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Use of saponin foam reinforced with colloidal particles as an application to soil remediation: experiments in a 2D tank

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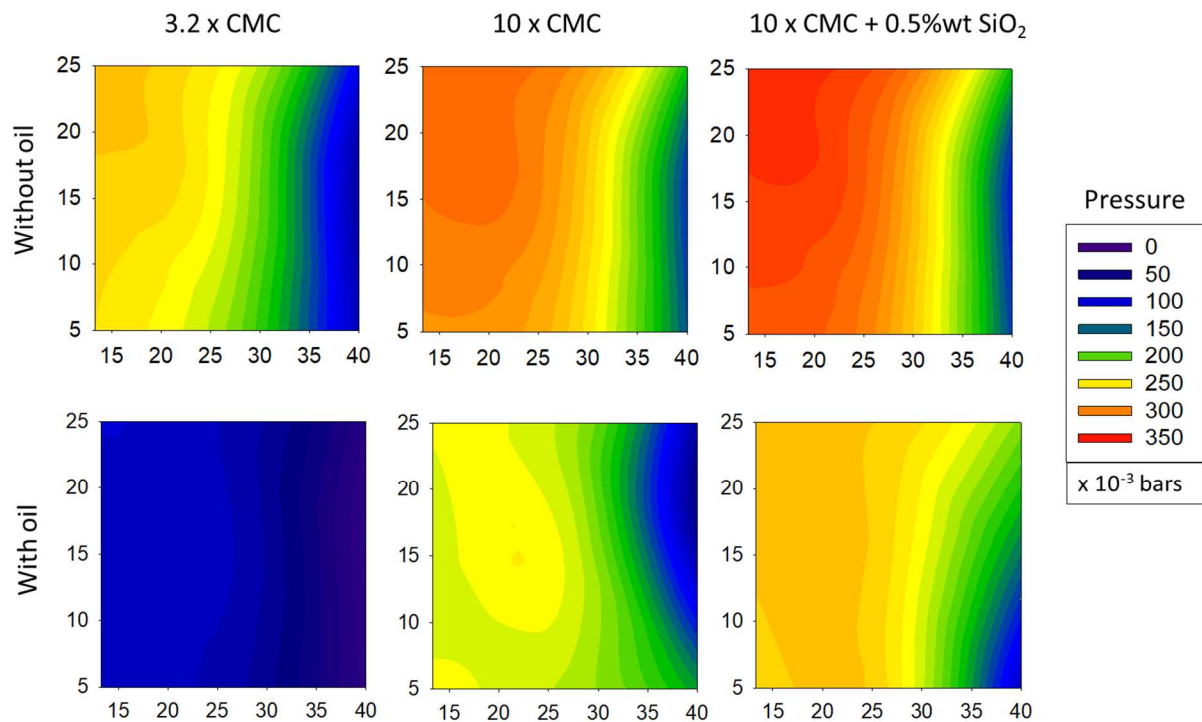
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Keywords: Foam, Porous medium, Colloidal particle, Light Non Aqueous Phase Liquid, 2D tank

Highlights

- A piston-like front is forming when injecting foam in a 2D-porous medium
- Oil presence disturbs foam displacement and foam front
- Solid silica particles increase foam resistance to oil induced destruction

Graphical abstract



Abstract

Foam can be used to achieve environmental remediation in case of contamination caused by light non aqueous phase spills. However, when it comes in contact with oily pollutants, foam becomes weaker and its life time is greatly reduced. Such weakening can be dampened by using silica particles -together with saponin surfactant- which were shown to reinforce foam in bulk and 1D sandpack experiments. Here is addressed both foam propagation in a 2D porous media when buoyancy and gravity interfere, and foam behaviour when in contact with floating oil. Therefore, macroscopic foam displacement, and specific liquid and gas phases behaviours were

29 studied in a 2D-tank. A piston-like displacement was observed during foam propagation in the
30 absence of oil, while foam liquid phase was influenced by gravity and did not propagate
31 homogeneously on entire tank height. In the presence of oil, foam was partly destroyed, which
32 increased the local permeability of gas and created new preferential paths for gas flow. This
33 effect was partially avoided via a surfactant concentration increase, but solid colloidal particles
34 turned out to be a more efficient stabilizing agent, by significantly increasing foam strength and
35 its oil-tolerance.
36

37 **1. Introduction**

38 Remediation of Light Non Aqueous Phase Liquid (LNAPL) contaminated soils is crucial for
39 public health and environmental issues. It can be achieved using different techniques, varying
40 with pollution type and contamination depth, soil permeability and soil geophysical properties.
41 Depending on the chosen treatment, remediation strategies can be *ex-situ*: the pollution is
42 treated outside the site, and excavation is necessary. However, due to the cost of excavation, the
43 use of *in-situ* remediation techniques is indicated. Among these techniques, surfactant flushing
44 allows reduction of the surface tension between water and the pollutant, easing pollutant
45 removal and solubilisation of the hydrocarbon molecules in surfactant micelles. Nevertheless,
46 the needed amount of surfactant may be too high, and the sweeping efficiency is sometimes low,
47 especially in heterogeneous porous media. To avoid these drawbacks, the use of aqueous foam is
48 recommended [1].

49 Liquid foam is made of a gaseous phase dispersed in a continuous aqueous phase. The thin
50 films separating gas bubbles are called lamellae and are stabilized by surfactants. These
51 amphiphilic molecules adsorb at the gas-water interface, decrease the interfacial tension,
52 limiting bubble coalescence and film rupture. Such a dispersion of gas in a liquid phase results in
53 a high viscosity fluid where gravity segregation, channelling and fingering are avoided [2] and,
54 consequently gas mobility is severely reduced [3].

55 Because of its high viscosity, foam can be used to block high permeability zones of a
56 heterogeneous porous medium, thus allowing other injected fluids to access low permeability
57 zones that are then more easily swept [4]. Foam can also serve as a tool in remediation strategy
58 to recover floating pollutant with a good sweeping efficiency, by pushing it to a pumping well
59 [5], or to bring oxidative chemicals to the contaminant source, where they will react with the
60 pollutant to form non-toxic compounds [6]. It can also serve to confine a polluted area waiting
61 for the appropriate treatment [7]. For the method that aims to recover a floating pollutant, the
62 objective is to inject foam underneath a LNAPL layer, so as to decrease the water flow towards
63 the pumping well in order to increase the pumping rate of the LNAPL. This may be achieved with
64 a foam of high sweeping efficiency and high viscosity.

65 However, to be of optimum quality and be efficient, foam has to fulfil two requirements. The
66 first requirement is to be of low sensitivity to buoyancy, and such a sensitivity is related to foam
67 structure, its quality and its viscosity. The second requirement is foam formulation, which
68 should be robust enough to resist oil-induced de-foaming effect. Indeed, foam is destabilized by
69 oil both in bulk and in porous medium [8]. This process has been extensively studied, and is
70 mainly governed by the destabilization of the foam-oil interface, called pseudo-emulsion film [9].
71 Therefore, additional foam reinforcement is necessary.

72 In that respect, it was concluded from previous experiments performed in 1D sandpack
73 columns, that the addition of native silica colloidal particles does effectively increase foam
74 resistance against oil-induced coalescence [10]. By irreversibly adsorbing at the gas-water
75 interface, silica particles increase the interfacial elasticity [11] and steric repulsion, thus
76 decreasing the film drainage rate [12]. Such a solid barrier in turn increases the strength of the
77 pseudo-emulsion film, and reinforces foam resistance against oil. To get a maximum foam

78 stability, depending on the system considered, silica particles are sometimes surface-treated to
79 adjust their degree of hydrophobicity to an optimum value [13]. Silica particles also have the
80 benefit of being natural products commonly used in food or medical applications [14].

81 To study buoyancy effects, and because they were negligible in 1D sandpack experiments,
82 the focus is here placed on foam displacement in a 2D-vertical porous medium to mimic the
83 application conditions. The objectives of the experiments are to characterize foam behaviour in a
84 vertical porous medium, and to investigate how the liquid and gas phases of foam typically flow.
85 Our work relies on the work of a few authors who have investigated foam propagation in 2D-
86 tanks for soil remediation [5,15,16]. Although, some authors studied foam reinforced with solid
87 colloidal particles in 2D-tanks, the performance of such Pickering-like foams was evaluated for
88 Enhanced Oil Recovery (EOR) applications [17,18]. And they used quite different operating
89 conditions and surfactants, injecting foam only in small containers where buoyancy was of less
90 relevance [17].

91 Moreover, given the environmental application, foam formulation should in fact, be as
92 friendly as possible. So saponin, a biodegradable surfactant was chosen for foam generation in
93 the present study. It is a plant-based surfactant with interesting foaming properties [19], and
94 has been successfully used for the removal of heavy metals and mixed contaminants via
95 desorption and solubilisation of contaminants [20]. It has also been used in synergy with solid
96 colloidal particles for food-grade foam stabilization

97 So, the main goal of this study is to explore the impact of foam formulation on individual
98 phase displacement in a 2D vertical porous medium, in the absence and in the presence of oil.
99 This was first achieved through the analysis of several macroscopic parameters: sequential
100 imaging, pressure field and water saturation (S_w). In these first experiments, no oil was present
101 since the objective was to determine how buoyancy modifies foam behaviour when surfactant
102 and colloidal particles concentrations vary. Later, foam behaviour was studied in the presence of
103 a top layer at residual oil saturation (S_{or}) to mimic a real operating situation and to study how
104 solid particles affect foam resistance against oil.

105

106 **2. Experimental**

107 *2.1. Chemicals*

108 The surfactant used was saponin (non-ionic, Sigma-Aldrich, France) with a critical micelle
109 concentration (CMC) of 0.062%wt. Native silica particles (LUDOX® TM-50, Sigma-Aldrich,
110 France) have a nominal size of 30 nm, as measured by Orts-Gils *et al.* [21], and were used as
111 received. As native solid particles suspensions were in aggregated state, they were
112 systematically sonicated 10 minutes by means of an ultrasonic bath equipment (Fisherbrand™
113 Elmasonic, Fisher Scientific France). Nitrogen of high purity (purity > 99.999%) was supplied by
114 Air Liquide (France). It was used to control the level of purity of the gas, and to avoid potential
115 oxidation of the chemicals by O₂. The pollutant oil used was MACRON 1821 F-4 (Houghton, US), a
116 refined cutting oil with a density of 0.818 at $T = 20^\circ\text{C}$. When needed, fluorescein sodium salt
117 (Sigma-Aldrich, France) was used as an inert dyeing agent.

118 *2.2. Preparation of foaming solutions and porous medium*

119 All foaming solutions were prepared using tap water which ionic strength was less than 10^{-2}
120 M. The surfactant (saponin) was dissolved in water at the desired concentration, expressed as a
121 multiple of critical micelle concentration ($\times\text{CMC}$), and stirred at 400 rpm for at least twenty
122 minutes.

123 To prepare aqueous solutions containing solid particles, silica particles were first
124 mechanically dispersed in a given amount of water, and vigorously sonicated for 10 minutes in

125 an ultrasonic bath. In parallel, the surfactant was dissolved in the same amount of water before
 126 blending the two solutions in convenient volume proportions.

127 A 40 cm long, 3 cm wide, and 30 cm high tank, built with 3 cm thick transparent PMMA sides
 128 was used as a container. It was then packed with clean sand purchased from Cantillana
 129 (Cantillana, France), with a D_{50} grain size of 279 μm .

130

131 *2.3. Experimental set-up*

132 The experimental setup is presented in Figure 1. To generate foam, aqueous foaming solution
 133 and nitrogen were simultaneously co-injected into the 2-D porous medium.

134 To inject aqueous foaming solutions, two piston pumps PHD ULTRA™ (Harvard Apparatus,
 135 US) were used with two syringes. To inject nitrogen, two mass flow meters (EL-FLOW®,
 136 Bronkhorst® France) were used in nominal conditions. Both gas and the foaming solution were
 137 injected at controlled flow rates.

138 Ten digital pressure sensors (Idroscan from AEP transducers, Italy) regularly distributed
 139 across the porous medium were used to measure the absolute pressure. The upper two taps
 140 situated at the tank sides were connected via a differential pressure transducer (Rosemount
 141 2051 Coplanar™, Emerson, France) and a camera (Panasonic Lumix DMC-TZ70) was used to
 142 take pictures of the tank during foam propagation. Finally, the effluents were weighed over time
 143 and a mass balance calculated.

144

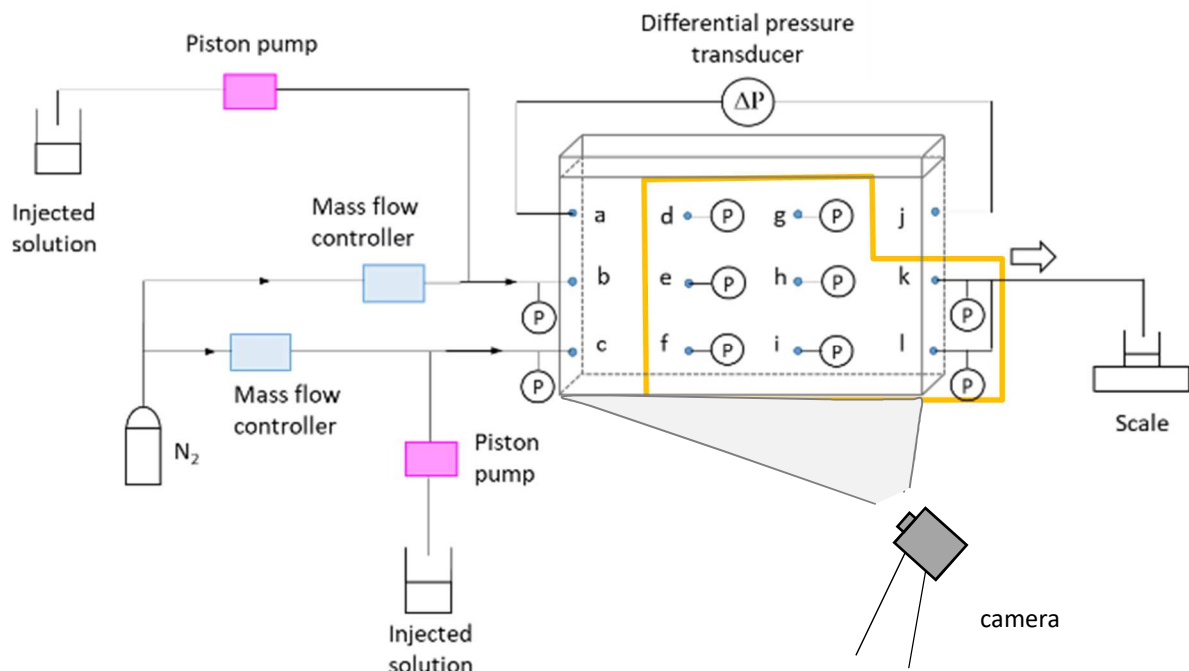


Fig. 1: Schematic representation of the experimental setup for foam injection in 2D porous medium. The pressure taps used to represent pressure maps are contoured in yellow

145 *2.4. Experimental procedure*

146 Experimental tests were designed to investigate different situations that are summarized in
 147 Table 1.

148 *Table 1: Summary of experiments*

Tests	Purpose	Experimental	Main experimental
-------	---------	--------------	-------------------

		conditions	conditions
Set 1: Foam displacement in a vertical 2D porous medium	Understand foam displacement in a vertical 2D porous medium through its liquid and gaseous phases	Observe a $10\times\text{CMC}$ foam front displacement and analyse velocities and pressures Add fluoresceine Inject N_2 in a $10\times\text{CMC}$ saturated medium	Experiments without oil
Set 2: Influence of surfactant concentration (C_s)	Choose the best experimental conditions	Decrease C_s to $3.2\times\text{CMC}$	
Set 3: Influence of solid colloidal particles addition	Test foam reinforcement via particles addition	Add $0.5\% \text{wt SiO}_2$ to a $10\times\text{CMC}$ foam	
Set 4: Foam displacement in the presence of oil	Understand foam displacement in the presence of oil	Observe a $10\times\text{CMC}$ foam front displacement and analyse velocities and pressures	Experiments with oil
Set 5: Influence of C_s in the presence of oil	Choose the best experimental conditions	Decrease C_s to $3.2\times\text{CMC}$	
Set 6: Influence of solid colloidal particles addition	Test foam reinforcement via particles addition in the presence of oil	Add $0.5\% \text{wt SiO}_2$ to a $10\times\text{CMC}$ foam	

149

150 To understand how foam behaves in a 2D porous medium, and how such behaviour is
151 modified in the presence of an oil layer, two sets of experiments were performed.

152 A first group of experiments was performed in the absence of oil. The effect of surfactant
153 concentration, injection strategy (gas/liquid co-injection versus Surfactant Alternating Gas
154 (SAG)), and solid particles addition were investigated. The last experiment was performed with
155 a dye added to the foaming solution during the co-injection process.

156 The second group of experiments was performed in the presence of oil in the upper part of
157 the 2D porous medium. The influence of surfactant concentration and solid particles on foam
158 flow was investigated.

159 Those experiments are here interpreted and discussed through the pressure measurements
160 and direct visualization of the foam front in the 2D porous media.

161

162 *2.4.1 Experiments in the absence of oil*

163 The container was filled with sand by gradually introducing sand and water, so that a water
164 saturated porous medium is obtained, with a known porosity and a known pore volume (PV). A
165 layer of clay of approximately 15 mm was then added at the top to ensure no-flux boundary
166 conditions. The top of the tank was then closed with a PMMA plug to mechanically tighten it.

167 To satisfy surfactant adsorption prior to any foam propagation, 3.3 pore volumes of
168 surfactant solution at a concentration $C_s = 10 \times \text{CMC}$ were injected into the water saturated
169 porous medium. This procedure is similar to that early used in 1D column experiments [10].

170 Gas and foaming solution were then co-injected at a total flow rate $Q_{tot} = 24.8 \text{ mL}\cdot\text{min}^{-1}$, with a
171 specified quality of 87.5% (volume fraction of gas). These conditions were previously
172 determined from column experiments to be the ones giving the strongest saponin foam [10].

173 Gas and foaming solution were separately injected through the two taps located at the bottom
174 of the tank (b and c), while opening the two opposite taps to atmospheric pressure. Once
175 injection began, pictures were taken every minute to record the foam front displacement.
176 Moreover, when performing experiments, the mass measurement of the outcoming liquid phase,
177 and pressure values at all taps locations led to the determination of the average water saturation
178 (S_w) of the porous medium:

$$S_w = \frac{V_w}{PV} \quad (1)$$

179 where V_w is the volume of remaining water, and PV is the total pore volume,

180

181 and a local resistance factor, called RF_p , defined as:

$$RF_p = \left[\frac{P_f}{P_w} \right]_{Q_{tot}} \quad (2)$$

182 where P_f and P_w are respectively the absolute pressure measured for foam and water at the
183 same flow rate and the same location.

184 For each pressure measurement tap, RF_p represents the increase in pressure due to the flow
185 of foam in the porous medium, and the higher the RF_p , the stronger the foam is. Values were
186 calculated after flow reached steady state for each tap, and a mean RF_p was calculated based on
187 RF_p values throughout the tank.

188 Because the mean RF_p does not take into account the local pressure charge, absolute pressure
189 values were used to draw 2D pressure maps throughout the tank. The pressure taps used to
190 create those maps are contoured in yellow in Fig. 1.

191

192 *Influence of surfactant concentration*

193 In order to study the influence of the surfactant concentration (C_s), two C_s values were
194 chosen as for previous column experiments [10]. One of the experiments was performed with C_s
195 = $3.2 \times \text{CMC}$, a formulation that has proven to give foam of intermediate strength, and another one
196 was conducted at $C_s = 10 \times \text{CMC}$, which showed a higher foam strength with a higher RF_p .

197 *Surfactant and colloidal particles.*

198 An experiment was carried out, using a $10 \times \text{CMC}$ saponin foaming solution containing 0.5%wt
199 SiO_2 , to see if colloidal particles strengthened foam similarly to what was observed in 1D column
200 experiments [10].

201 *Surfactant Alternating Gas experiment*

202 A surfactant alternating gas (SAG) experiment was carried out to observe the gas phase
203 displacement when injected alone. The aim was to observe whether the liquid phase
204 displacement influenced by any means the gas phase displacement.

205 To perform the SAG experiment, the porous medium was first saturated with a $10 \times \text{CMC}$
206 surfactant solution. Gas alone was then injected at the same total flow rate of $Q_{tot} = 24.8 \text{ mL}\cdot\text{min}^{-1}$
207 than for other experiments, and pictures taken every minute to record the gas displacement.

208 *Experiments with dyed water*

209 During foam displacement in porous medium, foam can be subject to buoyancy segregation,
210 with part of the gas phase being trapped in pores, while the rest stays mobile. This impacts the

211 liquid phase displacement during co-injection once the porous medium is filled with foam. In
212 order to dissociate the liquid phase flow from the foam flow, fluorescein was added at 0.05%wt,
213 as a dye to the surfactant solution prior to co-injection. The path taken by the liquid phase could
214 hence be clearly dissociated from the foam flow. Pictures were taken every minute to record the
215 liquid phase displacement.
216

217 2.4.2 Experiments in the presence of oil

218 Experiments of foam propagation in the presence of oil were carried out with a top layer at
219 S_{or} (residual oil saturation), to mimic the sublayer of an oil spread that exists at the interface
220 with an aquifer. By injecting foam via the two lower injection taps (b and c), a strong foam could
221 be generated before it comes in contact with oil.

222 These tests were done with 2/3 of the tank filled by gradually adding sand and water. In the
223 upper third only, oil was used instead of water. Water was then injected at the top entry, keeping
224 open the opposite exit. When no oil was produced anymore, indicating that S_{or} was reached in
225 that layer, water injection was stopped. After that, 3.3 PV of surfactant solution were injected to
226 saturate the medium before starting co-injection.

227 Based on visual observation, the instantaneous positions of the foam front were picked-up.

228 Water saturation and mean RF_p were calculated for each experiment, and measured absolute
229 pressures were used to draw 2D pressure maps.
230

231 3. Results and discussion

232 3.1. Foam propagation in the absence of oil

233 3.1.1 Influence of surfactant concentration

234 Pictures taken at a total injected pore volume of 0.28 are displayed in Figure 2, and a plot
235 that represents the time evolution of the foam front propagation is shown in Figure 3.

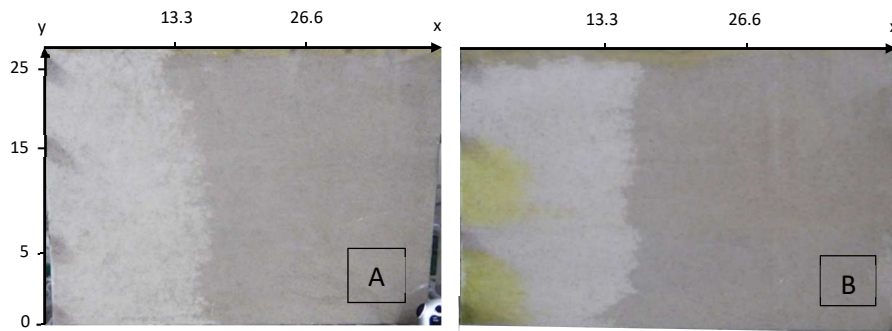


Fig. 2: Foam injection of 3.2×CMC (A), and 10×CMC (B) saponin foam after 0.28 PV injected

236
237 Pictures taken during foam displacement with $C_s = 3.2 \times \text{CMC}$ and $10 \times \text{CMC}$ (Fig. 2), show a
238 piston-like front during foam displacement with negligible buoyancy impact. This observation is
239 confirmed in Figure 3 where it can be seen, after the inlet effects, the propagation of a regular
240 and vertical front displacement.

241 The fact that the front is almost vertical proves that foam is generated wherever gas is
242 present, and that lamellae distribution is even on the full height. In fact, if foam was not formed,
243 only gas propagation would be observed, with quick path through the top of the porous medium.
244 Similarly, a weak foam formation would generate a gradually decreasing density of lamellae on
245 the full height of the container, that may lead to an oblique propagation front.

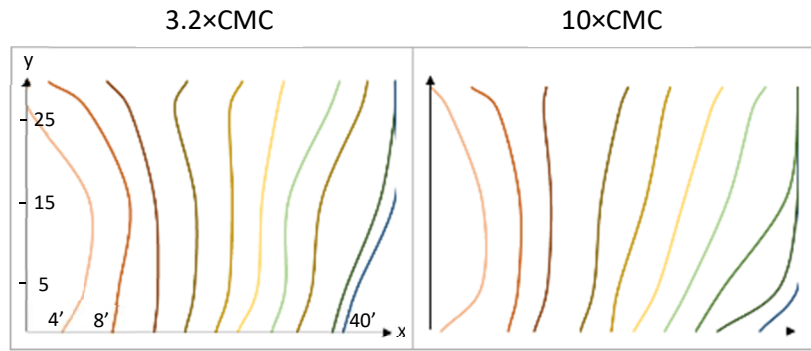


Fig. 3: Front propagation every four minutes at $C_s = 3.2 \times \text{CMC}$ and $C_s = 10 \times \text{CMC}$

246 Mean RF_p values, representative of foam strength, are displayed in Table 2. On this table are
 247 also reported the ultimate water saturation as deduced from mass balance. At equilibrium state
 248 the mean RF_p , is equal to 7.9 for $3.2 \times \text{CMC}$, significantly below that corresponding to $10 \times \text{CMC}$
 249 (9.7), meaning that foam strength does increase with C_s . In the meantime, S_w remains stable at
 250 0.36.

251

252 Table 2: Mean RF_p and S_w for three different foam formulations in the absence of oil, with and without silica particles

Formulation without oil	$3.2 \times \text{CMC}$	$10 \times \text{CMC}$	$10 \times \text{CMC} + 0.5\% \text{wt SiO}_2$
Mean RF_p	7.9	9.7	9.9
S_w	0.36	0.35	0.30

253

254 Those observations indicate that the foam is so strong that it propagates with a piston-like
 255 movement, and that the surfactant concentration has a minor impact on both S_w and the shape of
 256 the displacement front, while foam strength is noticeably improved.

257 3.1.2 Influence of presence of colloidal particles in the foaming solution

258 Figure 4 represents the picture taken at a total injected pore volume of 0.28 (Figure 4A) and
 259 a time evolution of the foam front (Figure 4B).

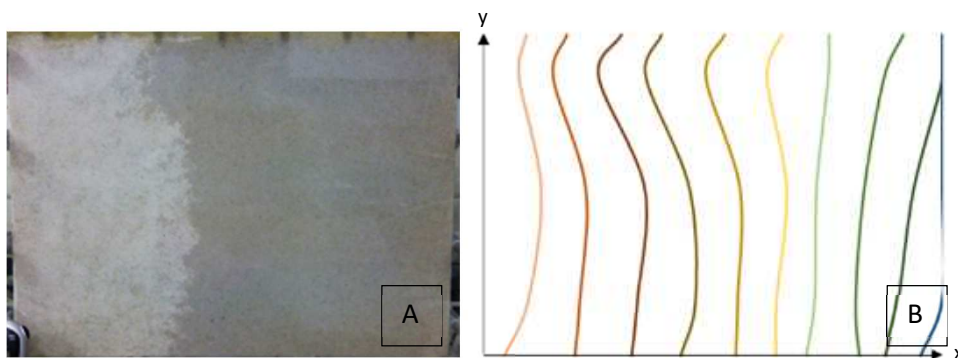


Fig. 4: Foam front after 0.28 PV injected (A) and front position every 4 minutes (B) at $C_s = 10 \times \text{CMC} + 0.5\% \text{wt SiO}_2$ saponin foam

260 The front shape and propagation observed in Figure 4A and B are very similar to the ones
 261 observed when foam is generated with surfactant alone. This result confirms that foam is
 262 generated wherever gas is present in the porous medium and that the presence of solid particles
 263 does not undermine foam generation and propagation.

264 Considering RF_p , its mean value is equal to 9.9, very close to 9.7 obtained in the absence of
265 particles. On the contrary, the ultimate water saturation S_w decreases from 0.35 to 0.30 (Table 2)
266 when solid colloidal particles are added to the saponin-based formulation, indicating a better
267 sweeping efficiency of the initially water saturated porous medium. In the meantime, a steady
268 piston-like foam front is observed, poorly affected by buoyancy. This decrease of S_w is
269 presumably due to the formation of more rigid lamellae, as solid colloid adsorption at the liquid-
270 gas interface generates lamellae that are more resistant to drainage. Thus, a slightly higher RF_p is
271 observed.
272

273 3.1.3 Comparison between liquid/gas co-injection and SAG

274 Figure 5 presents a picture of the foam front displacement taken at total pore volume
275 injected of 0.27PV when gas is injected in a porous medium that was beforehand saturated by
276 the foaming solution at $C_s = 10 \times \text{CMC}$.
277



Fig. 5: N_2 injection in a $C_s = 10 \times \text{CMC}$ surfactant saturated porous medium after 0.27 PV injected

278 A comparison with the previous figures shows that the front propagation is almost vertical
279 and is very similar to that previously obtained during co-injection. This proves that foam is
280 generated wherever gas and foaming solution are present in the porous medium and does not
281 depend on the injection process.
282

283 3.1.4 Injection of dyed foaming solution

284 To characterize the specific path taken by water and gas, an experiment was performed with
285 dyed water. Similarly to the other experiments, the porous medium was first saturated with
286 aqueous solution to satisfy surfactant adsorption. A foaming solution was then dyed by adding
287 fluorescein and co-injection was performed under the same conditions as before. The path of the
288 newly injected solution could then be followed as it appears in yellow in Figure 2B and Figure 6
289 after injection of respectively 0.28 and 2.4 PV.

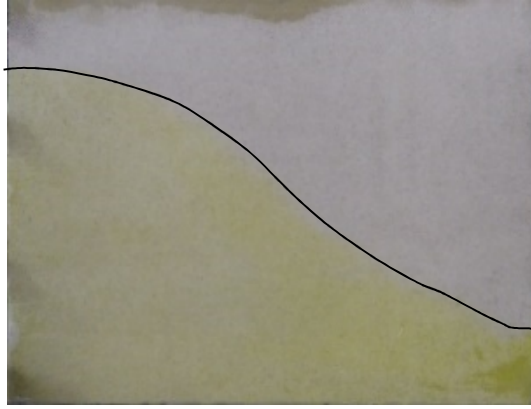


Fig. 6: Injection of a 10×CMC foam with a coloured liquid phase after 2.4 PV injected

290 In Figure 6, two zones with different colours are observed. Gas and aqueous dyed solution
 291 are co-injected at a given value of foam quality and, after 2.4 PV of total fluid injected, the entire
 292 tank is saturated with foam. However, a colour difference can be observed from top to bottom,
 293 which establishes the presence of a vertical foam quality stratification. The aqueous foaming
 294 solution in yellow is moving down slowly while gas is moving up without preventing foam
 295 formation and propagation in the porous medium.

296 This behaviour can be explained in the following way. Literature results shows [22] that as
 297 gas fraction increases, the apparent viscosity and capillary pressure P_c increase until they reach
 298 a maximum value at f_g^* . At that critical gas fraction, the apparent viscosity is maximum and P_c
 299 reaches its ultimate value P_c^* . Below f_g^* , foam is in the low quality regime: gas is discontinuous
 300 and trapped in a lamellae network. The pressure drop is independent of the gas velocity and
 301 depends on the liquid velocity. In contrast, for $f_g > f_g^*$ foam is in the high quality regime, where
 302 the pressure drop is dependent of the gas velocity and independent of the liquid velocity. For gas
 303 fraction well above f_g^* , the occurrence of bubbles coalescence increases drastically, leading to an
 304 increase in gas mobility and a decrease in the apparent viscosity. Consequently, in the vicinity of
 305 f_g^* , a given apparent viscosity may correspond to two f_g values: one of them $> f_g^*$ and the other $<$
 306 f_g^* .

307 In those experiments, nitrogen and the foaming solution were co-injected at $f_g = 87.5\%$,
 308 which was previously determined as being close to f_g^* [10]. However, in 2D experiments, due to
 309 the impact of buoyancy, the local gas fraction should span from lower quality in the bottom of
 310 the container to higher quality at the top. Moreover, the change of pressure with height is low
 311 (Figure 7), and results are consistent; foam quality is higher at the top, and the pressure drop is
 312 almost independent of the liquid phase velocity.

313 In other words, based on the water mobility map (Figure 6), a small spatial variation of S_w
 314 can largely impact the relative permeability to water k_{rw} [23] leading to an easier water flow in
 315 the lower part. In the meantime, the S_w gradient has little impact on the relative permeability to
 316 gas k_{rg} , thus explaining why the front displacement is almost vertical, and why the f_g gradient has
 317 a limited impact on the velocity height dependency. This specific study indeed corroborates the
 318 spatial variation observed of both velocity front displacement and resistance factor.

319

320 3.1.5 Pressure drop analysis

321 The behavior of foam generation and propagation in 2D porous media can be analyzed
 322 considering the absolute pressure measurements P_f and P_w at each pressure tap during co-
 323 injection. However, and for convenience, the study was restricted to pressure taps located at d, e
 324 and f measurement points (See Fig. 1), to follow foam displacement at three different heights (5,
 325 15 and 25 cm). Thereby, the resistance factor RF_p is plotted versus the injected pore volume

326 (corresponding to time) in Figure 7, for such a bottom, middle and top positions. Foaming
 327 conditions are the same as in Figure 2.
 328

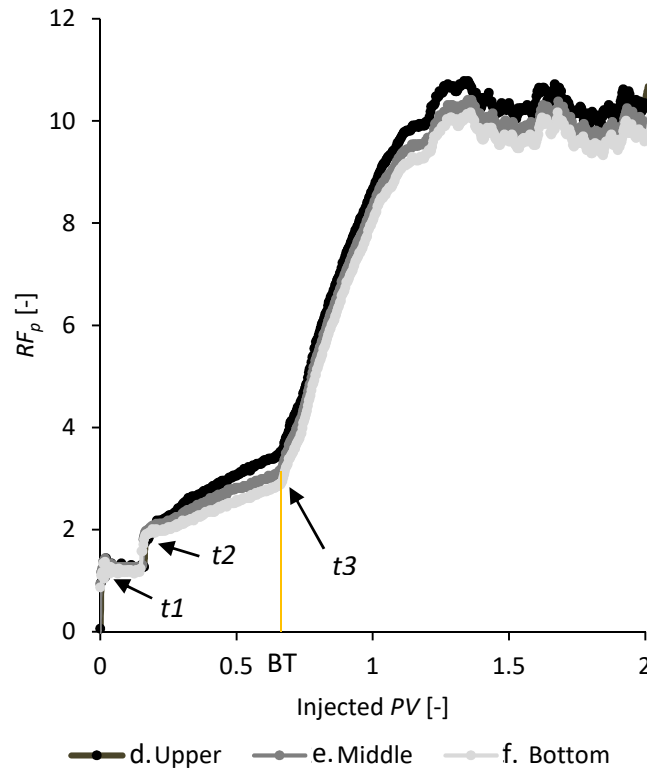


Fig. 7: Pressure variations at the 13.3 cm right of the tank for a foam formulation of 10×CMC with varying heights of 5 cm (Bottom), 15 cm (Middle) and 25 cm (Upper). Breakthrough (BT) location is indicated by a vertical line

329 Once co-injection begins at $t = t_1$, a sudden increase is observed as aqueous solution flows at
 330 that location. Between t_1 and t_2 , the plateau value equals unity as only water is flowing. At $t = t_2$,
 331 the pressure suddenly increases once foam reaches the pressure taps. Then, between t_2 and t_3
 332 foam steadily propagates within the porous medium and pressure linearly increases as a
 333 function of the injected volume, in a similar way to what was observed in 1D column
 334 experiments [10]. At $t = t_3$, foam breakthrough (BT) is observed while pressure keeps increasing.

335 This behaviour is in apparent contrast with what is usually observed in column experiments
 336 where pressure quickly stabilized after the breakthrough. In a previously published work,
 337 Portois *et al.* [23] have noted that when a pre-generated foam is injected in a porous medium
 338 initially containing a surfactant-free water, 8 PV beyond the BT were necessary to reach a steady
 339 state. They attributed this delay to surfactant adsorption. However, such an explanation cannot
 340 hold here because the porous medium was saturated with surfactant prior to nitrogen/foaming
 341 solution co-injection.

342 A possible explanation is that when foam locally breaks through, pressure at the
 343 corresponding exit point suddenly increases from water pressure to foam pressure. As a
 344 consequence, and to maintain the flow regime in the container, the pressure at taps d, e and f
 345 increases, keeping constant the pressure drop. This process continues until both exiting sides of
 346 the container are filled with foam, which is when the injected volume is around 1.2 PV.

347 In the last step, the pressure level is nearly stabilized, showing a new plateau that reflects the
 348 equilibrium between the lamella creation rate and its destruction, probably due to strong
 349 capillary pressure, high drainage and coalescence.

350 Experimental data (Figure 7) also show that the local pressure slowly increases from the
 351 bottom to the top of the tank. This indicates a slight foam weakening with height, as suggested

352 by the small change in the velocity front (Figure 4B), although one must keep in mind that when
353 gas fraction fluctuates around f_g^* , the local viscosity is only moderately changed.

354 3.2. Foam propagation in the presence of oil

355 In the previous section, foam formation and propagation were investigated in a 2D porous
356 media for different formulations, by focusing on the resistance factor and propagation front.
357 However, and for application purposes, the aim of the present study was to investigate how
358 foam behaves when it comes in contact with oil. To this end, the previous experiments have been
359 repeated with an upper layer of the porous medium now containing oil at residual saturation
360 (S_{or}). It is worth noting that, similarly to the previous experiments, the upper exit point was
361 closed. First, the influence of saponin concentration on the foam front displacement and
362 resistance factor were investigated, before considering the effect of the addition of SiO_2 solid
363 colloids.

364 In the first experiment, a $3.2 \times \text{CMC}$ based foam was injected in a porous medium saturated
365 with surfactant, with a top layer at S_{or} . Foam quality and total flow rate were the same as used
366 for experiments in the absence of oil. Such experiment was then repeated for concentrations of
367 $10 \times \text{CMC}$ of saponin and $10 \times \text{CMC}$ saponin + $0.5\% \text{wt SiO}_2$. Pictures taken after co-injection of 0.27

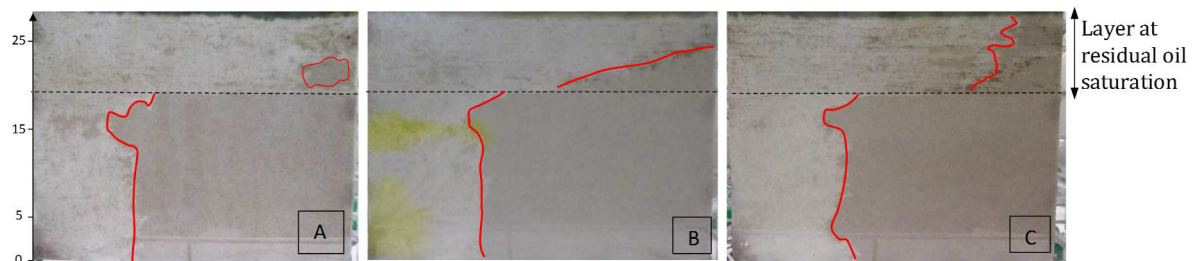


Fig. 8: Saponin foam in the presence of oil after 0.27 PV injected. Injection of $3.2 \times \text{CMC}$ (A), $10 \times \text{CMC}$ (B) and $10 \times \text{CMC} + 0.5\% \text{wt SiO}_2$ (C)

368 PV are displayed on Figure 8 for each formulation, and call for some preliminary remarks:

369 - Below the oily layer, the foam displacement front is almost vertical whatever the
370 formulation, with small fluctuations in the transverse direction.

371 - For $3.2 \times \text{CMC}$ of saponin (Figure 8A), a fast foam destruction is observed when it comes in
372 contact with oil. Then, a 3D connected gaseous phase forms and gas breakthrough happens
373 shortly after, with an apparent fingering effect, and a mean velocity much higher than in the rest
374 of the container.

375 - For $10 \times \text{CMC}$ of saponin (Figure 8B), the displacement front in the oily zone is more stable
376 than for low saponin concentration, even if oil-induced destruction through bubble coalescence
377 can still be observed. As a consequence, a partial phase segregation occurs, arising in a local
378 oblique displacement front with a mean velocity in the top layer more than twice the mean
379 velocity in the bottom layer.

380 - For $10 \times \text{CMC}$ of saponin + $0.5\% \text{wt SiO}_2$ (Figure 8C), the oily layer is more efficiently swept
381 and the displacement front is straightened. This brings out that SiO_2 particles effectively act as a
382 damping agent against oil-induced bubble coalescence. As recalled, in the absence of oil, SiO_2
383 addition moderately contributes to foam strengthening and mainly contributes to foam
384 stabilisation in the presence of oil. These foams, usually termed as Pickering-like foams are then
385 less brittle and have a higher resistance to oil-induced destruction.

386 It should be noted that for all these experiments, no noticeable oil was produced during co-
387 injection, and that S_{or} was nearly constant over time.

388 Besides these visual observations, water saturation S_w , as well as the local resistance factor
 389 RF_p were continuously determined during co-injection. In the present situation, some of the
 390 pressure sensors were located in the oil-free layer, and others in the oily layer. To illustrate the
 391 general features observed, Figure 9 shows the RF_p variations as a function of the total injected
 392 volume for a foaming solution that contains $10\times\text{CMC}$ saponin. The RF_p data correspond to the oil-
 393 free zone through the pressure measurements at locations e, f and in the oily layer through the
 394 pressure measurement at location d (see Figure 1). Regardless of the absolute values of RF_p , the
 395 RF_p vs PV curves in the oil-free part of the container are quite similar to those already obtained
 396 in the absence of oil.

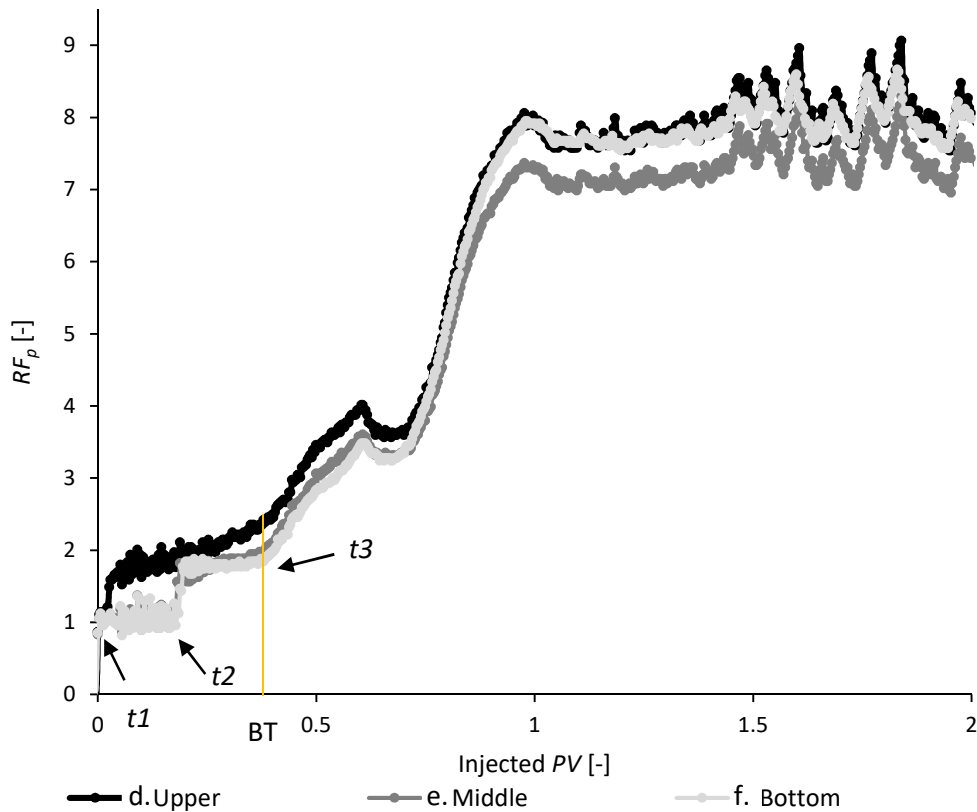


Fig. 9: RF_p variations at 13.3 cm right for a foam formulation of $10\times\text{CMC}$ in the presence of oil. Breakthrough (BT) is represented by the yellow line

397
 398 However, in the oily domain, the curve significantly changes especially before gas
 399 breakthrough. As the co-injection process begins, the pressure increases after a very short
 400 plateau regime while such a plateau holds in the oil-free zone until $t = t_2$. In fact, in the oily part
 401 of the container, when foam comes in contact with oil, some coalescence events occur and foam
 402 partially loses its structure and becomes weaker. Consequently, the lamellae density decreases
 403 and continuous gaseous channels are formed where gas quickly propagates. After gas
 404 breakthrough (BT), all pressure signals change in a similar way. But because the upper exit tap j
 405 is turned off, it is difficult to quantitatively compare visual observations with the RF_p versus PV
 406 curves.

407 However, to get an overall idea on how these formulations behave in the presence of oil, the
 408 average of ultimate RF_p values from the entire container can be compared. These data are given
 409 on Table 3, where both water saturation and the initial S_{or} in the top layer are also given. Firstly,
 410 whatever the formulation, the average RF_p values are lower in the presence of oil (Table 3): a
 411 consequence of the loss of foam structure due to the defoaming contribution of oil. Such a loss is

412 more remarkable in the case of 3.2×CMC saponin, and is significantly less pronounced for other
 413 formulations. Secondly, a velocity ratio “ V_r ” can be calculated by time averaging the front
 414 velocity in the top layer “ V_{tot} ” divided by that corresponding to oil-free zone before gas
 415 breakthrough “ V_{bottom} ”:

$$V_r = \frac{V_{tot}}{V_{bottom}} \quad (3)$$

416
 417 These data are also given in Table 3. The velocity ratio is well above unity whatever the
 418 formulation due to the oil defoaming nature, and this is more pronounced for 3.2×CMC for which
 419 foam is largely weakened in presence of oil. For higher saponin content, V_r ratio noticeably
 420 decreases, and such a decrease is even more pronounced when SiO_2 particles are added to the
 421 foaming solution. Besides, by considering S_w , the remaining water saturations are indeed higher
 422 than those previously obtained in the absence of oil.

423
 424 *Table 3: Mean RF_p , S_w , S_{or} and V_r for three different foam formulations with and without silica particles, in the presence of oil*

Formulation with oil	3.2×CMC	10×CMC	10×CMC + 0.5%wt SiO_2
$Mean\ RF_p$	2.2	8.0	7.8
S_w	0.43	0.41	0.42
S_{or}	0.023	0.022	0.020
V_r	4.03	2.74	2.59

425
 426 Otherwise it is more telling by considering pressure maps drawn by using pressures
 427 measured at steady state. To that end, such pressure maps are displayed in Figure 10 for the
 428 three formulations and for the two kinds of experiments.

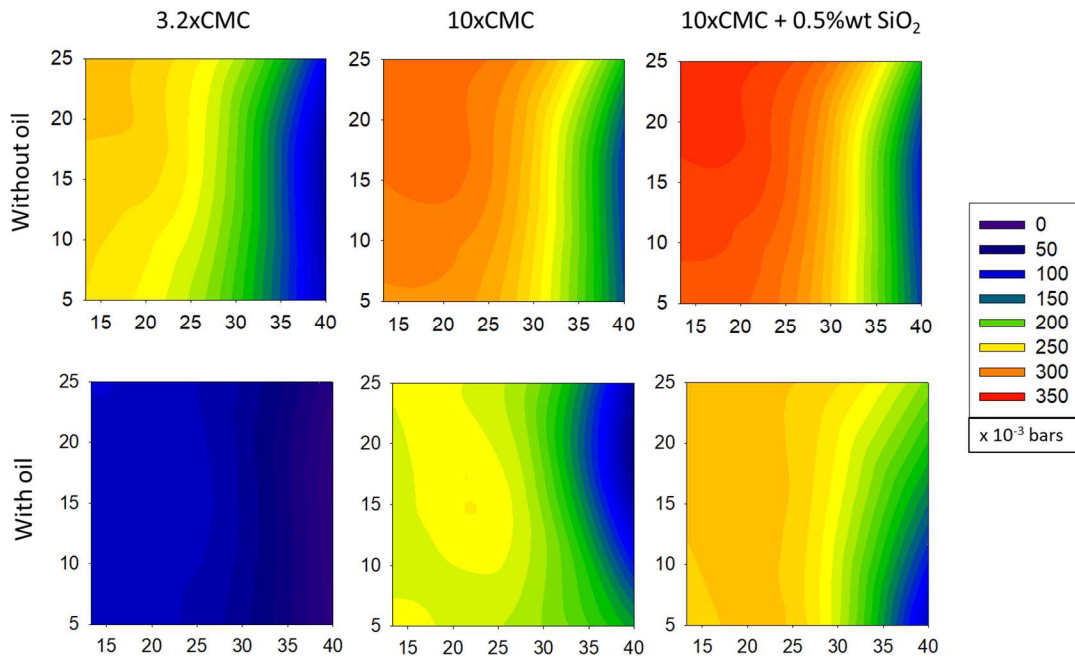


Fig. 10: Pressure maps at equilibrium for different foam formulations obtained with oil and without oil

429 It may be seen therefore that the increase in saponin and SiO_2 concentrations makes foam
 430 stronger, and that in the presence of oil, foam becomes weaker. However, the use of solid
 431 colloids such as silica particles appears to be a way to stem foam destruction by oil, as pressures
 432 are higher than in the case of silica-free formulations, and present as vertical fronts.

433 It appears that the presence of foam in the system not only allows a full sweeping of the
 434 porous medium, but also has a blocking effect on the full height of the tank, even in the presence
 435 of residual oil.

436 Thus, the suggested mechanism for foam propagation is the following: as gas and foaming
 437 solution starts invading the lower part of the porous medium, foam is created and starts
 438 propagating. Then, as foam reaches the upper layer containing oil, it is partly destroyed and
 439 locally generates a higher relative permeability to gas. It thus facilitates flow with a preferential
 440 path, visualized by a high front velocity. The increase in velocity in the top of the tank leads to an
 441 increased pressure. As gas and surfactant solution are injected into the porous medium, foam
 442 strengthens in the top layer and given the right formulation, a vertical front can be observed.

443 Meanwhile in the bottom layer, foam propagates with a lower velocity. It is slightly affected
 444 by the presence of oil in the top layer, because some gas is deviated to the top layer, implying
 445 that foam quality may drop below 87.5% in the bottom layer. As foam keeps propagating,
 446 pressure gradually reaches equilibrium, and after a few PV , stabilization is reached. Foam
 447 entirely fills the porous medium with homogeneous pressures on the full height, showing the
 448 foam ability to entirely block the porous medium, even in areas initially at S_{or} .

449 4. Conclusion

450

451 First, it is worth remembering that the goal of the present study was to investigate how the
 452 presence of oil impacts foam formation during a liquid-gas co-injection process. Literature and
 453 previous experiments have shown that organic phases, such as LNAPL, usually act as defoaming
 454 agents that thwart the use of foam in remediation treatments. So, the focus was here put on
 455 obtaining a strong foam that undergoes minimum buoyancy effects and is significantly resistant
 456 to oil. To meet these requirements, the synergy between a biological surfactant (saponin) and
 457 silica colloidal particles was explored to obtain a strong and stable foam. In the investigations,

458 gas-liquid co-injection experiments were carried out in a large size 2D porous medium in the
459 absence and in the presence of oil.

460 When no oil is present, even under circumstances of high foam quality and optimum total
461 flow rate, foam displacement is not trivial. Albeit foam visually sweeps the porous medium in a
462 piston-like way, buoyancy segregation still acts, and a gas/liquid saturation gradient takes place
463 across the flow direction. The corresponding local resistance factor, instantaneous velocity and
464 water saturation values are consistent with each other. This observed behaviour was coherent
465 with the variation of foam quality across the container and with the impact of such a variation on
466 foam viscosity, taking into account that the injected gas fraction was close to its critical value f_g^* .
467 As the surfactant concentration increases, foam strengthens due to a higher lamellae stability
468 that prevents bubbles to coalesce. If SiO₂ colloidal particles are incorporated in the formulation,
469 the resistance factor is slightly enhanced and S_w is substantially decreased. This may be
470 summarized by saying that SiO₂ addition probably arises in thicker lamellae without
471 significantly affecting the foam structure, and bubbles are in a shield consisting of solid SiO₂
472 colloidal particles.

473 By repeating the experiment in the presence of a layer initially at residual oil saturation,
474 formed foams are destroyed when they come in contact with oil, thus increasing the local gas
475 mobility while it seems unaffected in the rest of the container. However, foam resistance to oil-
476 induced destruction is less damaging when the surfactant concentration increases, and is
477 damped when SiO₂ particles are added to the formulation.

478 Finally, it should be reminded that the co-injection process is restricted to medium
479 permeability porous media, and that foam pre-generation is indicated in case of highly
480 permeable porous media [24, 25]. Moreover, after bubble generation, solid colloids can adsorb
481 at the gas-liquid interface due to their slow diffusion besides the significant energy intake
482 needed for particles adsorption. So, the process efficiency is multifactorial and depends, among
483 other things, on the characteristics of the porous medium, the oil composition, the nature of the
484 foaming solution and the gas and aqueous solution injection rates. Those characteristics should
485 hence be studied and taken into account before using the technique on the field.
486

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490

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