Figure 22 - TG and DTG curves of a) ANL and b) CX cement paste without LSs or with 0.8,	
1035	1.5, 2.0, 3.0 mass % of binder LSs mixed with IA and DA, for which hydration was stopped	
1036	after 28 days. The peaks corresponding to the decomposition of AFt, AFm, portlandite (CH)	
1037	and carbonates (C) are marked in the figures. ....	61
1038	Figure 23 – Mass loss (% of initial weight) of a) AFt, calcium sulfate hydrates (CSH <sub>x</sub> ), AFm,	
1039	C-S-H; b) CH; c) carbonates (C)vs. LSs dosage (mass % of binder) for ANL and CX cements	

1040 *with increasing amount of LSs added with IA and with DA. NB. The scale of the y-axis of*  
 1041 *figure a) is different than the one of the other figures. .... 61*  
 1042 *Figure 24 - Correlation between the calculated amount of ettringite\* and the particle surface*  
 1043 *area of solids in pastes of the two cements when LSs was added immediately with the mixing*  
 1044 *water (IA). \*: Amount of ettringite calculated considering the mass loss in the whole interval*  
 1045 *1 (50 - ca. 300 °C) ..... 62*  
 1046

1047

1048 Tables

1049 Table 1 – *Main phases in cement ANL and CX from XRD-Rietveld analysis <sup>a</sup>: results*  
 1050 *obtained with TGA analysis*

<b>Phase composition (mass</b>	<b>ANL</b>	<b>CX</b>
<b>% of powder)</b>		
<b>Alite</b>	60.5	54.3
<b>Belite</b>	14.2	18.8
<b>Aluminate cubic</b>	1.3	4.7
<b>Aluminate orthorhombic</b>	0.9	2.4
<b>Ferrite</b>	14.0	6.5
<b>Periclase</b>	0.4	1.1
<b>Quartz</b>	0.3	-
<b>Calcite</b>	3.2/ 3.8 <sup>a</sup>	3.6/ 3.7 <sup>a</sup>
<b>Portlandite</b>	1.1/ 1.4 <sup>a</sup>	2.6/ 2.5 <sup>a</sup>
<b>Anhydrite</b>	-	2.1

<b>Hemihydrate</b>	2.6	1.8
<b>Gypsum</b>	1.0	-
<b>Arcanite</b>		0.6
<b>Aphthitalite</b>	0.4	0.7
<b>Thenardite</b>	-	0.8

1051

1052 Table 2 – *Chemical composition of the cements given by the producers*

<b>Chemical compound</b>	<b>ANL</b>	<b>CX</b>
<b>(mass % of powder)</b>		
<b>CaO</b>	62.7	64.0
<b>SiO<sub>2</sub></b>	20.6	20.0
<b>Al<sub>2</sub>O<sub>3</sub></b>	4.4	4.6
<b>Fe<sub>2</sub>O<sub>3</sub></b>	3.5	2.6
<b>SO<sub>3</sub></b>	3.3	3.6
<b>MgO</b>	1.6	2.4
<b>K<sub>2</sub>O</b>	0.4	1.0
<b>Na<sub>2</sub>O</b>	0.3	0.2
<b>TiO<sub>2</sub></b>	0.2	0.2
<b>P<sub>2</sub>O<sub>5</sub></b>	0.2	0.2
<b>LOI (%) 1000 °C</b>	1.6	1.7
<b>Sum</b>	97.2	98.9

1053

1054 Table 3 - *Physical properties of the materials used*

	ANL	CX	Anhydrite	Hemihydrate	Gypsum
<b>Surface area (BET)</b> (m <sup>2</sup> /kg)	890	1330	3000	550	580
<b>Blaine surface</b> (m <sup>2</sup> /kg)	360	540			
<b>Density</b> (g/cm <sup>3</sup> )	3.1	3.1			
<b>d<sub>10</sub></b> (μm)	2.0	2.0			
<b>d<sub>50</sub></b> (μm)	12.0	10.0			
<b>d<sub>90</sub></b> (μm)	34.0	26.0			

1055

1056 Table 4 - *Chemical and physical properties of LSs*

<b>Mw</b>	g/mol	29000
<b>Mn</b>	g/mol	2100
<b>Organic S</b> (∞ SO <sub>3</sub> )	mass %	4.6
<b>SO<sub>4</sub><sup>2-</sup></b>	mass %	0.9
<b>Ca<sup>2+</sup></b>	mass %	4.6
<b>Na<sup>+</sup></b>	mass %	0.9
<b>-COOH</b>	mass %	7.1
<b>φ-OH</b>	mass %	1.4
<b>Total sugar</b>	mass %	8.3

1057

1058 Table 5 – *Analysed samples to obtain adsorption isotherms*

Material	LSs addition	
	procedure	LSs dosage (mass % of binder)
ANL cement	IA	0.1; 0.2; 0.4; 0.6; 0.8; 1.2; 1.5; 2.0; 3.0
	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

1059 Table 6 – *Mass loss (% dry binder) of ANL and CX cements with increasing amount of LSs*  
 1060 *added with IA and DA after 30 minutes of hydration. The mass loss is calculated in three*  
 1061 *temperature intervals: 1: ettringite, calcium sulfates, possibly C-S-H; 2: CH; 3: carbonates.*  
 1062 *The sum of the mass loss in interval 1 and 2 represents the amount of bound water. \*:40-350*  
 1063 *°C for CX cement*

Cement type	LSs dosage	Addition procedure	Interval 1	Interval 2	Interval 3	Bound water
			40-300 °C *	300-500 °C	500-850 °C	40-500 °C
Mass % of dry binder						
ANL	0		2.8	0.6	2.1	3.3
	0.8		2.5	0.4	2.6	3.0
	1.5	IA	3.9	0.8	4.8	4.7
	2.0		2.5	0.6	3.9	3.1
	3.0		3.0	0.7	4.4	3.7
	0.8	DA	2.7	0.2	2.7	2.8
	1.5		2.7	0.7	3.9	3.4

<b>CX</b>	0		2.9	0.8	2.0	3.7
	0.8		4.7	0.9	3.4	5.6
	1.5	IA	6.7	1.0	4.4	7.7
	2.0		5.7	1.0	5.3	6.7
	3.0		4.9	1.0	5.8	5.8
	0.8		2.4	0.8	3.0	3.1
	1.5	DA	2.8	0.9	4.1	3.7

1064

1065 Table 7 – Summary of the elements detected with XRD in ANL and CX cement pastes with  
 1066 0/0.8/1.5 mass % of binder LSs (IA) which hydration was stopped after 30 minutes

<b>Angle 2θ</b>	<b>Element</b>	<b>Symbol in graph</b>
<b>9.1</b>	Ettringite	AFt
<b>11.6; 20.7</b>	Gypsum	G
<b>12.2; 24.3</b>	C <sub>4</sub> AF	F
<b>14.9</b>	C <sub>3</sub> S	C <sub>3</sub> S
<b>23.0</b>	CaCO <sub>3</sub> /AFt	Cc/AFt
<b>25.4</b>	Anhydrite	A

1067

1068 Table 8 - Elemental concentration of Al, Fe, Ca, Si, and S in ANL and CX cements with 0, 0.8  
 1069 or 1.5 mass % of binder LSs after 30 minutes hydration, and in two LSs solutions (mmol/L):  
 1070 the 2.0 and 3.7 % LSs solutions were used for the cement samples with 0.8 and 1.5 mass % of  
 1071 binder LSs respectively

<b>Sample</b>	<b>LSs dosage</b>	<b>Al</b>	<b>Ca</b>	<b>Fe</b>	<b>S</b>	<b>Si</b>
	Mass % of binder			Mass %		
<b>ANL IA</b>	0	0.01	24	0	77	0.09
	0.8	0.01	26	0.01	96	0.11
	1.5	0.02	45	0.07	139	0.12
<b>ANL DA</b>	0.8	1.1	38	0.55	100	0.85
	1.5	3.6	52	1.4	72	2.6
<b>CX IA</b>	0	0.01	24	0	176	0.09
	0.8	0.01	10	0.02	169	0.30
	1.5	0.01	54	0.11	141	0.36
<b>CX DA</b>	0.8	0.01	28	0.11	176	0.23
	1.5	0.79	50	0.45	193	0.56
<b>2.0 % LSs sol.</b>		0.02	18	0.02	37	0.31
<b>3.7 % LSs sol.</b>		0.03	32	0.03	66	0.27

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1076

1077 Table 9 - *Elemental concentration of Ca and S in the pore solution (mmol/L) of calcium*  
 1078 *sulfate anhydrous, hemihydrate, and dihydrate, analysed after 30 minutes of hydration, and in*  
 1079 *two LSs solutions (mmol/L) (2.0 and 3.7 %)*

<b>Sample</b>	<b>LSs dosage</b>	<b>Ca</b>	<b>S</b>
	Mass % of binder	Mass %	
<b>CaSO<sub>4</sub></b>	0	34	68
	0.2	38	55
	0.4	36	55
	0.8	30	52
	1.5	30	57
<b>CaSO<sub>4</sub>·0.5H<sub>2</sub>O</b>	0	28	74
	0.2	83	93
	0.4	75	86
	0.8	67	83
	1.5	66	85
<b>CaSO<sub>4</sub>·2H<sub>2</sub>O</b>	0	20	57
	0.2	30	44
	0.4	42	53
	0.8	63	77
	1.5	72	89



<b>2.0 % LSs sol.</b>	18	37
<b>3.7 % LSs sol.</b>	32	66

1080

1081 Table 10 - *Mass loss (% dry binder) of ANL and CX cements with increasing amount of LSs*  
 1082 *added with IA and DA after 28 days of hydration. The mass loss is calculated in three*  
 1083 *temperature intervals: 1: AFt, calcium sulfates, AFm, possibly C-S-H, other hydrates; 2: CH;*  
 1084 *3: carbonates. The sum of the mass loss in interval 1 and 2 represents the amount of bound*  
 1085 *water.*

<b>Cemen</b>	<b>LSs</b>	<b>Addition</b>	<b>Interval</b>	<b>Interval</b>	<b>Interval</b>
<b>t type</b>	<b>dosage</b>	<b>procedure</b>	<b>1</b>	<b>2</b>	<b>3</b>
			40-420 °C	420-540 °C	540-850 °C
<b>Mass % of solid</b>					
<b>ANL</b>	0		19.3	5.6	3.8
	0.8	IA	21.0	5.7	4.7
	1.5		22.1	5.7	5.3
	0.8	DA	18.0	5.3	4.0
	1.5		-	-	-
	<b>CX</b>	0		21.3	5.8
0.8		IA	21.7	5.6	5.2
1.5			22.4	5.5	5.6
0.8		DA	21.8	6.0	4.6
1.5			20.9	5.8	5.5

1086

1087

1088 Table 11 – Comparison between the amount of LSs that could potentially adsorb in a  
1089 monolayer on the additional amount of ettringite formed for IA (“calculated  $\Delta$ ”), and the  
1090 difference in consumed LSs amount experimentally measured between the sample mixed with  
1091 IA and the one mixed with DA (“measured  $\Delta$ ”)

<b>Cement</b>	<b>LSs dosage</b>	<b>Calculated <math>\Delta</math></b>	<b>Measured <math>\Delta</math></b>
		<b>consumed LSs IA- DA</b>	<b>consumed LSs IA- DA</b>
	mass % of binder	mass % of binder	mass % of binder
<b>ANL</b>	0.8	0.07	0.25
	1.5	0.17	0.72
<b>CX</b>	0.8	0.12	0.16
	1.5	0.18	n.a.

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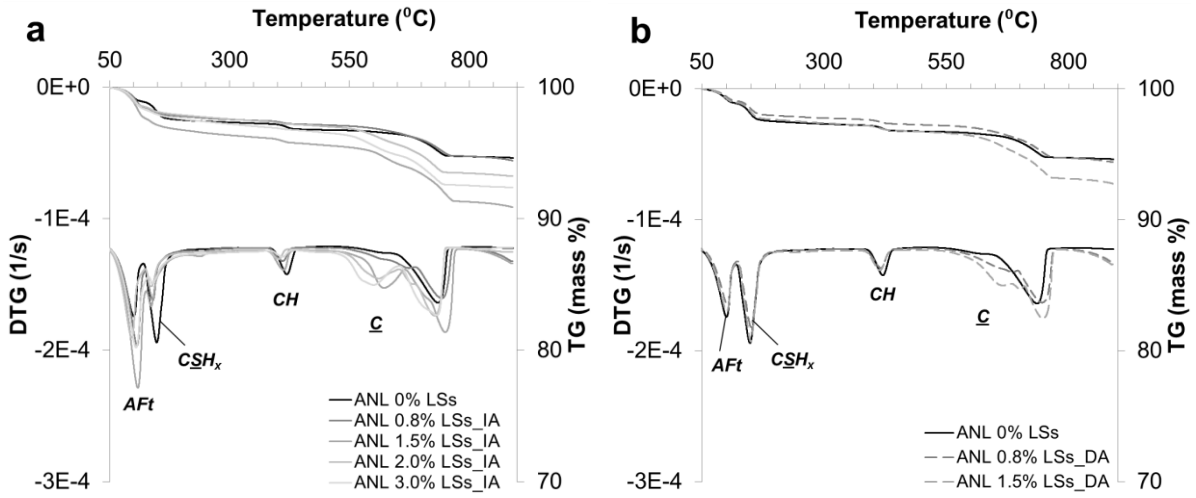
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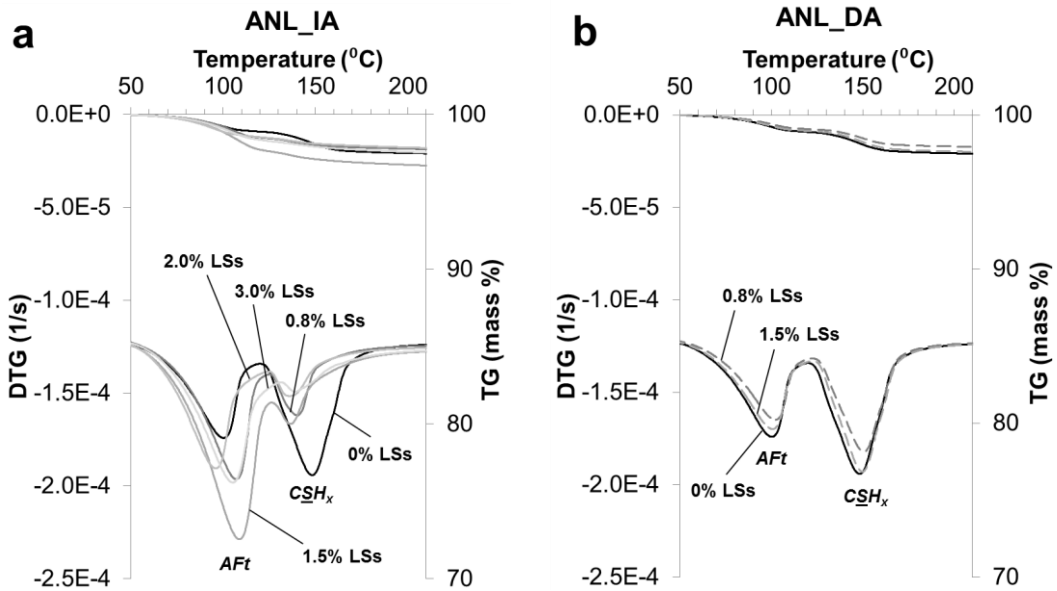
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1100 Figures



1101

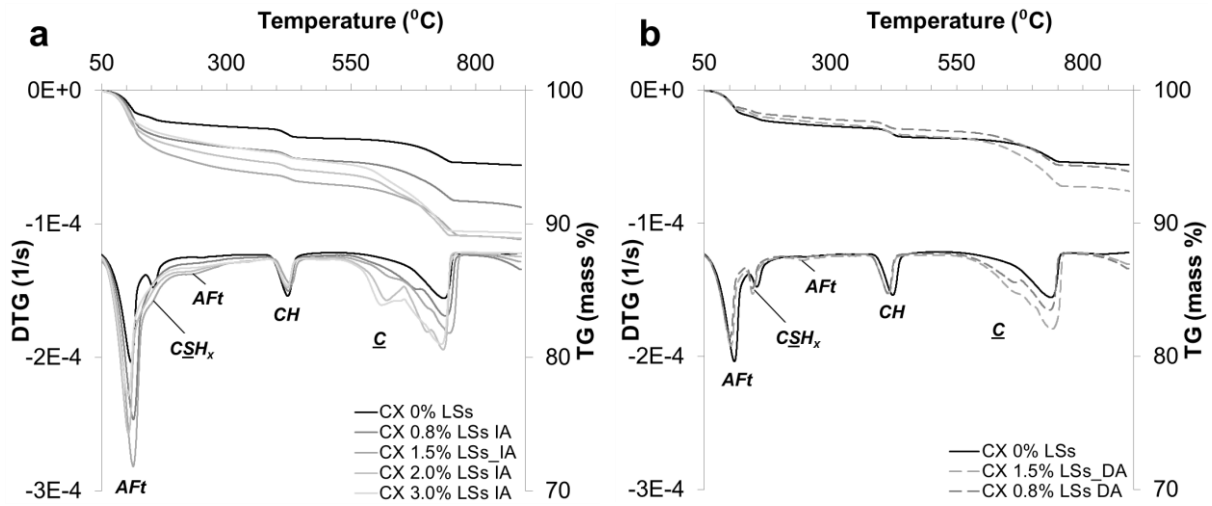
1102 Figure 1 – TG and DTG curves of ANL cement paste without LSs or a) with 0.8, 1.5, 2.0, 3.0  
1103 mass % of binder LSs mixed with IA, or b) with 0.8 and 1.5 mass % of binder LSs mixed with  
1104 DA. Hydration was stopped after 30 minutes. The peaks corresponding to the decomposition  
1105 of ettringite (AFt), calcium sulfates (CSH<sub>x</sub>), portlandite (CH) and carbonates (C) are marked  
1106 in the figures.



1107

1108 Figure 2 - TG and DTG curves of ANL cement paste without LSs or with a) 0.8, 1.5, 2.0, 3.0  
1109 mass % of binder LSs mixed with IA and b) 0.8, 1.5 mass % of binder LSs mixed with DA, for

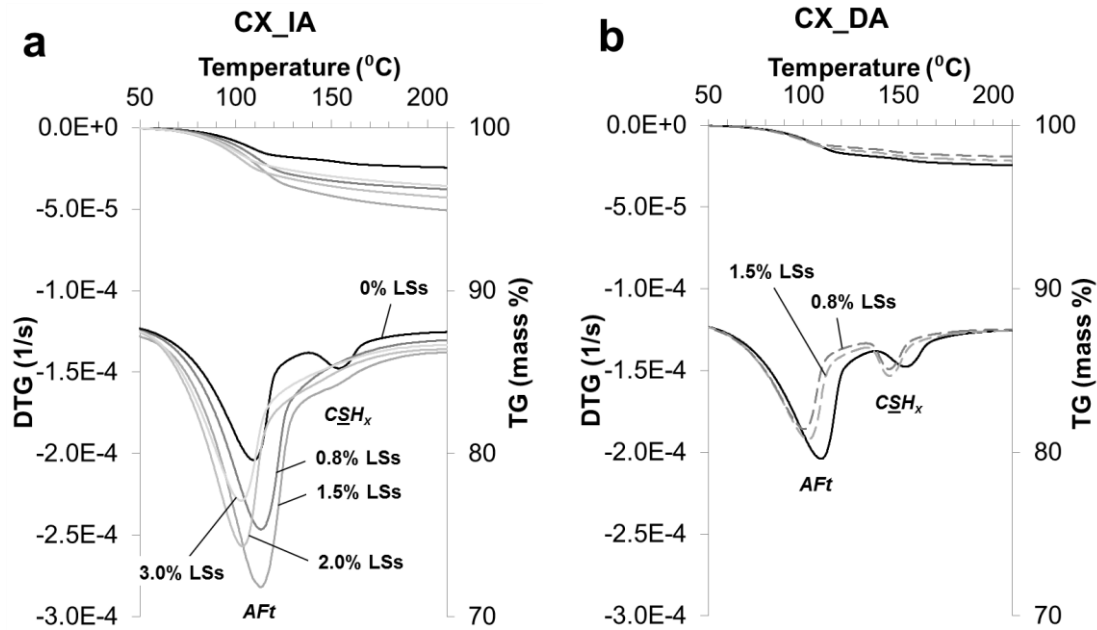
1110 which hydration was stopped after 30 minutes (Part of Figure 1; temperature range: 50-210  
 1111 °C). The peaks corresponding to the decomposition of ettringite (AFt) and calcium sulfates  
 1112 ( $CSH_x$ ) are marked in the figures.



1113

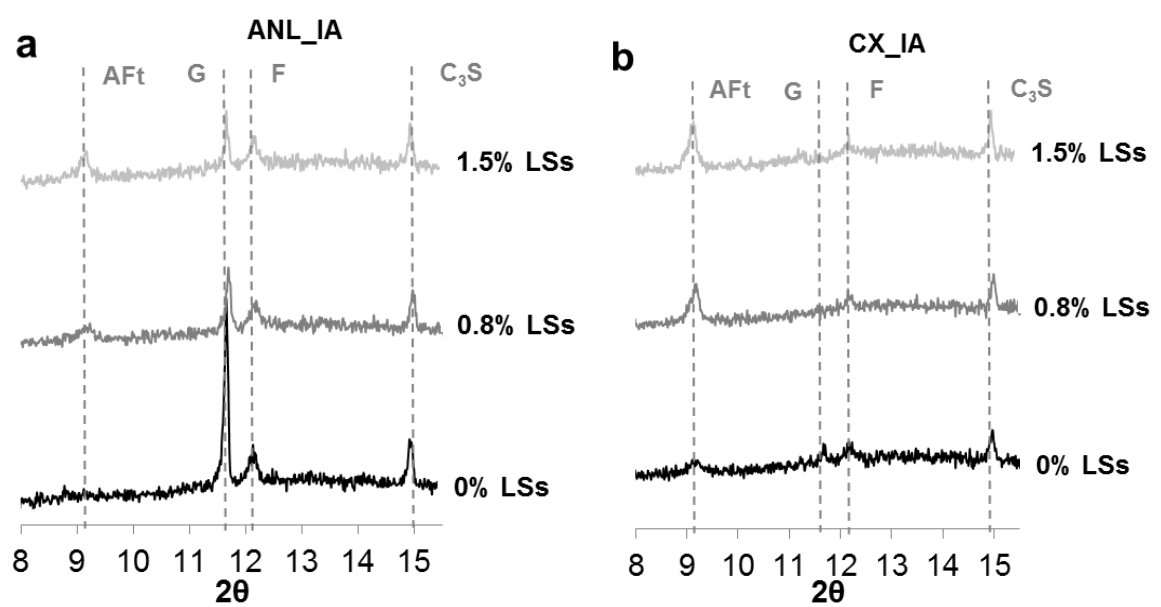
1114 Figure 3 – TG and DTG curves of CX cement paste without LSs or with 0.8, 1.5, 2.0, 3.0 mass  
 1115 % of binder LSs mixed with a) IA and b) DA, for which hydration was stopped after 30  
 1116 minutes. The peaks corresponding to the decomposition of ettringite (AFt), anhydrite,  
 1117 hemihydrate or gypsum ( $CSH_x$ ), portlandite (CH) and carbonates (C) are marked in the  
 1118 figures.

1119



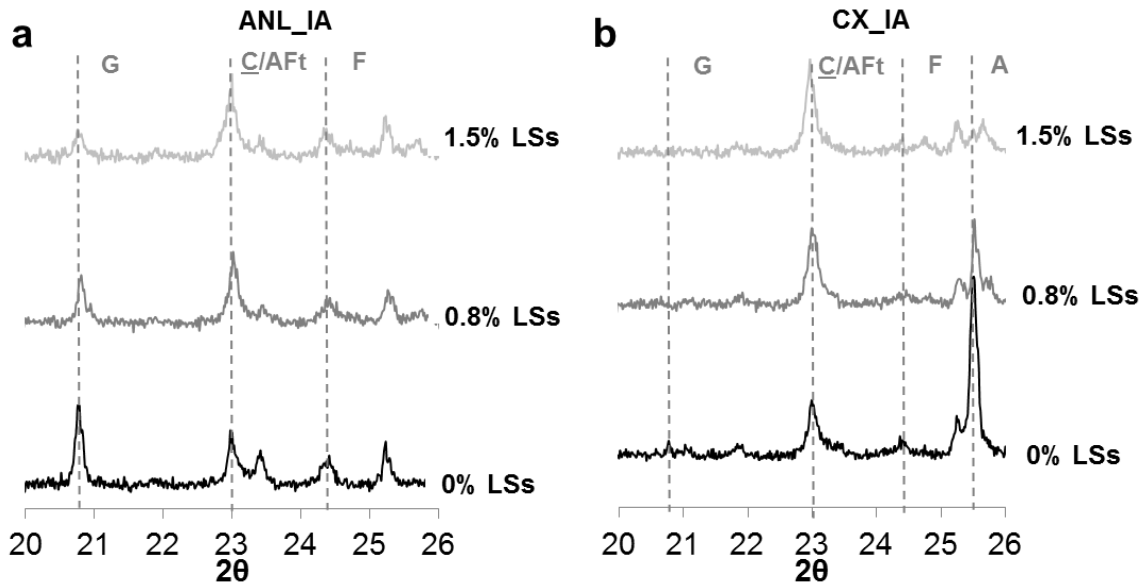
1120

1121 Figure 4 - TG and DTG curves of CX cement paste without LSs or with a) 0.8, 1.5, 2.0, 3.0  
 1122 mass % of binder LSs mixed with IA and b) 0.8, 1.5 mass % of binder LSs mixed with DA, for  
 1123 which hydration was stopped after 30 minutes (Part of Figure 3; temperature range: 50-210  
 1124 °C). The peaks corresponding to the decomposition of ettringite (AFt) and calcium sulfates  
 1125 ( $CSH_x$ ) are marked in the figures.



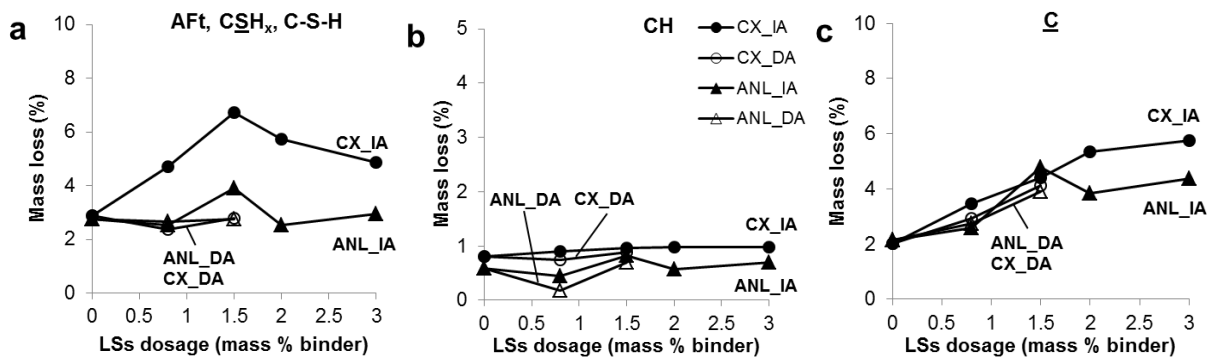
1126  
 1127

1128 Figure 5 – X-ray diffraction curves from  $2\theta = 9^\circ$  to  $15.5^\circ$  for a) ANL and b) CX cement  
 1129 pastes with 0, 0.8, 1.5 mass % of binder LSs (IA) which hydration was stopped after 30  
 minutes. Several peaks are displayed in the figures: AFt: ettringite; G: gypsum; F:  $C_4AF$ ;  $C_3S$



1130

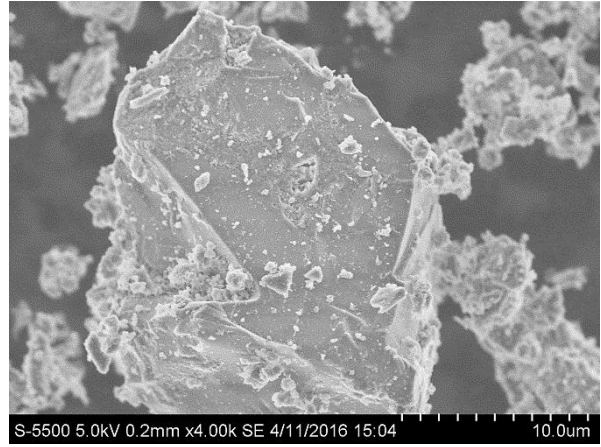
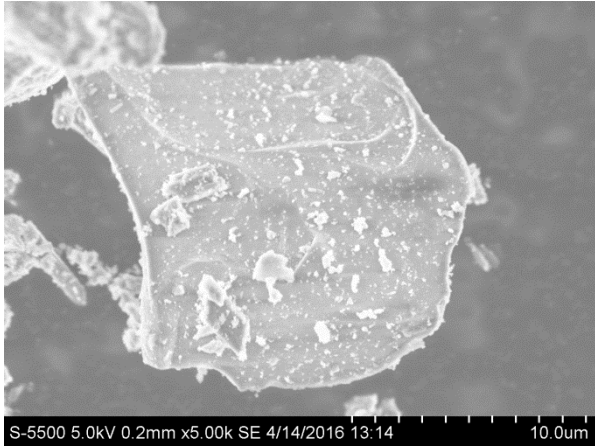
1131 Figure 6 - X-ray diffraction curves from  $2\theta = 20^\circ$  to  $26^\circ$  for a) ANL and b) CX cement pastes  
 1132 with 0, 0.8, 1.5 mass % of binder LSs (IA) which hydration was stopped after 30 minutes.  
 1133 Several peaks are displayed in the figures: G: gypsum; C: CaCO<sub>3</sub>; F: C<sub>4</sub>AF; A: anhydrite



1134

1135 Figure 7 – Mass loss (% of initial weight) due to a) ettringite (Aft), calcium sulfates (CSH<sub>x</sub>),  
 1136 possibly C-S-H; b) CH; c) carbonates (C) vs. LSs dosage (mass % of binder) for ANL and CX  
 1137 cements with increasing amount of LSs added with IA and with DA. The legend in figure b)  
 1138 also applies to figure a) and c). NB. The scale of the y-axis of figure b) is different from the  
 1139 one of the other figures.

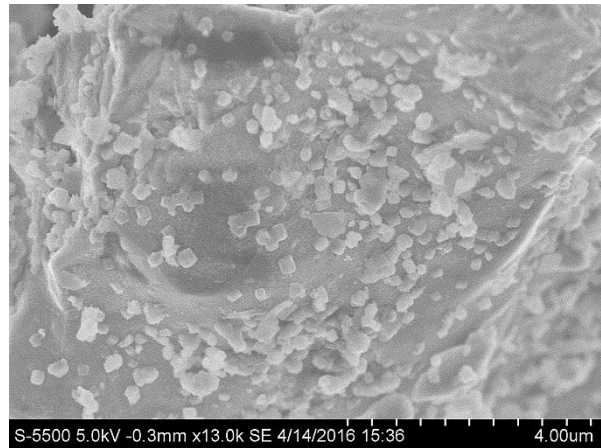
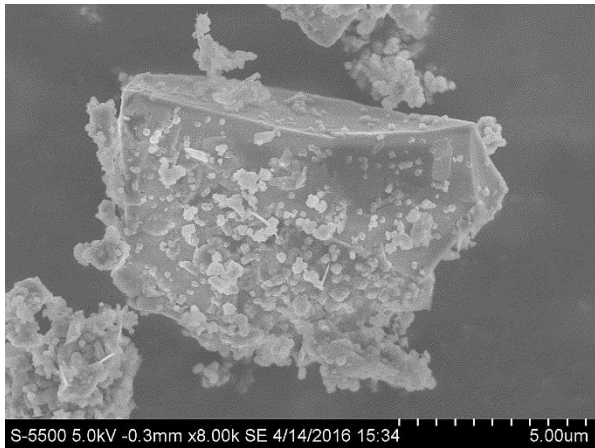
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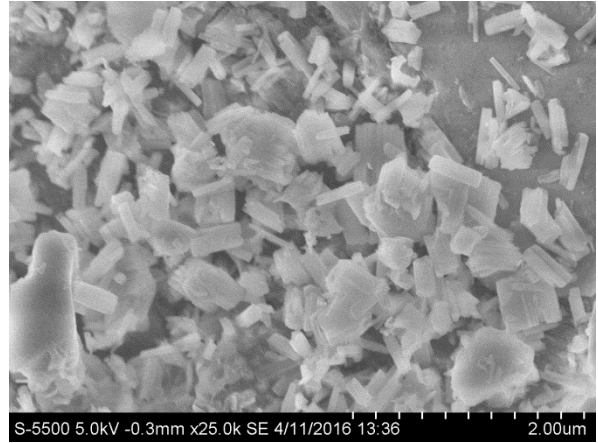
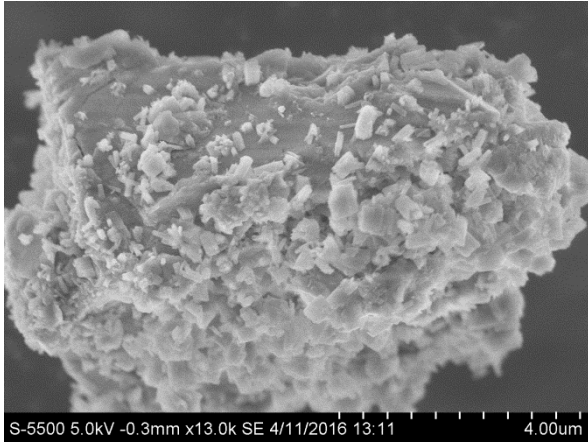
1142 Figure 8 – SEM images of cement grains of left) ANL and right) CX cement after 30 minutes  
1143 of hydration without LSs. Width of micrographs: 31  $\mu\text{m}$

1144



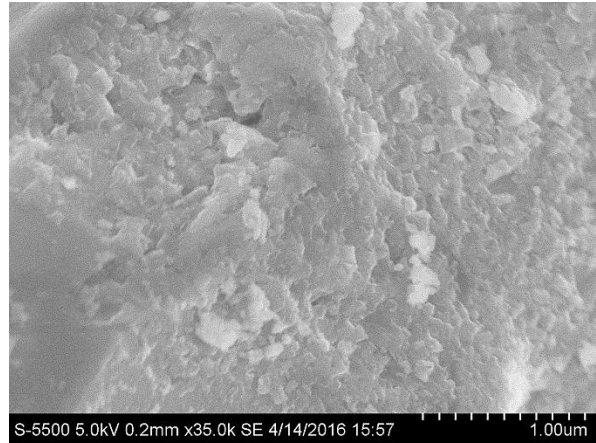
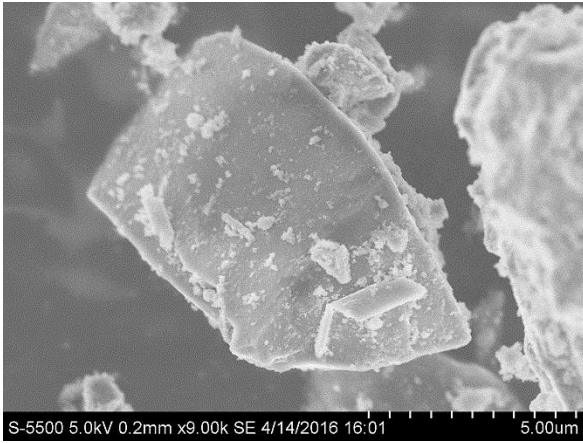
1145

1146 Figure 9 - SEM images of ANL cement grains after 30 minutes of hydration with 1.5 mass %  
1147 of binder LSs added with IA. Width of micrograph: left) 16  $\mu\text{m}$ , and right) 10  $\mu\text{m}$



1148

1149 Figure 10 - SEM images of CX cement grains with 1.5 mass % of binder LSs added with IA  
1150 after 30 minutes of hydration. Width of micrograph: left) 10 μm, and right) 5 μm

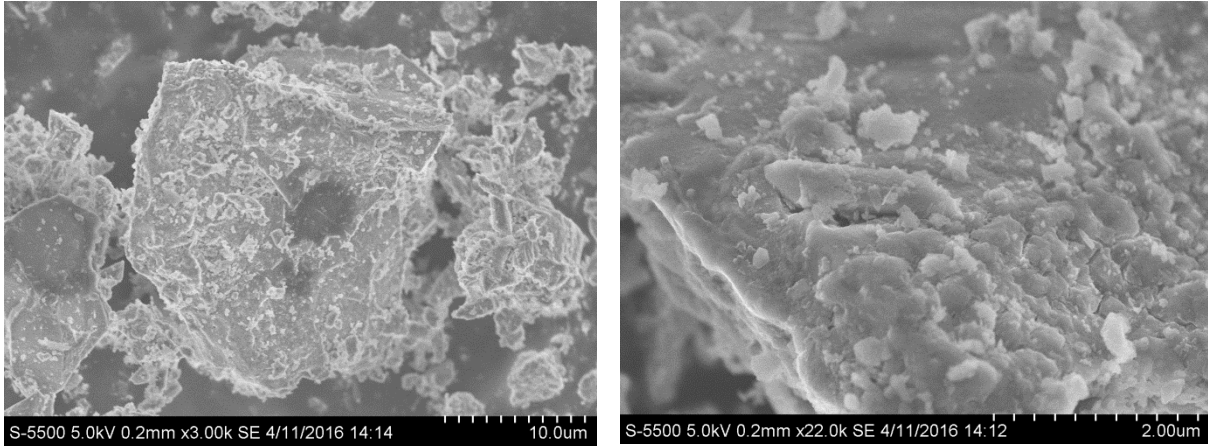


1151

1152 Figure 11 - SEM images of ANL cement grains with 1.5 mass % of binder LSs added with DA  
1153 after 30 minutes of hydration. Width of micrograph: left) 14 μm, and right) 4 μm

1154

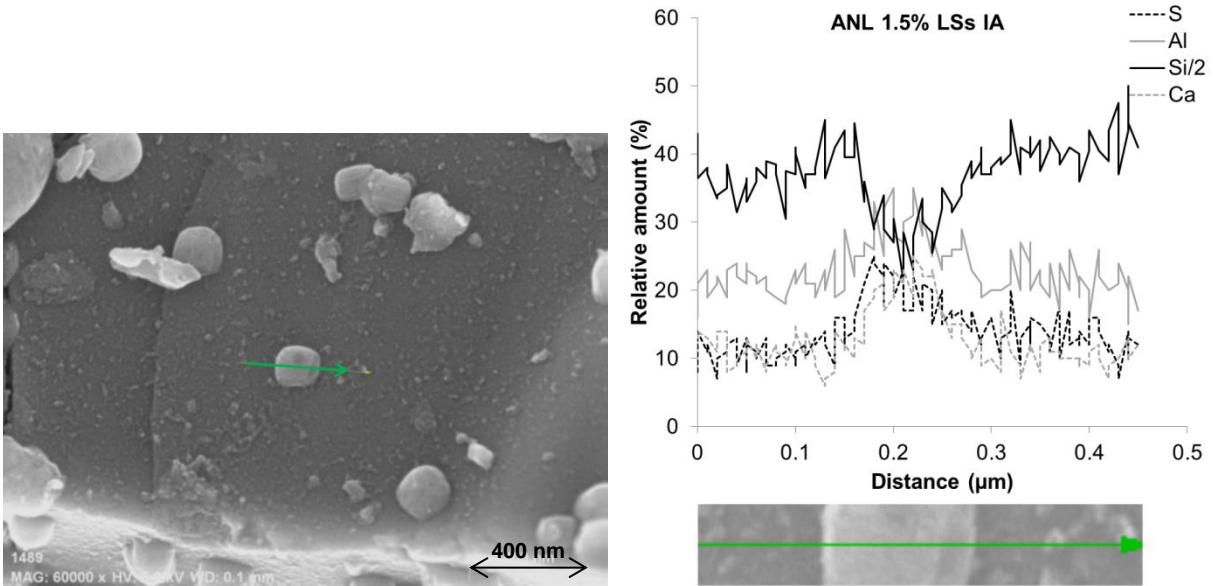




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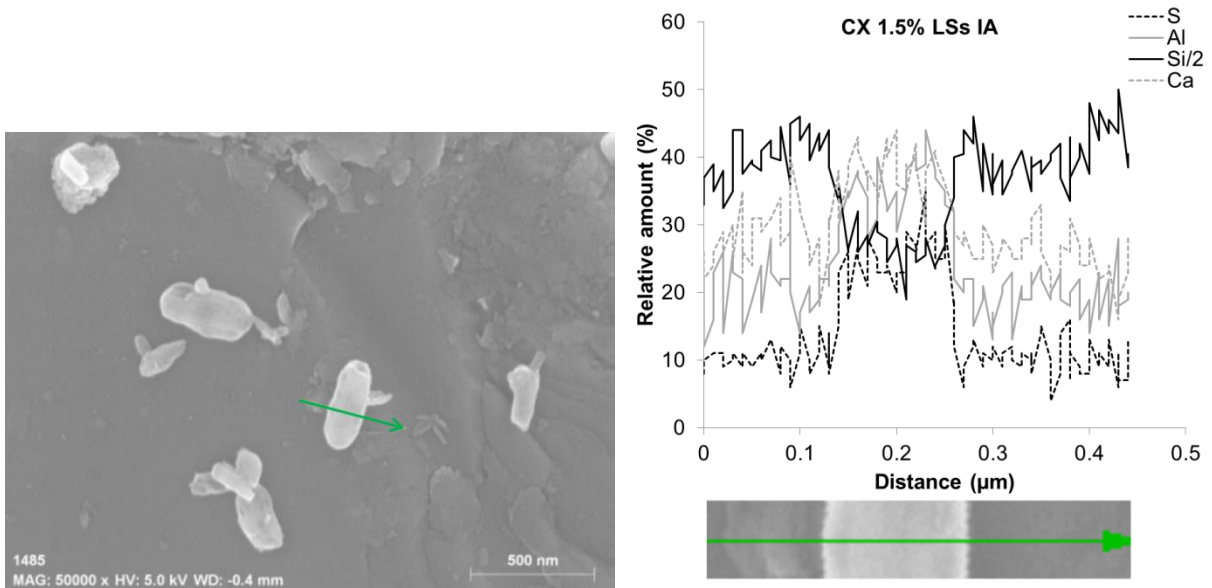
1156 Figure 12 - SEM images of CX cement grains with 1.5 mass % of binder LSs added with DA  
 1157 after 30 minutes of hydration. Width of micrograph: left) 42 μm, and right) 6 μm

1158



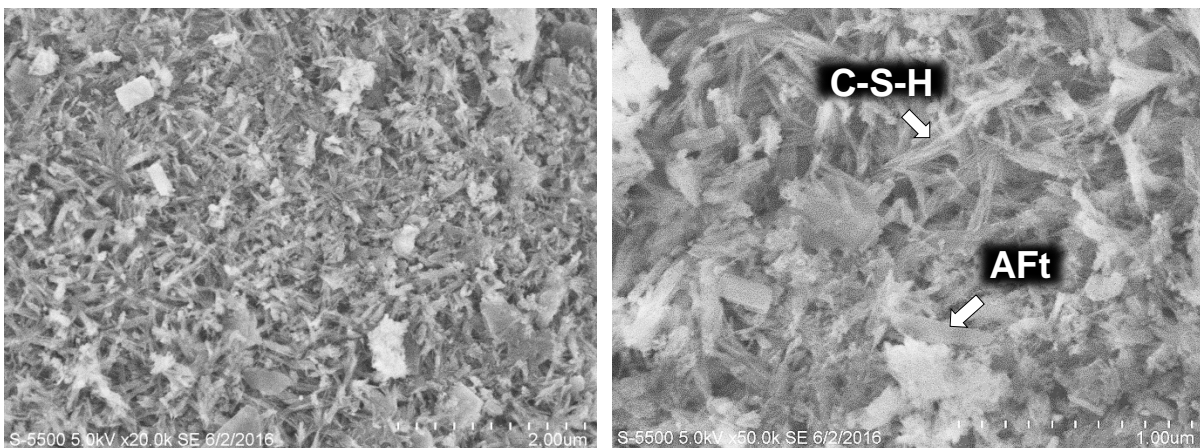
1159

1160 Figure 13 – Linear SEM-EDS analysis of a crystal on the surface of an unhydrated grain of  
 1161 ANL cement with 1.5 mass % of binder LSs added with IA after 30 minutes of hydration. The  
 1162 crystal analysed is shown in the centre of the micrograph (left; width of micrograph: 2 μm). It  
 1163 has to be noticed that the crystals turned to more rounded shapes during the scanning due to  
 1164 dehydration. The curve representing Si was scaled down by multiplying it by 0.5 for better  
 1165 graphical representation.



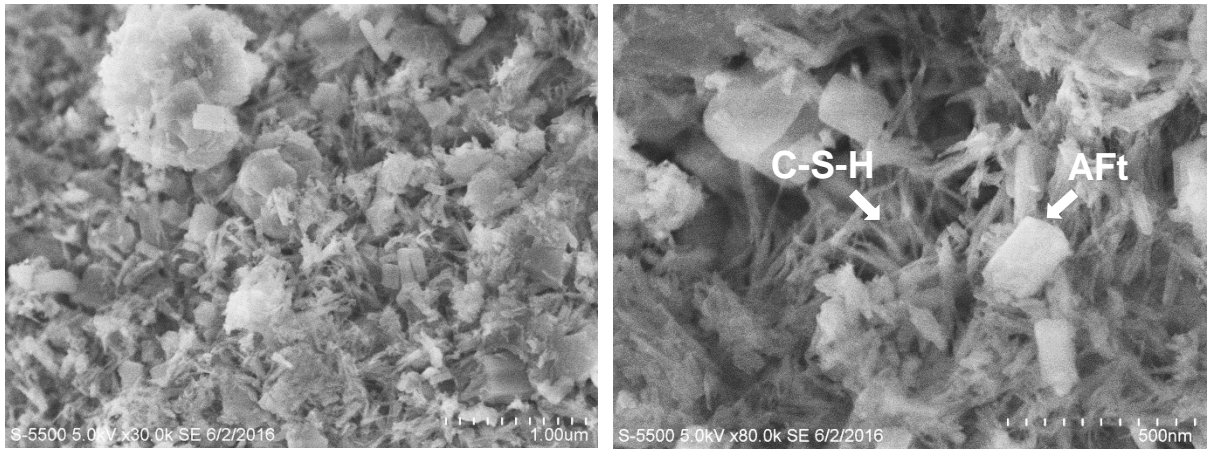
1166

1167 Figure 14 - *Linear SEM-EDS analysis of a crystal on the surface of an unhydrated grain of*  
 1168 *CX cement with 1.5 mass % of binder LSs added with IA after 30 minutes of hydration. The*  
 1169 *crystal analysed is shown in the centre of the micrograph (left; width of micrograph: 2.5 μm).*  
 1170 *It has to be noticed that the crystals turned to more rounded shapes during the scanning due*  
 1171 *to dehydration. The curve representing Si was scaled down by multiplying it by 0.5 for better*  
 1172 *graphical representation.*



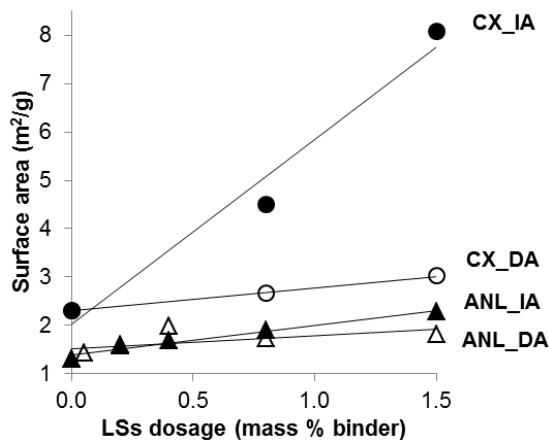
1173

1174 Figure 15 – *SEM images of ANL cement grains without LSs after 6 hours of hydration. Width*  
 1175 *of micrograph: left) 6 μm, and right) 2.5 μm. The identification of the hydrates (right) was*  
 1176 *based on visual appearance and comparison to literature, e.g.[33] .*



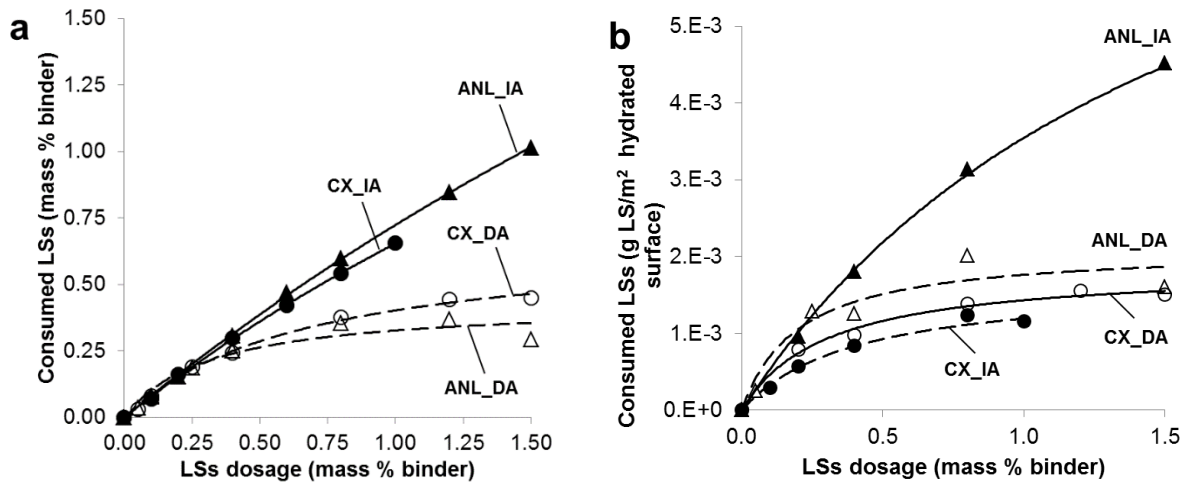
1177

1178 Figure 16 - SEM images of CX cement grains without LSs after 6 hours of hydration. Width of  
 1179 micrograph: left) 4  $\mu\text{m}$ , and right) 1.6  $\mu\text{m}$ . The identification of the hydrates was based on  
 1180 visual appearance and comparison to literature, e.g. [33].



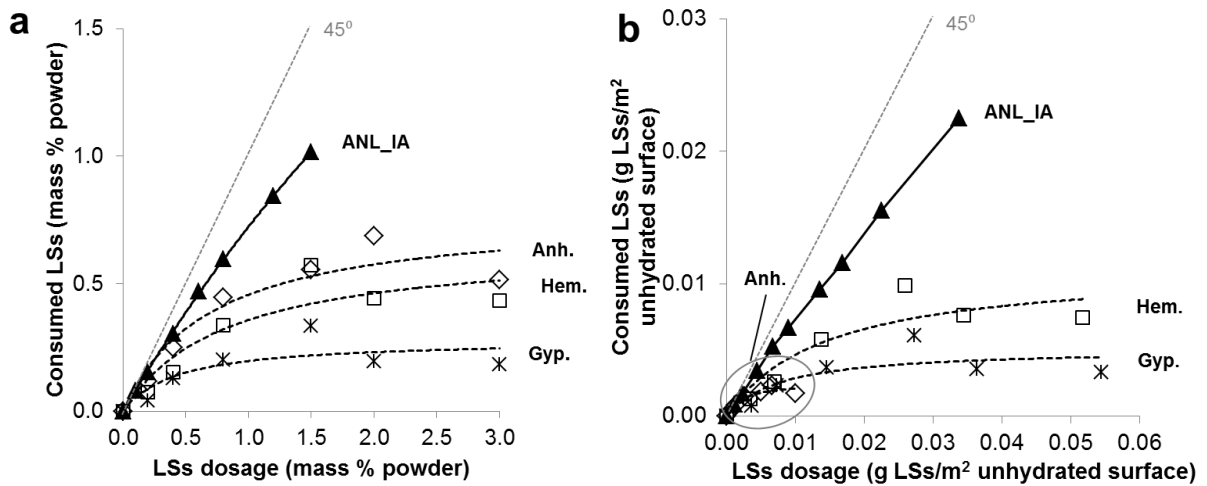
1181

1182 Figure 17 - Surface area of pastes of ANL and CX cements after 30 minutes of hydration vs.  
 1183 LSs dosage added (mass % of binder) both for IA and DA, after [18]. The specific surface  
 1184 area comprehends the surface area of unhydrated cement grains and hydrates.



1185

1186 Figure 18 – Amount of consumed LSs at 30 min. hydration vs. LSs dosage in neat ANL and  
 1187 CX cements for IA and DA, after [18]. The results are calculated as a) mass % of binder and  
 1188 as b) unit of surface area available for adsorption of hydrated pastes of ANL and CX cements

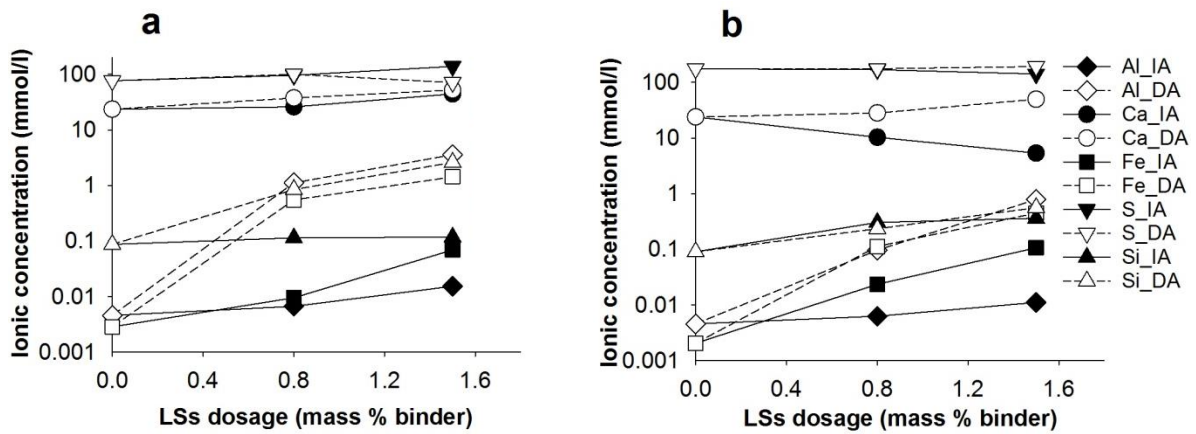


1189

1190 Figure 19 - Amount of consumed LSs at 30 min. hydration vs. LSs dosage added to calcium  
 1191 sulfate anhydrous (anh.), hemihydrate (hem) and dihydrate (gyp.) for IA. The results are  
 1192 calculated as a) mass % of powder, and b) g LSs/m² unhydrated surface

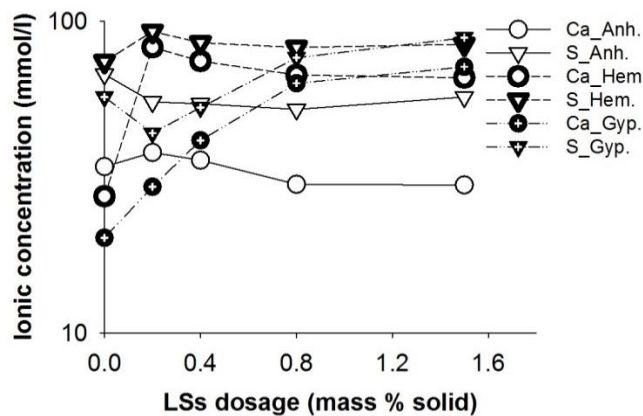
1193

1194



1195

1196 Figure 20 – Concentration of Al, Fe, Ca, Si, and S in the pore solution (mmol/l) expressed in  
 1197 logarithmic scale vs. total LSs added (mass % of binder) to a) ANL and b) CX cement pastes  
 1198 analysed after 30 minutes of hydration both for IA and DA. The legend in figure b) also  
 1199 applies to figure a).



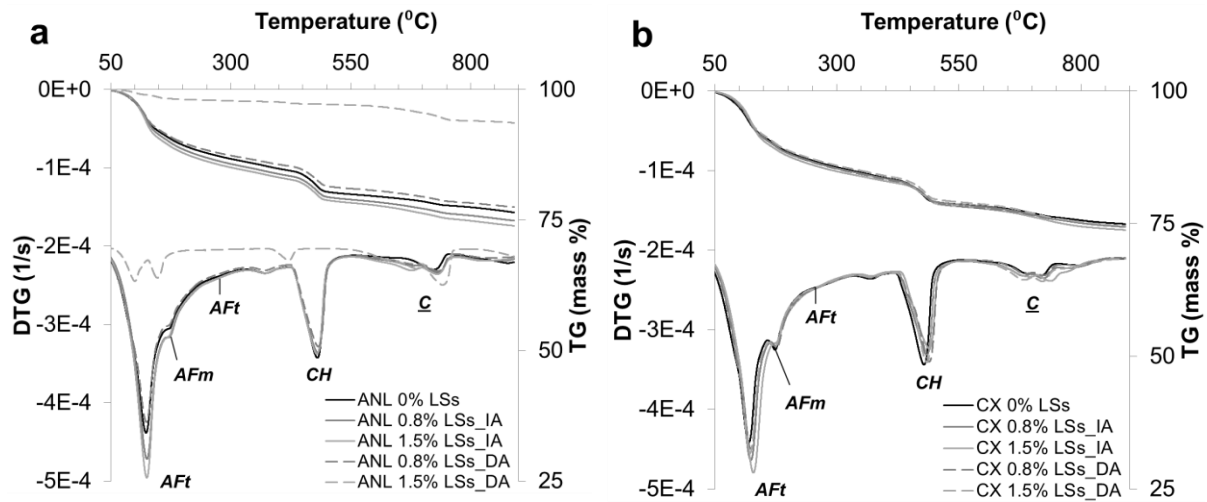
1200

1201 Figure 21 - Concentration of Ca and S in the pore solution (mmol/l) expressed in logarithmic  
 1202 scale vs. total LSs added (mass % of powder) with IA to calcium sulfate anhydrous,  
 1203 hemihydrate, and dihydrate, analyzed after 30 minutes of hydration

1204

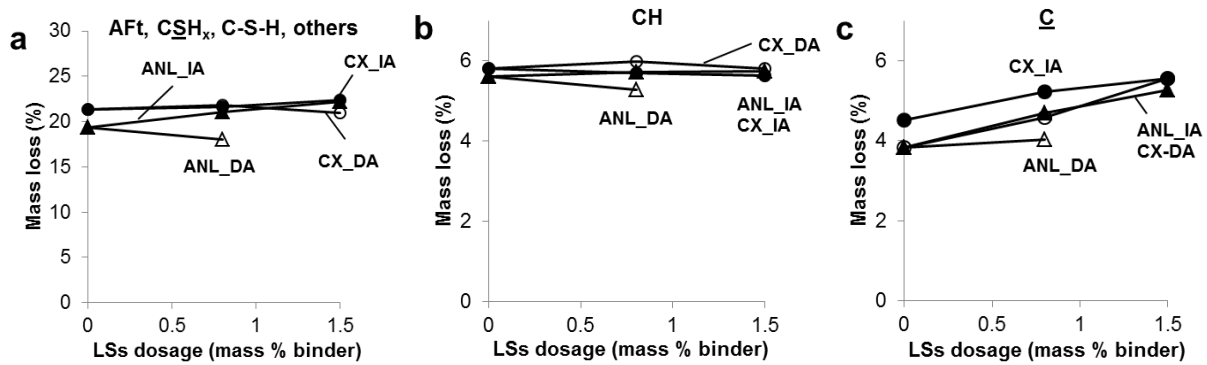
1205





1206

1207 Figure 22 - TG and DTG curves of a) ANL and b) CX cement paste without LSs or with 0.8,  
 1208 1.5, 2.0, 3.0 mass % of binder LSs mixed with IA and DA, for which hydration was stopped  
 1209 after 28 days. The peaks corresponding to the decomposition of AFt, AFm, portlandite (CH)  
 1210 and carbonates (C) are marked in the figures.



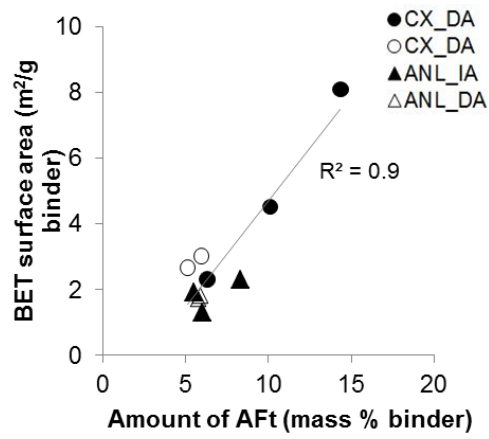
1211

1212 Figure 23 – Mass loss (% of initial weight) of a) AFt, calcium sulfate hydrates (CSH<sub>x</sub>), AFm,  
 1213 C-S-H; b) CH; c) carbonates (C) vs. LSs dosage (mass % of binder) for ANL and CX cements  
 1214 with increasing amount of LSs added with IA and with DA. NB. The scale of the y-axis of  
 1215 figure a) is different than the one of the other figures.

1216

1217

1218



1219

1220 Figure 24 - Correlation between the calculated amount of ettringite\* and the particle surface  
 1221 area of solids in pastes of the two cements when LSs was added immediately with the mixing  
 1222 water (IA). \*: Amount of ettringite calculated considering the mass loss in the whole interval  
 1223 I (50 - ca. 300 °C)