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Impact of Crude Oil on Pre-generated Foam in Porous Media

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Summary

As foam is injected into an oil reservoir, the region near an injector can become oil-free due to the relatively high capillary number. Foam created in this region encounters oil further out in the reservoir. The impact of oil on foam in porous media is usually investigated by co-injecting surfactant, gas and oil, or by injecting pre-generated foam into an oil-saturated core. However, the former experiment does not give information on the impact of oil on pre-generated foam, and from the latter experiment one cannot easily obtain data at different oil fractional flows, necessary to model the impact of oil on pre-generated foam.

Here the impact of crude oil on pre-generated foam is studied by co-injecting surfactant solution and gas into a relative narrow core (0.01 m diameter), and injecting oil into the porous medium some distance downstream from the inlet, through ports in the side of the porous medium. By injecting the three phases into the core we investigate the flow behaviour of foam with oil at fixed fractional flows of all three phases. The relatively narrow core allows rapid contact between the injected crude oil and pre-generated foam.

We observe a progressive decrease in the apparent viscosity of the foam after encountering oil. Foams with a higher gas fraction experience a more significant weakening by oil over the length of the core than foams with a lower gas fraction. By the end of the core, the apparent viscosities of foam with a higher gas fraction approach values observed with three-phase co-injection. Foam made with surfactant pre-equilibrated with the crude oil propagated for a shorter distance in presence of oil than foam made with surfactant that hasn't contacted oil before.

We present a novel, but relatively simple method to investigate the change of foam mobility as it encounters oil in a porous medium, at controlled fractional flows of all phases. We show that in our case the apparent viscosity of foam with oil can decrease by more than a factor of four over a distance of 0.15 m, indicating that foam and oil reach steady-state (as observed with three-phase co-injection) almost instantaneously compared to the length of a reservoir-simulation grid-block.

Introduction

Most research on the impact of (crude) oil on foam in porous media is conducted applying one of the following four methods:

- Pre-generated foam injection into a core pre-saturated with oil (Aarra and Skauge, 1994; Kristiansen and Holt, 1992; Tang, 2019)
- Co-injection of oil, gas, and surfactant into a core (Tang et al., 2018)
- Surfactant and gas injection into a core (partly) pre-saturated with oil (Raza, 1970; Simjoo, 2012)
- Pre-generated foam injection into a microfluidics chip, where oil is injected some distance from the main inlet (Schramm et al., 1993; Schramm and Novosad, 1990)

However, these processes do not necessarily represent what happens with the application of foam for enhanced oil recovery (EOR), where foam can sometimes be generated in the absence of oil near the well. This (pre-)generated foam then propagates into regions richer in oil, where the different phases interact.
A difference in flow characteristics between co-injection of three separate phases and co-injection pre-generated foam and oil arises from the difference in how oil impacts foam, i.e. by anti-foaming and/or de-foaming. Anti-foamers inhibit foam formation, and de-foamers destabilize an existing foam. For bulk foams outside porous media, de-foamers usually act on the outer surface of the foam (Pugh, 1996). By co-injecting gas, surfactant solution and oil, it is possible that foam is not created, due to strong anti-foaming impact by the oil. Tang (2019) sees a greater pressure gradient when injecting pre-generated foam than when co-injecting surfactant and gas into a core at waterflood-residual oil saturation. This indicates that, as with bulk foam, the impact of oil on pre-generated foam can be different from its impact on foam generation. By injecting foam pre-generated outside the porous medium, there is an uncertainty whether the characteristics of the injected foam are the same as in-situ-generated foam, especially if the foam generator has different properties than the core (Falls et al., 1989). Moreover, co-injecting oil and pre-generated foam from the core inlet can result in oil weakening the foam at the T-junction in the apparatus tubing or in the injection plate. Therefore, we choose to investigate the impact of crude oil on foam by co-injecting surfactant solution and gas from the face of the core, and oil some distance downstream from the coreface, to investigate the impact of crude oil on in-situ pre-generated foam. This is similar in intent to the experiments conducted by Schramm and Novosad (1990) in glass micromodels. For foams that are weakened by oil, they report that the foam lamellae transported oil droplets for some distance before rupturing, after which the following lamellae picked up and transported the oil droplets.
In the next section of this paper we present an overview of the materials we use for our experiments and experimental procedures. Using a relatively narrow core allows rapid contact between injected oil and foam, in a realistic porous medium much larger than pore dimensions. That section is followed by an overview and discussion of our experimental findings and then our conclusions.

Materials and procedure

We use anionic surfactant $C_{14/16}$ Alpha Olefin Sulfonate (AOS, brand-name Witconate, supplied by AkzoNobel) and a proprietary mixture of anionic and amphoteric surfactants, referred to here as surfactant A. We prepared all the surfactant solutions with 0.5 wt.% surfactant concentration. Synthetic seawater solution was used for the brine; see Table 1 for its composition. For AOS the critical micelle concentration (CMC) is roughly 0.003 wt.% at 23°C (Jones et al., 2016a). To satisfy adsorption, the core is flooded with more than 10 pore volumes of surfactant solution before conducting experiments. Nitrogen gas is injected into the core with a purity of 99.98%, supplied from a 200-bar gas cylinder. The crude oil has a viscosity of 3.8 ± 0.03 cP and density of 0.84 ± 0.01 g/cm^3, measured at 20°C. For our experiments with AOS we use Bentheimer sandstone, which has a porosity of about 0.25 (Peksa et al., 2015). By water-flooding the core we determined the permeability, k, to be $2.6 \pm 0.2 \times 10^{-12}$ m^2. The experiments with surfactant A are conducted with Berea sandstone, which has a porosity of about 0.2 (Kapetas et al., 2015; Øren and Bakke, 2003). By pumping water through a water-saturated core we determined the permeability to be $0.13 \pm 0.005 \times 10^{-12}$ m^2. The cores are 0.22 m in length and are 1 cm in diameter. The cores are coated in epoxy resin, which results in an effective core diameter of 0.94 cm, and are mounted in aluminium core-holders, as was done by Jones et al., (2016a, 2016b). Nitrogen and surfactant solution are injected from the bottom coreface, reached through relatively narrow tubes and connections, with an inner diameter of 0.75 mm, to minimise the droplet size of the entering phases. Oil is injected 5.5 cm from the main inlet; see Figure 1. For the experiments with AOS at 50, 70 and 95% foam quality, the oil was injected with a single syringe pump from a single inject port, and for all the other experiments with two syringe pumps from two different injection ports. The relatively narrow core allows rapid contact between the injected crude oil and pre-generated foam, especially when oil is injected from both sides. The experiments were conducted at a controlled temperature of 30°C with AOS, and at 90°C with surfactant A, and both with a back-pressure of 40 bar.

Table 1 Synthetic seawater composition

Salts	**Grams / litre**
NaCl	**25.4**
KCl	**0.673**
$MgCl_2$.6H2O	**10.2**
$CaCl_2$.2H20	**1.47**
Na_2SO_4	**3.83**

Table 2 *The measured and calculated surfactant and oil content of the surfactant solutions used.*

Description	Total carbon (ppm)	Oil content (wt.%)	Surfactant concentration (wt.%)
Initial AOS solution	**2878** ± 140 [a, b]	-	**0.50** ± 0.02 [a, b]
AOS solution with solubilized crude oil	**3329** ± 140 [b]	**0.14** ± 0.02 [b, c]	**0.37** ± 0.01 [c]; difference assumed due to surfactant lost to oil-water emulsion

[a] *values calculated with the active content in the initial AOS solution.*
[b] *values calculated with Shimadzu TOC analyser values.*
[c] *values calculated with the surfactant titration measurement.*

Interfacial-tension (IFT) values of <1 mN/m and 18 ± 1 mN/m were measured between crude oil and surfactant solution and synthetic seawater, respectively. These measurements were conducted using the Du Noüy–Padday method at room temperature (21 ± 1°C) and ambient pressure. Table 4 gives the relevant interfacial tensions for the crude oil and the aqueous solutions, and the respective values of entering, spreading, and bridging coefficients and lamella number.

Table 3 *Surface-tension values measured at ambient conditions.*

Surface tension (mN/m)	
Crude oil	**27** ± 1
Synthetic seawater	**73** ± 1
Synthetic seawater with 0.5 wt.% AOS C14-16	**28** ± 1

We prepared our surfactant solution with solubilized oil as follows: we mixed AOS surfactant solution (1029.1 +/- 0.1 g) and crude oil (198.9 +/- 0.1 g) in a 2-litre bottle, and stirred daily for 11 days. We then separated the surfactant solution from the crude oil and any separate emulsion layer by using a separation funnel. To remove any droplets from the surfactant solution, we centrifuged the solution at 2000 rpm for 2 hours, and finally filtered through a filter paper (Sartorius) with a pore size of 0.45 µm, under a pressure gradient imposed by a vacuum pump. The surfactant concentration in the surfactant solution equilibrated with crude oil was determined by titration to be 0.37 +/- 0.01 wt.%. From Total Oil Content (TOC) measurements (using a Shimadzu TOC analyser and a Skalar Primacs^{SLC} TOC analyser), we deduce that the solubilized crude oil content was 0.14 +/- 0.03 wt.%; see Table 2. We assume that the reduction in surfactant concentration by 0.13 wt.% detected by titration reflects surfactant consumption by emulsions or solubilisation into the oil when equilibrating the surfactant solution.
Core-flood experiments with both AOS and surfactant A were conducted with a total injection rate of 0.1 ml/min and 0.02 ml/min respectively, which is equivalent to superficial velocities of 6.8 ft/day and 2 ft/day. To minimize any impact of hysteresis while conducting the foam-quality scan, in collecting data we alternate between lower and higher foam qualities. We define the foam quality as the gas fraction of the combined gas and water injection rate (i.e., excluding oil).

Table 4 *Interfacial-tension values measured at ambient conditions, and the calculated entering, spreading and bridging coefficients, and lamella number. The measured interfacial tension between crude oil and surfactant solution was below the measurement range of the device (1 – 350 mN/m). We assume an interfacial tension of 1 mN/m in our calculation of the foam-stability coefficients.*

	Interfacial tension (mN/m)	Entering coefficient	Spreading coefficient	Bridging coefficient	Lamella number
Crude oil / synthetic seawater + 0.5 wt.% AOS C14-16	<**1**	**2**	**1-2**	**96**	**8**

After we reach steady-state in an experiment, we start to prepare the core for the following experiment. To achieve an oil saturation greater than will be achieved with the subsequent experiment we stop gas injection but continue injection of surfactant solution at 0.001 ml/min to prevent oil moving upstream. We inject at least 3 ml of oil (at 0.05 ml/min), more than one pore volume of the three downstream sections. This experimental procedure allows us to investigate the steady-state behaviour of pre-generated foam in the presence of crude oil at various oil fractional flows and initial oil saturations.

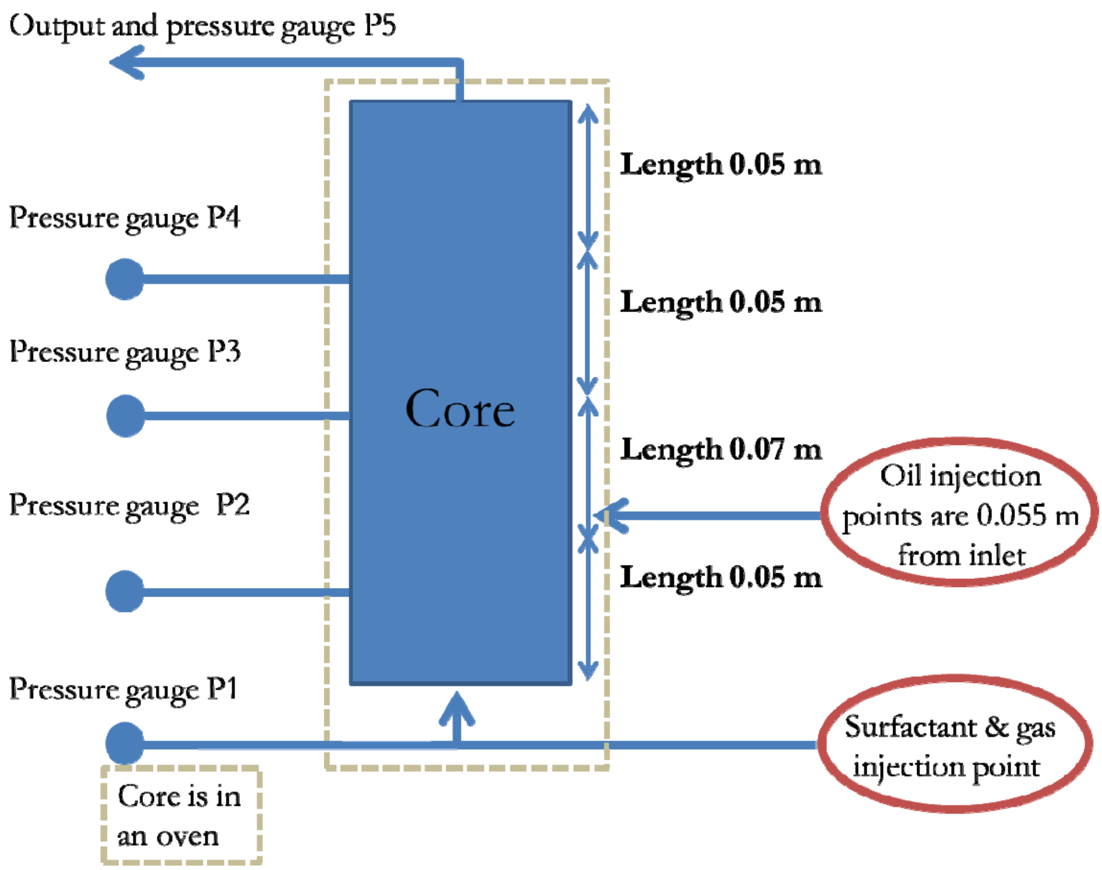


Figure 1 *Schematic of the apparatus used for this experiment. Note that there are two oil-injection points 0.055 m from the main inlet on opposite sides of the core. (Only one is shown here to avoid clutter.)*

Results and discussions

In each section of the core we calculate the "apparent viscosity" using the pressure gradient over that core and assuming single-phase flow. We define the dimensionless apparent viscosity as the ratio of apparent viscosities observed with pre-generated foam in the presence of oil to the apparent viscosity observed in section 2 in the absence of oil.

AOS foam and crude oil

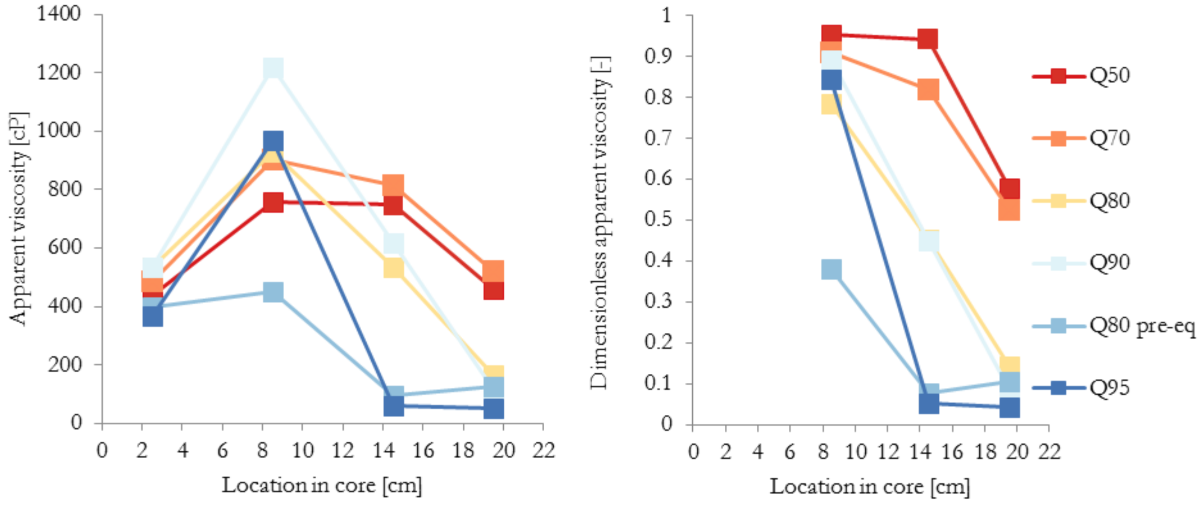
Figures 2A and B show the dimensional and dimensionless apparent viscosities, respectively, as a function of position along the core, for different foam qualities with AOS surfactant. AOS foam progressively weakens after it comes into contact with crude oil. Higher-quality foams experience a steeper and greater decline in apparent viscosity over the length of the core than lower-quality foams. The decline is most rapid with surfactant pre-equilibrated with the crude oil. However, apparent viscosity at the end of the core is similar for foam with pre-equilibrated surfactant (126 cP) and with surfactant which hadn't previously been in contact with oil (167 cP). Figure 3 shows apparent viscosity as a function of foam quality in the different sections of the core. It also shows the apparent viscosity observed in three-phase co-injection experiments, where the oil, surfactant solution and gas are injected from the same port, with a total velocity superficial velocities of 6.8 ft/day. Compared to the other reported experiments here, the three-phase co-injection experiments were conducted with the same materials and set-up, except with a shorter core (0.17 m vs. 0.22 m). The apparent viscosities are calculated over a section starting 5.25 cm from the inlet to 5.25 cm from outlet of the core. As foam propagates through the core, the apparent viscosity gradually decreases. We speculate that, in a sufficiently long core, apparent viscosities with pre-generated foam and oil would approach those with three-phase co-injection. It is unclear why apparent viscosity increases in the last section of the core with pre-equilibrated foam (Figure 2), as we did not observe this in any other experiments.

These results are consistent with the results of Schramm and Novosad (1990), who showed that foam lamellae in micromodels can travel some distance with oil droplets in them before rupturing. This indicates that pre-generated foam that comes into contact with oil in a porous medium does not necessarily collapse instantaneously, and can travel some distance on the core scale.

Aarra and Skauge (1994) and Kristiansen and Holt (1992) conducted similar experiments to these, where they pre-generated AOS-foam with qualities 65% - 95% outside their core and injected the foam into a core with crude oil at a residual saturation. As we do, they observed decreasing apparent viscosity along the length of the core for foam qualities between 65% and 95% in the presence of oil. Their results, together with ours, show that the impact of crude oil on pre-generated foam is a function not only of oil saturation and fractional flow, but also a function of foam quality.

Surfactant A foam and crude oil

Figures 4 and 5 show the apparent viscosity of foam with surfactant A in the absence of oil and of pre-generated foam in the presence of oil, respectively, over the length of the core. Similar to the experiments with AOS, the apparent viscosity decreases progressively after the first contact of the pre-generated foam with the crude oil. However, unlike the experiments with AOS, an abrupt increase in apparent viscosity is observed as the pre-generated foam first contacts oil. Figures 4 and 5 show that the apparent viscosity observed at first contact of oil and 40%-quality foam increases with an increasing fractional-flow of oil from 0 to 10%. We believe that the increase in apparent viscosity at first contact with oil reflects the decrease in relative permeabilities in three-phase flow and emulsion generation. Emulsion was observed in the core effluent. After first contact, a steeper decrease in apparent viscosity occurs with 10% oil fractional flow than with 1%. This is consistent with observations in microfluidics by Schramm and Novosad (1990), who showed that foam is weakened by oil droplets carried in the foam lamellae. Greater oil fractional flow means there are likely to be more oil droplets carried by the foam to destabilize it.



A B

Figure 2 *Left: apparent viscosity [cP] over the length of the core for different foam qualities with AOS. Right: dimensionless apparent viscosity [-] over the length of the core for the same experiments. All experiments were conducted with 0.1% oil fractional-flow.* Q50*: 50% foam quality, etc.* Pre-eq*: surfactant solution pre-equilibrated with oil.*

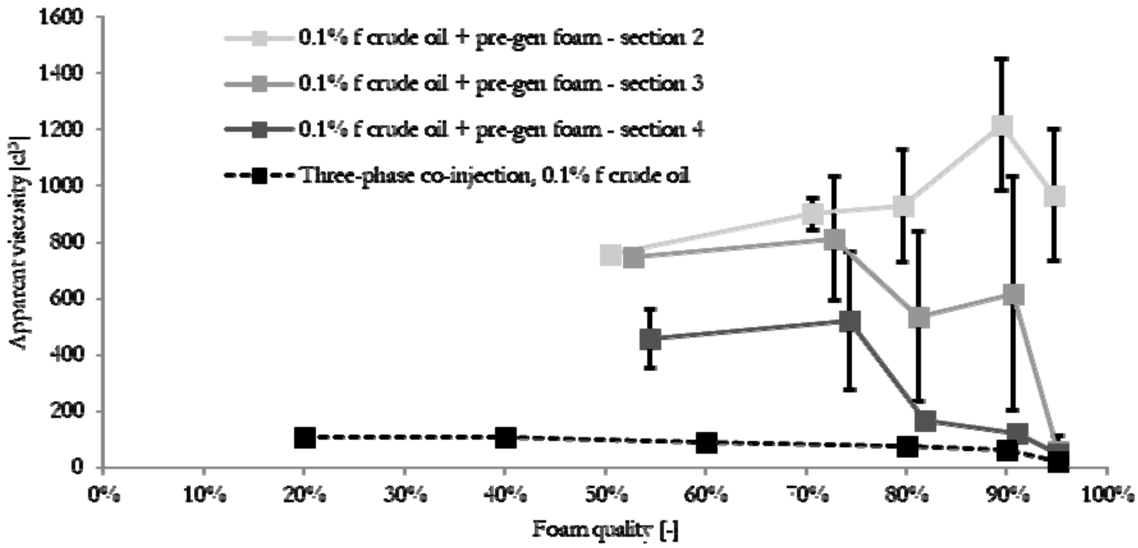


Figure 3 *Apparent viscosity as a function of foam quality for pre-generated foam in contact with oil in different sections of the core, compared to three-phase co-injection.* 0.1% f crude oil*: 0.1% injected fractional flow of crude oil.*

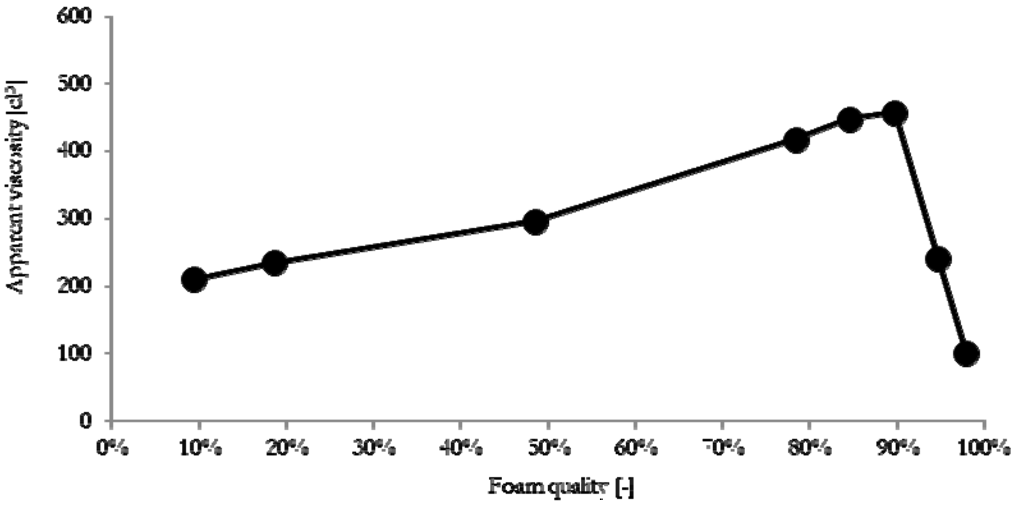


Figure 4 *Surfactant-A foam apparent viscosity as a function of foam quality, in the absence of oil, in the third section of the core.*

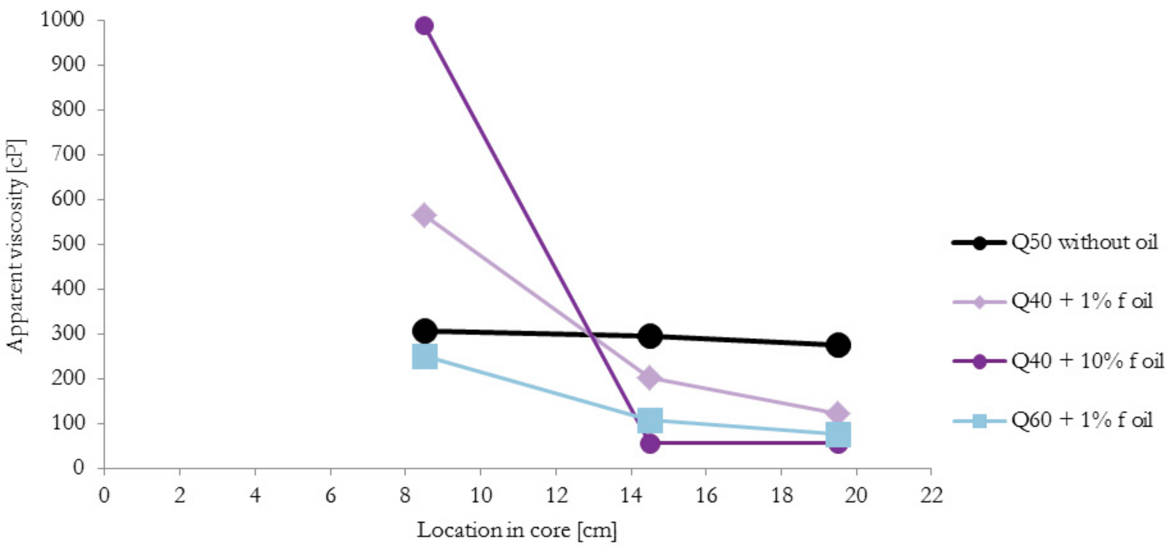


Figure 5 *Apparent viscosity of pre-generated foam with surfactant A and oil over the length of the core.* Q50*: 50% foam quality, etc.* f*: fractional flow of oil in injected fluids.*

Conclusions

We present a novel experimental approach to investigating the impact of oil on pre-generated foam with controlled oil flow rate. This approach allows one to investigate the weakening of pre-generated foam by oil as a function of distance travelled. Separate oil injection allows generation of foam without oil in the same porous medium before first contact with oil. The relatively narrow core diameter ensures rapid contact between foam and injected oil.

Pre-generated foam progressively weakened in presence of crude oil after first contact. The apparent viscosity can decrease by more than a factor four over a distance of 0.15 m. We speculate that in a sufficiently long core the pre-generated foam in contact with oil would gradually weaken until reaching the same apparent viscosity as with three-phase co-injection. Surprisingly, with surfactant A there is an increase in apparent viscosity as foam first encounters the crude oil, before progressively

weakening. We believe this reflects reduced gas and water relative permeabilities in three-phase flow, and possibly emulsification of oil in water.
Lower-quality foams propagated for a somewhat longer distance in the presence of oil than higher-quality foams, indicating that lower-quality foams are less susceptible (or less rapidly susceptible) to weakening by crude oil. (Distances in all cases are of course very short on a field scale.) Based on our experiments with 80% foam quality, we speculate that foam made with surfactant pre-equilibrated with the crude oil propagates for a shorter distance in presence of oil than foam made with surfactant that hasn't contacted oil before.

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