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Saponin foam for soil remediation: On the use of polymer or solid particles to enhance resistance to pollutant destruction

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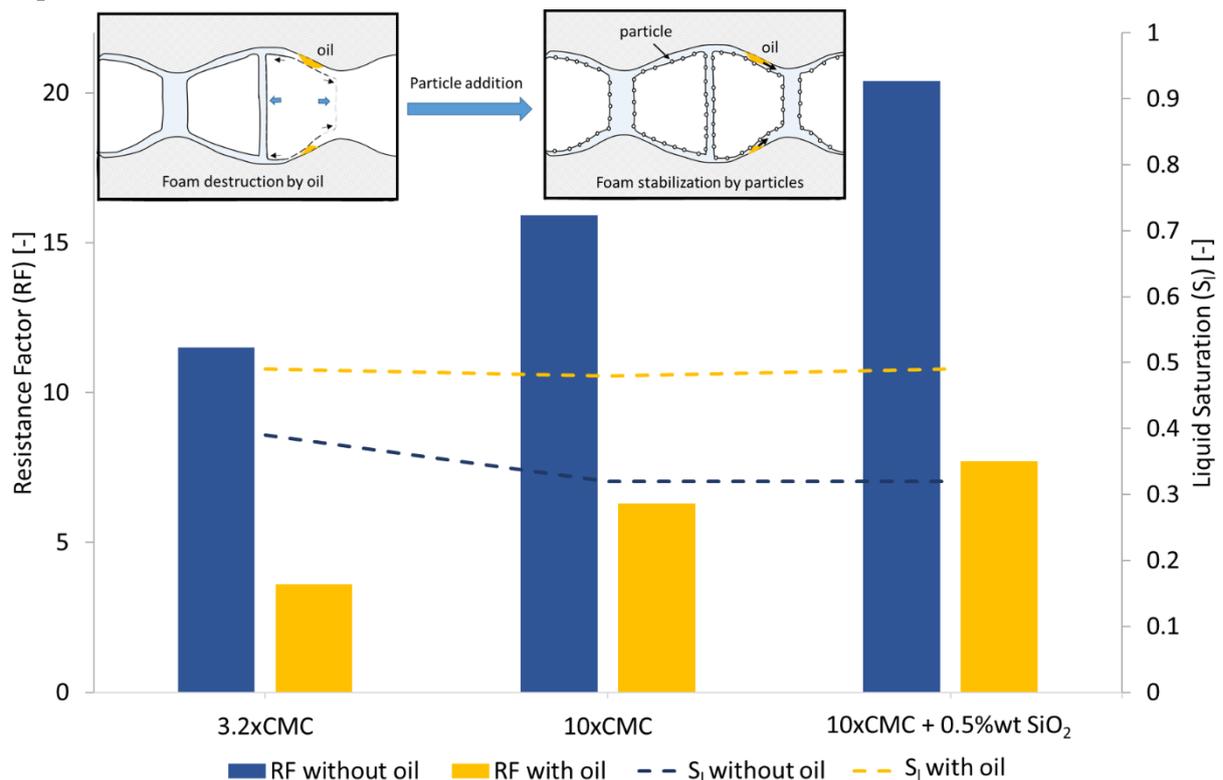
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Keywords: Foam; Porous media; Xanthan; Colloidal particle; Light Non-Aqueous Phase Liquid; Soil remediation

Highlights

- Addition of xanthan increases overall resistance factor but decreases foam strength
- Solid colloidal particles increase the foam's resistance to oil-induced destruction
- There is an optimal colloidal particle concentration for foam reinforcement

Graphical Abstract



Abstract

Foams can be used to remediate aquifer pollution due to industrial leaks. However, when in contact with oily pollutants, foams may collapse and thus have a very limited life-time. A suitable formulation of biodegradable foam that resists oil contact is therefore needed. Hence, the ability of xanthan polymer and silica colloidal particles to stabilise foam against oil was investigated.

1 Their performance in terms of stabilisation was evaluated via foam generation experiments in
2 columns of porous medium, conducted with and without oil. The results show that the addition
3 of xanthan polymer led to an increase in the viscosity of the solution, which thwarted the
4 formation of foam. It did not improve the resistance of foam to oil, but increased altogether the
5 resistance **factor up to more than twice the original value**. Concerning silica particles, it was
6 demonstrated that they both noticeably increased resistance factor and moderately stabilized
7 foam against oil **by 20 %** at optimum concentration. As such, this study presents a new way to
8 reinforce foam against oil for soil remediation issues.

10 **1. Introduction**

11 When a Light Non-Aqueous Phase Liquid (LNAPL) (an organic contaminant such as
12 hydrocarbon) is spilled, it can percolate due to gravity into the ground and reach an aquifer. It is
13 then dispersed, contaminating the aquifer, a potential source of drinkable water, and harming
14 aquatic living organisms. The possible consequences in terms of public health and
15 environmental issues are numerous and dire, and the removal of LNAPL is crucial.

16 Several remediation strategies can be used to reduce the existing pollution. There are two
17 main categories of these: *ex-situ* remediation techniques, which consist in excavating the
18 pollution in order to treat it, and *in-situ* techniques, which do not require soil displacement. The
19 latter approaches can thus be applied to a broader range of sites, but may present more
20 technical difficulties. Of the available solutions for *in-situ* remediation, gas sparging and flushing
21 are most commonly used. They consist of injecting gas or a surfactant solution, respectively, into
22 the porous media to mobilise the pollutant and pump it afterwards. However, due to the low
23 viscosity of the fluids, viscous fingering is observed, and fluids preferentially flow in high-
24 permeability layers.

25 Due to its interesting mobility control properties, foam has been considered for use in aquifer
26 remediation (Hirasaki *et al.*, 1997; Porto *et al.*, 2018). Liquid foam is basically a dispersion of
27 gas in liquid, and is stabilised by amphiphilic molecules called surfactants. Because of their
28 amphiphilic nature, surfactants adsorb at the gas-water interface, decrease interfacial tension
29 and stabilise lamellae and gas bubbles. As gas becomes trapped in water, its mobility is reduced,
30 mitigating channelling and gravity segregation (Apaydin and Kovscek, 2001). Gas dispersion
31 also increases fluid viscosity, and in the case of heterogeneous porous media, improves sweep
32 efficiency by diverting the flow to low-permeability regions (Tang and Kovscek, 2006). As a
33 result, the foam injection process has been proven to be more efficient than gas sparging or soil
34 flushing by surfactant solutions alone (Osei-Bonsu *et al.*, 2017; Xiao *et al.*, 2018). Moreover, foam
35 is mainly composed of gas, meaning that it also uses lower quantities of surfactant than soil
36 flushing processes, thus lowering environmental damage and being economically advantageous.

37
38 The use of foam can be considered for various remediation strategies. One technique consists
39 of injecting foam to push oil through the soil and to recover it afterward (Kilbane *et al.*, 1997). By
40 selectively blocking high-permeability areas of heterogeneous porous media, the placement of
41 foam allows for oil displacement in low-permeability zones, leading to higher sweep efficiency
42 (Kovscek and Bertin, 2003). The capability of foam to invade even low-permeability areas can
43 also be exploited to deliver remedial amendments. By transporting products such as phosphate
44 or nanoscale zero-valent iron (Shen *et al.*, 2011), foam facilitates a broad and homogeneous
45 distribution of these chemicals into the porous media. By reaching low-permeability zones via
46 foam displacement, remedial amendments can react with polluting chemicals. This reaction
47 produces non-toxic species, hence providing the necessary treatment for soil remediation
48 (Zhong *et al.*, 2011). Another approach is to use foam to confine pollutants to a defined area
49 before treating it (Porto *et al.*, 2018). Finally, foam can be used to block water beneath oil, thus

1 improving the selectivity of hydrocarbon pumping. The present research focuses on this
2 strategy.

3 When foam comes in contact with organic compounds, its stability is largely affected,
4 regardless of the surfactants used. This has been observed in both bulk and porous media
5 (Almajid and Kavscek, 2016), and mainly depends on the interfacial tensions between oil, gas
6 and water. This de-foaming process takes place via complex mechanisms, and recent theoretical
7 efforts have been carried out to model it (Denkov, 2004). Manlowe and Radke (1990) pointed
8 out that the stability of foam in porous media is dependent on the stability of the pseudo-
9 emulsion film separating oil and gas bubbles. This pseudo-emulsion film ruptures whenever its
10 drainage time is shorter than the contact time with oil.

11 Since oil destabilises foam, foam reinforcement is necessary in applications of this technique.
12 Several additives have been used for this purpose, including polymers and colloids (Binks *et al.*,
13 2017; Hernando *et al.*, 2018). The aim of polymer addition is to increase the bulk solution
14 viscosity of the aqueous phase, inducing long-term stability of the foam, while the aim of adding
15 colloidal particles is to create a mechanical barrier with the subsequent adsorption of particles
16 onto the surface of the bubble (Sun *et al.*, 2014). However, given the aim of soil remediation, any
17 negative impact of the surfactants or additives on the environment needs to be minimised, and a
18 choice of biodegradable chemical species with low toxicity is fundamental.

19
20 Most surfactants that have already been proven to stabilise foams in the presence of oil are
21 not environmentally friendly (Farajzadeh *et al.*, 2012; Osei-Bonsu *et al.*, 2015). However, due to
22 their low cost, such surfactants are usually favoured in Enhanced Oil Recovery (EOR), as it
23 requires large quantities of surfactant. Thus, an investigation of other types of surfactants is
24 required, and those from other industry fields can offer interesting alternatives.

25 Among the potential biodegradable surfactants, we focus here on a plant-based surfactant
26 called saponin, as it has promising properties (Pradhan and Bhattacharyya, 2017). It has been
27 used in solution for the removal of heavy metal and mixed contaminants via solubilisation and
28 desorption of contaminants (Chen *et al.*, 2008; Song *et al.*, 2008). It is one of the few
29 biodegradable surfactants that has also been used in foam reinforced with colloidal solid
30 particles for the stabilisation of food-grade products (Binks *et al.*, 2017).

31
32 Of the environmentally friendly polymers that can be used as additives, xanthan is a microbial
33 biodegradable polysaccharide with no environmental or health hazards, and is commonly used
34 in the food industry, and medical and environmental applications (Bilanovic *et al.*, 2016; Zhong
35 *et al.*, 2008). This product is well known for improving emulsion and the stability of colloidal
36 dispersions, as it increases the continuous phase viscosity and is thixotropic. It presents a very
37 high viscosity at low shear rates (or even a yield stress limit) and highly shear-thinning
38 behaviour at higher shear rates (Martínez-Padilla *et al.*, 2015; Zhong *et al.*, 2013). Although
39 xanthan may slightly decrease foamability (Martínez-Padilla *et al.*, 2015), it has been used by
40 many authors to improve the bulk stability of foams (Pu *et al.*, 2017), both with and without oil
41 (Sun *et al.*, 2015). It has also been shown that xanthan helps foam to improve oil recovery in core
42 experiments (Sun *et al.*, 2015; Wei *et al.*, 2018). Hence, xanthan was chosen as the reference
43 polymer in the present study.

44 Another way to reinforce the resistance of foam to oil is through the use of solid colloidal
45 particles. Many particles of various types, shapes and physico-chemical properties are currently
46 used, including alumina particles (Yang *et al.*, 2017), fly ash nanoparticles (Eftekhari *et al.*, 2015)
47 and silica particles (Nguyen *et al.*, 2014; Singh and Mohanty, 2015), all of which have been tested
48 in the presence of oil. However, their environmental impact varies with their chemical nature.
49 Silica particles are natural products that have been used in food grade applications (Dickinson,
50 2010). In order to include them in solution, they can be made partially hydrophobic through an

1 appropriate surface treatment, and they are used with surfactants to increase foam stability,
2 although they may decrease foamability in comparison with the surfactant alone (Sun *et al.*,
3 2014; Tang *et al.*, 1989; Zhang *et al.*, 2008). This justifies the choice of SiO₂ particles to test foam
4 reinforcement in this work.

5
6 Although some experiments have previously been performed in bulk to study the resistance
7 of foam to oil (Aveyard *et al.*, 1994), only a few have successfully been applied in porous media
8 (Bai *et al.*, 2018; Singh and Mohanty, 2015; Sun *et al.*, 2014). Moreover, these were used only for
9 EOR applications, rather than for environmental purposes. The main goal of this study is
10 therefore to investigate the influence of polymer or solid particles on foam stability and flow
11 resistance in porous media containing residual oil. Since field applications involve the blocking
12 effects of foam on water, this study focuses on both the sweeping efficiency and the foam water
13 content. Only environmentally friendly products were used, and the different foams were tested
14 both in the absence and the presence of oil in columns filled with a porous medium. The
15 injection parameters were first optimised to obtain the strongest foam, and these foams were
16 then reinforced with xanthan polymer or silica solid particles and tested in oil-free and oil-
17 containing porous media.

18 19 **2. Materials and Methods**

20 *2.1. Chemicals*

21 In this study, all selected surfactants were biodegradable and presented no environmental
22 hazard, as specified by their safety data sheet. The saponin (non-ionic, Fisher-Scientific, France)
23 had a measured critical micelle concentration (CMC) of 0.062%wt. The two other surfactants,
24 cocamidopropyl hydroxysultaine "CH" (zwitterionic, Cola@Teric CBS, Colonial Chemical, Inc.,
25 measured CMC = 0.01%vol) and sodium decylglucosides hydroxypropyl phosphate "SDHP"
26 (anionic, Suga@Fax D10, Colonial Chemical, Inc., measured CMC = 0.074%vol) were provided in
27 solution state.

28 In terms of additives, commercial FNCS xanthan was supplied by Jungbunzlauer (Austria AG).
29 The colloidal silica particles (LUDOX® TM-50, Sigma-Aldrich, France) had a nominal size of 30
30 nm, as measured by Orts-Gil *et al.* (2011). The pollutant oil was MACRON 1821 F-4 from
31 Houghton (US) with a density of 0.818 at $T = 20^{\circ}\text{C}$. Compressed nitrogen N₂ (purity > 99.999%)
32 was supplied by Air Liquide (France) and was used to avoid potential oxidation of the chemicals
33 by O₂ and to control the level of purity of the gas.

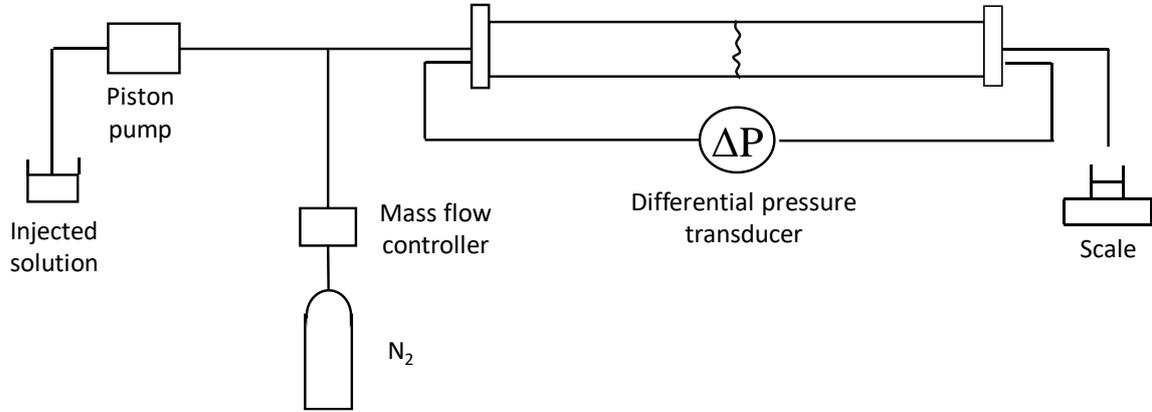
34 35 *2.2. Experimental facilities*

36 In order to measure the viscosity of the aqueous solutions with xanthan, five solutions with
37 xanthan concentrations of 100 to 500 ppm were prepared, and their shear viscosity was first
38 measured at various shear rates by means of a Kinexus controlled stress rheometer (Malvern
39 Instruments, UK) with a Peltier cylinder cartridge. All the samples were prepared with tap
40 water. The shear viscosity was measured at $20^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$, with a measurement range of between
41 1 and 1000 s⁻¹. Values at a shear rate of 12.5 s⁻¹, corresponding to the Newtonian plateau were
42 used to plot the shear rate versus the concentration of xanthan.

43 As the native solid particle suspensions were in an aggregated state, they were systematically
44 submitted to ultrasonic solicitation using ultrasonic bath equipment for 10 minutes
45 (Fisherbrand™ Elmasonic, Fisher Scientific France).

46 The experimental setup used for the coreflood experiments is presented in Fig. . A PHD
47 ULTRA™ piston pump (Harvard Apparatus, US) was used to inject the aqueous solutions. The
48 gas flow rate was controlled by a mass flow meter (EL-FLOW®, Bronkhorst® France) under
49 nominal conditions. Gas and aqueous solutions were co-injected into the column. The column
50 was a transparent PVC tube of length 40 cm and inner diameter 4.4 cm, which was sealed with

1 nylon caps at the inlet and outlet. A length of 40 cm was long enough to minimise the entrance
 2 and capillary end effects, as suggested in the literature (Eftekhari and Farajzadeh, 2017). The
 3 column was filled with sand from Cantillana (France), containing 98.4% SiO₂ grains with a D50
 4 of 279 μm, and a particle size distribution as shown in Fig. 2 (“Cantillana SAS,” n.d.).
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 Fig. 1: Schematic representation of the experimental setup for foam injection in the core experiments

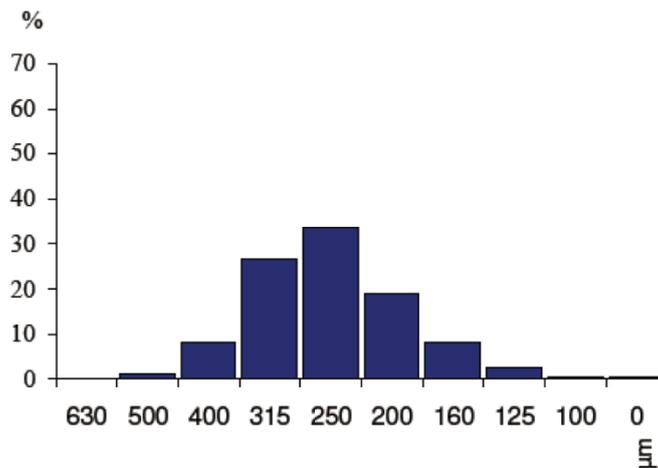


Fig. 2: Particle size distribution of the sand grains

9 The pressure drop between the inlet and the outlet of the column was measured with a
 10 differential transducer (Rosemount 2051 Coplanar™, Emerson, France) and values were
 11 recorded every 10 s.
 12

13 **2.3. Experimental procedure**

14 Various experimental tests were performed in this study, and these are presented in Table 1
 15 with the experimental approaches used.

16 *Table 1: Summary of experiments*

Tests	Purpose	Experimental approach
Set 1: Choice of surfactant	Selection of the surfactant	Try three different surfactants
Set 2: Optimisation of injection parameters	Choosing the experimental conditions	Vary both Q_{tot} and foam quality to achieve the lowest S_w and highest RF

Set 3: Effects of the addition of polymer	Testing foam reinforcement via polymer addition	Vary the polymer concentration in the absence of oil
		Vary the polymer concentration in the presence of oil
Set 4: Effects of the addition of solid colloidal particles	Test foam reinforcement via the addition of solid particles:	Vary the surfactant concentration
	Find optimum conditions in the absence of oil	Vary the particle concentration
	Test foam reinforcement in the presence of oil	Vary the surfactant concentration Test the addition of particles

1

2

2.3.1. Surfactant solutions

3

All experiments were performed at room temperature. All foaming solutions were prepared using tap water with an ionic strength of below 10^{-4} M. Before use, all aqueous solutions were stirred at 400 rpm for at least 10 minutes, except for the xanthan solutions, which required more than 12 h to ensure the complete dissolution of the polymer in water.

4

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All dispersions of solid particles were prepared by mechanical dispersion in a given amount of water, before sonication for 10 minutes in an ultrasonic bath. In parallel, the surfactant solutions were prepared by dissolution or dilution in the same amount of water. The two were then blended in convenient volume proportions.

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2.3.2. Coreflood tests

13

For the coreflood experiments, the column was placed vertically, and water and sand were gradually introduced by adding 2 cm of water and 2 cm of sand alternately. Gentle manual shaking was applied throughout the procedure to uniformly pack the sand grains. The sand packing porosity was calculated based on the exact amount of water and sand used. The column was then placed horizontally, and the absolute permeability was determined using Darcy's law by imposing various flow rates and measuring the pressure drop along the column.

14

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To saturate the medium and to cause surfactant adsorption on the sand grains, 3.3 pore volumes (PV) of solution were injected prior to co-injection. Similar procedures have previously been followed by other authors (Del Campo Estrada *et al.*, 2015; Eftekhari and Farajzadeh, 2017; Jones *et al.*, 2016), to ensure that any surfactant injected during co-injection only serves for foaming process.

19

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For each surfactant, the gas and foaming solution were co-injected into the column at a variable total flow rate (Q_{tot}). The liquid and gas (N_2) flow rates were varied to reach a target foam quality ($FQ=Q_{gas}/Q_{tot}$) while recording the induced pressure drop every 10 s.

23

24

25

26

During co-injection, two main parameters were observed to determine the foam properties: the resistance factor (RF , Eq. (1)) and the water saturation (S_w , Eq. (2)). These are defined as follows:

27

28

29

30

$$RF = \left[\frac{\Delta P_f}{\Delta P_w} \right]_{Q_{tot}} \quad (1)$$

31

32

where ΔP_f and ΔP_w are the pressure drops measured along the core when the foam and water are flowing, respectively, and

33

$$S_w = \frac{V_w}{PV} \quad (2)$$

where V_w is the volume occupied by the aqueous phase in the porous medium.

In the presence of the polymer, a modified resistance factor RF^* is calculated (Eq. (3)) to subtract the pure polymer viscosifying effect of the aqueous phase. This represents the ratio of the pressure drop of the foam ΔP_f to that of the continuous phase (CP) ΔP_{CP} at the same total flow rate, rather than water.

$$RF^* = \left[\frac{\Delta P_f}{\Delta P_{CP}} \right]_{Q_{tot}} \quad (3)$$

RF is related to the foam strength: the higher the RF , the higher the lamella density, and thus the stronger the foam. Meanwhile, S_w represents the amount of water remaining in the porous medium. A low value of S_w reflects a high efficiency of the foam in terms of displacing water, and shall reflect a decrease in water mobility through the foam.

The standard error for RF values was measured for three typical experiments, and it was found to be 0.68 with $3.2 \times \text{CMC}$ surfactant alone with four replicates, and 1.2 for $3.2 \times \text{CMC} + 1\% \text{wt SiO}_2$ in triplicate. Meanwhile, the standard error for RF^* with $3.2 \times \text{CMC} + 200 \text{ppm}$ xanthan was measured to be 0.21. The standard errors for the two other experiments were measured to be < 0.4 (data not shown). This set of standard errors demonstrates the reliability of the measurements.

Experiments in the presence of oil

In these experiments, the column was initially completely saturated with oil rather than water, and the procedure described above was followed. Water was injected until no oil was produced, allowing us to calculate the remaining oil saturation. This procedure led to a system at residual oil saturation, a situation encountered in the field at the interface between the aquifer and the LNAPL. To satisfy the conditions for surfactant adsorption, $3.3 PV$ of surfactant solution were injected before foam injection.

Experiments with the addition of polymer

Several solutions were prepared at fixed saponin concentration ($3.2 \times \text{CMC}$) to perform column experiments on the addition of polymer. Based on results in the literature (Pu *et al.*, 2017; Zhong *et al.*, 2013), a broad range of polymer concentrations of between 0 and 500 ppm was chosen to test the influence of polymer concentration on foam behaviour.

Experiments were then performed with oil. Two foaming solutions with different polymer concentrations were prepared, and were co-injected with gas into columns in a state of residual oil saturation. The polymer concentrations were chosen so that the same range of concentrations could be scanned as for the experiments without oil.

Experiments with the addition of particles

For these experiments, the range of particle concentrations was suggested by data in the literature, usually reaching a maximum of 1%wt (Binks *et al.*, 2017, 2007; Lv *et al.*, 2017) under comparable physico-chemical conditions but with different systems.

Experiments were performed following the same experimental procedure, first without and then with oil.

3. Results

3.1. Choice of surfactant

This first set of column experiments was performed in order to compare the saponin surfactant to two other surfactants previously used in the literature for similar purposes (Osei-Bonsu *et al.*, 2015; Simjoo *et al.*, 2013). Table 2 summarises the values of RF and S_w obtained in the steady state for the three selected surfactants. It is observed that both RF and S_w depend on the surfactant used. Based on its low S_w , SDHP is expected to be a promising surfactant, but its RF is below 10, which may lead to a weak foam. CH has a moderate RF but a high S_w , making it uninteresting for the purposes of application. Meanwhile, saponin shows both a relatively high RF and a low S_w , and was therefore selected at this stage for further experiment.

Table 2: Measured RF and S_w for different surfactants at $3.2 \times CMC$, $Q_{tot} = 6.3 \text{ mL} \cdot \text{min}^{-1}$ and at a quality of 87.5%

Surfactant	RF	S_w
Saponin	11.5	0.39
Cocamidopropyl hydroxysultaine (CH)	10.0	0.44
Sodium decylglucoside hydroxypropyl phosphate (SDHP)	6.6	0.34

3.2. Optimisation of injection parameters

This surfactant hierarchy is based on injection experiments performed at a single Q_{tot} and a given foam quality. The RF values may change at other flow rates. In order to identify the best flow conditions, analogous experiments were performed for a fixed saponin concentration of $3.2 \times CMC$ by varying both the foam quality and Q_{tot} over a wide interval.

The results are presented in terms of RF versus foam quality in Fig. 3. For all flow rates, the curves show a region of increase that corresponds to the low-quality regime, where the pressure gradient is independent of the gas flow rate, and a decreasing region that corresponds to the high-quality regime, where the pressure gradient is independent of the liquid flow rate. This is in accordance with the findings of other authors studying chemically different surfactants (Osterloh and Jante, 1992). The RF peak is located between 80% and 92% depending on the value of Q_{tot} , and it appears that the optimum foam quality increases as flow rate increases. Moreover, when the injection rate is high, RF decreases with the injection rate. This is in accordance with studies showing that foams of high quality are yield stress fluids with pronounced shear thinning behaviour (Denkov *et al.*, 2009; Princen and Kiss, 1987). For low injection rates, RF increases with the injection rate.

1

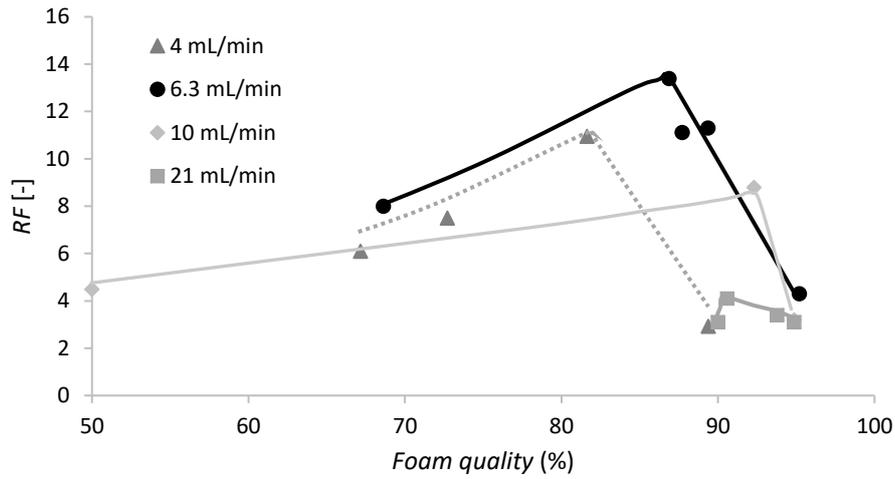


Fig. 3: RF for saponin injection at $3.2 \times \text{CMC}$ versus foam quality for different Q_{tot}

2 Fig. 4 shows the variation in S_w as a function of foam quality by gathering all S_w values
3 available, that correspond to any Q_{tot} values. In the low-quality regime, S_w decreases with the
4 foam quality. This indicates that as the foam quality increases, the sweep efficiency becomes
5 more effective, and the amount of water remaining is consequently low. For the strongest foams,
6 for which the quality is above 87%, S_w becomes almost constant. As the amount of gas in the
7 system increases, the number of bubbles increases and the lamella thickness decreases. At a
8 critical level of gas, the lamellae become too thin to be stable and collapse. An equilibrium is then
9 reached between the formation and destruction of lamella, and the water saturation remains
10 stable.
11

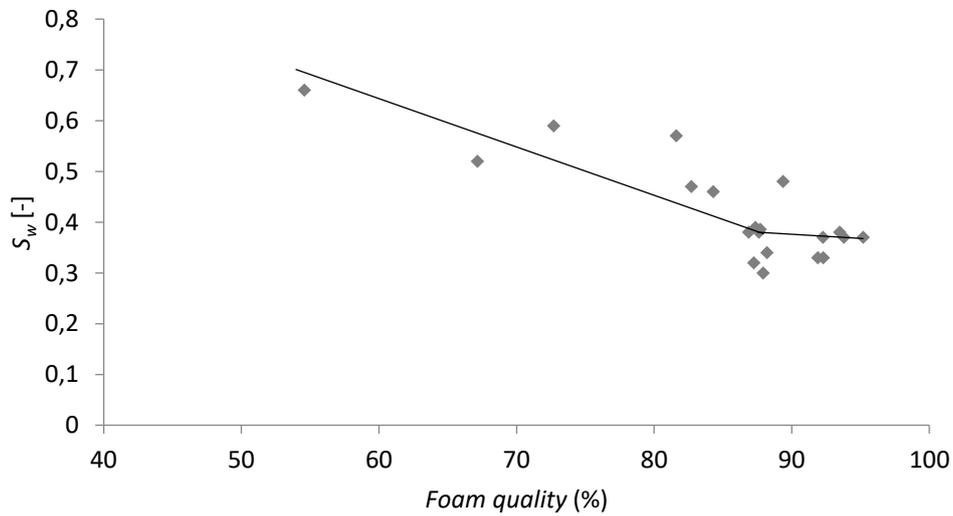


Fig. 4: Water saturation for saponin at $3.2 \times \text{CMC}$ versus foam quality

12

1 When plotted against the total flow rate (Q_{tot}) (see Fig. 5), S_w decreases with Q_{tot} in the low
 2 flow rate regime before reaching a limiting saturation at higher values of Q_{tot} . This graph shows
 3 that unlike RF , the values of S_w directly depend on Q_{tot} and to a lesser extent on the foam quality.
 4 For the remainder of the study, and to maximise sweep efficiency, the experimental conditions
 5 were chosen as a foam quality of 87.5% and Q_{tot} of 6.3 mL.min⁻¹.

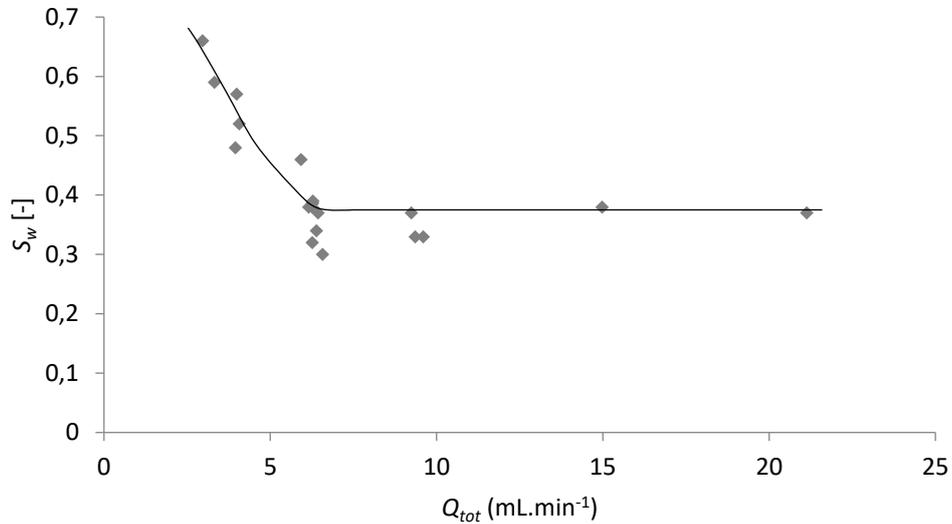


Fig. 5: Final water saturation versus Q_{tot} (mL.min⁻¹) for saponin-based foams at 3.2×CMC

6
 7 In summary, the optimum foam quality and flow rate are defined to give a strong saponin
 8 foam in a porous medium, with high RF and low S_w . This foam can then be reinforced with
 9 polymer in order to observe the resistance of the foam to oil, and how it behaves when polymer
 10 is added.

3.3. Effects of the addition of polymer

3.3.1. Oil-free conditions

11
 12 An example of the RF and S_w curves obtained as a function of the injected PV is presented in
 13 Fig. 6. Similar curves were obtained for other xanthan concentrations. In the beginning, RF
 14 increases steadily while S_w decreases linearly, indicating a piston-like foam displacement, until
 15
 16

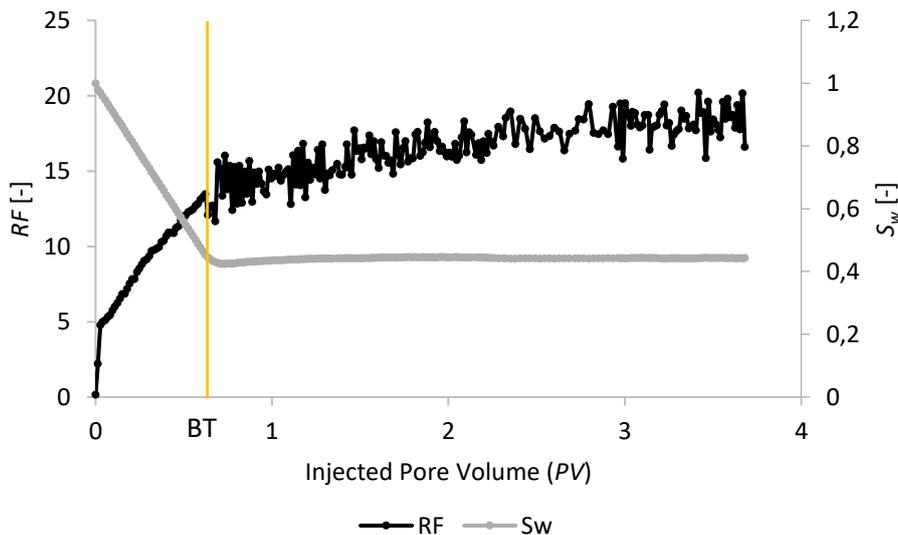


Fig. 6: RF and S_w versus injected pore volume for 3.2×CMC saponin with 200 ppm xanthan; breakthrough (BT) location is indicated by a vertical line

1 gas breakthrough. After this, S_w stabilises quickly as rearrangement of the foam takes place
 2 throughout the column, as can be observed from the slight increase in RF after gas breakthrough
 3 and the subsequent steady-state regime. The final RF and S_w values for various xanthan
 4 concentrations are shown in Table 3.

5 The first analysis concerns the onset of gas breakthrough (BT), i.e. the time of outgassing
 6 from the sand column. It can be observed that $BT \times S_w$ is almost constant regardless of Cx ,
 7 meaning that the time to breakthrough is mainly a consequence of the water content reached in
 8 presence of foam. Early breakthrough is a consequence of low gas saturation.

9 These results show that RF rises progressively with xanthan concentration (Cx). However, in
 10 contrast to the results in Section 3.2, S_w also increases, indicating the effects of the addition of
 11 xanthan. An opposite trend is seen for RF and RF^* (Table 3). As Cx increases, RF increases and
 12 RF^* decreases. An in-depth description of mechanism underlying the observed relationship
 13 between RF , RF^* and S_w is given in Section 4.1.

14
 15 Table 3: Shear viscosity at 12.5 s^{-1} , RF , pressure drop ratio $\Delta P_{polymer}/\Delta P_w$, RF^* , S_w , BT and $BT \times S_w$ at $3.2 \times CMC$ of saponin and
 16 various xanthan concentrations

Cx (ppm)	$\mu \cdot 10^{-3}$ (Pa.s)	RF	$\Delta P_{polymer}/\Delta P_w$	RF^*	S_w	BT (PV)	$BT \times S_w$
0	1.1	11.5	1.0	11.5	0.39	0.67	0.261
100	2.3	10.0	1.6	6.5	0.38	0.64	0.243
200	3.7	18.4	2.4	7.8	0.43	0.64	0.275
300	5.7	22.4	4.3	5.6	0.45	0.65	0.292
400	8.1	23.4	5.6	4.2	0.45	0.62	0.279
500	11.5	24.3	7.8	3.1	0.52	0.52	0.270

17 18 19 3.3.2. Experiments in the presence of oil

20 Similar experiments were performed with oil, to observe the resistance of the foam against
 21 oil-induced destruction. In these experiments, S_o^i corresponds to the oil saturation immediately
 22 before foam injection, which varies from one experiment to another. Measurements taken after
 23 foam injection showed that the oil saturation remained almost constant during the experiment.
 24 The results for the presence of oil are shown in Table 4, together with the results for xanthan-
 25 free solutions.

26 Table 4: RF , pressure drop ratio $\Delta P_{polymer}/\Delta P_w$, RF^* , S_w , S_o^i and foam breakthrough onset BT at $3.2 \times CMC$ of saponin in the
 27 presence of oil for various xanthan concentrations

Cx (ppm)	RF	$\Delta P_{polymer}/\Delta P_w$	RF^*	S_w	S_o^i	BT (PV)
0	3.5	1.0	3.5	0.31	0.18	0.51
200	4.0	2.8	1.4	0.48	0.12	0.38
500	6.4	6.0	1.1	0.44	0.21	0.31

28
 29 When RF^* is considered, a significant loss is observed compared to experiments in the
 30 absence of oil. Indeed, RF^* decreases rapidly with xanthan concentration, and it is likely that the
 31 foam bubbles are collapsing in contact with oil.

32 Compared to the use of polymers, it is well known that solid colloidal particles can efficiently
 33 stabilise both foams and emulsions against coalescence (Singh and Mohanty, 2015). These
 34 Pickering-like foams are of increasing interest to researchers, and most studies concern the
 35 determination of the optimum physico-chemical conditions of a given system. In the following, a

1 preliminary evaluation of the ability of colloidal SiO₂ particles to efficiently stabilise foams is
 2 presented for porous media in the absence or presence of oil.

3 3.4. Addition of Solid Colloidal Particles

4 3.4.1. Optimisation of foam/particle mixture

5 Effects of surfactant concentration in oil-free conditions

6 Since the addition of xanthan did not lead to foam reinforcement against oil (i.e. RF^* did not
 7 increase), colloidal particles were considered for use in formulating an oil-resistant foam. Native
 8 SiO₂ colloidal particles were chosen to perform coreflood experiments. Before reinforcement
 9 with colloidal particles, the influence of the surfactant concentration (C_s) on sweep efficiency
 10 was investigated. For a saponin surfactant, C_s was varied between $3.2 \times CMC$ and $15 \times CMC$ for a
 11 foam quality of 87.5% and $Q_{tot} = 6.3 \text{ mL} \cdot \text{min}^{-1}$. The obtained values of RF and S_w are shown in Fig.
 12 7.
 13

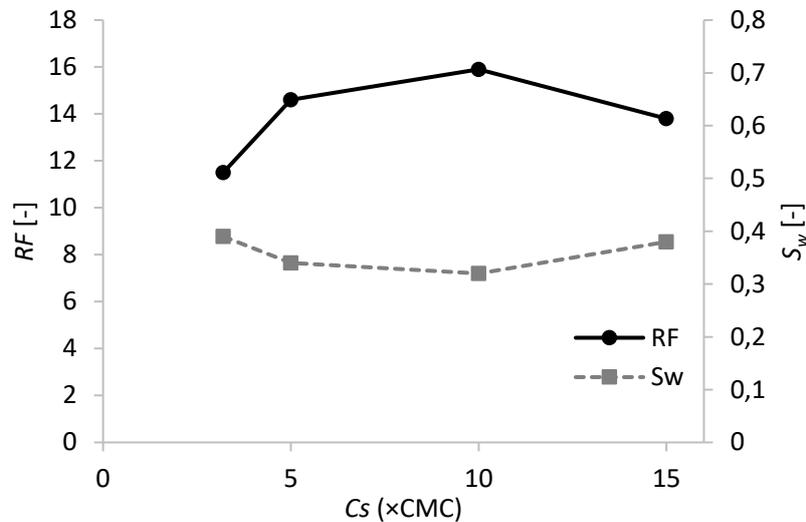


Fig. 7: Measured RF and S_w at different saponin concentrations

14 As can be seen from Fig. 7, RF and S_w are well correlated. As C_s is increased to $10 \times CMC$, RF
 15 increases and S_w decreases; this behaviour is characteristic of foams that become stronger with
 16 more efficient sweeping. Conversely, when the concentration is high enough (e.g. $15 \times CMC$), RF
 17 drops and S_w rises, indicating less efficient sweeping. Further explanations of the mechanisms
 18 involved are given in Section 4.2.
 19

20 Effects of colloidal particle concentration in oil-free systems

21 For a given $3.2 \times CMC$ saponin foam, the effect of silica particle concentration on the properties
 22 of the foam was studied. In these experiments, two concentrations of SiO₂ were used. Table 5
 23 shows the obtained values of RF and S_w .

24 Table 5: Measured RF and S_w at $3.2 \times CMC$ of saponin in oil-free experiments, with and without colloidal solid particles

	RF	S_w
Saponin alone	11.5	0.39
Saponin + SiO ₂ (0.5%wt)	14.2	0.41
Saponin + SiO ₂ (1%wt)	11.5	0.38

26

As can be seen from Table 5, the addition of particles at 1%wt does not change the values of S_w or RF . An increase in RF is observed when silica is added at 0.5%wt, without modifying the S_w value.

Optimal addition of particles in an oil-free system

Given the previous results on the importance of surfactant concentration, the saponin concentration was then changed to $10\times CMC$, while maintaining a SiO_2 concentration of 0.5%wt. When solid particles are added at $10\times CMC$, RF increases from 15.9 to 20.4, but S_w remains unchanged at 0.32 in comparison with saponin alone (Table 6). This indicates that the particles do not change the macroscopic foam structure and that the sweep efficiency remains the same. As the ultimate goal was to develop foam formulations that resist oil-induced destruction within porous media, core experiments were performed in the presence of oil.

3.4.2. Experiments in the presence of oil

In the same way as the oil-free system, the effect of surfactant concentration was investigated in experiments with oil. When the surfactant concentration is increased from $3.2\times CMC$ to $10\times CMC$, RF increases from 3.6 to 6.3 (with oil) (see Table 6).

Table 6: Measured RF , S_w and S'_o at $10\times CMC$ of saponin with and without oil, and with and without colloidal particles

		RF	S_w	S'_o
Without oil	Saponin alone	15.9	0.32	0
	+ SiO_2 (0.5%wt)	20.4	0.32	0
With oil	Saponin alone	6.3	0.36	0.12
	+ SiO_2 (0.5%wt)	7.8	0.36	0.11

In the oil-free system, the addition of 0.5%wt SiO_2 substantially increases RF , especially for $10\times CMC$ saponin solutions. Thus, $10\times CMC + 0.5\%wt SiO_2$ was used in experiments in the presence of oil. The results show an increase in RF from 6.3 (without particles) to 7.7 when silica is added at 0.5%wt (see Table 6). In these experiments, both S'_o and S_w remain the same, and are similar to those for the oil-free experiments in which S_w remains unchanged.

To obtain a comprehensive overview of these experiments, the main results for the addition of SiO_2 particles are presented in Fig. 8. The effects of surfactant concentration with and without oil can be observed. The increase in RF with increasing surfactant concentration is linked to a decrease in S_w in the absence of oil. The importance of particle addition is also shown in the figure: it causes an increase in RF in the presence of oil, while S_w remains unchanged.

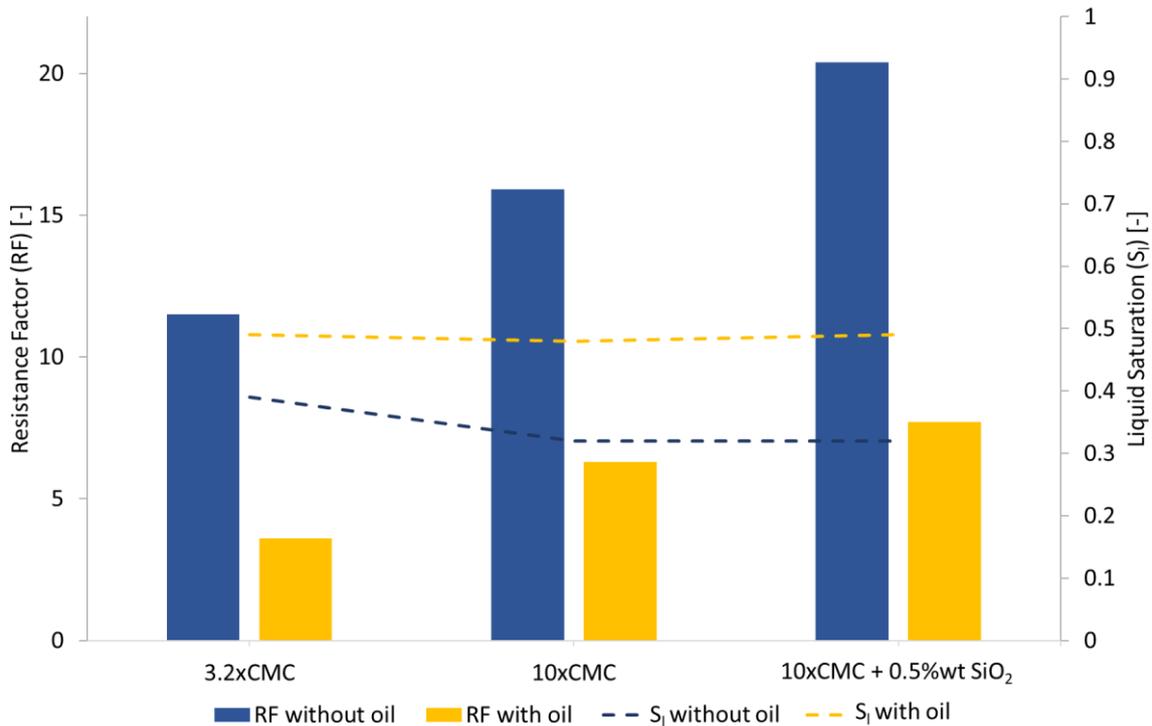


Fig. 8: RF and S_l for different saponin formulations with the addition of particles

1

2

3 4. Discussion

4 4.1. Polymer effect

5 The first analysis concerns the shear viscosity values obtained at 12.5 s^{-1} . When the values
 6 obtained at different xanthan concentrations are compared with those reported by other
 7 authors (Zhong *et al.*, 2013), they appear to be low. However, the use of tap water implies the
 8 presence of ions, and particularly cations. According to Zhong *et al.* (2013), this concentration of
 9 cations leads to a decrease in the viscosity of xanthan solutions. This phenomenon is explained
 10 by the ionic neutralisation of the local anionic charges of xanthan, leading to a molecular
 11 contraction and hence lower viscosity.

12 Regarding the variation in RF , it can be shown that the overall resistance factor RF for
 13 polymer foams has two contributions. The first is a structural contribution RF^* that mainly
 14 depends on the number density of the bubbles, their size and the interface rheology, which itself
 15 relies on the possible interaction between polymer and surfactant molecules. The second is a
 16 continuous phase contribution due to the bulk viscosity. By increasing C_x , the relative
 17 continuous phase viscosity $\Delta P_{polymer}/\Delta P_w$ increases, thus increasing RF inside the column, as
 18 confirmed by the increase in shear viscosity.

19 Phenomenologically, when a hydrosoluble polymer and a surfactant are simultaneously
 20 present, the foaming process is believed to occur as follows (Hernando *et al.*, 2018). After the
 21 mechanical creation of the gas/liquid interface, a process of coalescence immediately occurs.
 22 Within this period, however, the surfactant molecule reaches the gas/liquid interface,
 23 preventing coalescence. In the presence of the polymer, the process of collapse in the early
 24 foaming stages is delayed due to polymer-induced steric repulsion in the liquid films. As a
 25 consequence, the surfactant molecules have a longer time to reach the interface, hence
 26 promoting the foaming process.

27 However, depending on the type of interaction between the polymer and the surfactant,
 28 surfactant molecules may not be free to reach the interface. In fact, in the case of a strong

1 surfactant-polymer interaction, a surfactant-polymer complex is formed that slows down
2 adsorption at the surface, decreases the amount of free monomers in solution and thus
3 decreases foamability. This strong interaction can be found for surfactants and polymers of
4 opposite charge (Petkova *et al.*, 2012).

5 Conversely, in the case of a weakly interacting system, surfactant monomers can quickly
6 adsorb at the surface during foaming, and the polymer stabilises the new lamella via steric
7 repulsion, thus improving foamability. A system of this type can be found with a non-ionic
8 polymer and a charged surfactant (Petkova *et al.*, 2012).

9 Meanwhile, for non-interacting systems, the foamability is thwarted by mitigation of the
10 interface creation rate and a decrease in the diffusion coefficient of the surfactant molecules. In
11 this case, no polymer co-adsorption on the surfactant, or change of gas/water interfacial tension
12 is expected (Hernando *et al.*, 2016; Petkova *et al.*, 2012). A loss of foamability, even of limited
13 magnitude, is accompanied by a gain in stability. The obtained films are thicker than when the
14 surfactant is used alone and have a low drainage velocity, and lamellae that contain polymers
15 are stabilised by long-range steric interactions (Gochev, 2015).

16 In this situation, it is likely that a weaker foam is created with thicker lamellae, leading to
17 higher S_w , early breakthrough and lower RF^* .

18 The RF^* , S_w and breakthrough variations observed in the present study also reveal difficulties
19 in foam formation, a phenomenon that could be due to the formation of a surfactant-polymer
20 complex via strong interactions.

21 However, in the present study, xanthan and saponin are both non-ionic chemicals whose
22 interactions can take place via hydrogen bonding, a weaker interaction than electrostatic
23 bonding. Formation of a surfactant-polymer complex may not explain the observed behaviour,
24 and it appears that the decrease in foam strength depends mainly on the continuous phase
25 viscosity increase.

26
27 Similar experiments were performed with oil to determine the potential oil resistance, and to
28 identify whether the foam creation mechanism observed previously was reproduced. It appears
29 that the expected stabilization of foam against destruction by oil is not induced by xanthan
30 addition. The same degradation of the foam was observed by Hernando *et al.* (2016) in foams
31 reinforced with non-ionic polyacrylamide, where it was shown that oil acted as a defoaming
32 agent. In an equivalent way to the oil-free experiments, the observed increase in RF is due only
33 to the increase in the continuous phase viscosity, and is hindered by structural loss of the foam.
34 As a corollary, BT decreases and S_w becomes significant in the presence of polymer.

35 Overall, it appears that the addition of xanthan to a saponin foaming solution results in an
36 increase in the continuous phase viscosity that mitigates liquid drainage and thickens lamellae.
37 It also increases RF , thanks to the viscous contribution, but at the same time hinders the
38 generation of foam, leading to weaker foam in oil-free sandpacks. Moreover, no positive
39 stabilisation effect was observed in the presence of oil, as reported by Shen *et al.* (2006). It is
40 therefore not a suitable way to increase foam strength in the presence of oil, but can still be
41 useful if the aim is only to increase the overall RF .

42 43 4.2. Surfactant concentration

44 To interpret data from the variations in surfactant concentration, the dynamic displacement
45 of foam in porous media is considered. In fact, during foam flow, lamellae are continuously
46 stretched at the pore body and compressed at the pore throat, where the distance between the
47 walls is smaller, as illustrated in Fig. 9. As surfactant unimers on gas/liquid interface are in
48 dynamic equilibrium with surfactant micelles, compensation for the lack of surfactant molecules
49 during the stretching period is more nearly instantaneous as C_s increases. This leads to lamellae
50 that are more stable against breakage, and stronger foam is transported along the core.

1 However, above a certain value of C_s , the aqueous film may be depleted in the surfactant
 2 micelles compared to the nodes due to the important amount of surfactant present. More space
 3 is available in the nodes for micelles to be packed in, a situation that is not encountered at
 4 standard surfactant concentrations. Thus, an additional attractive force of osmotic origin
 5 contributes to the disjoining pressure, leading to the thinning of lamellae and coalescence of less
 6 resistant foams.

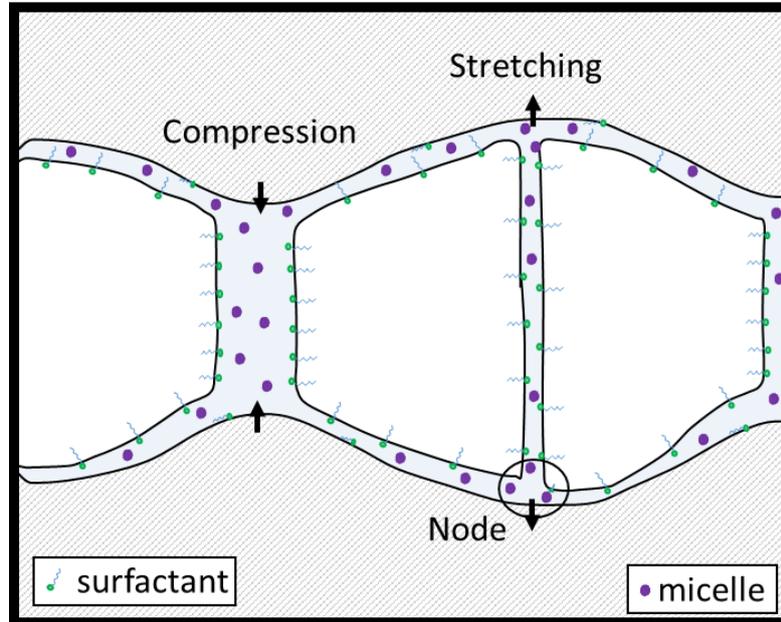


Fig. 9: Sketch illustrating foam displacement at pore scale

7 Indeed, according to Jones *et al.* (2016), relatively low surfactant concentrations are needed
 8 for stabilisation in bulk foam, where large bubbles are formed with low gas/water interface
 9 area. Conversely, higher surfactant concentrations are necessary to obtain a similar surface
 10 coverage in porous media, as the bubbles are of smaller size and of the same order of magnitude
 11 as pore bodies.

13 4.3. Particle addition

14 The results for $3.2 \times \text{CMC}$ in the absence of oil show similar values of RF and S_w , without
 15 particles and with $1\% \text{wt SiO}_2$ (Table 5), suggesting that particles do not have any impact on how
 16 the foam rearranges itself inside the porous media. It therefore appears as if the surfactant alone
 17 is responsible for foamability and foam stability.

18 However, an increase in RF is noted when silica is introduced at only $0.5\% \text{wt}$, with no
 19 significant increase in the aqueous phase viscosity. The apparent aqueous phase viscosity was
 20 determined by measuring RF^* , which was equal to RF , implying that the pressure gradients
 21 during the flow of water or surfactant solution are the same. Thus, both solutions have the same
 22 apparent viscosity. The increase in RF suggests an improvement in gas/water interface rheology
 23 when SiO_2 is added at this concentration. For other systems, it is usually reported that a loss of
 24 foam strength, or equivalently RF , is observed when the particle concentration exceeds a certain
 25 threshold value due to particle aggregation (AlYousef *et al.*, 2018; Veyskarami and Ghazanfari,
 26 2018) or surfactant adsorption on the surface of the particles, thereby limiting the amount of
 27 available surfactant (Yang *et al.*, 2017). Thus, the limiting solid concentration should be below
 28 $1\% \text{wt}$.

29 The increase in RF that is observed when SiO_2 is added to a 3.2 or $10 \times \text{CMC}$ solution indicates
 30 a microscopic foam change. This probably arises from particles gathering at the gas/water
 31 interface, as this would be promoted by a large number of surfactant molecules. This in turn

1 would strengthen the interface rigidity and induce a higher RF . To interpret this finding, it
2 should be borne in mind that the best adsorption of solid colloids has been reported for partially
3 hydrophobic particles, with a ratio of hydrophobic to hydrophilic sites ratio that depends on the
4 system of interest (Binks and Horozov, 2005; Tang *et al.*, 1989). It is therefore possible that
5 when free surfactant molecules are available to change the hydrophobicity of colloids, this
6 makes the adsorption of particles at gas/water interface more energetically favourable, thus
7 increasing the interface rigidity. As Yang *et al.* (2017) reported for a different system, with the
8 appropriate surface charges and right surfactant/particle ratio, surfactants could adsorb at the
9 particle surface and improve the stability of the foam. Both the particle network created in the
10 film and the adsorption of the modified particles at the interface contribute to the increase in the
11 bulk stability of the foam and its blocking ability in porous media.

12 In the oil-free system, the correlation between surfactant concentration and RF increase is
13 explained by the need for additional surfactant due to dynamic foam displacements. In the
14 presence of oil, surfactant concentration and the increase in RF also seem to be correlated. Indeed,
15 since the surfactant is involved in the oil/water emulsion, a higher surfactant concentration is
16 needed for the formation of foam.

17 The increase in RF when 0.5%wt SiO_2 is added to the solution in the presence of oil is similar
18 to the results of oil recovery experiments by Sun *et al.* (2014), in which they added 0.5% SiO_2 to
19 an SDS foam. Although they reported a slightly higher increase, the surfactant was different, which
20 could lead to different particle/surfactant interactions and potentially stronger adsorption at the
21 interface.

22 The subsequent increase in RF observed with the addition of particles suggests that colloidal
23 particles do reach the gas/water interface and create a barrier against the oil-induced coalescence
24 of bubbles. This phenomenon is illustrated in Fig. 10, where the presence of oil leads to the foam
25 collapsing in the absence of particles. As particles are added to the formulation, they adsorb at the
26 interface, rigidify it and stabilise the foam against the oil. The thermodynamics of systems with
27 solid particles constituting a rigid barrier at the gas/water interface depends on the contact angle,
28 which itself relies on the degree of hydrophobicity of the particles. When the gas/water interface
29 is covered by solid colloids, they effectively mitigate the entry of oil droplets at the interface, but
30 this is in competition with the opposing capillary effect that takes place between adjacent
31 adsorbed particles (Denkov, 2004).

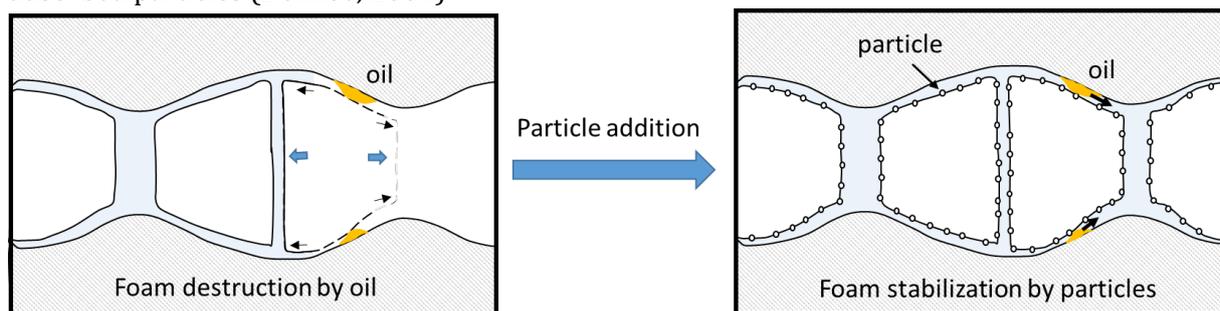


Fig. 10: Sketch illustrating the mechanism of foam reinforcement by particles against oil in porous media

32

33 4.4. Applicability in the field

34 If a foam is used as a blocking agent for water flow, the value of S_w should be as low as
35 possible. For the injection of foam into surficial aquifers, the RF should be significantly higher
36 than 1 for the foam to act as a sweeping agent, but should not be too high due to injectivity
37 constraints. A value slightly lower than or close to 10 is acceptable for practical purposes (Maire
38 *et al.*, 2018; Portois *et al.*, 2018). It is shown in Table 6 that for the optimised experiments, these
39 conditions are met, with RF being close to 8 while the S_w is quite low at around 0.36.

1 In the presence of xanthan, the obtained *RF* was lower than with particles (6.4 compared to
2 7.8), and it has been shown that this effect is mainly due to an increase in the viscosity of the
3 fluid in lamellae, while the foam itself seemed to be weakened. This effect, which is not clearly
4 visible in 1D experiments, should be visible in 2D experiments. Indeed, in 2D or 3D situations, a
5 weak foam tends to lead to preferential pathways and thus to a low sweep efficiency. Therefore,
6 in order to reach an homogeneous foam distribution, the addition of particles is preferable over
7 xanthan polymer.

8 Finally, when considering foam technology for soil remediation, several practical aspects
9 should be taken into account, such as the cost and possible technical issues.

10 Since foam is mainly composed of gas, the main cost of the procedure lies in the
11 biodegradable surfactant and particles used. Silica particles are easily available and affordable,
12 whereas a biodegradable surfactant can be more expensive.

13 However, apart from the cost of the surfactant, the procedure is still shown to be less
14 expensive, easier and more feasible than other techniques. In fact, the bare ground needed for
15 excavation is not necessary, little equipment is needed, and the sweeping efficiency is high. Thus,
16 foam is an ideal candidate for a heterogeneous porous medium, particularly when compared to
17 gas sparging or soil flushing. Several challenges still remain, such as the development of oil-
18 resistant foams on a larger scale, or the implementation of a push-and-pump technique in which
19 foam would be injected into the same well where oil is pumped. The use of foam is also still
20 contraindicated in scenarios with fast-flowing underground water, as this technique is still
21 under development.

22 Finally, even with a biodegradable surfactant used in food-grade applications, the addition of
23 this chemical may impact the environment to some extent. Although the health and
24 environmental issues caused by a pollutant are substantially more important than those of a
25 biodegradable surfactant, a risk assessment is always required.

26 27 **5. Conclusions**

28 The objective of the present study was to obtain a biodegradable formulation, consisting of
29 surfactant and additives, that can ensure the stability of foam stability in porous media in the
30 presence of organic pollutants. The findings of the present study can be summarised as follows:

- 31 - Saponin appears to be the most effective biodegradable surfactant of the three
32 alternatives considered here.
- 33 - Coreflood experiments confirm the detrimental effects of oil on the stability of foam both
34 in bulk and in porous media for all formulations studied.
- 35 - The addition of xanthan is less efficient than colloidal solid particles for foam
36 reinforcement, as it increases only the continuous phase viscosity, inducing an increase in
37 flow resistance and a decrease in water saturation. In this respect, environmentally
38 friendly interacting polymer-surfactant systems may be of interest.
- 39 - Particle addition is shown to inhibit the destruction of foam in the presence of oil by
40 creating a physical barrier at the gas/water interface. In the present study, the optimum
41 concentration of saponin and SiO₂ were found to be 10×CMC and 0.5%wt, respectively.

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17
18 September 10th 2019,

19 To Charles Werth,

20
21
22
23 Dear Sir,

24
25 We would like to respond to comments concerning our paper “Saponin foam for soil
26 remediation: on the use of polymer or solid particles to enhance resistance to pollutant
27 destruction”.

28
29 Please find below the response to comments of the Reviewer 1 on the paper, as the other two
30 reviewers already gave positive reviews. For some of the comments we do not fully agree with
31 Reviewer 1, thus we ask for and hope that, considering that the other two reviewers were
32 satisfied, you will be able to accept the manuscript.

33
34 We thank you in advance for the time taken to consider our revised manuscript.

35
36 Yours faithfully,

37
38
39 Natacha Forey, Olivier Atteia, Abdelaziz Omari and Henri Bertin
40
41

1 The first comment referred to the addition of quantitative data in the abstract. This was
2 taken into account and the abstract was consequently modified (see lines3-5 p.2).

3 Then, the reviewer suggested improvement of the manuscript with the help of a native
4 English speaker. The manuscript has therefore been revised by a professional English speaker.

5 In the first comments Reviewer 1 argued that the solutions were not completely stable and
6 homogeneous during the injection period. We replied that the microscope was not the best way
7 to judge the stability of the injected solution.

8 To that concern, it can be first replied that although the microscope may shear the
9 solutions and break the possible weak interactions existing between the different particles, it does
10 give a qualitative statement about stability. Another way to judge stability would be to study a
11 possible particles sedimentation. In their experiments with nanoparticles, Binks *et al.* (2015) used
12 photography to monitor the stability of solution that sediment. However, our solutions showed
13 no visual sedimentation, indicating that any aggregation would be smaller than 200 μm , the limit
14 of visual detection by the human eye. It is also possible that the size of the possible aggregates is
15 not small enough to lead to segregation. Authors used laser diffraction analysis (Binks *et al.* 2017;
16 Karakashev *et al.* 2011) to measure the size of their particles, however, this cannot be used to
17 access the stability of the solution, since stirring is necessary during the measurement, which
18 supply a shearing effect and can break any possible aggregation.

19 The fourth comments required duplicate or triplicate tests, we have to emphasize the fact
20 that in experiments of foam injection in porous medium, authors usually do not run duplicate or
21 triplicate given the long-time of 2 to 3 days necessary to perform one single coreflood
22 measurement (Aarra *et al.* 2014; Boeije *et al.* 2018; Eftekhari *et al.* 2015; Jones *et al.* 2018; Ma *et*
23 *al.* 2013; Pang 2010; Wang *et al.* 2015; Zeng *et al.* 2016). In our study triplicates were run for five
24 different tests, which all showed a good reproducibility. For all those reasons, and given the
25 necessity to move forward on to the next part of the project, on 2D-tank experiments, it was
26 chosen not to perform duplicates.

27 Finally, the reviewer commented on the fact that there was a lack of consideration about
28 the mass recovery of the different chemicals.

29 For each experiment involving oil, the amount of recovered oil is lower than 3.5 mL, which
30 represents less than 2% of the initial amount present in the column. It is difficult to be more
31 precise than that, particularly in the presence of surfactants, because it is very difficult to separate
32 surfactants from oil, and even when achieved, the extraction factor is not up to 100% (Gao *et al.*

1 2014; Anon 2017; Anon 2018). The same applies to polymer separation, whose amount cannot
2 easily be measured when mixed with surfactants.

3 COT (Carbon Organic Total) could be used to measure the amount of carbon in a sample,
4 and then lead to the sum of components. However, another mean would still be necessary to
5 differentiate surfactants from polymer or surfactants from oil.

6