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Contribution of turbidimetry on the characterization of cement pastes bleeding

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Abstract

The aim of this paper is to examine the contribution of turbidimetry measurements on the characterization of cement pastes bleeding. In some cases (e.g. presence of superplasticizer), the bleed water becomes turbid due to finest particles dispersion and the boundary between the bleed water and the consolidated paste becomes difficult to detect. Turbiscan device allows detecting this boundary more accurately than traditional tests. The role of superplasticizer and solid volume fraction on bleeding is examined. The bleeding measurements highlight the role of superplasticizer on bleeding and its kinetics. The effect of superplasticizer may be explained by better dispersion leading to release of water trapped between agglomerates. Furthermore, the existence of critical volume fraction, above which no bleeding occurs, close to that corresponding to the appearance of contacts between particles is shown. Finally, using rheological measurements, the correlation between the yield stress and bleeding has been possible.

Keywords

Bleeding; Cement paste, Settlement, Yield stress, Superplasticizer

1 **1. Introduction**

2 Stability of concentrated mineral suspensions must be well controlled and is of great importance
3 in several domains as ceramics, covering industry, paper industry... notably cement and
4 concrete. For the latter, comprehension of fresh state behavior of cement based materials
5 allowed manufacturing special concretes such as self-compacting concretes (SCC) (Gaimster
6 and Dixon, 2003; Okamura and Ozawa, 1996; Shi et al., 2015) and high performance concretes
7 (HPC). In practice, fresh concrete should be quite fluid and resistant to instability phenomena
8 (Kovler and Roussel, 2011; Navarrete and Lopez, 2017). A fluid concrete would be more
9 sensitive to instability such as segregation and bleeding. Furthermore, it is well known that the
10 fresh state of concrete affects strongly its strength and durability. For instance, excessive
11 bleeding weakens the bond between cement matrix and aggregates and induces a
12 heterogeneity of strength (Josserand et al., 2006). The bleeding can also cause major
13 disorders, in particular for cementitious post-tensioning tendon grout. The European standard
14 EN 447 limits the bleeding of these grouts to 0.3% after 3 hours at rest. Despite its negative
15 consequences, mild bleeding can ensure a wet curing of concrete which limits the effects of
16 drying shrinkage.

17 At the cement paste scale, bleeding occurs due to the difference between density of cement
18 particles and water. It usually corresponds to the accumulation of clear water at the surface
19 (Josserand et al., 2006; Kovler and Roussel, 2011; Perrot et al., 2012). Gravity is the driving
20 force at the origin of bleeding. It induces the settlement of the solid particles causing in turn the
21 upward displacement of water. Bleeding can thus be described as a settlement and
22 consolidation process governing by the permeability of the network of interacting particles
23 (Josserand et al., 2006). Powers (Powers, 1968) considered bleeding as a special case of
24 sedimentation and described it by a general law derived from Poiseuille's law of capillary flow.
25 He proposed a relation which can assess the initial bleeding rate as a function of solid volume
26 fraction (Powers, 1968). The bleeding rate can be assumed to follow the Kozeny-Carman
27 equation (Powers and Dahl, 1939), but Peng et al. (Peng et al., 2017) showed that this is not
28 relevant since bleeding rate is not constant. In a recent study, Massoussi et al. (2017) suggest
29 that bleeding cannot be simply described by a consolidation process, but is of obvious
30 heterogeneous nature leading to the formation of preferential water extraction channels

31 (Massoussi et al., 2017). By using numerical image acquisition, Massoussi et al. (2017) showed
32 that the bleeding process is composed of five stages: the induction period, the accelerating
33 regime, the constant water extraction rate period, the consolidation regime and the final
34 consolidated state. In their study, the effect of superplasticizer has not been examined.

35 In general, sedimentation in suspensions can be defined as the downward displacement of
36 particles and depends mainly on particle size, density, and surface properties (Autier et al.,
37 2014; Eckert et al., 1996). However, depending on solid volume fraction, there are different
38 types of sedimentation. The extreme situations occur for very low volume fraction (diluted
39 suspension) in which unit particles and agglomerates can settle independently, and for high
40 volume fraction in which particles can interact (interparticle forces and direct contacts) forming a
41 network that consolidate under its own-weight. Bleeding thus occurs when this network of
42 interacting particles exists. In this case, in addition to sediment layer, a sharp front of a clear
43 supernatant layer appears and increases over time (bleeding layer). In the case of suspension
44 with superplasticizer, due to the dispersion of finest particles and the decrease of magnitude of
45 interparticle forces, different zones can be observed: a turbid supernatant (turbid bleeding)
46 containing finest particles which settle very slowly, and sediment with one or several zones with
47 various concentrations. Whatever the mode of sedimentation, the suspension at the equilibrium
48 is composed of a layer of more or less clear supernatant above a consolidating sediment
49 (Eckert et al., 1996; Fitch, 1983; Peng et al., 2017). In this study, the bleeding corresponds to
50 the supernatant layer forming above compact sediment, even for cement paste with low solid
51 volume fractions.

52 There are several methods to measure bleeding such as those defined in the standards (EN
53 447, ASTM C243, ASTM C1741-18, ASTM C940 - 98a). However, the majority of these
54 methods are difficult to use without a sharp bleeding front (Josserand and De Larrard, 2004;
55 Massoussi et al., 2017; Radocea, 1992). For instance, methods based on the visual
56 measurement of bleeding thickness cannot be used without a clear bleeding front. Another test
57 based on the measurement of hydrostatic pressure (HYSPT) allow bleeding rate to be
58 measured, but by assuming sharp bleeding front and homogeneous zone below bleed water
59 (Peng and Jacobsen, 2013). Furthermore, Peng et al. (Peng et al., 2017) found that the
60 bleeding rate of fresh cement paste determined by the Kozeny-Carman equation (Powers,

61 1968) and visual measurements remains constant whatever the water to cement ratio and the
62 bleeding step. Josserand and de Larrard (Josserand and De Larrard, 2004) proposed a method
63 which consists in sucking bleed water with pipette, but this method is more suitable for concrete
64 than for cement pastes.

65 It thus appears that conventional bleeding tests are not always suitable for accurately
66 measuring bleeding, especially when the latter is turbid. In addition, the incorrect determination
67 of the bleeding could lead to false interpretations. In fact, Daczko (Daczko, 2012) reported that
68 the absence of sharp bleeding front (e.g. turbid bleeding) does not guarantee that a mixture is
69 stable. Test based on turbidity measurement could make it possible to measure the evolution of
70 turbid bleeding more accurately than conventional tests (Peng et al., 2017). In fact, the
71 Turbiscan device is able to detect nascent destabilization phenomenon in concentrated
72 suspensions much faster than visual testing.

73 Furthermore, it appears that bleeding is related to rheological properties of the paste at rest. For
74 instance, the self-compacting concrete is able to flow under its own-weight and can stay
75 homogeneous. The first property is related to the stress required to initiate flow, i.e the yield
76 stress, while the second involves the resistance of particles to bleeding and segregation. In
77 addition, instabilities at rest occurs when the yield stress of suspending matrix is not sufficient to
78 stabilize the particles (Roussel, 2006). It thus appears that yield stress and bleeding are two
79 properties closely related. Attempts to correlate yield stress and bleeding can be found in the
80 literature (El Bitouri and Azéma, 2021; Perrot et al., 2012). Perrot et al. (Perrot et al., 2012)
81 found that this correlation is indirect and difficult to use in practice. They based their conclusion
82 on the fact that at the critical water to cement ratio below which no bleeding occurs, the cement
83 paste without SP displayed a yield stress of about 300 Pa, while cement paste with 3% of SP
84 displayed a yield stress of 40 Pa. However, their study was based on visual observation with
85 two measurement of bleeding at 1 and 2 hours, and turbid bleeding and the retarding effect of
86 SP were not mentioned.

87 The yield stress takes its origins from direct contacts and interparticle forces which contribute to
88 form an internal network of particles able to resist to applied stress (Dzuy and Boger, 2002;
89 Roussel et al., 2010). The role of solid volume fraction on the yield stress is crucial and well
90 documented in literature (Flatt, 2004; Flatt and Bowen, 2006; Mehdipour and Khayat, 2018;

91 Perrot et al., 2012; Toutou and Roussel, 2006; Zhou et al., 2002). Different critical volume
92 fractions corresponding to the dominating physical phenomena are defined (Roussel et al.,
93 2010). At rest, there is a volume fraction threshold below which cement paste doesn't display
94 any yield stress. This threshold is known as percolation volume fraction (ϕ_{perc}) above which a
95 network of interparticle forces appears in the material (Eckert et al., 1996; Roussel et al., 2010).
96 In literature, the values of the percolation volume fraction are ranging from 0.2 to 0.4 (Flatt and
97 Bowen, 2006; Perrot et al., 2012; Toutou and Roussel, 2006). Furthermore, it is well known that
98 yield stress and viscosity diverges when solid volume fraction reaches a critical value (ϕ_{div})
99 (Roussel et al., 2010). The divergence of yield stress results from rigid contact between cement
100 particles. It has to be kept in mind that this critical value is different from the maximum dense
101 packing due to agglomeration of particles (Roussel et al., 2010). The addition of superplasticizer
102 allows dispersing the agglomerates and thus to get closer to the real maximum packing (ϕ_m).
103 Furthermore, it is shown that a transition volume fraction of the order of $0.8 \phi_{div}$ separates
104 suspensions in which the yield stress is mainly due to interparticle forces network and
105 suspensions in which the yield stress is mainly due to a direct contacts network. Roussel et al.
106 (Roussel et al., 2010) showed that below a percolation threshold (ϕ_{perc}), there are no direct
107 contacts nor interparticle forces forming a network able to resist to applied stress, and thus, the
108 cement paste doesn't display any yield stress. Also, in cement paste with volume fraction below
109 the percolation threshold, cement particles can settle independently (hindered sedimentation).
110 Above the percolation threshold, a network of interacting particles consolidates under its own
111 weight, which corresponds to bleeding domain. From a critical solid volume fraction, bleeding
112 becomes negligible (Perrot et al., 2012).

113 The aim of this paper is to examine the contribution of turbidimetry measurements on the
114 characterization of cement pastes bleeding. The role of superplasticizer and solid volume
115 fraction is examined. Since bleeding and yield stress originate from the same mechanisms, their
116 correlation is also investigated. For this, rheological measurements are performed to examine
117 the effect of superplasticizer and particle size on the different transition volume fractions: the
118 percolation threshold (ϕ_{perc}), the transition volume fraction to frictional regime ($0.8 \phi_{div}$), and the
119 apparent dense packing (ϕ_{div}).

120

121 **2. Materials and methods**

122 **2.1 Materials**

123 The experiments were carried out by using cement (CEM II/A-L 42.5 N). Particle size
124 distributions (in water) were determined by a laser granulometer S13320 from Beckman Coulter
125 Company with an adapted optical model. As shown in Fig. 13, cement exhibited a broad particle
126 size distribution ranging from 0.04 to 92.1 μm , with a main mode of about 17.30 μm .

127 A commercial polycarboxylate based superplasticizer with an equivalent dry extract content of
128 20 wt% is used.

129 **2.2 Sample preparation**

130 Cement pastes were mixed with deionized water in a planetary agitator according to the
131 following sequence: 5 minutes mixing at 500 rpm, scraping the mixer walls to homogenize the
132 mix (30 seconds), 5 minutes mixing at 500 rpm.

133 For cement pastes with superplasticizer, the binder and 90 wt% of the total water were mixed
134 according to the following mixing procedure: 5 minutes mixing at 500 and scraping the mixer
135 walls to homogenize the mix, 10 min resting. The superplasticizer and the remaining 10% of the
136 water were then added to the mix which was mixed for 5 min at 500 rpm. Two dosage of
137 superplasticizer were studied: 0.1 and 1 wt% of dry substance.

138 Cement pastes were prepared at the ambient temperature ($22^{\circ}\text{C}\pm 2$) with water to cement ratios
139 (w/c) ranging from 0.2 to 1 which corresponds to solid volume fractions ranging from 0.24 to
140 0.56 (Table 5). The initial solid volume fraction is calculated according to:

$$\phi = (1 + \rho_c W / \rho_w C)^{-1} \quad (1)$$

141 Where : ϕ is the initial solid volume fraction, ρ_c and ρ_w are respectively the density of cement
142 (3.14 g/cm^3) and water, C and W are respectively the mass of cement and water.

143 All the tests were performed at the ambient temperature ($22^{\circ}\text{C}\pm 2$) during the dormant/induction
144 period of cement hydration and hence changes due to chemical activity are not considered. The
145 initial setting time measured by Vicat's needle in accordance with ASTM C191 standard in neat
146 cement paste is of about 130 minutes. The addition of superplasticizer induces retarding effect
147 leading to an increase of initial setting time.

148 **2.3 Bleeding experiments**

149 Bleeding measurements were carried out using an analyzer of concentrated suspensions, the
150 Turbiscan LAB from Formulaction France. Turbiscan device consists of a vertical light scanner
151 (near-infrared light source ($\lambda=860$ nm)) with backscattering and transmission sensors able to
152 detect nascent destabilization phenomenon in concentrated suspensions (Mengual et al., 1999).
153 The transmission sensor detects the light transmitted across the sample (at 0° from the incident
154 beam), while the backscattered detector receives the light scattered backward by the sample (at
155 135° from the incident beam). The vertical scanner, which moves along the whole sample height
156 (with a measuring step of $40\mu\text{m}$), recorded the transmission (T) and backscattered (BS) profiles
157 each 1 minute during the first hour and then each 5 min for the following 1 hour (Fig. 14). The
158 rates of transmitted (T) and backscattered (BS) light are related to the solid volume fraction ϕ
159 and the mean particles diameter d (Mengual et al., 1999) as follows :

$$\%T \approx \exp\left(-\frac{A\phi}{d}\right) \quad (2)$$

$$\%BS \approx \frac{B\phi}{d} \quad (3)$$

160 Where: A and B are constant parameters. Thus, changes in transmission (or/and backscattered)
161 signal results from change in solid volume fraction and/or mean diameter.

162 Fig. 14 shows an example of sedimentation column with the recorded transmitted and
163 backscattered signals. At the beginning of the experiment, the paste is opaque and there is zero
164 transmission (x-axis) along the height of the cell (y-axis). With increasing time, a supernatant
165 gradually forms at the top of the cell, characterized by an increase in transmission. The height of
166 this supernatant corresponds to the bleeding layer. The evolution of bleeding front (boundary
167 between the supernatant and the consolidated paste) can be characterized by the displacement
168 of the transmission and backscattering signals (Fig. 14). The recorded profiles obtained by
169 Turbiscan allow determining the bleeding layer, whether clear or turbid, more accurately than
170 traditional bleeding test methods (Massoussi et al., 2017; Peng et al., 2017; Perrot et al., 2012).
171 Moreover, Turbiscan allows quantifying the bleeding rate and solid volume fraction (and/or
172 mean diameter) of each layer in the sedimentation column.

173 After mixing, a 55 mm height and 25 mm diameter cylindrical tube is filled with paste. The initial
174 height of the paste is of 45 mm for all tests, corresponding to a volume of 27 ml. After filling, the

175 tube is immediately sealed to prevent water evaporation and introduced in the Turbiscan device.
176 It is worth noting that the bleeding measurements could be affected by the wall effect. The
177 diameter of the tube is large enough to limit the wall effect since the disturbed thickness is of
178 few microns (Ben Aïm, 1970). Massoussi et al. (Massoussi et al., 2017) found that cement
179 pastes bleeding is not affected by the presence of the interface between the material and the
180 tube wall for diameter larger than 2.2 cm.

181 Bleeding is determined as the ratio of the height of the supernatant (transmission zone) H_{sup} to
182 the initial height of the cement paste H_c :

$$\text{Bleeding (t)} = 100 \times H_{sup}(t)/H_c \quad (4)$$

183 **2.4 Rheological measurements**

184 Rheological measurements were carried out using an experimental Couette rheometer AR2000
185 ex from TA instruments equipped with a four blades vane geometry (internal diameter = 28 mm,
186 the outer cup diameter = 30 mm). The geometry constants were calibrated using Couette
187 analogy (Aït-kadi et al., 2002).

188 The performed measurement procedure consists of a stress growth experiment which allows
189 measuring the static yield stress (Dzuy and Boger, 2002; Mahaut et al., 2008). The stress
190 growth procedure starts with a strong pre-shear (100 s^{-1} during 200 s) followed by a resting time
191 of 200 s, and then a small rotational velocity corresponding to a shear rate of 10^{-2} s^{-1} is applied
192 to the vane geometry. On the shear rate vs. strain curve obtained for yield stress measurement
193 (Fig. 15), the stress begins to increase linearly with the strain to reach a peak followed by a
194 steady state flow. The peak defines the static yield stress which corresponds to the minimum
195 stress to induce flow.

196 **3. Results**

197 **3.1 Effect of solid volume fraction on bleeding**

198 The evolution of bleeding as a function of water to cement ratio (and corresponding volume
199 fraction) is shown in Fig. 16. This evolution consists of two stages. In the first stage, bleeding
200 increases linearly with time. The slope of this linear zone defines bleeding rate. Above this linear
201 zone, bleeding reaches a plateau (bleeding capacity). It can be observed that bleeding reaches
202 a steady state before 2 hours (consolidation regime). Beyond this time, the contribution of

203 hydration reactions on the stabilization of the cement paste is not negligible (setting time). The
204 bleeding capacity corresponds thus to the value of bleeding reached at 2 hours.

205 The evolution of bleeding capacity and its rate as a function of solid volume fraction is shown in
206 Fig. 17. It can be noted that both the bleeding and its rate decrease with the increase of solid
207 volume fraction. For low solid volume fractions, which correspond in practice to that of cement
208 grouts, bleeding capacity is high. It has to be kept in mind, that bleeding less than 5% is
209 considered as acceptable in such materials (Azadi et al., 2017). The bleeding of cement grout is
210 reduced by the addition of others components (e.g. bentonite).

211 From solid volume fraction of 0.35, the bleeding is less than 5% and becomes negligible at 0.44.
212 This volume fraction domain corresponds to standard water to cement ratio in concretes.

213 **3.2 Effect of superplasticizer on bleeding**

214 The effect of superplasticizer on bleeding is illustrated in Fig. 17 and Fig. 18. It appears that
215 bleeding and its rate increase with the increase of superplasticizer dosage. However, the time
216 required to reach the plateau increases with increasing superplasticizer dosage.

217 It thus seems that the addition of superplasticizer (with the studied dosages) leads to an
218 increase of both bleeding capacity and bleeding rate, but also the time required to reach the
219 plateau. This effect may be explained in part by a change in the cement particles assembly
220 since the addition of superplasticizer allows a better dispersion of the cement particles. The
221 permeability of solid skeleton is thus expected to increase. However, Perrot et al. (Perrot et al.,
222 2013) found that the addition of superplasticizer reduces the initial bleeding rate and increases
223 bleeding capacity. They reported that the better dispersion of cement particles in the presence
224 of superplasticizer induces a finer porous network that increases the flow resistance inside the
225 material. They found that the permeability is decreased by about a decade and the bleeding rate
226 is decreased by the same order of magnitude in the presence of superplasticizer (dosage
227 between 0 and 3%). Caution should be exerted about the effect of superplasticizer on the
228 permeability of fresh cement paste due to the complexity of measurement methods and the
229 specificities of the porous medium (compressibility, hydration). Moreover, the apparent
230 permeability of fresh cement paste is not constant and depends on the bleeding stage.
231 Massoussi et al. (Massoussi et al., 2017) reported that during the accelerating period of
232 bleeding, the apparent permeability of the paste increases due to the formation and percolation

233 of the water extraction channels. The effect of superplasticizer on the permeability of fresh
234 cement paste remains misunderstood and requires more investigations.

235 Furthermore, the increase of bleeding and its rate in the presence of superplasticizer could be
236 explained, in part, by a deagglomeration effect. In fact, the addition of superplasticizer allows a
237 better dispersion of cement particles, releasing water trapped by agglomerates. It should be
238 noted that the permeability and the deagglomeration effects could be probably linked which
239 could leads to a localization effect (localized bleeding). More investigations are needed to clarify
240 the mechanisms at the origins of increasing bleeding and its kinetics in the presence of
241 superplasticizer.

242 The rate of excess water released (Fig. 18) due to the better dispersion of cement particles can
243 be assessed and quantified, through the difference of the bleeding thicknesses at 2h (H_{sup})
244 between cement paste without superplasticizer and cement paste with 1% SP as follows:

$$\%Excess\ water = (H_{sup}(SP = 1\%) - H_{sup}(SP = 0\%)) \times A / V_i \quad (2)$$

245 Where: A is the area of the Turbiscan tube, V_i is the initial volume of water. The height of the
246 column H_c is constant. The presence of finest particles in the supernatant is neglected.

247 Fig. 19 presents the rate of excess water extracted as a function of volume fraction. The excess
248 water extracted represents between 12% and 2% of the initial water volume. It is interesting to
249 note that this rate decreases with the increase of solid volume fraction. This indicates that the
250 dispersion effect of superplasticizer is attenuated with the increase of solid volume fraction. In
251 fact, when solid volume fraction reaches a high value, there is an appearance of direct contacts
252 between cement particles which block the dispersive action produced by electrosteric effect.
253 The latter is effective when the interparticle forces are the dominating physical phenomenon in
254 the suspension. When contacts between particles appear, it is more difficult to disperse them.
255 The network of cement particles is compact and the bleeding becomes negligible.

256 Superplasticizers can have a deleterious effect on bleeding. For example, with a water to
257 cement ratio of 0.6, increasing the dosage of superplasticizer leads to a significant increase in
258 bleeding as shown in Fig. 18. It should be noted that the use of superplasticizers is generally not
259 necessary at such water to cement ratio. Furthermore, the water to cement ratio (and the
260 corresponding volume fraction) from which the bleeding becomes negligible decreases

261 (increases) with the increase of the superplasticizer dosage (Fig. 17). Thus, the de-
262 agglomeration effect, generally required to increase the workability of cementitious materials,
263 can therefore prove to be deleterious for bleeding. When superplasticizer is employed, it is
264 therefore important to determine the bleeding layer correctly. This is not always obvious,
265 especially when the bleeding front is not sharp. The contribution of turbiscan device on the
266 determination of the bleeding front is illustrated in Fig. 20 for cement paste with 0.1% SP
267 (w/c=0.9). After 2 hours of settling, according to the transmitted signal (T), only a small bleeding
268 layer is observed (peak between 42 and 44 mm). No transmission is observed in the rest of the
269 column that remains turbid. However, a decrease of the backscattered signal (BS) is observed
270 between 33 and 42 mm. The rate of backscattered signal remains constant after 2 hours
271 between 0 and 33 mm. The decrease in the backscattered signal suggests a decrease of solid
272 volume fraction (eq 3). The boundary of this layer with reduced volume fraction is not sharp and
273 difficult to determine with some bleeding tests (e.g. visual observation in a graduated cylinder,
274 numerical image acquisition). The real front of bleeding at 2 hours is located at 33mm as shown
275 in Fig. 20. In order to confirm that this turbid layer can be considered as bleeding, some
276 samples are left in the closed tube until hardened. As shown in Fig. 20, the turbid layer clarifies
277 over time and its thickness little changes. The hardened paste located at the bottom of this layer
278 presents different contrasts visible as a decrease in the backscattered rate.

279 **3.3 Bleeding and yield stress**

280 The yield stress measurements were performed to examine the effect of superplasticizer on
281 transition volume fractions. As shown in Fig. 21, the yield stress increases with solid volume
282 fraction ϕ . The percolation volume fraction, from which cement paste without superplasticizer
283 exhibits a minimum stress, corresponds to 0.31. The addition of superplasticizer (SP) increases
284 this percolation volume fraction (0.41 for 0.1% SP and 0.52 for 1% SP). In fact, in cement paste
285 with superplasticizer, due to the dispersive action by electrosteric effect, it is more difficult to
286 form a percolated network of particles.

287 Furthermore, the value of ϕ_{div} can be derived from experimental data by plotting the asymptote
288 of the curve presented in Fig. 21. The solid volume fraction ϕ_{div} , for which yield stress diverges,
289 is thus of about 0.56 for cement paste without superplasticizer. It depends on the agglomeration

290 state of the suspension since it increases with the incorporation of superplasticizer (0.59 for
291 0.1% SP and 0.61 for 1% SP).

292 The measured static yield stresses can be fitted by the following relationship (represented by
293 the dotted lines in Fig. 21) derived from the YODEL (Yield stress mODEL)(Flatt and Bowen,
294 2006):

$$\tau_0 \cong k \frac{\phi^2(\phi - \phi_{perc})}{\phi_{div}(\phi_{div} - \phi)} \quad (2)$$

295 Where: k is a fitting parameter (Table 3), ϕ is the solid volume fraction, ϕ_{perc} the percolation
296 volume fraction and ϕ_{div} is the solid volume fraction for which the yield stress diverges.

297 As reported by Roussel et al. (Roussel et al., 2010), the solid volume fraction of 0.8 ϕ_{div}
298 separates the suspensions in which the yield stress is mainly due to a network of interparticle
299 forces and the suspensions in which the yield stress is mainly due to direct contacts network
300 (Perrot et al., 2013; Roussel et al., 2010).

301 The transition volume fractions corresponding to the percolation threshold (ϕ_{perc}), the
302 appearance of contacts (0.8 ϕ_{div}), and the apparent dense packing (ϕ_{div}) are plotted as a function
303 of superplasticizer dosage (Fig. 22). These critical volume fractions allow assessing the
304 dominating physical phenomenon as reported by Roussel et al. (Roussel et al., 2010).

305 Below the percolation threshold, the interparticle forces are not able to maintain particles in
306 suspension. The settling of cement particles can be described by hindered sedimentation. From
307 the percolation threshold, the magnitude of interparticle forces increases leading to the
308 formation of a network of particles able to withstand a stress. This network consolidates under
309 its own weight leading to the bleeding. When the contacts appear, the network of cement
310 particles is compact and the bleeding becomes negligible.

311 It is interesting to note that the addition of superplasticizer leads to an increase of transition
312 volume fractions. The domain in which the interparticle forces are the dominating phenomenon
313 is thus reduced with the increase of superplasticizer dosage. It is the same case for the domain
314 in which the contacts are predominant (Fig. 22).

315 Since the yield stress and bleeding originate from the network of interacting particles, their
316 correlation seems to be possible and interesting from a practical point of view. Fig. 23 shows the
317 yield stress and the bleeding as a function of solid volume fraction. It can be noted that the

318 critical solid volume fraction above which no bleeding occurs (ϕ_c) is different from the
319 percolation threshold (ϕ_{perc}). The bleeding phenomenon concerns suspensions in which a
320 network of interacting particles exists. Below the percolation threshold, bleeding is important
321 while the yield stress is negligible. Bleeding becomes negligible and yield stress diverges when
322 solid volume fraction is close to that corresponding to the appearance of the contacts between
323 cement particles ($0.8 \phi_{div}$). In fact, from this solid volume fraction, the appearance of rigid
324 contacts between particles leads to a compact network. The percolation of the low amount of
325 water available becomes difficult, and the fresh cement paste thus remains homogeneous and
326 cannot bleed.

327 Furthermore, there is a minimum yield stress above which no bleeding occurs. This minimum
328 yield stress of about 10 Pa does not depend on the superplasticizer dosage as shown in Fig. 23.
329 Fig. 24 presents the correlation between yield stress and bleeding. Two extreme domains can
330 be observed. The first domain corresponds to a negligible bleeding with a high yield stress and
331 the second domain corresponds to a negligible yield stress and an important bleeding. These
332 two domains are not of interest for cementitious materials, since a high yield stress does not
333 allow sufficient workability to be obtained, and significant bleeding can have deleterious
334 consequences. Between these domains, yield stress and bleeding seem to be correlated and
335 this correlation does not depend on the superplasticizer dosage. This domain is of interest for
336 cementitious materials since a compromise between workability and bleeding (stability) can be
337 obtained. The yield stress is low enough to ensure workability, and high enough to limit
338 bleeding.

339 **4. Conclusions**

340 The aim of this paper is to investigate the contribution of Turbiscan device on the
341 characterization of mineral suspensions bleeding especially cement pastes bleeding compared
342 to alumina suspensions. The effect of superplasticizer, solid volume fraction and particles size
343 on bleeding is also examined. The main results of this paper are:

- 344 • The use of Turbiscan device allows turbid bleeding to be characterized more accurately
345 than traditional tests, although no interface between the bleed water and the paste can
346 be seen by visual observation.

- 347 • The use of superplasticizers leads to an increase in bleeding and its rate. This effect
348 may be explained by particles dispersion which release water trapped between
349 agglomerates.
- 350 • Rheological measurements show that critical volume fractions depend on the
351 superplasticizer dosage.
- 352 • A critical solid volume fraction (ϕ_c) above which no bleeding occurs is close to the
353 transition volume fraction ($0.8\phi_{div}$) corresponding to the appearance of rigid contacts
354 between particles. This critical volume fraction increases as a function of
355 superplasticizer dosage.
- 356 • Correlation between yield stress and bleeding is possible. A minimum yield stress, not
357 superplasticizer dosage dependent, above which no bleeding occurs is of about 10-50
358 Pa.

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Table 1. Granular and physical characteristics of cement

	cement
Measured density	3.14
specific surface (cm ² /g)	3700 (Blaine)
Principal mode (μm)	22.73
dmean (μm)	17.30
dmin (μm)	0.04
dmax (μm)	92.09

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Table 2. Water to cement ratios (w/c) used and the corresponding solid volume fractions

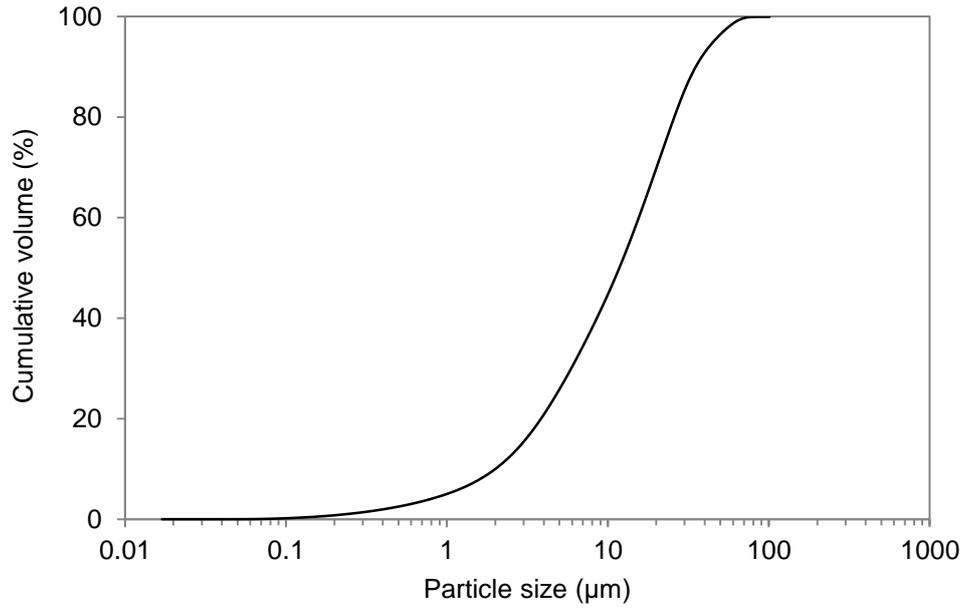
w/c ratio	solid volume fraction
0.25	0.56
0.3	0.52
0.35	0.48
0.4	0.44
0.45	0.41
0.5	0.39
0.6	0.35
0.7	0.31
0.8	0.28
0.9	0.26
1	0.24

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Table 3. Parameters used to fit the experimental data

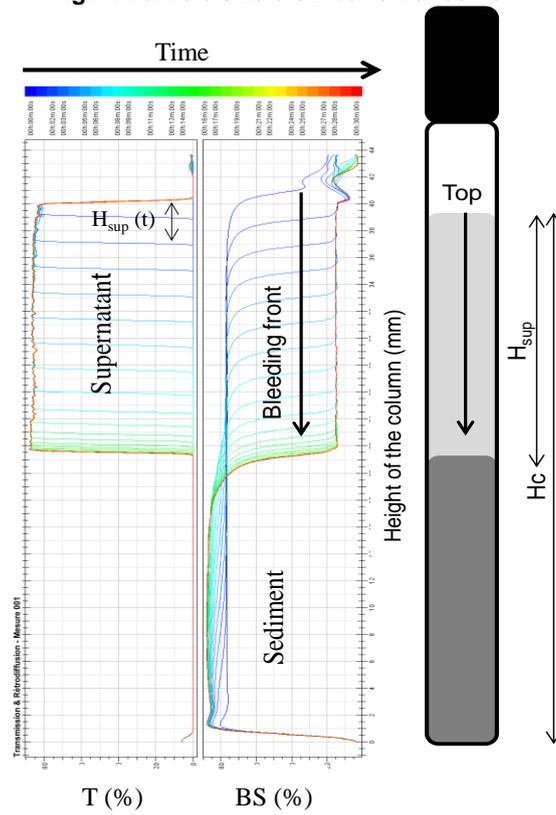
SP dosage (%)	0	0.1	1
percolation volume fraction ϕ_{perc}	0.31	0.42	0.52
maximum volume fraction ϕ_{div}	0.56	0.59	0.61
fitting parameter (k)	65	65	65

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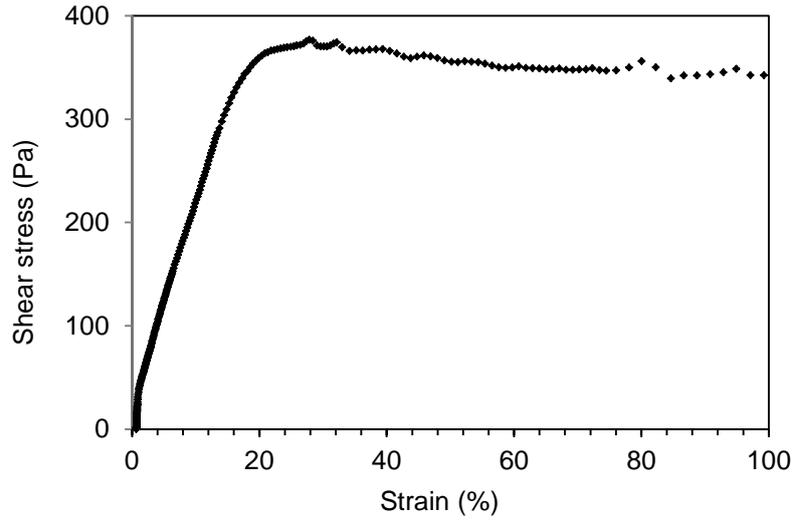
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Fig. 1. Particle size distribution of cement



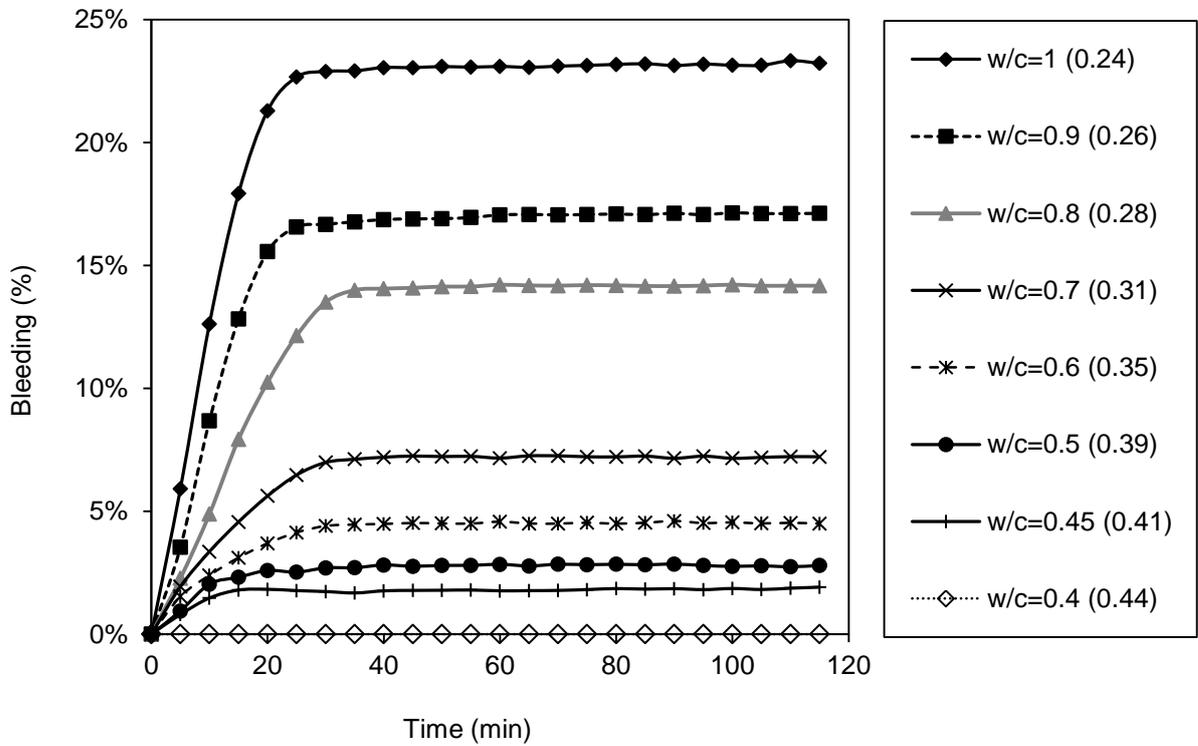
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Fig. 2. Illustration of sedimentation column and transmission and backscattered patterns



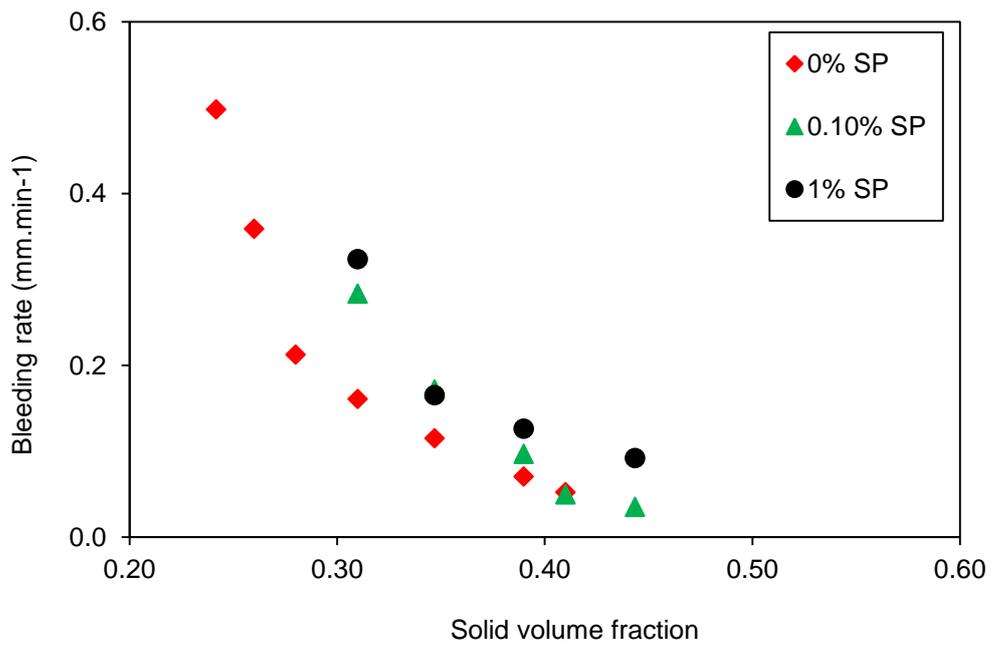
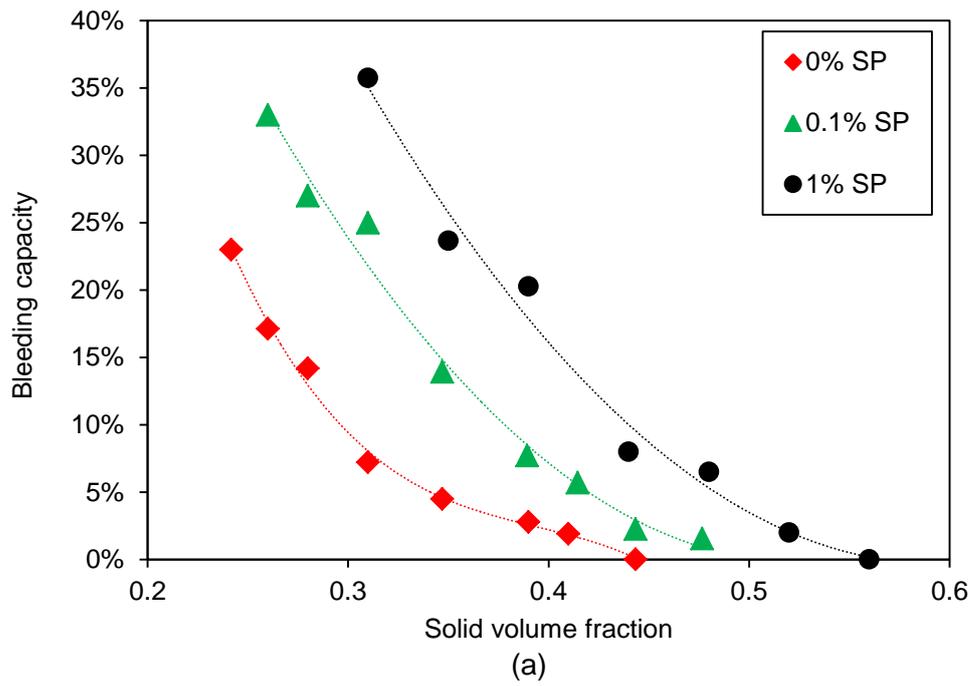
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Fig. 3. Shear stress as a function of shear strain for cement paste without SP and with a water to cement ratio of 0.25 ($\phi=56\%$)



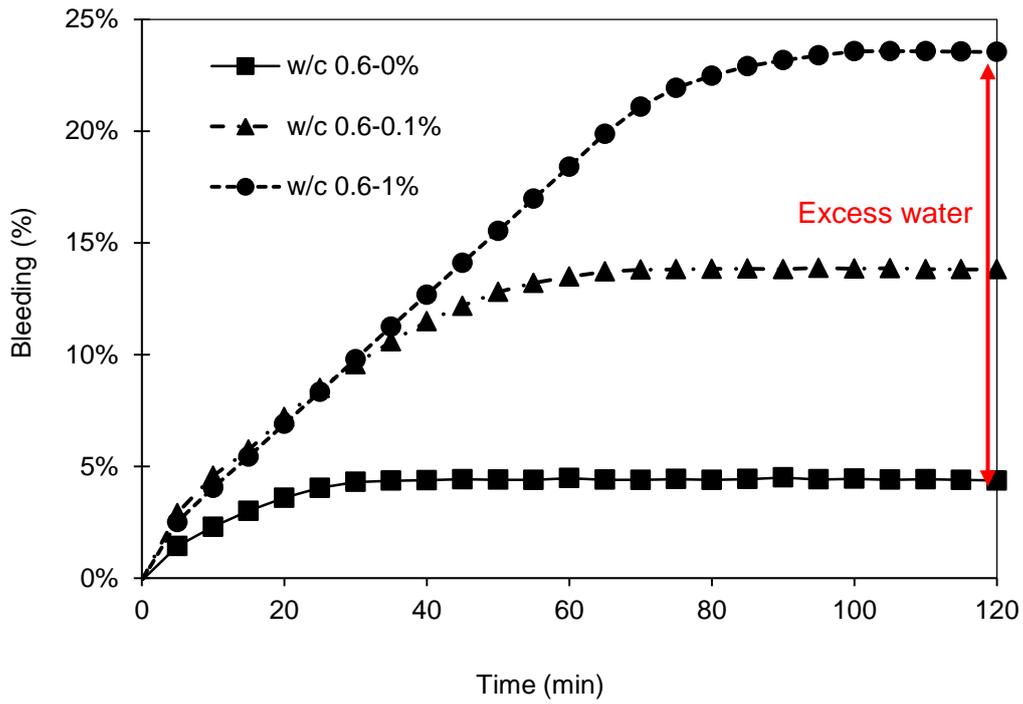
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Fig. 4. Evolution of bleeding as a function of water to cement ratio for cement pastes, in brackets is the solid volume fraction



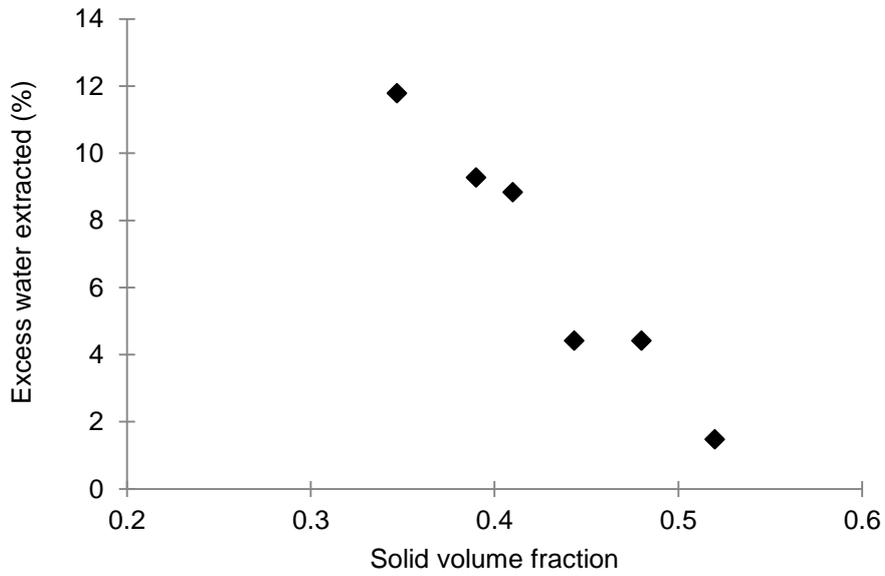
(b)
Fig. 5. Bleeding capacity (a) and bleeding rate (b) as a function of solid volume fraction

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Fig. 6. Evolution of bleeding for cement pastes with time for w/c ratio of 0.6 (solid volume fraction of 0.35)



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Fig. 7. Excess water extracted as a function of solid volume fraction

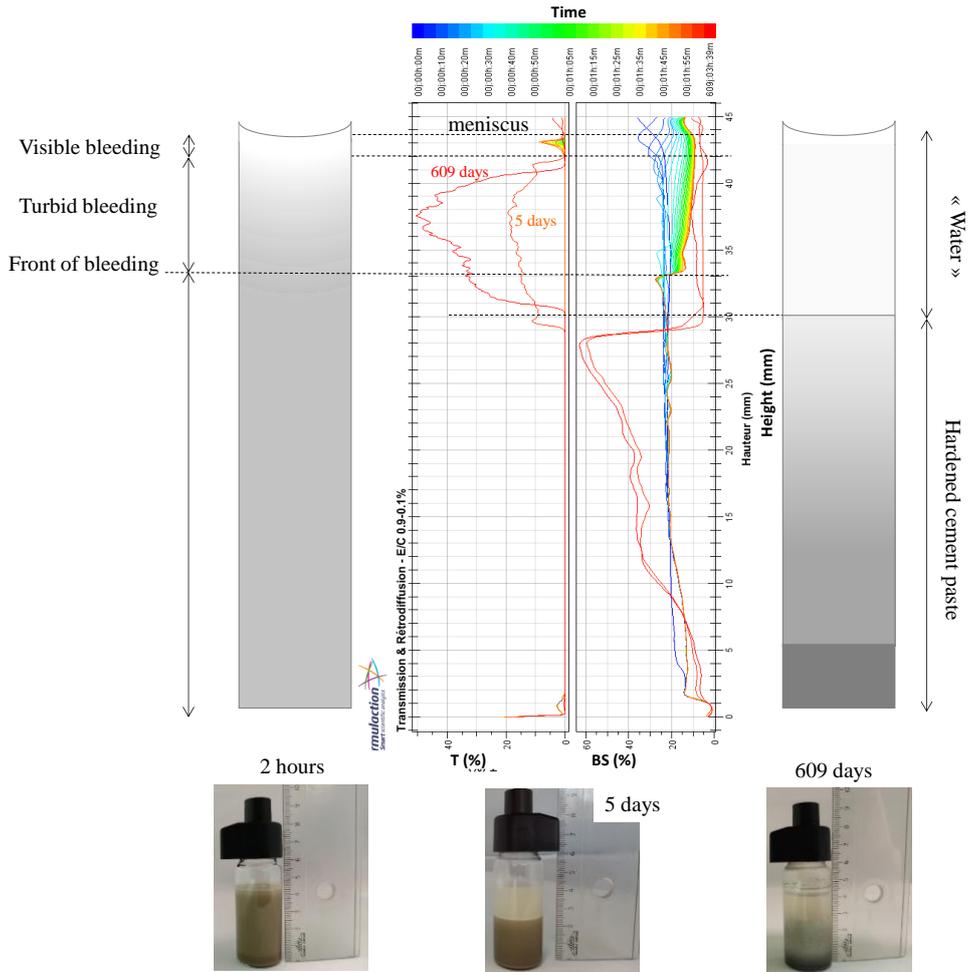
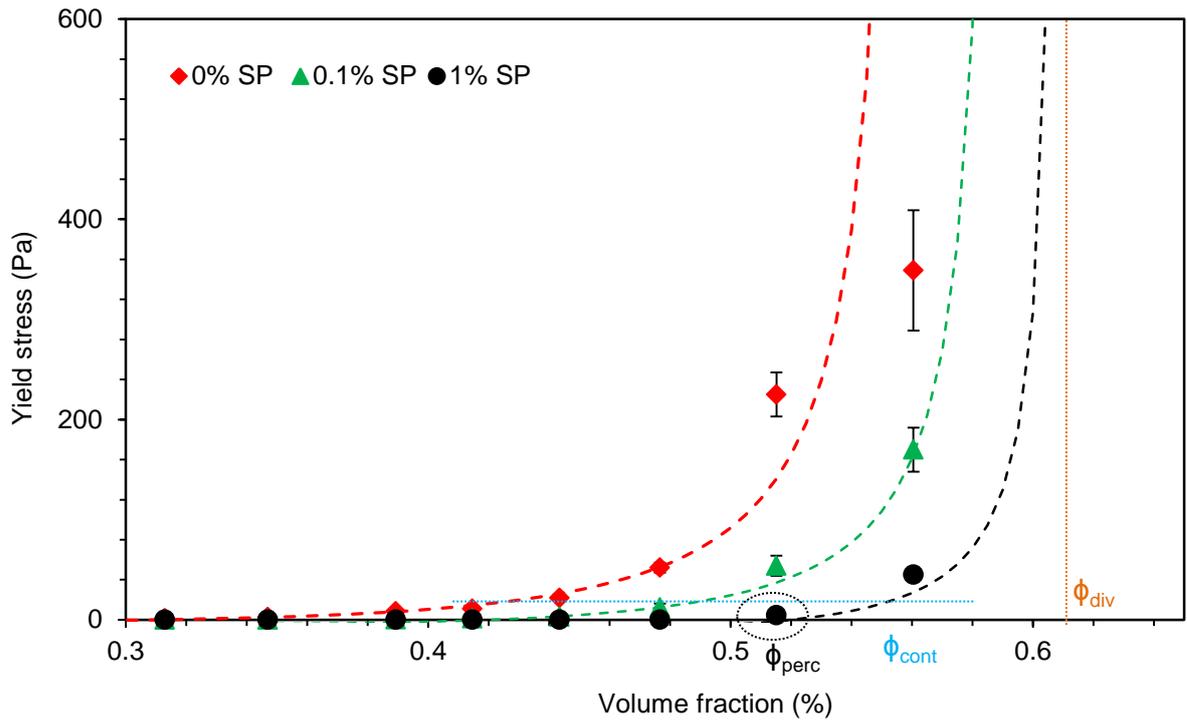
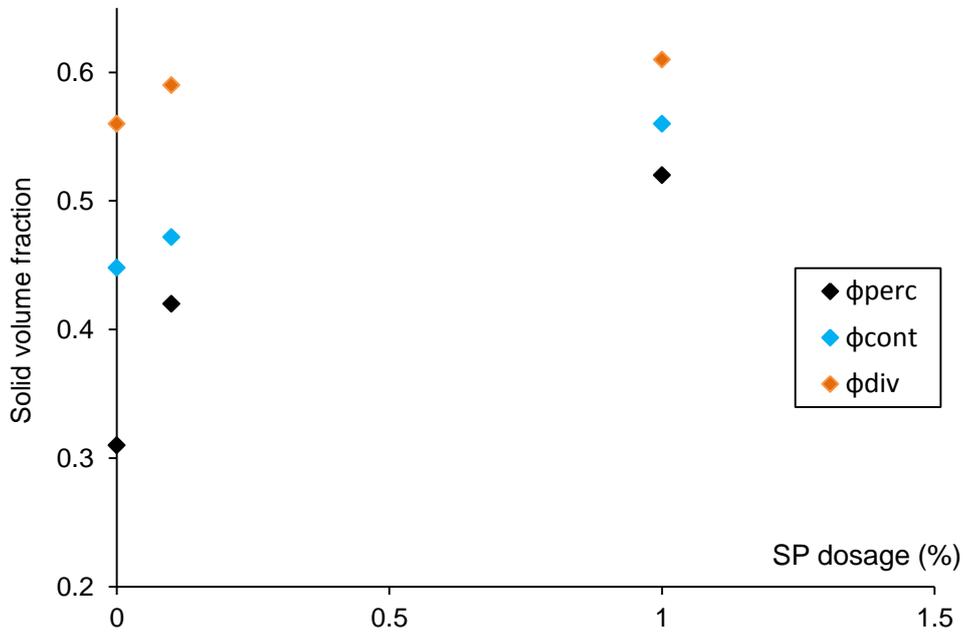


Fig. 8. Bleeding measurement for cement paste with w/c=0.9 and SP=0.1%



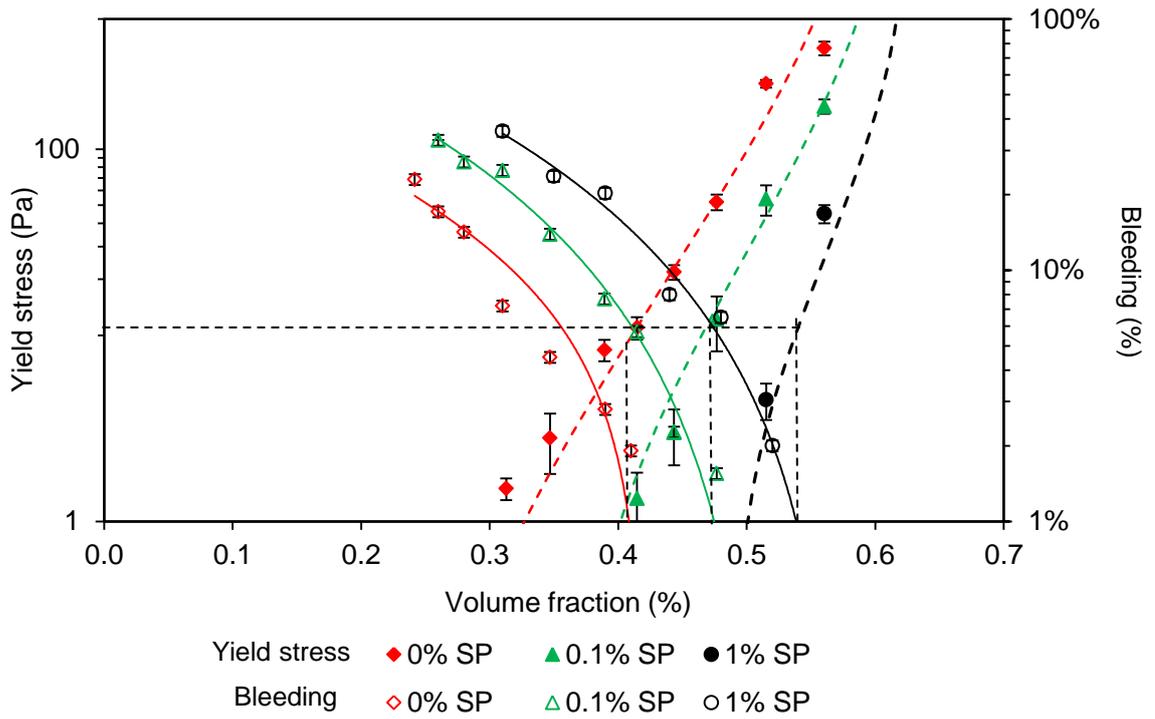
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Fig. 9. Yield stress as a function of solid volume fraction for cement paste containing 0, 0.1 and 1 wt% of PCE



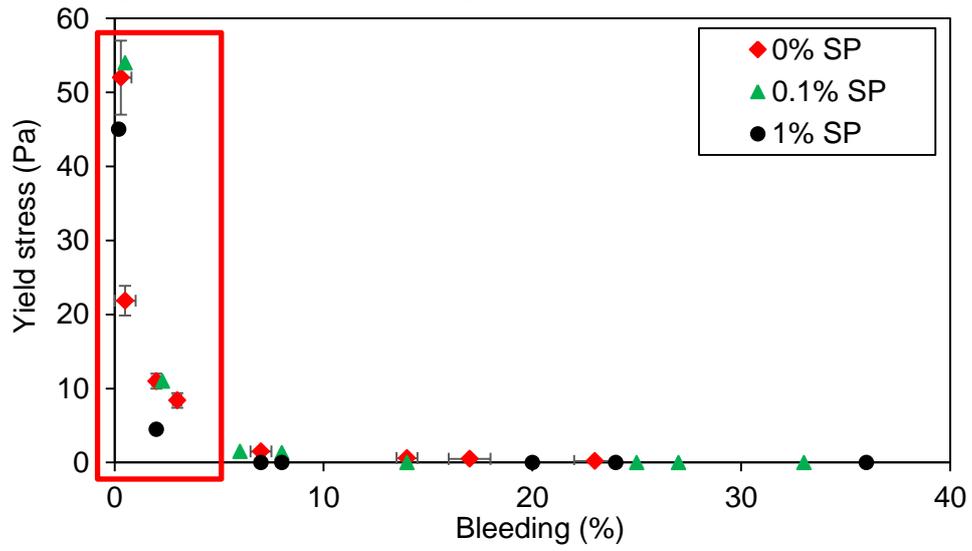
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Fig. 10. Transition volume fractions as a function of superplasticizer dosage



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Fig. 11. Yield stress and bleeding as a function of solid volume fraction



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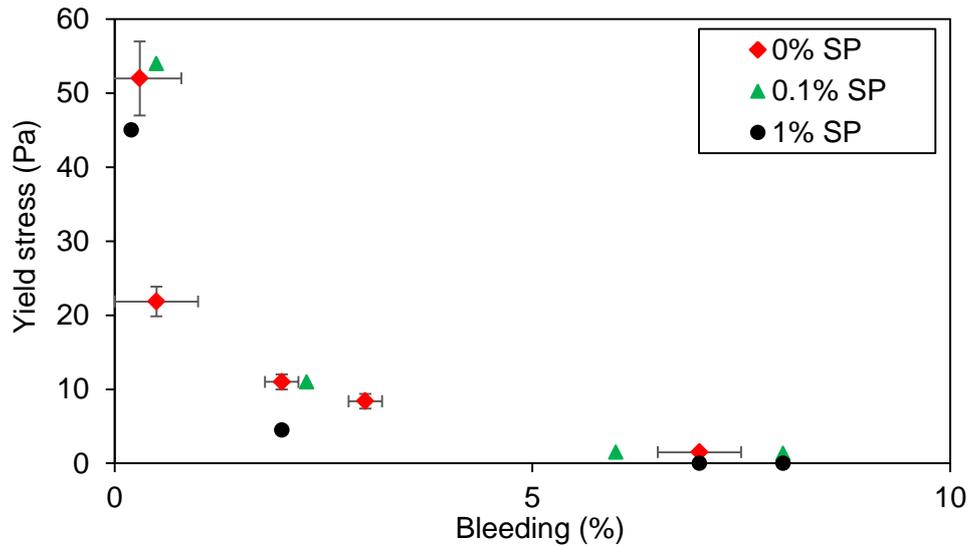


Fig. 12. Correlation between yield stress and bleeding

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