

1 **THE ROLE OF SOLVENT QUALITY AND OF COMPETITIVE ADSORPTION ON**  
2 **THE EFFICIENCY OF SUPERPLASTICIZERS IN ALKALI-ACTIVATED SLAG**  
3 **PASTES**

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10  
11 **ABSTRACT**

12 The loss of dispersing ability by polycarboxylates ether superplasticizers in alkali-activated slag  
13 cements has been widely reported. However, no clear-cut explanation of this phenomenon can  
14 be found to date. Therefore, the behaviour of poly(methacrylate-g-poly(ethylene glycol))  
15 superplasticizers in NaOH or Na<sub>2</sub>CO<sub>3</sub>-activated slag pastes was investigated. The observed loss  
16 of efficiency of the polymer was not due to a specific property of the slag particles, nor to  
17 structural degradation of the polymer in the alkaline solutions. Actually, the ionic strength of  
18 the activating solution decreased the solvent quality and changed the polymer conformation,  
19 leading to a deterioration of the steric repulsion brought by the side-chains. Moreover, in the  
20 Na<sub>2</sub>CO<sub>3</sub>-activated systems, the adsorption behaviour of the polymers was also significantly  
21 altered. Here, this was not caused by a low calcium concentration or by a preferential adsorption  
22 of the superplasticizer on calcite crystallites. The most plausible explanation was a competitive  
23 adsorption with CO<sub>3</sub><sup>2-</sup> ions.

24 **Keywords:** cement, rheology, polymer, alkali activation, admixtures, solubility, PCE, MPEG

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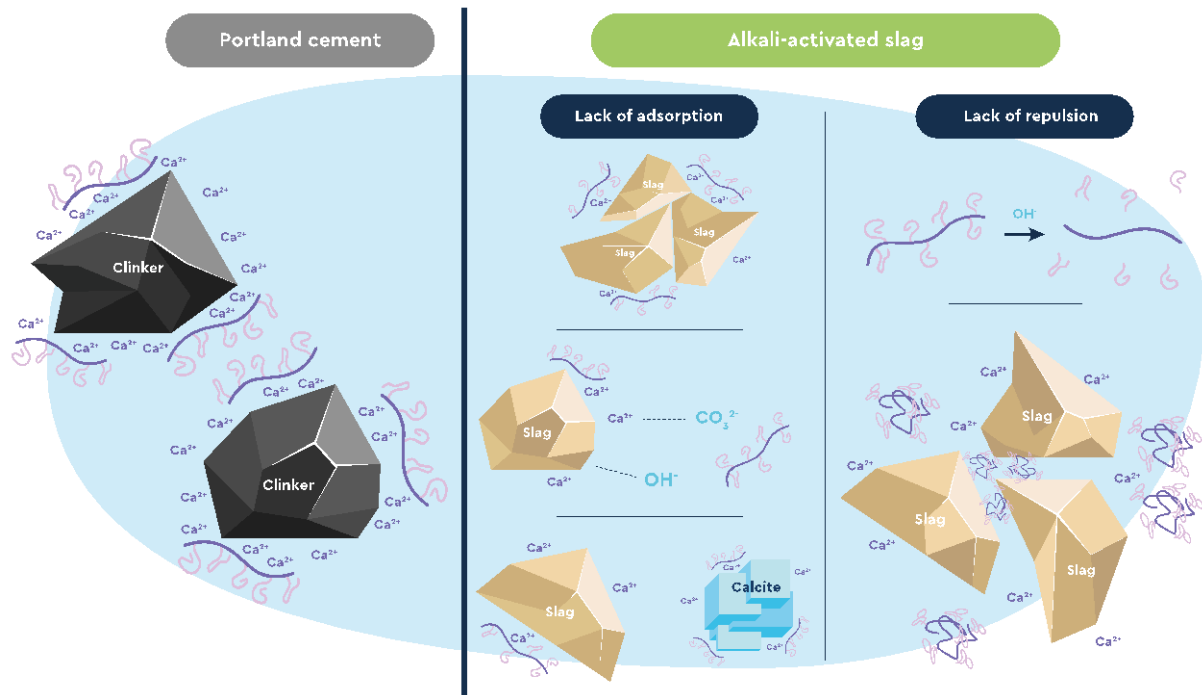
## 26 **1. INTRODUCTION**

27 Alkali-activated slag, consisting of ground-granulated blast furnace slag and an alkaline  
28 activator, is a novel low carbon cementitious material receiving increased attention worldwide.  
29 This is mainly due to its reduced environmental impact compared to ordinary Portland cement  
30 (OPC) while having similar performances [1–4] .

31 Still, one major impediment remains regarding its use at a large scale: to cast and pump concrete  
32 or mortars properly, a high and time-controlled fluidity is needed. This property is usually  
33 obtained by adding superplasticizers to the mix, polymers which adsorb on the surface of  
34 cement grains and keep them from flocculating. One of the most widely used families of  
35 superplasticizers is made of comb-shaped polymers based on the polycarboxylate ether (PCE)  
36 chemical structure [5]. These superplasticizers consist in a – usually anionic – charged  
37 backbone which adsorbs on the anionic charged sites of the cement particles, thanks to a surface  
38 charge inversion by the calcium cations present in the interstitial solution. Grafted side-chains  
39 of polyethylene glycol (PEG) extend in the interstitial solution, inducing a steric repulsion  
40 which keeps the particles from flocculating [6–9].

41 Yet, many studies show that the traditional superplasticizers used in OPC have little or no  
42 dispersing efficiency in alkali-activated slag cements [10–12]. Different explanations have been  
43 suggested in the literature. They are schematically represented in Figure 1. A first possibility is  
44 the degradation of the polymer structure by the alkaline environments of the activating solutions  
45 [12,13]. The steric repulsion could also be impacted by a lack of solubility of the  
46 superplasticizers as proposed in the study of Conte and Plank [14]. Another explanation could  
47 be a lack of adsorption of the polymers on the slag’s surface. This could be due either to a lower  
48  $\text{Ca}^{2+}$  concentration in the interstitial solution, to a difference of surface chemistry between slag  
49 and clinker’s particles [15,16], to competitive adsorptions between the superplasticizers and  
50 other anions in solution [17], or to a different affinity of the polymer between the slag grains

51 and the hydrates formed very early [18]. However, no conclusive explanation has so far  
 52 transpired, and no satisfactory solution has been found to address the challenge of the fluidity  
 53 control of alkali-activated cements.



54  
 55 **Figure 1: Schematic representation of the molecular origin of fluidification, or lack thereof, of**  
 56 **clinker or activated slag pastes by PCEs. PCE adsorbs on clinker via charge inversion due to  $\text{Ca}^{2+}$ ,**  
 57 **and the swollen PEO side-chains prevents particle aggregation (left). This effect is lost in activated**  
 58 **slag pastes. This could be explained by poor PCE adsorption due to an insufficient amount of  $\text{Ca}^{2+}$**   
 59 **(middle-top), to competitive adsorption between PCE and anions of the activating solutions**  
 60 **(middle-centre), or to preferential adsorption of the PCE on precipitated very early reaction**  
 61 **products such as calcium carbonates (middle-bottom). This could also be due to hydrolysis of the**  
 62 **polymer (right- top) or to a collapse of the PEO side-chains (right-bottom) in the activating**  
 63 **solution.**

64 In this context, the aim of this study is to improve our understanding of the factors hindering  
 65 the dispersing properties of polycarboxylates-based superplasticizers (PCE), a member of the  
 66 poly(methacrylate-g-poly(ethylene glycol)) family also called MPEG, in slag cements activated

67 with NaOH or Na<sub>2</sub>CO<sub>3</sub>. For this purpose, the dispersing ability of the polymers was evaluated  
 68 by rheological studies, and their chemical stability in the activating solutions was assessed by  
 69 size exclusion chromatography. Moreover, adsorption measurements using the depletion  
 70 method were used to investigate the affinity of the superplasticizer to the slag surface and  
 71 determine if a competitive adsorption with the activator anions took place. These measurements  
 72 were coupled to a study of the superplasticizer solubility and conformation using cloud point  
 73 measurements and capillary viscometry. Finally, the interstitial concentration of calcium was  
 74 measured by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and a  
 75 possible competitive adsorption between slag and calcite was investigated.

## 76 2. MATERIALS AND METHODS

### 77 2.1. Materials

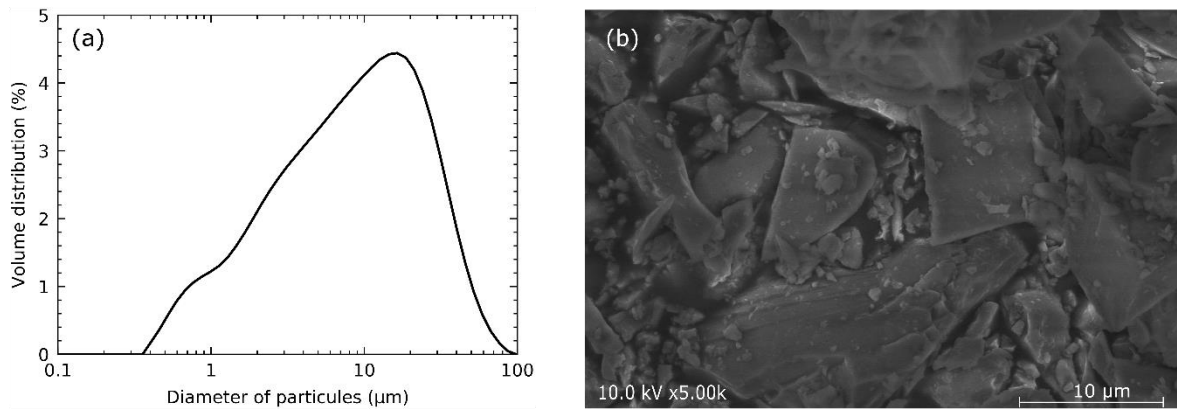
78 A ground granulated blast-furnace slag supplied by CHRYSO SAINT-GOBAIN France was  
 79 used in this study. Its chemical composition, determined by X-ray fluorescence (XRF) by an  
 80 external contractor (Université Paris Cité, France), is summarised in Table 1.

81 **Table 1 : The chemical composition of the slag determined by XRF (wt %). LoI.: Loss on ignition**  
 82 **measured at 1000 °C.**

	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MnO	LoI.
Slag	37.33	40.88	9.76	0.31	6.35	0.30	0.40	0.56	0.18	3.95

83 A specific surface area of  $0.85 \pm 0.02$  m<sup>2</sup>/g was measured by krypton adsorption following the  
 84 BET method (see below). Figure 2a presents the particle size distribution of the slag dispersed  
 85 in isopropanol and measured by laser light diffraction (Mastersizer, Malvern Panalytical),  
 86 courtesy of Dr. Y. Keskin (Navier laboratory, Marne la Vallée, France), with a D<sub>v50</sub> value of  
 87 9.15 μm. The particles have irregular shapes with sharp edges, as shown on the SEM image

88 (Figure 2b). The image was taken on a JEOL 6300F field emission electron microscope, at 10  
89 kV, in high-vacuum mode.



90 **Figure 2: (a) Particle size distribution of the blast furnace slag. (b) SEM image of the blast furnace**  
91 **slag particles.**

92 In some samples, the slag was replaced by a calcite powder from Sigma-Aldrich with a specific  
93 surface area of  $0.58 \pm 0.06 \text{ m}^2/\text{g}$ , or one supplied by CHRYSO SAINT-GOBAIN France with  
94 a surface area of  $2.1 \pm 0.3 \text{ m}^2/\text{g}$ .

95 Sodium hydroxide (NaOH) pellets EMPLURA<sup>®</sup> or sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) powder  
96 >99.5% from Sigma-Aldrich were used for the preparation of the activating solutions. Each  
97 were dissolved in ultrapure water (conductivity of 18.2 mΩ/cm) in the appropriate amounts in  
98 order to obtain an alkaline solution with the target activator's concentration. With some  
99 exceptions (as specified), the activating solutions had a composition corresponding to a paste  
100 formulation of 4.0 % Na<sub>2</sub>O by weight of slag and a water/slag (w/s) weight ratio of 0.4. This  
101 composition allowed having a reasonable setting time for the activation with NaOH and  
102 satisfactory consistencies for all the pastes.

103 Three poly(methacrylate-g-poly(ethylene glycol)) superplasticizers, supplied by CHRYSO  
104 SAINT-GOBAIN France, were used in this work. Their average structure can be described  
105 using Gay and Raphaël's nomenclature for comb copolymers [19,20]. The polymers are  
106 composed of  $n$  segments, each containing  $N$  backbone monomers and one side-chain of  $P$

107 monomers. The superplasticizer average structures were *n8.5N5P17*, *n10N5P45* and  
 108 *n10N5P114*. Thereafter, the polymers will be referred respectively as PCE17, PCE45, and  
 109 PCE114 since only the side-chain length varied significantly. Their characteristic molecular  
 110 parameters are given in Table 2. They were used as dilute solutions containing a defoamer and  
 111 neutralized by NaOH. For the size-exclusion chromatography and the capillary viscometry  
 112 measurements, solutions without defoamer were used. The water added by the polymer solution  
 113 was considered in the calculation of the w/s ratio of the pastes. Except for the cloud point  
 114 measurements, the superplasticizer used was PCE45, namely, the one with the medium length  
 115 side-chains.

116 **Table 2: Characteristic molecular parameters of the superplasticizers used.**

<b>Superplasticizer</b>	<b>n</b>	<b>N</b>	<b>P</b>	<b>M<sub>w</sub> (g/mol)</b>	<b>M<sub>n</sub> (g/mol)</b>	<b>Đ (M<sub>w</sub>/M<sub>n</sub>)</b>
<b>PCE17</b>	8.5	5	17	31900	11000	2.9
<b>PCE45</b>	10	5	45	51000	25000	1.8
<b>PCE114</b>	10	5	114	152700	54500	2.8

## 117 **2.2. Sample preparation and tests performed**

118 A precise mass of polymer solution, depending on the dosage used and the dry extract of the  
 119 solution, was firstly combined with the activating solution in a container with a diameter of 52  
 120 mm. Then, 50 g of slag was added into the solution. The alkali-activated slag paste was prepared  
 121 by immediate mixing with an overhead stirrer, using a radial flow stirring blade of 29 mm  
 122 diameter. The mixing procedure was the following. First, the paste was blended at 500 rpm for  
 123 30 s. Then, for an additional 30 s, a fast (1500 rpm) mixing was applied. This was followed by  
 124 a rest time of 30 s and a final 1 min of fast mixing.

125 For adsorption and pore solution composition measurements, the slag pastes were left at rest  
 126 for 10 min after the protocol described above and then homogenised by stirring for 1 min at 500

127 rpm. The resulting sample was filtered by two superimposed filter papers (20 - 25  $\mu\text{m}$  and 11  
128  $\mu\text{m}$  particle retention) set in a Büchner funnel, using a vacuum pump. The aqueous phase was  
129 then filtered again with 1.2  $\mu\text{m}$  PSE syringe membranes. This choice of a relatively coarse  
130 membrane insured that no polymer was retained by it when in good solvent and that the overall  
131 filtration process remained short enough (5 min) to neglect further advancement of hydration.

### 132 **2.2.1. Isothermal micro-calorimetry**

133 The hydration heat of the slag cements was measured at 25°C with a TAM Air isothermal  
134 micro-calorimeter from TA Instruments, at IETcc-CSIC (Madrid, Spain). A total mass of 5.0 g  
135 of cement paste was weighed into the mix-ampoules right after the mixing. The mix-ampoules  
136 were placed in the calorimeter at the same time as a reference composed of a precise mass of  
137 ultrapure water in order to have a similar calorific capacity as the cement samples. The resulting  
138 heat flows were normalised by the slag mass.

### 139 **2.2.2. Polymer adsorption measurements**

140 The amount of superplasticizer adsorbed on slag particles was determined by Total Organic  
141 Carbon (TOC) measurements using a TOC-L analyser from Shimadzu. For each activator, the  
142 TOC analyser was first calibrated with a “blank” sample (slag paste without any  
143 superplasticizer added) to assess the amount of organic carbon dissolved from the slag powder.  
144 The pore solutions, obtained as described above, were acidified with 20 % HCl to remove  
145 inorganic carbon and lower the pH to values tolerable by the analyser.

146 The affinity of the superplasticizers with the calcite surface was also assessed using the same  
147 protocol. Slag was replaced by calcite in quantities such as to keep the same total solid surface  
148 area.

### 149 **2.2.3. Effect of the polymer on the slag paste rheology**

150 The rheology of the samples was measured 5 min after the beginning of the mixing. Rheological  
151 parameters of pastes over time were determined at 25°C using a DHR 3 rheometer from TA  
152 Instruments equipped with a vane geometry. The paste rheological behaviour and the dispersing  
153 effect of the superplasticizers were characterized by determining flow curves. First, a shear  
154 ramp from 1 s<sup>-1</sup> to 200 s<sup>-1</sup> was applied for 1 min. This was followed by a 45 s pre-shearing at  
155 200 s<sup>-1</sup>. Finally, the flow curve was measured by steps of decreasing shearing rates from 200 s<sup>-1</sup>  
156 to 0.01 s<sup>-1</sup>. To ensure that the sample was in steady state conditions, points were taken only  
157 when the deviation of the torque stayed under 4.0 % during 3 s or if the measurement took more  
158 than 30 s to stabilize. This last case happened at very low shear rates, when the steady state  
159 could not be reached anymore, because the shearing energy was too low to fight the  
160 structuration of the pastes.

### 161 **2.2.4. Polymer's chemical stability and size-exclusion chromatography (SEC)**

162 The polymers were first diluted with the activating solutions for 30 min, at molalities of 3.2  
163 mol/kg and 1.6 mol/kg for NaOH and Na<sub>2</sub>CO<sub>3</sub> respectively. The solutions were then dialysed  
164 using a SpectraPor membrane (MWCO: 1 kDa) against ultrapure water. The water was changed  
165 every day until its pH reached the neutral value of 7. The polymers were then freeze-dried and  
166 subsequently redispersed in a 0.2 M NaNO<sub>3</sub> solution. The final solutions with a concentration  
167 in polymer of 2 g/L were analysed by SEC with a Viscotek TDA 302 system triple detector  
168 equipped with three OH-pak SB-806M HQ columns in series and a guard column. The mobile  
169 phase was a 0.2 M NaNO<sub>3</sub> aqueous solution and the flow-rate was 0.7 mL/min. 100 µL of each  
170 sample was passed in the set of columns. The number- and weight average molar masses  
171 (respectively M<sub>n</sub> and M<sub>w</sub>) and dispersity ( $\bar{D}=M_w/M_n$ ) were derived from a universal calibration  
172 curve based on poly(ethylene oxide) standards from Malvern.



### 173 **2.2.5. Polymer cloud point measurements**

174 The solubility of the polymers, depending on their side-chain length and the activator, was  
175 assessed by UV-visible spectroscopy and visual determination of their cloud point. The cloud  
176 point was defined in the following manner. Solutions of 1 g/L of polymer in ultrapure water  
177 were prepared. The activators were then added progressively until the solutions became turbid  
178 to the eye. The corresponding activator molality is called the cloud point. The validity of this  
179 qualitative cloud point procedure was checked by absorbance measurements with a UV-vis  
180 Hewlett-Packard 8453 spectrophotometer at a wavelength of 600 nm, using a quartz cell (see  
181 Supplementary material, Figure S1).

### 182 **2.2.6. Polymer conformation and capillary viscometry**

183 Changes in conformation of the superplasticizers in the activating solutions were estimated by  
184 capillary viscometry. Solutions containing different concentrations of polymer in the different  
185 activating solutions were prepared and studied with a Ubbelohde viscometer using a 0.53 mm  
186 diameter capillary tube. The apparatus' thermostat was set to 25°C. Each reported value is the  
187 average of 10 measurements.

188 The intrinsic viscosities  $[\eta]$  were obtained thanks to the empirical Fedors model [21] for  
189 polyelectrolyte solutions

$$190 \quad \frac{1}{2(\sqrt{\eta_{sp}+1}-1)} = \frac{1}{[\eta]} \times \left( \frac{1}{C} - \frac{1}{C_m} \right) \quad \text{Eq. 1}$$

191 where  $\eta_{sp}$  is the specific viscosity,  $C$  the polymer concentration and  $C_m$  the critical concentration  
192 corresponding to the particles close packing. This model was derived from an equation used for  
193 Newtonian suspensions of rigid particles and is generally suited for polymer solutions with  
194 specific viscosities comprised between 1 and 100.

195 Finally, the sizes of the superplasticizers were determined using the Fox-Flory [22,23] equation

$$196 \quad [\eta] = \phi' \frac{R^3}{M} \quad \text{Eq. 2}$$

197 that links the intrinsic viscosity to the polymers' radius  $R$  and to their molar mass  $M$ , and where  
198  $\phi'$  is equal to  $3.08 \times 10^{24} \text{ mol}^{-1}$  for polymers with high polydispersities. It should be noted that  
199 the Fox and Flory theory was developed for dilute solutions of linear and flexible polymers in  
200 thermodynamic good solvent conditions. Consequently, the sizes calculated with this equation  
201 cannot be considered as true polymer sizes for the comb copolymers used, but it does provide  
202 the trend of the effect of the solvent on their size. We thus refer to the radius obtain from  
203 equation 2 as a viscosimetric radius.

#### 204 **2.2.7. Pore solution analysis by ICP-OES**

205 Elementary composition of the pore solutions was measured at the ISTeP laboratory of  
206 Sorbonne Université (Paris, France) by Inductively Coupled Plasma – Optical Emission  
207 Spectrometry (ICP-OES) with a 5100 SVDV Agilent analyser. The interstitial solutions,  
208 obtained by filtration as explained above, were first acidified with  $\text{HNO}_3$  2% in a proportion of  
209 1:10 to prevent the precipitation of solids. The samples were then further diluted with  $\text{HNO}_3$   
210 2% to proportions of 1:1000, 1:200, 1:100 and 1:50 to explore different concentration ranges.

#### 211 **2.2.8. Characterization of the hydrates by X-Ray Diffraction (XRD)**

212 To characterize the hydrates formed during the slag reaction with the different activators, the  
213 hydration of the samples was stopped after 9 h for the NaOH-activated pastes and after 131 h  
214 for the  $\text{Na}_2\text{CO}_3$ -activated. To stop them, the samples were washed twice with ultrapure water  
215 and then with isopropanol, following the protocol given by Palacios et al. [24]. Next, they were  
216 dried in a vacuum desiccator at room temperature and finely ground in a mortar. Finally, the  
217 powders obtained were analysed in a Phillips PW 1700 diffractometer equipped with a  
218 X'Celerator detector, in  $\theta$ - $2\theta$  configuration. The X-rays corresponding to the Copper  $K_{\alpha 1}$  line  
219 ( $1.540562 \text{ \AA}$ ) were produced with applied voltage and intensity of 40 kV and 40 mA  
220 respectively. Data were collected between  $5$  and  $60^\circ$ , with steps of  $0.0170^\circ$ .

### 221 **2.2.9. Specific surface area measurements**

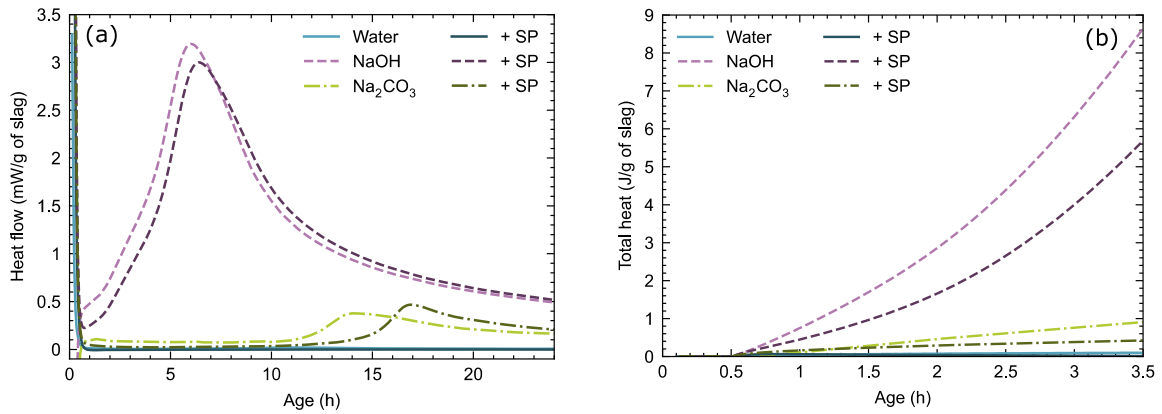
222 The sample specific surface areas were obtained after krypton adsorption-desorption  
223 experiments at 77 K, using the BET method, by an external contractor (LIEC, Nancy, France).  
224 The measurements were conducted on an adsorbometer Belsorp-Max II from MicrotracBEL  
225 Corp. The samples were degassed beforehand under vacuum to eliminate any superficial  
226 impurity. For calcite and anhydrous slag samples, the degassing was conducted at 120°C for 18  
227 h. The specific surface area of cement pastes stopped right after the mixing was also assessed.  
228 These samples being more sensitive to thermal changes, the degassing was conducted at 80°C  
229 for 48 h.

## 230 **3. RESULTS AND DISCUSSION**

### 231 **3.1. Hydration kinetics of the alkali-activated slag pastes**

232 First and foremost, the kinetics of the hydration reaction of the activated and non-activated  
233 cements was studied by isothermal micro-calorimetry. The heat flows measured over 24 hours  
234 are presented on Figure 3. Only alkali-activated systems exhibited measurable heat flows due  
235 to the exothermic dissolution of the slag and hydrates precipitation. This indicates that (i) the  
236 hydration of slag in water was, as expected, very slow, and that (ii) the presence of activators  
237 was required for the cement to set.

238 Figure 3 also shows that the addition of superplasticizer to non-activated slag cements did not  
239 have any effect on its hydration. However, the superplasticizer had a small retarding effect on  
240 the hydration of the NaOH or Na<sub>2</sub>CO<sub>3</sub> activated slags, since the heat flow peaks are delayed by  
241 0.5 h and 3.5 h respectively.



242 **Figure 3: Isothermal micro-calorimetry measurements (25 °C) of the evolution of the heat flow**  
 243 **over 24 hours (a) and of the total heat over 3.5 hours (b) of a slag cement hydrated in water (solid**  
 244 **line), with Na<sub>2</sub>CO<sub>3</sub>- (dotted lines) or NaOH- (dashed lines) activations at 4%wt. Na<sub>2</sub>O by weight**  
 245 **of slag, and a w/s ratio of 0.4. Measurements were also performed in presence of 0.5 wt% (13.4**  
 246 **g/L) of the superplasticizer PCE45 (SP).**

247 An important observation is that the heat released during the first fifteen minutes of hydration  
 248 was minimal in all cases – not taking into account the initial dissolution heat. Even for the  
 249 NaOH system, it remains at values typical of what is observed during ordinary cement dormant  
 250 period (see for example results reported in [3]). Extrapolating to time zero the heat flux  
 251 observed at 0.5 h, one can estimate an upper limit of 0.2 J/g slag for the heat released during  
 252 the first 15 minutes in the most reactive (NaOH) system. Taking an approximate value of 300  
 253 J/g slag for the total heat of reaction[25], one infers that, at the very most, less than 1‰ of the  
 254 slag had reacted after 15 minutes. Furthermore, Krypton adsorption measurements (Table 3)  
 255 resulted in BET specific surface for samples stopped right after the mixing similar to the one of  
 256 the initial anhydrous slag (see section 2.1.). This meant that even in the case of NaOH  
 257 activation, the amount of surface area created during the first minutes of hydration could be  
 258 neglected. In addition, XRD or NMR could detect no reaction products before a few hours  
 259 (Figure S2). All these observations allow defining a 15 minutes-time window during which one  
 260 can neglect hydrate formation, in first approximation. As a result, the following study of the  
 261 superplasticizers was performed at hydration times within that time window, during which the

262 solid surface area can be considered constant and during which superplasticizer-hydrate  
263 interactions do not need to be considered on first analysis.

264 **Table 3: Specific surface areas of non-activated, and 4%wt. Na<sub>2</sub>O NaOH or Na<sub>2</sub>CO<sub>3</sub>-activated slag**  
265 **samples right after the mixing. The pastes were prepared with a w/s ratio of 0.4. The values are**  
266 **given with an error of  $\pm 0.02$  m<sup>2</sup>/g.**

System	Water	NaOH	Na <sub>2</sub> CO <sub>3</sub>
Kr BET (m <sup>2</sup> /g)	0.82	0.85	0.83

### 267 3.2. Dispersing ability of the superplasticizer

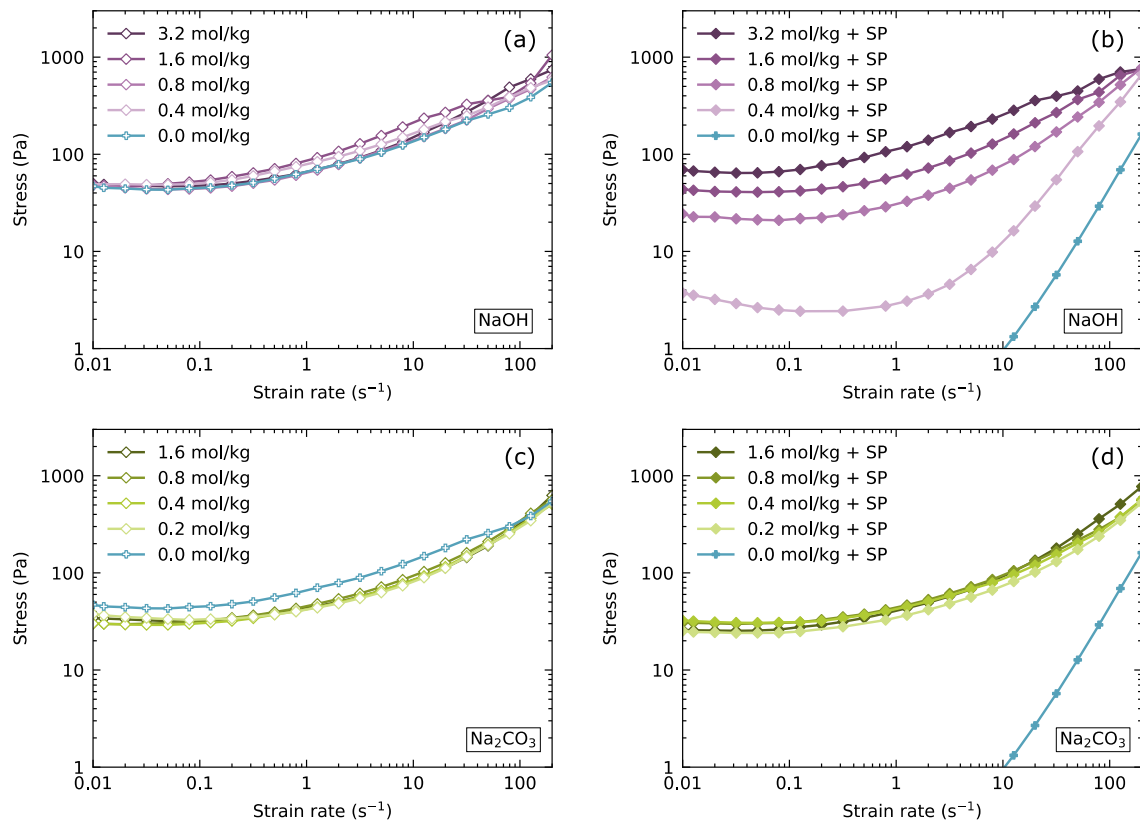
268 The dispersing ability of the superplasticizer was assessed by flow curves measurements in the  
269 slag cements with different activator molalities. The samples were prepared at a constant w/s  
270 ratio of 0.4, but the activator quantity was varied between 4.0 and 0.5 wt% of Na<sub>2</sub>O. Rheology  
271 experiments started five minutes after the beginning of the mixing and lasted about five  
272 minutes. Therefore, they took place before any important hydrates' precipitation, according to  
273 the calorimetry measurements (see Figure 3).

274 The results are presented in Figure 4 and show the expected rheological behaviours of cement  
275 pastes – which are yield stress fluids [26]. The yield stress  $\tau_c$  is estimated by fitting the curves  
276 with the Herschel-Bulkley model:

$$277 \quad \tau > \tau_c \Rightarrow \tau = \tau_c + k\dot{\gamma}^n \quad \text{Eq. 3}$$

278 where  $\tau$  is the shear stress,  $\dot{\gamma}$  the strain rate, and  $k$  and  $n$  are material parameters. This empirical  
279 model is valid for steady state flow conditions with shear rates comprised between  $10^{-2}$  and  
280  $100$  s<sup>-1</sup>. The behaviour of the slag pastes without any superplasticizer (Figures 4a and 4c) was  
281 similar whether the cement was activated or not, with a yield stress of 25 to 45 Pa. Moreover,  
282 the activator molality did not have a significant effect on the rheological behaviour of the slag  
283 pastes in these cases.

284 When the superplasticizer was added (Figures 4b and 4d), different behaviours appeared. In the  
 285 case of a non-activated slag cement, i.e. in water, the addition of the superplasticizer led to a  
 286 drastic decrease, below 1Pa, of the apparent yield stress. Even though the measurements were  
 287 not done in steady state conditions anymore, this proves that the superplasticizer had a great  
 288 dispersing ability in suspensions of slag in water.



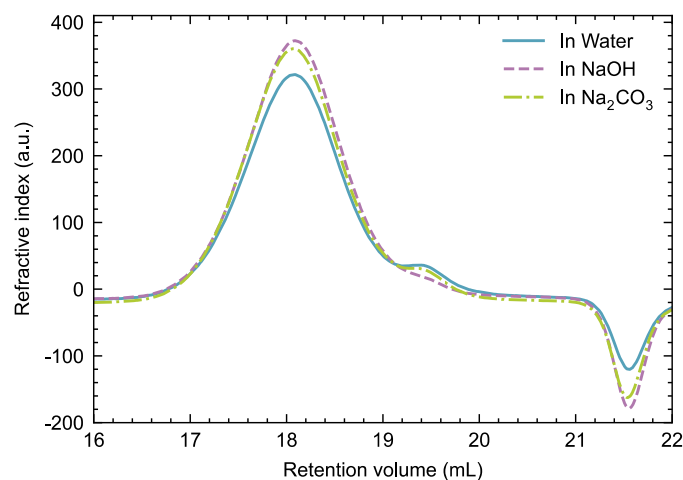
289 **Figure 4: Flow curves obtained for slag cements activated with NaOH (a and b) and Na<sub>2</sub>CO<sub>3</sub> (c**  
 290 **and d), without (a and c) and with 0.5 wt% by slag (13.4 g/L) of PCE45 (b and d) depending on**  
 291 **the activator molality. The w/s ratio is kept at 0.4, and the wt% of Na<sub>2</sub>O is varied. For stresses**  
 292 **under 1 Pa, systems are too fluid to be stable and sediment under gravitation forces. Results below**  
 293 **1 Pa are thus not reported.**

294 On the contrary, the addition of the superplasticizer in alkali-activated slag pastes at 4.0 wt%  
 295 of Na<sub>2</sub>O and a w/s ratio of 0.4 (3.2 mol/kg of NaOH or 1.6 mol/kg of Na<sub>2</sub>CO<sub>3</sub>) was associated  
 296 with negligible changes of rheological behaviour. For NaOH-activated slag (Figure 4b), some

297 fluidity was regained when the activator molality was diminished, but never reached the one  
298 measured in non-activated slag cements. The  $\text{Na}_2\text{CO}_3$  activation had an even worse effect on  
299 the rheological curves, as it totally inhibited the dispersing effect of the superplasticizer at all  
300 the concentrations investigated (Figure 4d).

301 In summary, the polymer could disperse slag particles in water, as expected, but lost this ability  
302 in presence of activators, partially in the case of NaOH and totally in the case of  $\text{Na}_2\text{CO}_3$ . These  
303 observations demonstrate that the efficiency problem of the superplasticizers was not due to an  
304 intrinsic surface property of slag but to an effect of alkaline activators. Moreover, the two  
305 activators did not have the same influence on the superplasticizer, as a gradual loss of efficiency  
306 was observed with NaOH while  $\text{Na}_2\text{CO}_3$  completely inhibited the polymer's action. Hence, the  
307 two systems will be discussed separately for the remainder of the article.

308 First and foremost, the chemical stability of the PCEs in 3.2 mol/kg NaOH-solution or 1.6  
309 mol/kg  $\text{Na}_2\text{CO}_3$ -solution was checked by SEC (Figure 5). It is established that the polymers  
310 were not significantly hydrolysed in the activating solutions within the time scale of the  
311 experiments as expected for superplasticizers with polymethacrylic acid backbones  
312 (MPEG)[27]. Other hypothesis had to be explored to explain the PCEs efficiency losses in the  
313 systems under investigations.



314 **Figure 5: Size-exclusion chromatography curves showing the evolution of the refractive index**  
315 **depending on the retention volume for the superplasticizer PCE45 after contact with the**  
316 **activating solutions.**

317

### 318 **3.3. The case of NaOH-activation**

#### 319 **3.3.1. Superplasticizer's adsorption on slag**

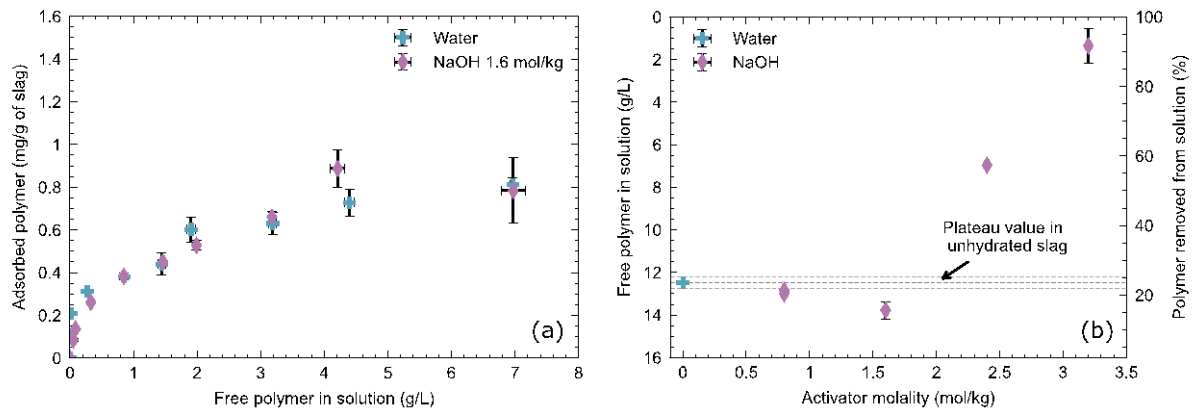
320 As stated in the introduction, a possible explanation for the efficiency loss of the  
321 superplasticizer is a lack of adsorption of the polymer chains on slag grains. In order to explore  
322 this hypothesis, adsorption measurements were conducted on slag pastes with a higher w/s ratio  
323 of 0.8 to facilitate the collection of the interstitial solutions. The quantity of superplasticizer  
324 added to the system was varied to plot effective “adsorption isotherms” (Note that these  
325 measurements cannot be strictly considered as isotherms since they are not performed at  
326 thermodynamic equilibrium; furthermore, there is no guarantee that they solely reflect  
327 adsorption processes, as will be discussed below.). These analyses consisted in the  
328 measurement of the quantity of polymer in the interstitial solution of cement pastes with Total  
329 Organic Carbon equipment. Knowing the initial quantity of polymer added to the cement paste,  
330 the quantity of polymer removed from solution or adsorbed to the slag surface was then  
331 deduced. The results are presented on Figure 6a.

332 For both systems, the curves exhibit a generic Langmuir-type adsorption isotherm shape with  
333 a steep initial increase of the amount of adsorbed polymer, characteristic of a high polymer  
334 affinity for the surface of slag grains [9]. This increase is followed by an adsorption pseudo  
335 plateau corresponding to the full coverage of the slag particles' surface. The polymer's  
336 adsorption plateau in NaOH solutions or in pure water was reached for a similar value in both  
337 cases, around 0.8 mg/g corresponding to 0.95 mg/m<sup>2</sup>.

338 These results indicate that the superplasticizer adsorption on slag was not modified in NaOH  
339 solutions, despite the loss of dispersing ability observed by rheology at the same NaOH



340 concentration (1.6 kg/mol). This result is different from the observations of Marchon et al. [17]  
 341 who showed that the addition of NaOH in an OPC blended with fly ash leads to a decreased  
 342 adsorption of PCEs. This difference was probably due to the contrast in composition and surface  
 343 between clinker and slag particles. Indeed, the adsorption of the superplasticizers on slag was  
 344 low compared to OPC systems (77 % of PCE remaining in solution at the plateau in our slag  
 345 samples against 56 % in the OPC blended system [17]). Also, while the calcium concentration  
 346 in solution is always relatively high and stable (imposed by portlandite equilibrium) in OPC  
 347 systems, in slag it can vary. The use of NaOH activates slag hydration, making more calcium  
 348 available to permit PCE adsorption (as seen in Table 5). This could counterbalance and mask a  
 349 possible competitive adsorption of the hydroxides as observed in OPC.



350 **Figure 6: (a) Evolution of the quantity of adsorbed superplasticizer (PCE45) on non-activated or**  
 351 **NaOH-activated slag depending on the quantity of free polymer in solution. The w/s ratio was 0.8,**  
 352 **with 4.0 wt% of Na<sub>2</sub>O by weight of slag when using NaOH, leading to a NaOH molality of 1.61**  
 353 **mol/kg. (b) Evolution of the quantity of free polymer (PCE45) in solution or polymer**  
 354 **removed from solution (right axis) depending on the NaOH molality. The superplasticizer was**  
 355 **added in proportions of 0.6 wt% by weight of slag (16.9 g/L) and the w/s ratio was 0.4. The Na<sub>2</sub>O**  
 356 **dosage is varied to change the activator molality.**

357 To further study the superplasticizer properties in the activated slag binders, adsorption  
 358 measurements were conducted while varying the activators' molality. These experiments were

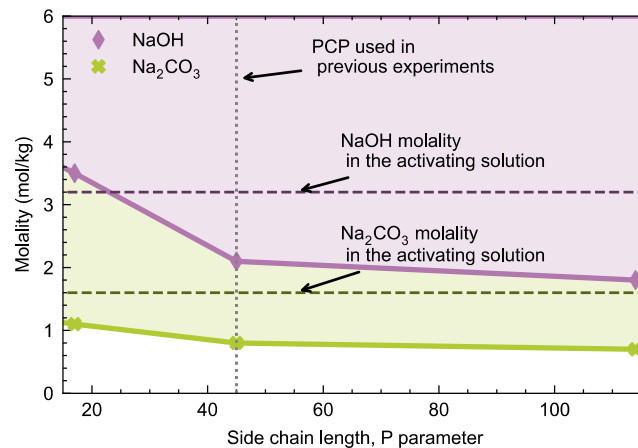
359 run on slag pastes with a w/s ratio of 0.4 and a polymer content of 0.6 wt% by weight of slag  
360 which is on the adsorption isotherm plateau. In order to change the activators' molality while  
361 keeping the initial quantity of polymer and the w/s ratio constant, the quantity of activator by  
362 weight of slag was varied from 0 wt% Na<sub>2</sub>O to 4 wt% Na<sub>2</sub>O for NaOH (maximum molality of  
363 3.2 mol/kg).

364 The results are presented on Figure 6b. First, it can be noticed that, for a non-activated cement  
365 paste, i.e. in water, the quantity of free polymer in solution was 12.5 g/L, which corresponds to  
366 a little more than 20 % of the total polymer content adsorbed on slag surface under these  
367 conditions. For low NaOH molalities (0.8 and 1.6 mol/kg), polymer adsorption was similar to  
368 the one observed in non-activated conditions, as already seen in Figure 6a. For the highest  
369 NaOH concentrations in Figure 6b, the concentration of free polymer in solution decreased,  
370 leading to seemingly quasi total "adsorption" of polymer. This result was clearly not attributable  
371 to a Langmuir-type adsorption phenomenon. Another phenomenon than adsorption was at play  
372 here, which further separated the polymer from the interstitial solution.

### 373 **3.3.2. Superplasticizer's solubility in NaOH solution**

374 To investigate the phenomenon inducing a higher apparent adsorption of superplasticizers at  
375 high NaOH molality, the interaction between superplasticizers and activating solutions was  
376 studied independently from the slag. Indeed, during the paste preparations with a w/s ratio of  
377 0.4 and 4.0 wt% of Na<sub>2</sub>O, corresponding to an activator molality of 3.2 mol/kg for NaOH, it  
378 was observed that the addition of the superplasticizer to the activating solutions led to turbid  
379 solutions. However, this phenomenon did not occur when the superplasticizer was added in  
380 pure water. Hence, arises the question of the polymer solubility in the activating solutions.

381 The issue of superplasticizers solubility has been recently discussed by Conte and Plank [14]  
 382 who showed by macroscopic observations that the solubility of PCEs can be insufficient in slag  
 383 cements activated with NaOH or Na<sub>2</sub>CO<sub>3</sub> and that this solubility depends on the side-chain  
 384 length of the superplasticizers, their charge density and their chemical composition.  
 385 As in the study previously mentioned, the solubility of the superplasticizers was assessed by  
 386 cloud point measurements at ambient temperature, and this for superplasticizers with different  
 387 side-chain lengths (parameter *P* in Gay and Raphaël's nomenclature). The backbone chain  
 388 length varied only slightly (parameter *n* from 8.5 to 10).  
 389 The cloud points were measured at polymer concentrations equal to the ones in [14] for sake of  
 390 comparison. They are reported in Figure 7. The activator molalities corresponding to the cloud  
 391 points were lower when the side-chain length was increased. This observation means that the  
 392 polymer was more sensitive to the activator, and less soluble, for greater side-chain lengths.



393 **Figure 7: Cloud points measurements for superplasticizers with different side-chain lengths (*P*),**  
 394 **at 1 g/L of polymer. For molality of activators higher than the cloud points, the polymer solutions**  
 395 **were turbid.**

396 It is now interesting to compare these results with the conditions used in the alkali-activated  
 397 pastes. For slags activated with 4.0 wt% of Na<sub>2</sub>O by weight of slag and a w/s ratio of 0.4, the  
 398 NaOH molality is 3.2 mol/kg. As figured by the corresponding horizontal dashed line in Figure

399 7, this molality did not correspond to a swollen state for PCE45 and PCE114, meaning these  
400 polymers were not fully soluble even at the low polymer concentration of 1 g/L. They are likely  
401 to be even less soluble at the higher concentrations of 13-17 g/L used in the present study. Only  
402 the superplasticizer with small side-chains, PCE17, was in a swollen state at this NaOH  
403 molality.

404 The absence of dispersing effect of the superplasticizer (Figure 4b) and the aberrant values of  
405 adsorption (Figure 6b) in activated cements at 3.2 mol/kg of NaOH can thus be explained by a  
406 first order phase transition from dispersed to aggregated states. Indeed, this concentration being  
407 above the cloud point of PCE45, the decrease of solubility of the polymers led to their  
408 aggregation. The polymer was then retained by the filters used for the collection of the  
409 interstitial solution, inducing very high apparent “adsorptions” (Figure 6b). Furthermore, the  
410 PEG side-chains are collapsed and not extended in the interstitial solution under these  
411 conditions and cannot play their role of steric repulsion between the slag’s particles (Figure 4b),  
412 potentially accounting for the loss of efficiency of the superplasticizer.

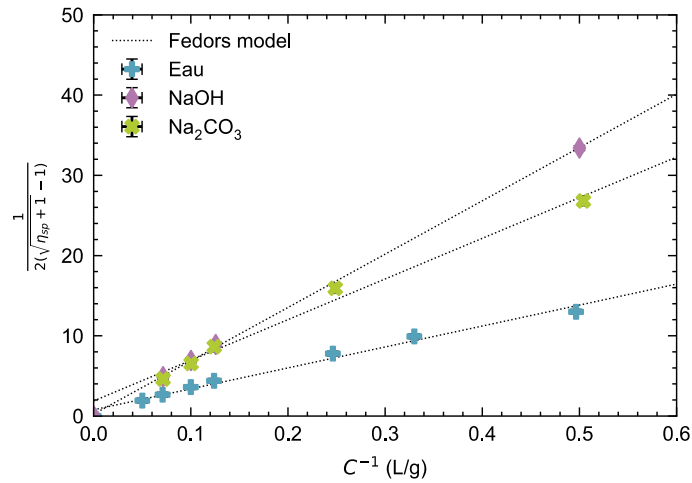
413 However, a transition from solvated to aggregated states cannot explain the observed loss of  
414 efficiency below the cloud point. A better solubility of the polymers can be obtained either by  
415 lowering the activator molality (going from the top to the bottom of Figure 7) or by reducing  
416 the side chain length (going from the left to the right of Figure 7). Some rheology measurements  
417 were thus conducted with PCE17 in non-activated and NaOH-activated slag (w/s of 0.4, 4.0  
418 wt% of Na<sub>2</sub>O, 3.2 mol/kg of NaOH), as shown on Figure S3 in the Supplementary Material.  
419 This superplasticizer did improve the fluidity of the non-activated slag but lost its efficiency in  
420 the NaOH-activated paste, even though its “cloud point” is above the NaOH molality in these  
421 conditions. This result is similar to what was observed with PCE45. Indeed, Figure 4b showed  
422 that PCE45 had no dispersing ability in NaOH-activated slag at a molality of 1.6 mol/kg, which  
423 is also slightly below the PCE45 “cloud point” in NaOH solution. Furthermore, as seen in

424 Figure 4b, the fluidity of PCE45 did not transition abruptly when going above the cloud point.  
425 Instead, the loss was gradual when the NaOH molality increased toward the cloud point, a  
426 behaviour that is not compatible with a first order phase transition from solvated to aggregated  
427 state. Solubility in its strict sense cannot fully account for the fluidity loss.

### 428 **3.3.3. Influence of NaOH on the superplasticizer's viscometric radius**

429 To further investigate potential conformational changes of the superplasticizers in the NaOH  
430 solution below its cloud point, the PCE45 solutions specific viscosities were measured by  
431 capillary viscometry. Variations of specific viscosities reveal conformational changes and allow  
432 to estimate qualitatively variations of the hydrodynamic size of the superplasticizer according  
433 to Fedors model[20,21]. Since this model is strictly valid only for polymers in their swollen  
434 state, the measurements were done in water and in NaOH at 1.61 mol/kg, which corresponds to  
435 the molality used previously for the adsorption isotherm (Figure 6a). Furthermore, it was  
436 verified that all solutions (polymer concentrations from 0 to 14 g/L) were clear (below their  
437 cloud points) and the polymers could be considered as swollen.

438 The evolution of the specific viscosities depending on the polymer concentration is plotted on  
439 Figure 8 and the values are fitted with Fedors model (Eq. 1). The intrinsic viscosities and the  
440 viscometric radii obtained from the Fox-Flory equation are reported in Table 4. A significant  
441 decrease of the superplasticizer viscosimetric radii was observed in the NaOH-solution  
442 compared to the pure water solution, even though the NaOH molality used were below the cloud  
443 point and thus corresponded to swollen state conditions.



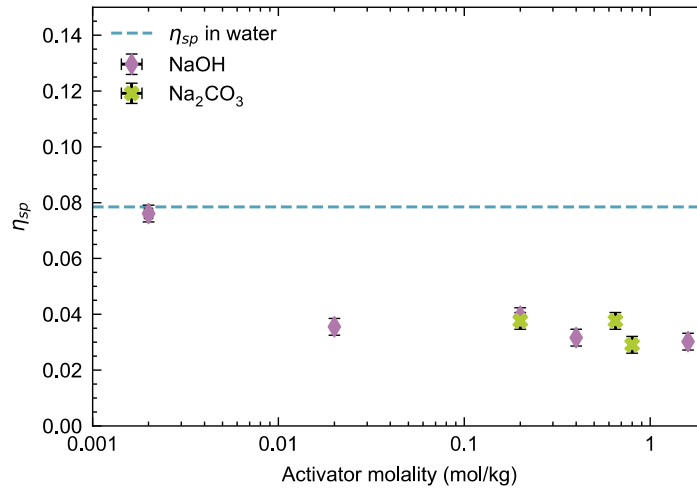
444 **Figure 8: Evolution of the polymer (PCE45) solutions' specific viscosity depending on the polymer**  
 445 **concentration from 0 to 14 g/L. The values are plotted accordingly to Fedors model in order to**  
 446 **obtain the intrinsic viscosity of the superplasticizer in the different solutions. The activator**  
 447 **molalities were 1.61 mol/kg for the NaOH solution and 0.65 mol/kg for the Na<sub>2</sub>CO<sub>3</sub> solution. All**  
 448 **solutions were clear and thus below their cloud points.**

449 **Table 4: Intrinsic viscosities and viscometric radii of the superplasticizer in water, 1.61 mol/kg of**  
 450 **NaOH, or 0.65 mol/kg of Na<sub>2</sub>CO<sub>3</sub>, calculated with the Fedors equation and the Fox and Flory**  
 451 **model (see part 2.2.5.). The values are given with an error of  $\pm 2$  mL/g for the intrinsic viscosities**  
 452 **and  $\pm 0.2$  nm for the viscometric radii.**

	Water	NaOH	Na <sub>2</sub> CO <sub>3</sub>
<b>Intrinsic viscosity (mL/g)</b>	39	15	20
<b>Viscometric radius (nm)</b>	8.6	6.3	6.8

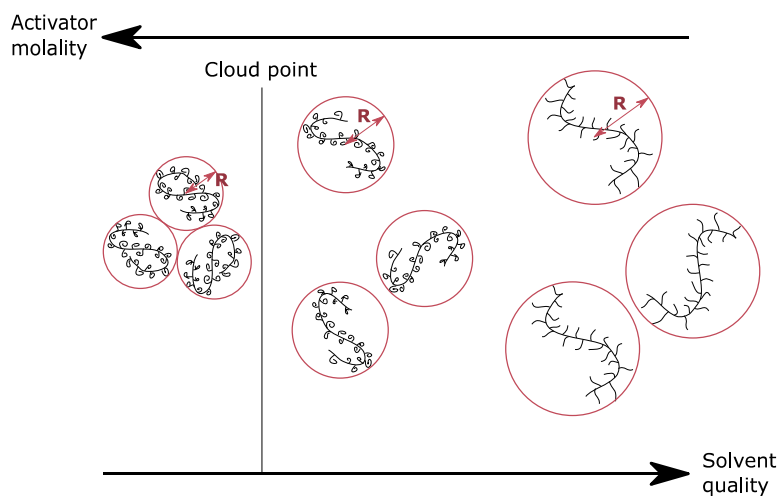
453 To further study this effect, the activator molality was decreased, keeping the polymer  
 454 concentration constant (2 g/L). The specific viscosities measured are presented in Figure 9,  
 455 without using Fedors model as the polymer concentration was kept constant. The specific  
 456 viscosities decreased only slowly with the activator molality but eventually reached the value  
 457 measured in pure water for a molality of 0.002 mol/kg. Therefore, the polymer radius increased  
 458 when the NaOH molality decreased. Interestingly, the viscosities were always lower than the

459 one of PCE in pure water despite the fact that all these measurements were performed in clear  
 460 solutions (not turbid).



461 **Figure 9: Evolution of the polymer (PCE45) solutions' specific viscosity depending on the activator**  
 462 **molality. The polymer concentration was 2 g/L.**

463 These experiments showed that, even when the polymer solutions were macroscopically clear,  
 464 the presence of NaOH led to a decrease of the solvent quality for the superplasticizers and thus  
 465 to its partial shrinking, as represented on Figure 10. The side-chains were not extended in the  
 466 solution and could not play their role of steric repulsion between the slag grains. As NaOH  
 467 molality decreases, the solvent quality improved and the side-chains further expanded in the  
 468 interstitial solution. The dispersing action was hence gradually recovered.



469 **Figure 10: Schematic representation of the evolution of the polymer's conformation depending on**  
470 **the solvent quality. R is the polymer's viscometric radius.**

471 It can thus be concluded that the lack of efficiency of the superplasticizers in NaOH-activated  
472 slag cements is not simply due to a phase separation when they are not in a swollen state but  
473 also to a gradual decrease of the solvent quality with the concentration of the NaOH activating  
474 solution, which limits the steric repulsion of the side-chains. The question now is to see if the  
475 same explanation for the efficiency loss of PCE applies to Na<sub>2</sub>CO<sub>3</sub> activation or if other  
476 phenomena must be explored.

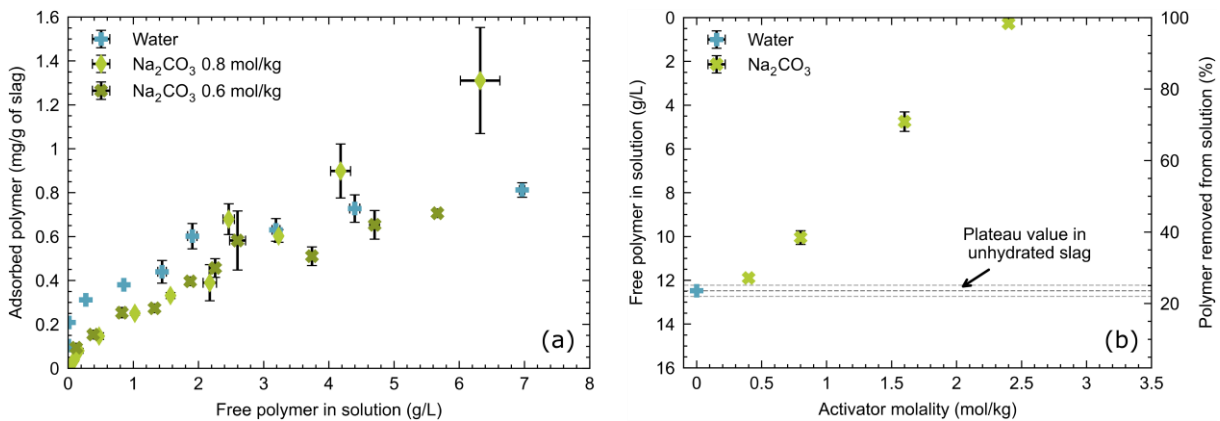
### 477 **3.4. The case of Na<sub>2</sub>CO<sub>3</sub>-activation**

#### 478 **3.4.1. Superplasticizer adsorption on slag**

479 First, as for NaOH, the adsorption behaviour of the superplasticizer PCE45 was studied in  
480 Na<sub>2</sub>CO<sub>3</sub>-activated systems. This time, two w/s ratios (0.8 and 1.0) were used to see the effect  
481 of the Na<sub>2</sub>CO<sub>3</sub> molality on the effective adsorption isotherms. The curves obtained (Figure 11)  
482 present a different shape than the previous isotherms obtained with NaOH (Figure 6a): the  
483 initial slope was slower compared to non-activated and NaOH-activated slag no apparent  
484 inflexion point marked the approach to a plateau value. For PCE45 concentrations below 2.5  
485 g/L, effective adsorption appeared generally reduced in the Na<sub>2</sub>CO<sub>3</sub> system compared to non-  
486 activated and NaOH-activated slag. This meant that contrary to NaOH, the Na<sub>2</sub>CO<sub>3</sub> solution  
487 significantly disturbs the polymer adsorption. This result does not depend on the w/s ratio (nor  
488 on the activator molality) indicating that mainly surface adsorption phenomena are at play at  
489 low concentrations of polymer. For PCE45 concentrations above 2.5 g/L, on the other hand,  
490 and for a w/s ratio of 0.8, corresponding to the highest Na<sub>2</sub>CO<sub>3</sub> concentration, no plateau is  
491 observed and the amount reached is even higher than the one resulting from adsorption observed  
492 in water. This last result is confirmed by the results shown in Figure 11b where increasing



493 adsorption values and less polymer in the interstitial solution are observed as the  $\text{Na}_2\text{CO}_3$   
 494 molality is increased up to 6 wt%  $\text{Na}_2\text{O}$  for  $\text{Na}_2\text{CO}_3$  (maximum molalities of 2.4 mol/kg). These  
 495 results reflect that as for  $\text{NaOH}$ , at high concentration of polymers, a phenomenon other than  
 496 simple physical adsorption is at play.



497 **Figure 11: (a) Evolution of the quantity of adsorbed superplasticizer on slag without an activator**  
 498 **(in water) or activated with  $\text{Na}_2\text{CO}_3$  depending on the quantity of free polymer in solution. The**  
 499 **non-activated paste had a w/s ratio of 0.8. The  $\text{Na}_2\text{CO}_3$  samples were all activated with 4.0 wt%**  
 500  **$\text{Na}_2\text{O}$  by weight of slag, and two w/s ratio were tested: 0.8 corresponding to a  $\text{Na}_2\text{CO}_3$  molality of**  
 501 **0.81 mol/kg, and 1.0 corresponding to a molality of 0.65 mol/kg. (b) Evolution of the quantity of**  
 502 **free polymer (PCE45) (left axis) in solution or polymer removed from solution (right axis)**  
 503 **depending on the  $\text{Na}_2\text{CO}_3$  molality. The superplasticizer was added in proportions of 0.6 wt% by**  
 504 **weight of slag (16.9 g/L) and the w/s ratio was 0.4. The  $\text{Na}_2\text{O}$  dosage is varied to change the**  
 505 **activator molality.**

### 506 3.4.2. Superplasticizer solubility in $\text{Na}_2\text{CO}_3$ solution

507 As well as for the  $\text{NaOH}$  system, the high adsorption values observed can be explained by a  
 508 lack of solubility of the superplasticizers in the  $\text{Na}_2\text{CO}_3$  solutions. Indeed, the cloud points  
 509 measurements conducted (see Figure 7) showed that the addition of  $\text{Na}_2\text{CO}_3$  also impacted the  
 510 solvent quality for the superplasticizers, leading to even lower values of cloud points with  
 511  $\text{Na}_2\text{CO}_3$  than with  $\text{NaOH}$ . This trend, which follows the Hofmeister series, is common when

512 studying the solubility of PEG [28–30], or of polymers containing PEG segments[31], and is  
 513 linked to the higher valency and radius of  $\text{CO}_3^{2-}$  compared to  $\text{OH}^-$  [32]. Furthermore, as for  
 514 NaOH, the capillary viscometry measurements resulted in a lower viscometric radius of PCE45  
 515 in 0.65 mol/kg  $\text{Na}_2\text{CO}_3$  solutions than in pure water (Figure 8, Table 4 and Figure 9).  
 516 However, the dispersing ability of the superplasticizers was not gradually recovered when using  
 517 lower molalities of  $\text{Na}_2\text{CO}_3$  (Figure 4d), contrary to the NaOH-activated system. This shows  
 518 that the lack of solubility and the change of conformation were not the only phenomena at play  
 519 here. The mechanisms were thus more complex and warranted further investigations.

### 520 **3.4.3. Investigation of the lower superplasticizer adsorption in $\text{Na}_2\text{CO}_3$ systems**

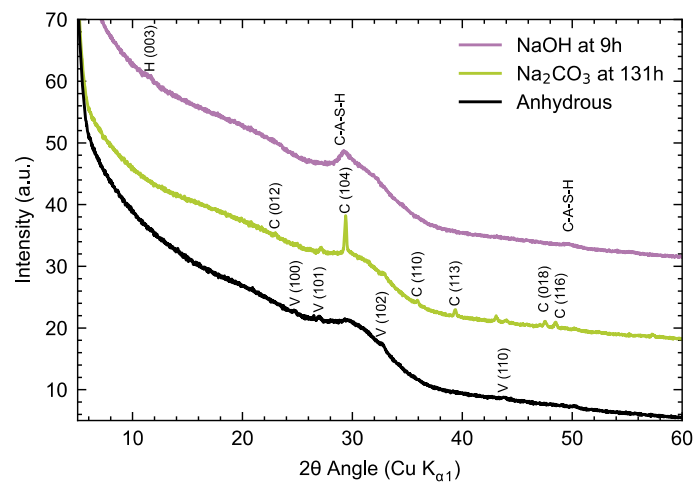
521 As was shown in section 3.4.1., the adsorption of the superplasticizer on the slag particles was  
 522 modified when the cement was activated with  $\text{Na}_2\text{CO}_3$ . Two possible explanations are  
 523 examined hereafter.

524 The first conjecture is that the calcium concentration in the interstitial solution was too low.  
 525 Indeed, it is well known that calcium cations serve as a link between the negatively charged  
 526 surface of cementitious or slag particles and the negative backbone of the superplasticizers.  
 527 However, even though the calcium concentration in solutions (Table 5) was lower in  $\text{Na}_2\text{CO}_3$ -  
 528 activated pastes (as well as in NaOH-activated pastes) compared to what is measured in  
 529 ordinary Portland cement [33,34], the value was similar to the one obtained for non-activated  
 530 slag cement. The previous observations thus cannot be explained by a lower calcium  
 531 concentration in the interstitial solution.

532 **Table 5: Calcium concentrations in the interstitial solution of the different slag cements, measured**  
 533 **by ICP-OES. The values are given with an error of  $\pm 6 \mu\text{mol/L}$ .**

System	Water	NaOH	$\text{Na}_2\text{CO}_3$
[Ca] mmol/L	0.406	0.750	0.437

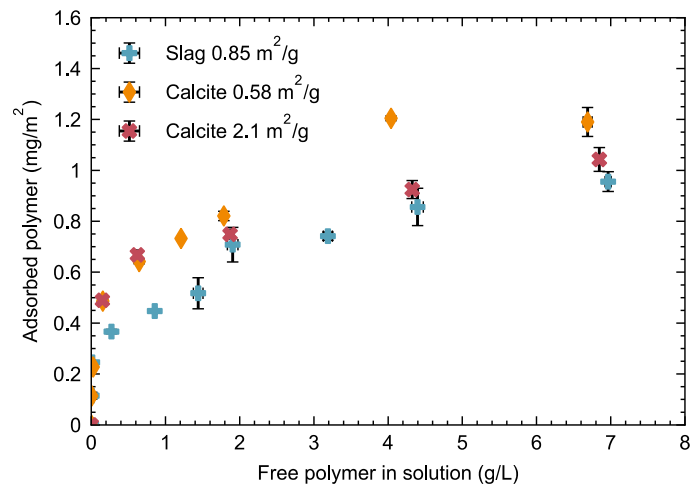
534 The second conjecture is a preferential adsorption of the superplasticizer on reaction products  
 535 which would have already been formed in low quantities even at early hydration times. The  
 536 activated slags were thus analysed by XRD at different times of reaction. The results are  
 537 presented on Figure 12. The anhydrous slag leads to a diffractogram with a large bump around  
 538  $30^\circ$  corresponding to its amorphous content. Some small peaks were also visible which can be  
 539 associated with the presence of a low quantity of vaterite in the initial slag.



540 **Figure 12: X-ray diffractograms of anhydrous slag and of the NaOH- and Na<sub>2</sub>CO<sub>3</sub>-activated slag**  
 541 **cements, with a w/s ratio of 0.4 and 4.0 wt% of Na<sub>2</sub>O. The peaks are referenced with the**  
 542 **corresponding Miller indexes between brackets according to the PDF files. The different phases**  
 543 **visible are CaCO<sub>3</sub> crystallised as calcite (noted C, file 00-005-0586) and as vaterite (noted V, file**  
 544 **01-072-0506), hydrotalcite Mg<sub>2</sub>Al(OH)<sub>4</sub>(CO<sub>3</sub>)<sub>0.5</sub>H<sub>2</sub>O (noted H, file 01-089-0460) and a C-A-S-H**  
 545 **taken accordingly to the tobermorite-11Å structure (file 00-045-1480).**

546 When slag was activated with NaOH, peaks corresponding to a C-A-S-H gel [35–38] was  
 547 present at 9 h, as it is the primary hydration product of cementitious binders, together with some  
 548 peaks corresponding to hydrotalcite as a secondary hydrate. In the case of an activation with  
 549 Na<sub>2</sub>CO<sub>3</sub>, calcite [36,39] was detected at 131 h, as well as a very amorphous alumino-silicate  
 550 gel, mostly visible on the NMR spectra (Figure S2).

551 As a result, adsorption measurements of the superplasticizer on calcite were conducted to  
 552 investigate if the formation of this phase could explain the apparent lower adsorption values  
 553 measured previously in the case of  $\text{Na}_2\text{CO}_3$  activation (Figure 11). Indeed, one could conjecture  
 554 that due to high concentration of carbonates some very small calcite crystallites, undetectable  
 555 by XRD, would be already formed at the time of the adsorption measurements and that the  
 556 superplasticizer would adsorb on them. The TOC apparatus would still measure this fraction  
 557 of the PCE as part of the solution since some calcite crystallites could be small enough to pass  
 558 through the  $1.2\ \mu\text{m}$  filters used to separate the interstitial solution. Different studies [40–44]  
 559 have already shown that superplasticizers can adsorb well on calcite and that this mineral can  
 560 be used as a reference system for early-age cementitious materials. This is a plausible  
 561 hypothesis that is explored in the following paragraph.



562 **Figure 13: Adsorption isotherms of the superplasticizer PCE45 on slag and two calcites of**  
 563 **different specific surface area. These experiments were conducted with a constant total surface of**  
 564 **solid corresponding to the samples at  $w/s = 0.8$ .**

565 The adsorption isotherms on slag and calcite are presented on Figure 13. Contrary to what was  
 566 done for the previous adsorption studies, in this case, it is better to look at the values given in  
 567  $\text{mg/m}^2$  of solid since they take into account the different specific surface areas of calcite and

568 slag. For this purpose, we have considered that the specific surface area of the slag was not  
569 significantly changed during the first 15 minutes of reaction (see Table 3).

570 Figure 12 shows that the quantities of superplasticizer adsorbed on calcite are equal or a little  
571 higher than on slag. Therefore, the polymer could indeed adsorb on the calcite precipitated in  
572 the Na<sub>2</sub>CO<sub>3</sub>-activated slag pastes. Nevertheless, taking the Ca concentration measured by ICP-  
573 OES in the liquid phase of this sample (0.4 mmol/L, see Table 5) as an estimate of the order of  
574 magnitude of Ca precipitated as calcite nuclei, the quantity of polymer adsorbed on calcite at  
575 the plateau (1.1 mg/m<sup>2</sup>) cannot account for the difference of adsorbed polymer between the  
576 Na<sub>2</sub>CO<sub>3</sub>- or non-activated samples (5.5 mg/m<sup>2</sup> according to the data of Figure 11). The specific  
577 surface of the calcite crystallites needed for this hypothesis to be true can be estimated to 3500  
578 m<sup>2</sup>/g. This very high value is aberrant as it would require crystallite sizes of the atomic order.  
579 The orders of magnitude involved are thus not in favour of the calcite adsorption hypothesis.  
580 Consequently, the competitive adsorption of the polymers on calcite cannot by itself explain  
581 the lower affinity of the superplasticizers to the slag surface in Na<sub>2</sub>CO<sub>3</sub>-activated systems.  
582 However, the formation of calcite showed there is a strong interaction between Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>  
583 . Therefore, there could be a competition between the CO<sub>3</sub><sup>2-</sup> anions and the superplasticizers for  
584 the adsorption sites at the slag surface, explaining the shape of the isotherms measured  
585 previously (Figure 11). This last explanation, however plausible, could not be tested with the  
586 experimental means of the current study and thus remains hypothetical.

#### 587 **4. CONCLUSIONS**

588 This paper provides results on the behaviour of polycarboxylates ether superplasticizers in  
589 alkali-activated slag. Two systems were considered, with NaOH and Na<sub>2</sub>CO<sub>3</sub> as alkaline  
590 activators.

591 First and foremost, it was shown that the dispersing efficiency of the superplasticizers in non-  
592 activated slag cement was good, with satisfying adsorption and rheological behaviours. The

593 chemical stability of the polymers in the activating solutions was also confirmed by SEC  
594 analyses. Therefore, the question of the solubility of the superplasticizers in the activating  
595 solutions (NaOH and Na<sub>2</sub>CO<sub>3</sub>), which has only been investigated once before, was examined.  
596 A qualitative correlation between the solubility of the polymers and the adsorption measures  
597 was found. However, the full dispersing ability of the polymers, as manifested in the rheology  
598 of the paste, was not retrieved in the swollen state. Capillary viscometry was thus conducted to  
599 study the conformation of the polymers in the corresponding activating solutions. A smaller  
600 viscometric radius was measured for the superplasticizers in the NaOH and Na<sub>2</sub>CO<sub>3</sub> solutions.  
601 Since the viscometric radius of comb copolymers scales with the coil size of the side-chains,  
602 this meant that the side-chain extension was also reduced. This could very well lead to a  
603 degradation of the steric repulsion between particles, which is the mechanism of action of  
604 superplasticizers, thus explaining their loss of efficiency in alkali-activated slag cements.  
605 Furthermore, it appeared that the superplasticizer adsorption as well was hindered in Na<sub>2</sub>CO<sub>3</sub>-  
606 activated slag cements. This observation could not be explained by the low Ca concentration in  
607 the cement pore solution nor by the competitive adsorption of the superplasticizer between the  
608 slag and the precipitated calcite. Finally, by elimination, the most plausible hypothesis seemed  
609 to be a competitive adsorption between the superplasticizer and the CO<sub>3</sub><sup>2-</sup> brought by the  
610 activator but this remained an open question.

611 To summarize, it was found that the solubility of MPEG polymers in NaOH and Na<sub>2</sub>CO<sub>3</sub>  
612 activating solutions represents a limiting factor for their dispersing capability. Furthermore, the  
613 presence of activator anions alters both the adsorption of the polymer and its conformation. The  
614 present study thus suggests that, to improve the rheology of alkali-activated slag cements, it  
615 will be necessary to formulate polymers less sensitive to the ionic strength of the activating  
616 solutions than the superplasticizers currently used by the industry in ordinary Portland cements.

617 **CRedit authorship contribution statement**

618 **Clara Paillard:** Conceptualisation, Methodology, Investigation, Writing – Original Draft,  
619 Visualization; **Marien Aparicio Cordoba:** Investigation; **Nicolas Sanson:** Conceptualization,  
620 Methodology, Writing – Review & Editing, Supervision; **Jean-Baptiste d’Espinose de**  
621 **Lacaille:** Conceptualization, Methodology, Writing – Review & Editing, Supervision;  
622 **Guylaine Ducouret:** Methodology; **Pascal Boustingorry:** Conceptualisation, Methodology,  
623 Writing – Review & Editing; **Marie Jachiet:** Conceptualization, Methodology, Writing –  
624 Review & Editing; **Claire Giraudeau:** Conceptualisation, Methodology, Writing – Review &  
625 Editing; **Vanessa Kocaba:** Conceptualization, Methodology, Writing – Review & Editing.

626 **Declaration of competing interests**

627 The authors declare that there is no conflict of interest.

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- 636 [1] F.G. Collins, J.G. Sanjayan, Workability and mechanical properties of alkali activated  
637 slag concrete, *Cement and Concrete Research*. 29 (1999) 455–458.  
638 [https://doi.org/10.1016/S0008-8846\(98\)00236-1](https://doi.org/10.1016/S0008-8846(98)00236-1).
- 639 [2] A. Fernández-Jiménez, F. Puertas, Effect of activator mix on the hydration and strength  
640 behaviour of alkali-activated slag cements, *Advances in Cement Research*. 15 (2003)  
641 129–136. <https://doi.org/10.1680/adcr.2003.15.3.129>.
- 642 [3] A. Gruskovnjak, B. Lothenbach, L. Holzer, R. Figi, F. Winnefeld, Hydration of alkali-  
643 activated slag: comparison with ordinary Portland cement, *Advances in Cement*  
644 *Research*. 18 (2006) 119–128. <https://doi.org/10.1680/adcr.2006.18.3.119>.
- 645 [4] J.S.J. Van Deventer, J.L. Provis, P. Duxson, Technical and commercial progress in the  
646 adoption of geopolymer cement, *Minerals Engineering*. 29 (2012) 89–104.  
647 <https://doi.org/10.1016/j.mineng.2011.09.009>.
- 648 [5] T. Tsubakimoto, M. Hosoido, H. Tahara, Copolymer and method for manufacture  
649 thereof, US4471100A, 1984.
- 650 [6] P.F.G. Banfill, A discussion of the papers “rheological properties of cement mixes” by  
651 M. Daimon and D. M. Roy, *Cement and Concrete Research*. 9 (1979) 795–796.  
652 [https://doi.org/10.1016/0008-8846\(79\)90075-9](https://doi.org/10.1016/0008-8846(79)90075-9).
- 653 [7] E.M. Gartner, H. Koyata, P. Scheiner, Influence of aqueous phase composition on the  
654 zeta potential of cement in the presence of water-reducing admixtures, *American*  
655 *Ceramic Society*. 40 (1994) 131–140.
- 656 [8] G. Gelardi, R.J. Flatt, 11 - Working mechanisms of water reducers and superplasticizers,  
657 in: P.-C. Aïtcin, R.J. Flatt (Eds.), *Science and Technology of Concrete Admixtures*,  
658 Woodhead Publishing, 2016: pp. 257–278. <https://doi.org/10.1016/B978-0-08-100693-1.00011-4>.
- 660 [9] D. Marchon, S. Mantellato, A.B. Eberhardt, R.J. Flatt, 10 - Adsorption of chemical  
661 admixtures, in: P.-C. Aïtcin, R.J. Flatt (Eds.), *Science and Technology of Concrete*  
662 *Admixtures*, Woodhead Publishing, 2016: pp. 219–256. <https://doi.org/10.1016/B978-0-08-100693-1.00010-2>.
- 664 [10] E. Douglas, J. Brandstetr, A preliminary study on the alkali activation of ground  
665 granulated blast-furnace slag, *Cement and Concrete Research*. 20 (1990) 746–756.  
666 [https://doi.org/10.1016/0008-8846\(90\)90008-L](https://doi.org/10.1016/0008-8846(90)90008-L).
- 667 [11] F. Puertas, A. Palomo, A. Fernández-Jiménez, J.D. Izquierdo, M.L. Granizo, Effect of  
668 superplasticisers on the behaviour and properties of alkaline cements, *Advances in*  
669 *Cement Research*. 15 (2003) 23–28.
- 670 [12] M. Palacios, F. Puertas, Effect of superplasticizer and shrinkage-reducing admixtures on  
671 alkali-activated slag pastes and mortars, *Cement and Concrete Research*. 35 (2005)  
672 1358–1367. <https://doi.org/10.1016/j.cemconres.2004.10.014>.
- 673 [13] M. Palacios, F. Puertas, Stability of superplasticizer and shrinkage-reducing admixtures  
674 in high basic media, *Materiales de Construcción*. 54 (2004) 65–86.
- 675 [14] T. Conte, J. Plank, Impact of molecular structure and composition of polycarboxylate  
676 comb polymers on the flow properties of alkali-activated slag, *Cement and Concrete*  
677 *Research*. 116 (2019) 95–101. <https://doi.org/10.1016/j.cemconres.2018.11.014>.



- 678 [15] A. Habbaba, J. Plank, Interaction between polycarboxylate superplasticizers and  
679 amorphous ground granulated blast furnace slag, *Journal of the American Ceramic*  
680 *Society*. 93 (2010) 2857–2863. <https://doi.org/10.1111/j.1551-2916.2010.03755.x>.
- 681 [16] A. Habbaba, J. Plank, Surface chemistry of ground granulated blast furnace slag in  
682 cement pore solution and its impact on the effectiveness of polycarboxylate  
683 superplasticizers, *Journal of the American Ceramic Society*. 95 (2012) 768–775.  
684 <https://doi.org/10.1111/j.1551-2916.2011.04968.x>.
- 685 [17] D. Marchon, U. Sulser, A. Eberhardt, R.J. Flatt, Molecular design of comb-shaped  
686 polycarboxylate dispersants for environmentally friendly concrete, *Soft Matter*. 9 (2013)  
687 10719–10728. <https://doi.org/10.1039/C3SM51030A>.
- 688 [18] J. Plank, C. Hirsch, Impact of zeta potential of early cement hydration phases on  
689 superplasticizer adsorption, *Cement and Concrete Research*. 37 (2007) 537–542.  
690 <https://doi.org/10.1016/j.cemconres.2007.01.007>.
- 691 [19] C. Gay, E. Raphaël, Comb-like polymers inside nanoscale pores, *Advances in Colloid*  
692 *and Interface Science*. 94 (2001) 229–236. [https://doi.org/10.1016/S0001-](https://doi.org/10.1016/S0001-8686(01)00062-8)  
693 [8686\(01\)00062-8](https://doi.org/10.1016/S0001-8686(01)00062-8).
- 694 [20] G. Gelardi, N. Sanson, G. Nagy, R.J. Flatt, Characterization of Comb-Shaped  
695 Copolymers by Multidetector SEC, DLS and SANS, *Polymers*. 9 (2017) 61.  
696 <https://doi.org/10.3390/polym9020061>.
- 697 [21] R.F. Fedors, An equation suitable for describing the viscosity of dilute to moderately  
698 concentrated polymer solutions, *Polymer*. 20 (1979) 225–228.  
699 [https://doi.org/10.1016/0032-3861\(79\)90226-X](https://doi.org/10.1016/0032-3861(79)90226-X).
- 700 [22] M. Rubinstein, R.H. Colby, *Polymer physics*, Oxford University Press, Oxford ; New  
701 York, 2003.
- 702 [23] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953.
- 703 [24] M. Palacios, S. Gismera, M.M. Alonso, J.B. d’Espinose de Lacaillerie, B. Lothenbach,  
704 A. Favier, C. Brumaud, F. Puertas, Early reactivity of sodium silicate-activated slag  
705 pastes and its impact on rheological properties, *Cement and Concrete Research*. 140  
706 (2021) 106302. <https://doi.org/10.1016/j.cemconres.2020.106302>.
- 707 [25] M. Königsberger, J. Carette, Validated hydration model for slag-blended cement based  
708 on calorimetry measurements, *Cement and Concrete Research*. 128 (2020) 105950.  
709 <https://doi.org/10.1016/j.cemconres.2019.105950>.
- 710 [26] N. Roussel, *Understanding the rheology of concrete*, Woodhead Publ., Oxford, 2012.
- 711 [27] G. Gelardi, S. Mantellato, D. Marchon, M. Palacios, A.B. Eberhardt, R.J. Flatt, 9 -  
712 Chemistry of chemical admixtures, in: P.-C. Aïtcin, R.J. Flatt (Eds.), *Science and*  
713 *Technology of Concrete Admixtures*, Woodhead Publishing, 2016: pp. 149–218.  
714 <https://doi.org/10.1016/B978-0-08-100693-1.00009-6>.
- 715 [28] F.E. Bailey, R.W. Callard, Some properties of poly(ethylene oxide)1 in aqueous  
716 solution, *Journal of Applied Polymer Science*. 1 (1959) 56–62.  
717 <https://doi.org/10.1002/app.1959.070010110>.
- 718 [29] H.D. Willauer, J.G. Huddleston, R.D. Rogers, Solute Partitioning in Aqueous Biphasic  
719 Systems Composed of Polyethylene Glycol and Salt: The Partitioning of Small Neutral  
720 Organic Species, *Industrial & Engineering Chemistry Research*. 41 (2002) 1892–1904.  
721 <https://doi.org/10.1021/ie010598z>.

- 722 [30] M.J. Hey, D.P. Jackson, H. Yan, The salting-out effect and phase separation in aqueous  
723 solutions of electrolytes and poly(ethylene glycol), *Polymer*. 46 (2005) 2567–2572.  
724 <https://doi.org/10.1016/j.polymer.2005.02.019>.
- 725 [31] B.A. Deyerle, Y. Zhang, Effects of Hofmeister Anions on the Aggregation Behavior of  
726 PEO–PPO–PEO Triblock Copolymers, *Langmuir*. 27 (2011) 9203–9210.  
727 <https://doi.org/10.1021/la201463g>.
- 728 [32] Y. Marcus, ViscosityB-coefficients, structural entropies and heat capacities, and the  
729 effects of ions on the structure of water, *Journal of Solution Chemistry*. 23 (1994) 831–  
730 848. <https://doi.org/10.1007/BF00972677>.
- 731 [33] F. Caruso, S. Mantellato, M. Palacios, R.J. Flatt, ICP-OES method for the  
732 characterization of cement pore solutions and their modification by polycarboxylate-  
733 based superplasticizers, *Cement and Concrete Research*. 91 (2017) 52–60.  
734 <https://doi.org/10.1016/j.cemconres.2016.10.007>.
- 735 [34] D. Rothstein, J.J. Thomas, B.J. Christensen, H.M. Jennings, Solubility behavior of Ca-,  
736 S-, Al-, and Si-bearing solid phases in Portland cement pore solutions as a function of  
737 hydration time, *Cement and Concrete Research*. 32 (2002) 1663–1671.  
738 [https://doi.org/10.1016/S0008-8846\(02\)00855-4](https://doi.org/10.1016/S0008-8846(02)00855-4).
- 739 [35] A. Fernández-Jiménez, F. Puertas, Setting of alkali-activated slag cement. Influence of  
740 activator nature, *Advances in Cement Research*. (2001) 7.
- 741 [36] A. Fernández-Jiménez, F. Puertas, I. Sobrados, J. Sanz, Structure of calcium silicate  
742 hydrates formed in alkaline-activated slag: influence of the type of alkaline activator,  
743 *Journal of the American Ceramic Society*. 86 (2003) 1389–1394.  
744 <https://doi.org/10.1111/j.1151-2916.2003.tb03481.x>.
- 745 [37] R.J. Myers, S.A. Bernal, J.L. Provis, Phase diagrams for alkali-activated slag binders,  
746 *Cement and Concrete Research*. 95 (2017) 30–38.  
747 <https://doi.org/10.1016/j.cemconres.2017.02.006>.
- 748 [38] F. Bonk, J. Schneider, M.A. Cincotto, H. Panepucci, Characterization by multinuclear  
749 high-resolution nmr of hydration products in activated blast-furnace slag pastes, *Journal*  
750 *of the American Ceramic Society*. 86 (2003) 1712–1719. [https://doi.org/10.1111/j.1151-](https://doi.org/10.1111/j.1151-2916.2003.tb03545.x)  
751 [2916.2003.tb03545.x](https://doi.org/10.1111/j.1151-2916.2003.tb03545.x).
- 752 [39] A.R. Sakulich, S. Miller, M.W. Barsoum, Chemical and microstructural characterization  
753 of 20-month-old alkali-activated slag cements, *Journal of the American Ceramic*  
754 *Society*. 93 (2010) 1741–1748. <https://doi.org/10.1111/j.1551-2916.2010.03611.x>.
- 755 [40] G. Bossis, P. Boustingorry, Y. Grasselli, A. Meunier, R. Morini, A. Zubarev, O.  
756 Volkova, Discontinuous shear thickening in the presence of polymers adsorbed on the  
757 surface of calcium carbonate particles, *Rheologica Acta*. 56 (2017) 415–430.  
758 <https://doi.org/10.1007/s00397-017-1005-4>.
- 759 [41] F. Dalas, A. Nonat, S. Pourchet, M. Mosquet, D. Rinaldi, S. Sabio, Tailoring the anionic  
760 function and the side chains of comb-like superplasticizers to improve their adsorption,  
761 *Cement and Concrete Research*. 67 (2015) 21–30.  
762 <https://doi.org/10.1016/j.cemconres.2014.07.024>.
- 763 [42] N. Mikanovic, K. Khayat, M. Pagé, C. Jolicoeur, Aqueous CaCO<sub>3</sub> dispersions as  
764 reference systems for early-age cementitious materials, *Colloids and Surfaces A:*  
765 *Physicochemical and Engineering Aspects*. 291 (2006) 202–211.  
766 <https://doi.org/10.1016/j.colsurfa.2006.06.042>.

- 767 [43] S. Pourchet, S. Liautaud, D. Rinaldi, I. Pochard, Effect of the repartition of the PEG side  
768 chains on the adsorption and dispersion behaviors of PCP in presence of sulfate, *Cement*  
769 *and Concrete Research*. 42 (2012) 431–439.  
770 <https://doi.org/10.1016/j.cemconres.2011.11.011>.
- 771 [44] J.A. Richards, R.E. O’Neill, W.C.K. Poon, Turning a yield-stress calcite suspension into  
772 a shear-thickening one by tuning inter-particle friction, *Rheologica Acta*. 60 (2021) 97–  
773 106. <https://doi.org/10.1007/s00397-020-01247-z>.  
774