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# Yield stress of aerated cement paste

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## Abstract

Yield stress of aerated cement paste is studied. Samples are prepared by mixing aqueous foam with cement paste, which allows controlling bubble size, gas volume fraction and yield stress of the cement paste. Two distinct behaviors are observed depending on the surfactant used to prepare the precursor aqueous foam: (i) For a surfactant with low adsorption ability with respect to cement grains, bubbles tend to decrease the yield stress of the paste with magnitude governed by the Bingham capillary number, which accounts for bubble deformability. (ii) For a surfactant with high adsorption ability, bubbles increase significantly the yield stress. This behavior is shown to result from the surfactant-induced hydrophobization of the cement grains, which adsorb at the surface of the bubbles and tend to rigidify them. Within this regime, the effect of air incorporation is comparable to the effect of added solid particles.

*Keywords:*

rheology (A), cement paste (D), bubbles

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## 21 1. Introduction

22 Yield stress of a cement paste, mortar or concrete is a crucial property.  
23 For instance, sufficient yield stress can stop bleeding [1]. When material is  
24 poured in a formwork, yield stress can have negative effects if it prevents proper  
25 filling of the mold [1] but it helps to reduce the lateral formwork pressure [2].  
26 In the case of mortar sprayed on a vertical support, yield stress dictates the  
27 maximum thickness of the layer [3]. Among cementitious materials, aerated  
28 materials raise growing interest. Entrainment of air bubbles into concrete, up  
29 to 10% by volume, is known to improve its durability in environments exposed  
30 to freeze-thaw cycles [4]. At higher air content, aerated construction materials  
31 are promising for various industrial applications thanks to their low densities,  
32 low raw material needs, and improved thermal and acoustic properties.

33 The goal of this paper is to understand the effect of air bubbles on the yield  
34 stress of cement pastes containing air below 40% by volume. These materials  
35 will be referred to as "aerated cement paste" or "bubbles suspensions in cement  
36 paste" as the word "foams" usually refers to materials with higher air volume  
37 content, above 64% [5], where bubbles are densely packed and deformed by their  
38 neighbors. In foams, bubble interactions induce specific rheological properties  
39 [5], that are not discussed in this paper.

40 Various observations have been reported in the literature concerning the rhe-  
41 ological properties of aerated cement pastes or mortars. *Aïtcin* [4] notes that  
42 entrained bubbles improve workability of concrete whereas *Rixom and Mailva-*  
43 *ganam* [6] reports a large increase of viscosity with the amount of entrained  
44 air. These opposite results may arise from the different experimental protocols  
45 and the different paste formulations. Actually, quantifying the effect of air in-  
46 clusions on cement paste rheology, independently from the paste formulation,  
47 requires to determine normalized rheological quantities, e.g. yield stress  $\tau_y$  of

48 the aerated paste divided by the yield stress  $\tau_{ref}$  of the suspending paste. Mi-  
 49 cromechanical analysis shows that the normalized yield stress is a function of  
 50 air volume content  $\Phi$  and of the deformation of the bubbles when the fluid is  
 51 yielding [7, 8]. Deformability of the bubbles is characterized by the Bingham  
 52 capillary number  $Ca_y$ , which compares the suspending fluid yield stress  $\tau_{ref}$   
 53 and the bubble capillary pressure  $2\gamma/R$ :

$$Ca_y = \frac{\tau_{ref}}{2\gamma/R} \quad (1)$$

54 where  $\gamma$  is the air-liquid surface tension and  $R$  is the bubble radius. Such  
 55 a behavior has been confirmed experimentally when  $Ca_y \rightarrow \infty$  and  $Ca_y \rightarrow$   
 56 0 [9, 10] for model yield stress fluids, i.e. aerated concentrated emulsions.

57 The case of aerated cement paste is much more complex due to the po-  
 58 tentially strong effect of added surfactants on the suspending fluid yield stress  
 59  $\tau_{ref}$  [11]. In order to tackle this issue we prepare aerated cement paste by incor-  
 60 porating aqueous foam into cement paste within conditions where both water  
 61 and surfactant amounts are controlled. In the first part of the study, the effects  
 62 of both water and surfactants on the suspending fluid yield stress are quan-  
 63 tified. The dimensionless yield stress  $\tau_y/\tau_{ref}$  of the prepared aerated cement  
 64 pastes is then assessed as a function of bubble size and air volume content for  
 65 two different surfactants.

## 66 **2. Materials and methods**

### 67 *2.1. Materials*

68 We use a CEM I cement from Lafarge, Saint Vigor factory. Specific surface  
 69 area is  $0.359 \text{ m}^2/\text{g}$  and chemical composition is given in Table 1.

70 Two surfactants will be used: TTAB (tetradecyltrimethylammonium bro-  
 71 mide) is a cationic surfactant provided by Sigma-Aldrich, its molar mass is 336

C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	CaO/SiO <sub>2</sub>	MgO	Na <sub>2</sub> O +0.658 K <sub>2</sub> O	SO <sub>3</sub>	Gypsum
62%	16%	2.1%	15%	3	1.1%	0.34 %	2.6%	2.4%

Table 1: Chemical composition of CEM I cement from Lafarge, Saint Vigor

72 g/mol. Bio-Terge<sup>®</sup> is an anionic surfactant provided by Stepan, its molar mass  
73 is 315 g/mol.

74 Interaction of both surfactants with the same cement as used in this paper  
75 have been previously studied [11]. Adsorption isotherm of surfactants on cement  
76 grains have been measured and surfactant Critical Micelle Concentration (CMC)  
77 have been measured in DI water and in cement synthetic cement pore solution.  
78 For TTAB, CMC is 1.5 g/L in water and 0.5 g/L in cement pore solution.  
79 Regarding Bio-Terge, its CMC is 2 g/L in water and 0.5 g/L in cement pore  
80 solution. The main results of this paper will be recalled in the discussion.

## 81 2.2. Method

### 82 2.2.1. Preparation of aerated and reference cement pastes

83 As the yield stress of cementitious materials depends on their shear history,  
84 the same time schedule has been followed for all samples. First, distilled water  
85 and cement at water-to-cement mass ratio  $W/C_i$  are mechanically mixed for 3  
86 min. Then, the paste is left at rest for 20 minutes to allow for the formation of  
87 sulfo-aluminates [12]. After 20 minutes, foam is added to the cement paste and  
88 carefully incorporated with a spoon. Hand mixing allows us to check visually  
89 that the bubbles size is kept constant during incorporation of the foam. Mixing  
90 duration is 4 minutes, and it is carried out always by the same operator in order  
91 to be similar in all experiments. 30 minutes after initial cement paste mixing,  
92 the rheometer cup is filled and rheometry starts.

93 Unfoamed samples, the so-called "reference cement pastes", were prepared  
94 for comparison purpose with foamed samples. In these cases, the above-described

95 procedure was followed except that pure surfactant solution was added (28 min  
96 after initial cement paste mixing) instead of foam.

97 The weight of water contained into the foam added to the cement paste is  
98 measured in order to calculate the new effective water-to-cement ratio,  $W/C_f$ ,  
99 which characterizes the suspending cement paste in the aerated sample. Final  
100 air content  $\Phi$  is assessed by weighting the aerated paste in the rheometer cup.  
101 Indeed, the density  $\rho$  of the sample is related to the air content by  $\rho(\Phi) =$   
102  $\rho_0(1 - \Phi)$ , where  $\rho_0 = (W/C_f + 1)/(W/C_f/\rho_w + 1/\rho_c)$  is the density of the  
103 suspending cement paste, with  $\rho_w$  (resp.  $\rho_c$ ) the density of water (resp. of  
104 cement). The maximal relative error on the measured air fraction is 4%.

105 Note that in the chosen procedure, foam or surfactant solution is added  
106 more than 20 minutes after first mixing of cement and water, so surfactant is  
107 not expected to interfere in the formation of first hydration products [12].

### 108 *2.2.2. Foam production*

109 Aqueous foam is generated according to the method described in [13]. In  
110 brief, bubbles are created with a small T junction with two inputs: surfactant  
111 solution and nitrogen. Within such conditions, foams are made of bubbles  
112 having the same diameter, which is set by the flow rates of both nitrogen and  
113 surfactant solution. The foam is collected (bubble by bubble) in a column and  
114 it is wetted from the top to prevent it from drying and breaking. Once foam is  
115 ready to use, it is pushed from the column at constant flow rate.

### 116 *2.2.3. Samples*

117 We study seven sets of samples. For each set, both initial water-to-cement  
118 ratio (i.e. before addition of foam) and foam characteristics (surfactant and  
119 bubble size) are kept constant.

120 Sets of reference samples are prepared to match with each set of bubble

	Surfactant	Surfactant concentration	Bubble diameter	$W/C_i$	Reference set
Set T1	TTAB	4.5 g/L	475 +/- 10 $\mu\text{m}$	0.382	R_T1
Set T2	TTAB	4.5 g/L	270 $\mu\text{m}$	0.335	R_T2
Set T3	TTAB	4.5 g/L	475 +/- 10 $\mu\text{m}$	0.325	R_T3
Set T4	TTAB	4.5 g/L	475 +/- 10 $\mu\text{m}$	0.305	R_T4
Set T5	TTAB	4.5 g/L	780 +/- 20 $\mu\text{m}$	0.335	R_T2
Set B1	Bio-Terge	30 g/L	440 +/- 5 $\mu\text{m}$	0.329	R_B1
Set B2	Bio-Terge	8 g/L	590 +/- 10 $\mu\text{m}$	0.335	R_B2
-	-	-	-	0.305 to 0.405	R_0

Table 2: Characteristics of each set of aerated cement paste samples. The corresponding reference paste for each set contains the same surfactant at the same concentration, and the same initial water-to-cement ratio. Note that sets T2 and T5 share the same reference R\_T2.

121 suspensions, i.e. they are prepared with the same surfactant solution and from  
122 the same initial cement paste, but they contain no bubble. In addition, reference  
123 set R\_0 refers to yield stress measurement on surfactant-free paste.

#### 124 2.2.4. Yield stress measurement

125 Yield stress measurements are carried out with a vane-in-cup geometry in  
126 Ultra+ Kinexus Rheometer from Malvern. The six-blade vane tool is 5 cm high  
127 and 25 mm wide. We use a striated cup to avoid wall slip: diameter is 37 mm  
128 and height 62.5 mm. The cup is filled with aerated or reference cement paste  
129 with a spoon, then the Vane tool is slowly inserted into the paste. Pre-shear  
130 is prevented before measurement in order to avoid material flow and buoyancy-  
131 induced bubble migration [2, 14, 15].

132 Yield stress is measured with a start of flow sequence at a constant shear rate  
133  $\dot{\epsilon} = 0.01\text{s}^{-1}$  for 10 minutes [16]. For all samples, stress increases up to the yield  
134 stress and then decreases. The yield stress is reached for shear strain values  
135 between 40 and 45%. This value is low enough to enable correct measurement  
136 of yield stress with a Vane tool [17].

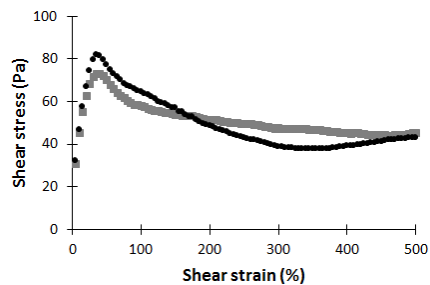


Figure 1: Start of flow curves for yield stress measurement of an aerated cement paste (grey) and the corresponding reference paste (black). Examples correspond to set T3 with air content 31% and the corresponding reference sample from set R.T3.

### 137 **3. Results**

#### 138 *3.1. Reference yield stress*

139 Yield stresses for reference samples are plotted in Fig. 2. As expected, when  
 140 no surfactant is added, the yield stress decreases when the final water-to-cement  
 141 ratio increases. For each reference data set containing TTAB surfactant, the  
 142 yield stress decreases when the amount of added TTAB solution increases. The  
 143 same trend is observed with Bio-Terge solution at the smallest concentration  
 144 (R\_B2), even if the decrease is lower than for TTAB. On the contrary, when  
 145 30 g/L Bio-Terge surfactant solution is used (R\_B1), the yield stress increases  
 146 with the amount of added solution.



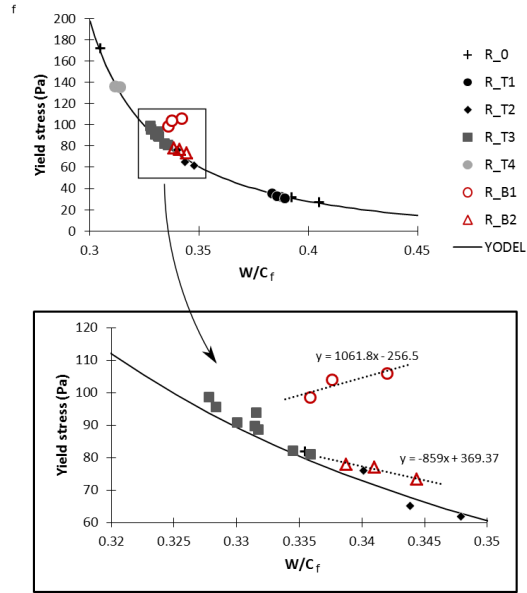


Figure 2: Yield stress of reference cement pastes. Yield stresses for pastes with no surfactant (R\_0) or TTAB surfactant (R\_T1 to R\_T4) are fitted with equation 3 with  $\Phi_{perc} = 0.32$ ,  $\Phi_{max} = 0.545$  and  $m_1 = 65 Pa$ . In the case of Bio-Terge surfactant, linear regressions for each set of data are plotted with dotted lines.

### 147 3.2. Aerated cement paste

148 Yield stresses measured for each data set at different air contents are given  
 149 in Figs. 3 and 4. Evolution of yield stress with increasing air content is not the  
 150 same for all data sets: it is constant in set T1, it decreases in sets T2 to T5 and  
 151 increases for B1 and B2.

## 152 4. Discussion

### 153 4.1. Reference yield stress with surfactant

154 Ionic surfactants, mainly anionic, can strongly modify yield stress when they  
 155 are added to a cement paste [11]. At low concentration, adsorbed surfactant  
 156 monolayer turns cement grains to hydrophobic grains which induces attractive  
 157 interactions. At macroscopic scale, this results in the increase of the yield stress.

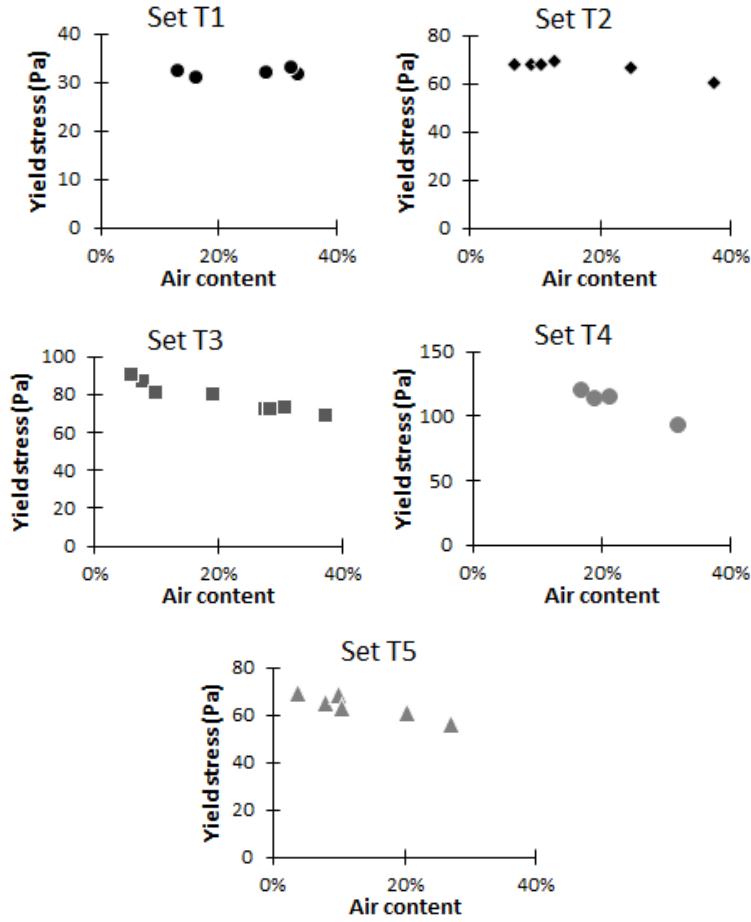


Figure 3: Yield stresses of aerated cement pastes made with TTAB surfactant. Bubble diameter is 475  $\mu\text{m}$  for T1, T3 and T4, 270  $\mu\text{m}$  for T2 and 780  $\mu\text{m}$  for T5. Initial water-to-cement ratio is 0.382 for T1, 0.335 for T2 and T5, 0.325 for T3 and 0.305 for T4.

158 At high surfactant concentration, surfactant agglomeration on the surface of the  
 159 cement grains leads to steric repulsion between them and a drop of the paste  
 160 yield stress.

161 As surfactant concentration has a significant effect on the yield stress, let us  
 162 calculate the final concentrations  $C_{TA,f}$  after mixing foam and cement paste.  
 163 They depend on the concentration in the foaming solution  $C_{TA,i}$ , on the initial

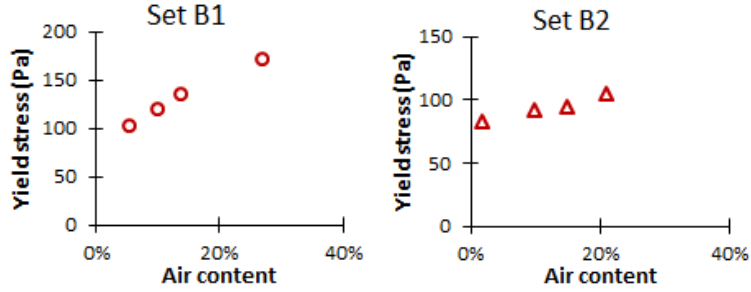


Figure 4: Yield stresses of aerated cement pastes made with Bio-Terge surfactant. For B1, bubble diameter is  $440 \mu\text{m}$ , initial water-to-cement ratio is 0.329, and surfactant concentration in foam is 30 g/L. For B2, bubble diameter is  $590 \mu\text{m}$ , initial water-to-cement ratio, 0.335, and surfactant concentration in foam, 8 g/L.

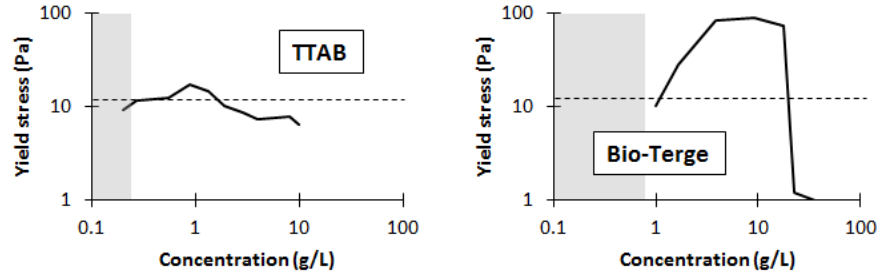


Figure 5: Effect of surfactant concentration on the yield stress of cement pastes at  $W/C_f = 0.5$  prepared following the protocol described in [11]. Repetition of a reference test in [11] showed that the error is about 5% of the yield stress value. Dotted line shows yield stress of the paste with no surfactant (12 Pa). Grey areas show the surfactant concentrations used in the present study.

164 water-to-cement ratio of the precursor cement paste  $W/C_i$  and the final water-  
 165 to-cement ratio  $W/C_f$ :

$$C_{TA,f} = C_{TA,i} \frac{W/C_f - W/C_i}{W/C_f} \quad (2)$$

166 Calculated values range from 0.03 to 0.2 g/L for samples containing TTAB  
 167 and between 0.08 and 0.8 g/L for Bio-Terge. In Fig. 5, yield stress is given as a  
 168 function of surfactant concentration for cement pastes at  $W/C_f = 0.5$  prepared

169 as in [11], with the same cement as this work, and containing TTAB or Bio-  
 170 Terge. The figure shows that for both surfactants, the estimated concentrations  
 171 are well below the concentrations at which maximum yield stresses are expected.  
 172 Surfactants are therefore in the low concentration regime, where yield stress can  
 173 be enhanced by hydrophobic interactions, but due to the very low concentrations  
 174 used, we can expect this effect to be insignificant. Further analysis is made below  
 175 for each surfactant.

#### 176 4.1.1. Reference yield stress with TTAB

177 In Fig. 2, all yield stresses of cement pastes containing no surfactant or  
 178 TTAB follow the same curve. First of all, this shows that TTAB, at the low  
 179 concentrations we use here, has no effect on yield stress. In addition, yield  
 180 stress depends only on the total water content in the cement paste, including  
 181 both initial mixing water and foaming solution added later.

182 We choose to fit TTAB reference curve with equation 3 [18]:

$$\tau_{ref} = m_1 \frac{\Phi_p^2(\Phi_p - \Phi_{perc})}{\Phi_{max}(\Phi_{max} - \Phi_p)} \quad (3)$$

183 In this equation,  $m_1$  accounts for the intensity of the interactions between  
 184 cement grains, whose major components are Van der Waals, electrostatic and  
 185 steric forces [18].  $\Phi_p$  is the solid volume fraction and is related to the water-to-  
 186 cement ratio and to the densities of water  $\rho_w$  and cement  $\rho_c$ :

$$\Phi_p = 1/(1 + \rho_c/\rho_w W/C_f) \quad (4)$$

187  $\Phi_{perc}$  and  $\Phi_{max}$  are respectively is the percolation threshold and the maximal  
 188 solid fraction of the cement grains.

189 This curve is shown in Fig. 2 with parameters  $\Phi_{perc} = 0.32$ ,  $\Phi_{max} = 0.545$   
 190 and  $m_1 = 65 \text{ Pa}$ .

191 *4.1.2. Reference yield stress with Bio-Terge*

192 When Bio-Terge solution is added to cement paste, yield stress is higher than  
 193 for samples containing TTAB or for surfactant-free pastes at the same water-  
 194 to-cement ratio. In fact, addition of Bio-Terge solution into a cement paste  
 195 has two consequences: solid fraction  $\Phi_p$  decreases and the intensity of of the  
 196 attractive forces between cement grains increases. As a result, reference yield  
 197 stress  $\tau_{ref}$  cannot be fitted by equation 3. Therefore, we choose to describe the  
 198 corresponding data with linear regressions:  $\tau_{ref} = 1062 W/C - 257$  for set R\_B1  
 199 and  $\tau_{ref} = 369 - 859 W/C$  for set R\_B2.

200 *4.2. Dimensionless yield stress*

201 Results for the normalized yield stress, i.e.  $\tau_y/\tau_{y,ref}$ , are shown in Fig. 6.

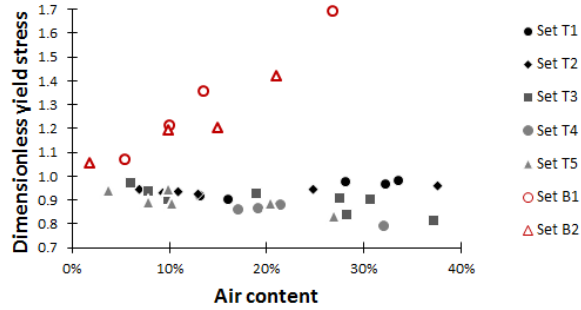


Figure 6: Dimensionless yield stress for all samples (see Table 2 for characteristics of the samples).

202 First of all, data corresponding to the different samples presented in Figs. 3  
 203 and 4 collapse on two consistent sets characterized by the surfactant used. For  
 204 Bio-Terge samples, the dimensionless yield stress increases with air content. On  
 205 the other hand, with TTAB surfactant, all the measured value are below the  
 206 reference yield stress; the lowest measured dimensionless yield stresses are 0.8  
 207 (f.i. set 4 at 30% air content).

208 There is no major effect of Bio-Terge concentration nor bubble size on the  
209 dimensionless yield stress. During preparation however, we noted that incorpo-  
210 rating aqueous foam in cement paste was more difficult for B2, where Bio-Terge  
211 concentration is lower, because the bubbles tend to break during hand mixing.

212 Observation of the bubbles after they have risen at the top surface of the  
213 sample has revealed a fundamental difference for the surfactant samples: bub-  
214 bles in Bio-Terge samples are covered with a layer of cement grains (Fig. 7-right)  
215 whereas bubbles in TTAB are bare (Fig. 7-left). Actually bare bubbles are dif-  
216 ficult to observe because they usually break as soon as they reach the sample  
217 surface. On the contrary, in Bio-Terge samples at rest, only few bubbles break.  
218 The difference observed for the rheological behavior of the two surfactant sam-  
219 ples seems to be related to the different nature of the bubbles surface. We  
220 consider each case in the following.

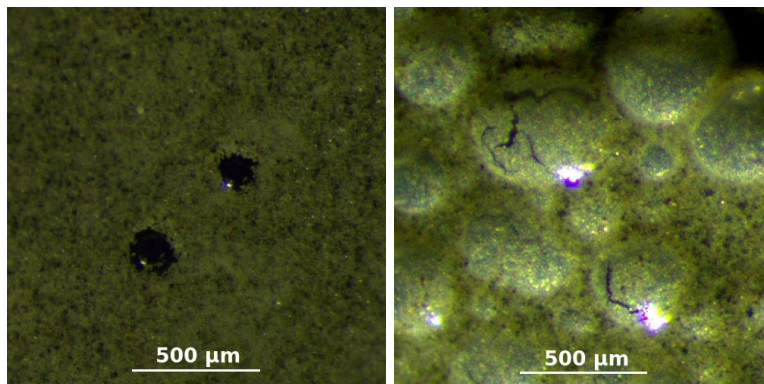


Figure 7: Left: sample from set T1 containing TTAB. Right: sample from set B1 containing Bio-Terge. Note that bubbles tend to break rapidly when exposed to air, especially for samples containing TTAB, so that the number of the bubbles on each picture is not representative of the air content.

#### 221 4.2.1. Bare bubbles (TTAB)

222 The effect of such bubbles are expected to be described by micromechanical  
223 models for capillary inclusions [7, 8], which are based on the Bingham capillary

224 number  $Ca_y = \tau_{y,ref}R/(2\gamma)$ . Theoretical dimensionless yield stress for non-  
 225 deformable bubbles  $Ca_y \rightarrow 0$  is given by [7, 8]:

$$\tau_y/\tau_{ref} = \sqrt{(1-\Phi)\frac{5+3\Phi}{5-2\Phi}} \text{ when } Ca_y \rightarrow 0 \quad (5)$$

226 When the bubbles are fully deformable ( $Ca_y \rightarrow \infty$ ), the relation becomes:

$$\tau_y/\tau_{ref} = \sqrt{(1-\Phi)\frac{3-3\Phi}{3+\Phi}} \text{ when } Ca_y \rightarrow \infty \quad (6)$$

227 Equations 5 and 6 are plotted in Fig. 8. Both curves have also been obtained  
 228 experimentally for bubble suspensions in a model yield stress fluid (concentrated  
 229 oil-in-water emulsion) [9, 10]. In [10], experimental results fitted with equation 5  
 230 for experimental Bingham capillary numbers within the range  $0.0069 \leq Ca_y \leq$   
 231  $0.11$  and with equation 6 for  $Ca_y = 0.57$ .

232 Let us calculate  $Ca_y$  for each TTAB data set. As mentioned previously,  
 233 reference yield stress  $\tau_{ref}$  decreases with increasing liquid content as described  
 234 by equation 3. Besides, at low surfactant concentration, surface tension  $\gamma$  de-  
 235 creases when concentration increases. Such a variation is reported in [11] as a  
 236 function of TTAB concentration in the interstitial solution of the cement paste.  
 237 By assuming that TTAB concentration in solution is close to the total TTAB  
 238 concentration, i.e. that the amount of adsorbed molecules is negligible, surface  
 239 tension can be described by  $\gamma = 31 - 6.8 * \ln(C_{res})$  within the range 0.02-0.2 g/L  
 240 (this formula has been obtained by fitting experimental results from [11], with  
 241  $\gamma$  in mN/m and  $C_{res}$  in g/L). Using those  $\gamma$  values and equation 3, experimental  
 242 values of  $Ca_y$  are calculated and given in Table 3. In Fig. 8, dimensionless yield  
 243 stress results of aerated cement paste with TTAB are plotted for comparison  
 244 with both theoretical curves.

245 At low air content, experimental dimensionless yield stresses are systemat-

Set	$Ca_y$
T1	0.08
T2	0.10
T3	0.21 - 0.23
T4	0.34 - 0.36
T5	0.28 - 0.30

Table 3: Bingham capillary numbers for experiments with TTAB

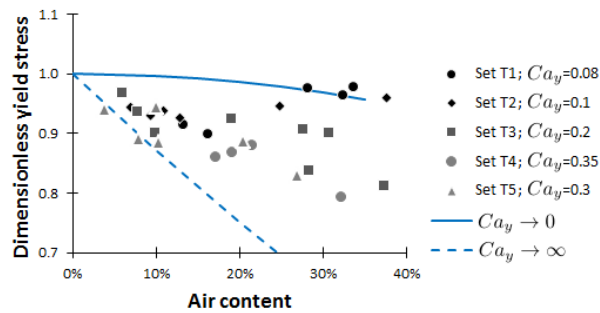


Figure 8: Dimensionless yield stress for samples made with TTAB. Theoretical curves, which have been observed experimentally on model yield stress fluid by Ducloué [19], are indicated for non-deformable bubbles (full line) and fully deformable bubbles (dotted line).

246 ically lower than theoretical values. This behavior is possibly an experimental  
 247 artifact and shows that despite all our effort to keep the same preparation proto-  
 248 col for aerated and reference samples, shearing of the paste during hand mixing  
 249 may be influenced by the presence of bubbles.

250 However, all the results fall within the range of expected values between the  
 251 two theoretical curves. Moreover, the dimensionless yield stress values stretch  
 252 as a function of  $Ca_y$ . This can be seen mainly at high air content: the higher  
 253 the capillary number, the lower the dimensionless yield stress.

#### 254 4.2.2. Particle covered bubbles (Bio-Terge)

255 Yield stress measured for aerated Bio-Terge cement pastes is well above the  
 256 upper bound predicted by theory based on  $Ca_y$  (i.e. equation 5). The particle



257 layer attached to the bubble surface suggests that the behavior in the case of  
258 Bio-Terge lies in the modified surface properties of the bubbles.

259 Particle covered interfaces have first been reported by *Ramsden* [20] and  
260 *Pickering* [21]. Bubbles covered by a dense layer of irreversibly adsorbed parti-  
261 cles, called armored bubbles, are known to be very stable compared to surfactant  
262 stabilized bubbles: the particle armor can prevent bubble rupture (or coales-  
263 cence) [22, 23, 24] and volume decrease due gas transfer (ripening) [25, 26, 27,  
264 28, 29].

265 First requirement to allow solid particle adsorption at air-water or oil-water  
266 interface is that the particles must be partially hydrophobic. Then, the elec-  
267 trostatic barrier to particle adsorption must be low enough [30]. Increase of  
268 contact angle of water on cement grains has been observed in the presence of  
269 low amount of Bio-Terge, so we can assume that the first point is fulfilled. Ce-  
270 ment grains have a size comprised between a few micrometers and 100  $\mu\text{m}$  with  
271 average value close to 10  $\mu\text{m}$  [16]. Due to their irregular shape, radius of curva-  
272 ture of the edges is several orders of magnitude below the grain size [31], which  
273 decreases the adsorption barrier [30]. In addition, cement solution contains a  
274 high concentration of dissolved ions [12], and this high electrolyte content re-  
275 duces electrostatic repulsion between charged particles and interface, which also  
276 decreases the adsorption barrier [30]. All these aspects show that cement par-  
277 ticles covered by a monolayer of Bio-Terge molecules are good candidates to  
278 adsorb at air-water interfaces.

279 In the micro-mechanical model for the bubbles, the stress of the air-fluid  
280 interface is characterized by one value, i.e. the surface tension  $\gamma$ . However,  
281 previous studies showed that this simple behavior cannot account for particle  
282 stabilized interfaces, where complex behavior arises from the kinetics and irre-  
283 versibility of the adsorption of the particles at the interface [30] and leads to

284 an additional extra stress. In the case of an isotropic interface between two  
 285 Newtonian fluids, the extra stress can be expressed as a function of two scalars,  
 286 namely the shear surface viscosity  $\mu_{s,s}$  and the dilatational surface viscosity  $\mu_{s,d}$   
 287 [32]. The resistance of surface viscosity to the shear stress from the bulk around  
 288 the inclusion can be quantified by the Boussinesq numbers  $Bq_s = \mu_{s,s}/(\mu_{ext}R)$   
 289 and  $Bq_d = \mu_{s,d}/(\mu_{ext}R)$ , where  $\mu_{ext}$  is the viscosity of the external fluid. De-  
 290 termination of the value of the surface rheological properties of cement covered  
 291 bubbles is far out of the scope of this paper. Though, the wide literature re-  
 292 lated to the rheology particle covered interfaces can highlight the behavior of  
 293 adsorbed cement grains. We will recall here the main literature results. To get  
 294 a more complete understanding of this complex issue, one can read the recent  
 295 reviews from *Thijssen and Vermant* [33], *Maestro* [34] and *Pitois and Rouyer*  
 296 [35].

297 Adsorption of particles to an interface can enhance both the dilatational  
 298 [36] and the shear [37] surface viscosities. High surface viscosities indicate that  
 299 under applied stress, deformation of the interface is slow. When particle volume  
 300 fraction is high, surface viscosities diverge and the interface exhibits a yield stress  
 301 behavior [38, 39, 40, 37], i.e. as long as the applied stress is below the yield  
 302 stress, it behaves like a solid membrane. When interactions between particles  
 303 are weak, yield stress behavior happens for particle surface fractions reaching  
 304 the so-called *jamming surface fraction* [36]. On the contrary, when attractive  
 305 interaction between the particles at the interface makes them agglomerate, the  
 306 critical volume fraction leading to the yield stress behavior can be greatly re-  
 307 duced [38, 39, 40, 37]. Note that for particles adsorbed at an interface, attractive  
 308 interactions include capillary forces which are enhanced by the roughness of  
 309 the particles [38, 39]. Cement-grains covered interfaces are therefore likely to  
 310 exhibit a surface yield stress.

311 In addition, the complex rheological properties affect the deformability of the  
 312 bubbles. Recent numerical work performed on droplets in shear flow has shown  
 313 that the deformation  $D = (L - B)/(L + B)$  (where L and B are the major and  
 314 minor axes of the deformed droplet) of the inclusion is greatly influenced by the  
 315 surface viscosities [41]. For flow conditions which leads to a high deformation  
 316  $D \geq 0.35$  when  $Bq_s = Bq_d = 0$ , the deformation D is divided by a factor 2  
 317 when  $Bq_s = Bq_d = 10$  or when  $Bq_d = 0$  and  $Bq_s = 10$ . For our system, the  
 318 viscosities are expected to diverge, so we can assume that these values of the  
 319 Boussinesq number are by far exceeded. Therefore, the bubbles must remain  
 320 spherical during the start-of-flow experiment performed on the aerated cement  
 321 pastes prepared with Bio-Terge.

322 Eventually, adsorption of hydrophobic cement grains at the surface of the  
 323 bubbles leads to two effects: (1) the immobilization of the interface of the bub-  
 324 bles due to a surface yield stress and (2) the reduction of the bubble defor-  
 325 mation. Due to these two effects, armored bubbles are expected to behave as  
 326 non-deformable solid inclusions.

327 In order to compare directly the armored bubbles with solid inclusions, addi-  
 328 tional measurements were performed with solid beads instead of bubbles. Pro-  
 329 cedure followed for the tests is the same as described in paragraph 2.2.1; at 27  
 330 minutes after preparation of the cement paste, we added to the paste 500  $\mu\text{m}$   
 331 diameter polystyrene beads or 2 mm diameter glass beads. These additional  
 332 samples contain no surfactant, so reference yield stress is given by equation 3.

333 The micromechanical analysis for solid inclusions assumes no-slip conditions  
 334 at their surface [7], and the corresponding theoretical dimensionless yield stress  
 335 is:

$$\tau_y/\tau_{ref} = \sqrt{\frac{(1 - \Phi)}{(1 - \Phi/\Phi_m)^{2.5\Phi_m}}} \quad (7)$$

336 where  $\Phi_m$  is the maximal packing fraction of the beads within shearing con-  
 337 ditions. This curve has been experimentally validated in model yield stress  
 338 materials [14] and in cement paste [16].  $\Phi_m$  value measured in cement paste is  
 339 0.56.

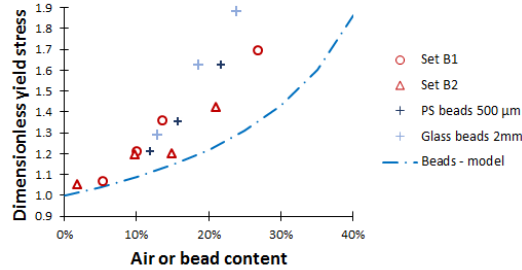


Figure 9: Dimensionless yield stress for samples made with Bio-Terge. Dotted line correspond to the theoretical curve for a suspension of solid spheres with maximal solid fraction 0.56. Crosses correspond to measurements carried out with 500  $\mu\text{m}$  polystyrene beads or 2 mm glass beads.

340 In Fig. 9, we can see that our experimental results for Bio-Terge bubbles and  
 341 for beads are consistent with equation 7, showing significant increase of the yield  
 342 stress as a function of inclusion volume fraction, with no effect of inclusion size.  
 343 Experimental data are slightly above the theoretical values, which could be re-  
 344 lated to our experimental method and the difficulty to follow accurately the same  
 345 protocol for cement paste with and without inclusions. However, experimental  
 346 dimensionless yield stresses for bead suspensions coincide with dimensionless  
 347 yield stress of bubbles suspensions prepared with Bio-Terge surfactant. There-  
 348 fore, armored bubbles behave mainly like solid spheres in the cement paste at  
 349 the onset of yielding.

## 350 5. Conclusion

351 We have investigated the effect of added bubbles with well controlled size  
 352 and volume fraction on the yield stress of aerated cement paste. Bubbles were

353 stabilized with two surfactants, which are known to have different adsorption  
354 behavior with respect to cement grains.

355 The behavior of the bubbles is strongly affected by the surfactant. When sur-  
356 factant has low affinity to cement grains, the dimensionless yield stress depends  
357 only on the Bingham capillary number  $Ca_y$ , which accounts for the deformabil-  
358 ity of the bubbles. For  $Ca_y \sim 0.1$ , i.e. for small bubbles and/or low cement paste  
359 yield stress, the yield stress is almost unchanged with respect to the bubble-free  
360 paste. On the contrary, when  $Ca_y \gtrsim 0.2$ , i.e. for large bubbles and/or high  
361 cement paste yield stress, a small decrease of the dimensionless yield stress with  
362 air volume content can be observed.

363 Totally different behavior is observed when surfactant adsorbs on cement  
364 grains. Effect of bubbles is comparable to solid inclusions, and no effect of bubble  
365 size can be seen. We attribute this effect to the in-situ hydrophobization of the  
366 cement grains and their irreversible adsorption at the bubbles surface, which  
367 changes completely the surface properties of the bubbles. In such a case, the  
368 yield stress of the aerated cement paste increases significantly while its density  
369 decreases in proportion of air introduced in the paste.

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