Pore-scale dynamics of foam flow in porous media

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5.4 Summary and conclusion ................................................................. 130
5.5 References ..................................................................................... 132

Chapter 6: Summary and conclusions ............................................... 137
Applicability of this research ............................................................ 138
Future work ....................................................................................... 139
Abstract

Abstract of thesis submitted by Mohammad Javad Shojaei for the Degree of Doctor of Philosophy and entitled “Pore-scale dynamics of foam flow in porous media” on 1\textsuperscript{st} September 2019.

Understanding the dynamics of foam flow in porous media is of great importance to many industrial processes such as soil remediation, CO2 sequestration, and enhanced oil recovery. The efficiency of the foam-liquid displacement depends on several parameters relating to the surfactant properties, boundary conditions, and the transport properties of the porous media. Thus, it is essential to understand the dominant mechanisms controlling foam flow in porous media.

In this dissertation, several parameters such as the surfactant properties, external conditions for instance gravitational effect, the pore size of porous media and the aperture variation of the fracture have been shown to influence the dynamics of foam flow in porous media. The obtained results revealed the adverse effect of fluid separation by gravity segregation and fingering of the gas phase into the foam bank at high flow rates on the efficiency of the foam displacement in porous media. However, our results showed pore size of porous media has a stronger influence on foam stability compared to the effect of type of oil. Also, it was found that there is no meaningful correlation between the stability of oil in bulk-scale to pore scale. The obtained results in fractured media showed that fracture wall roughness strongly increases the foam’s apparent viscosity and shear rate. Moreover, foam bubbles traveling in regions of larger aperture exhibit larger velocity, size, a higher coarsening rate, that are subjected to a higher shear rate. Additionally, in this dissertation, the effect of the synergy between different surfactant types and nanoparticles on the stability of foam was investigated.
The results reported in this dissertation shed new insight into the behavior of foam in porous media. The results of this dissertation have been published in 3 peer-reviewed journal papers with another one under review.
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Dedication

To my parents Zahra and Hossein, and my sister and brother Susan and Mohammad Kazem, and my cutest nephews Armin and Artin!
Acknowledgments

Firstly, I would like to express my sincere gratitude to Dr. Nima Shokri, who by his unrivaled support has guided me through this thesis. I am grateful for his kindness, mentorship, and relentless commitment to my academic progress. I have been extremely blessed to work with such a serious yet very friendly and supportive supervisor.

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Finally, and most importantly, I would like to thank my entire family especially my parents who have sacrificed a lot for me to reach this position. I am very grateful for their unconditional love and support.
Chapter 1: **Introduction: Foam Flow in Porous Media**

Understanding the dynamics and behavior of foam flow in porous media is an important topic which is relevant in various industrial applications such as in the soil remediation, CO2 sequestration, enhanced oil recovery. The foam flow dynamics in porous media are strongly influenced by the properties of the surfactant solutions, the external conditions, and the properties of the porous media. Thus, it is vital to understand the important parameters and mechanisms controlling the foam flow behavior under a given boundary condition.

1.1 Foam

Foam consists of a gas phase made discontinuous by the thin liquid films called lamellae, which can profoundly reduce the mobility of gas [1, 2]. The viscosity of foam could be up to 1000 times higher than their constituents (surfactant and gas) that makes it a desirable fluid for fluid displacement [3, 4].

Three main mechanisms of foam generation in porous media are snap-off, lamella division, and leave behind [5, 6]. Snap off happens subsequent of capillary pressure reduction in pore throats and accumulation of liquid [7]. Snap off is a repetitive process, and the generated foam bubbles usually have the size of pore throats. Lamella divides when a foam bubble greater than pore size approaches a branching point in porous media [8]. Lamellae leaves behind when two gas bubbles approach a pore body by converging of two bubbles in the downstream of the pore [8]. Foam flows in porous media in a continuous phase or discontinuous phase [7]. Foam flows continuously when gas goes through the porous media without interruption by lamella. In discontinuous flow, gas is transferred as a chain of gas bubbles which are separated by lamella [9].
Another important aspect of the foam flow in porous media is how to have a stabilized foam. Gas diffusion, capillary coalescence, and the detrimental effect of oil are three main mechanisms of foam coalescence in porous media [10, 11]. Gas diffuses between two adjacent gas bubbles with different sizes from the small bubble with high capillary pressure to large bubble with low capillary pressure. In the capillary suction mechanism, lamella breaks as its thickness pass a critical value. Lamella thickness is controlled by fluid exchange into and out of lamella [12]. At high capillary pressure, the liquid is back to the plateau border from lamella and coalescence occurs when the thickness thin to a critical thickness [13]. The detrimental effect of oil on foam stability is another factor that destabilizes the foam [14].

Despite the advances toward a complete understanding of the foam flowing in porous media, there is still a need to contribute to the fundamental aspects of the mechanism that determines foam flow dynamics under a given boundary condition. Such information will be useful to accurately control the process of flow displacement.

1.2 Foam models

Almost all foam models change the property of gas and assume the property of the liquid phase remains constant. During the flow of foam in porous media, the gas phase could be trapped through the stationary lamella, and subsequently, the mobility of the gas phases decreases. The extent of gas trapping in porous media depends on flow rate, pore geometry, and pore size distribution, liquid phase content, and bubble size. Also, as gas bubbles move through the porous media, the lamella around the gas bubbles have contact and friction with the pore surface, which causes another source of pressure drop and mobility reduction. There are two types of models for simulation foam flow in porous media named population-balance model and implicit-texture model. The Population-balance model deals explicitly with foam bubble size, while the implicit-texture model implicitly considers the effect of foam on apparent
viscosity through a mobility reduction factor. These models did not consider the impact of gravity segregation on foam generation and propagation inside the porous media. Moreover, in fractured porous media, the effect of aperture variation of fracture on the apparent viscosity of foam and foam coarsening has not reflected in these models that we studied those effects experimentally in this work.

1.3 Definition of key parameters and concepts

As this thesis is paper-based, we go through some of the critical parameters and concept that was used in the following chapters.

**Foam quality**: Foam quality is the volume fraction of gas in the foam network that can be calculated by dividing the flow rate of gas to total flow rate (flow rate of gas + flow rate of liquid) i.e. $\frac{q_g}{q_g + q_l}$

**Capillary number**: Capillary number is a dimensionless number that represents the relative effect of viscous force to the capillary force which define as $\frac{V \mu}{\sigma}$. Here V is the flow rate of foam, $\mu$ is the viscosity of foam, and $\sigma$ is the interfacial tension between displacing fluid and displaced fluid.

**Apparent viscosity**: The apparent viscosity at a given flow rate was calculated using Darcy’s law when the system reaches to steady-state (no further change in pressure drop), i.e. $\mu_{app} = \frac{K \Delta P}{q L}$. Here, K is the permeability of porous media, $\Delta P$ is the pressure drop across the model, $q$ is the flow velocity, and $L$ is the length of the micromodel.

**Permeability**: Permeability is the ability of a porous media to transmit fluids, usually measured in darcies or milli-darcies. In our experiments, we calculated it through the Darcy equation by
flowing water at different flow rates and the measured the pressure drop. The average value was selected and reported.

**Porosity**: Porosity is the percentage of the volume within porous media that can contain fluids. For a model, we saturate the model with water and measure its volume. Then the porosity was calculated by dividing the measured volume to the total volume.

**Plateau border**: In a foam network, the Plateau border is the junction area where three films intersect.

### 1.4 Experimental set-up and image processing

In all chapters, experimental tools such as Hele-Shaw cell, Vosges sandstone fracture, micromodel, and glass bead were employed to study foam flow and foam behavior at different boundary conditions. In some of these experiments, we injected pre-generated foam, and in some others, in-situ foam generation was used for placing foam inside the media. Pre-generated foams were created by simultaneous injection of surfactant and gas into a foam generator fitted with a sintered glass disc (Scientific Glass, UK) with a pore size distribution between 40 and 60 μm. While, in-situ foam generation achieved by injection of gas and surfactant inside the porous media through different mechanisms of snap-of, lamellae division, and leave behind depending on the flow rate and properties of porous media. In all set-up, we connected pressure transducers to the inlet and outlet (in some experiments, the outlet was connected to the atmosphere) to measure the pressure drop along the system to calculate the apparent viscosity of foam. Also, we placed a camera at the top of the system to monitor the flow of fluids inside the media. Gas and liquid injections were controlled by a mass flow controller connected to a PC and high precise pump, respectively. More details of these experimental set-ups were given
in each chapter. ImageJ and customized MATLAB codes were used for image segmentation and obtaining the desired data from the recorder image. To distinguish between the different fluids inside the porous media, firstly, we have the model wholly saturated with displaced fluid. We could distinguish between the displacing fluid and the grain that can be done by two main ‘peaks’ in the gray value histogram of each image. The first peak specifies displaced fluid while the second peak characterises to grains. A threshold for distinguishing between these two peaks was calculated through the histogram of the pixel values of the model where the derivative of the gray value changed from negative to positive. Some further modifications were done by ImageJ, to track the interface between the displacing fluid and displaced fluid at the desired time steps.

1.5 Aims and objectives

Motivated by the importance of the application of foam in various industrial applications, the key objectives of the present thesis were to describe:

1. How boundary conditions such as flow rate and gravitational segregation influence foam flow behavior in porous media.

2. How the properties of porous media or fractured porous media such as the pore size distribution or aperture variation of fracture influence the foam flow behavior.

3. How additives such as nanoparticles affect the stability of foam bubbles.

To address this, a series of experiments were conducted under various boundary conditions to study foam behavior.
1.6 Thesis overview

**Chapter 1** provides a brief introduction about foam and its relevance in key industrial applications.

**Chapter 2** is about the effect of fingering of highly mobile gas and gravitational effect on foam flow in porous media. This chapter was published in “Industrial & Engineering Chemistry Research - ACS Publications”.

**Chapter 3** is about the investigation of the effect of oils with varying chain length and pore size of porous media on the stability and displacement efficiency of foam in porous media. This chapter was published in “Industrial & Engineering Chemistry Research - ACS Publications”.

**Chapter 4** is about the effect of the aperture variation of fracture on the dynamics of foam flow in fractured porous media. This chapter was published in “Journal of Colloid and Interface Science - Elsevier”.

**Chapter 5** is about the effect of the synergy between nanoparticle and surfactants with different surface charges on foam stability. This chapter was submitted to RSC Advances for possible publication.

**Chapter 6** consists of a summary of the research undertaken and reviews the conclusions reached.
1.7 References


Chapter 2: Foam flow investigation in 3d printed porous media: fingering and gravitational effects

This chapter has been published in Industrial & Engineering Chemistry Research - ACS Publications, 2018, 57, 7275-7281. The objective of this work was to study the effect of fingering of highly mobile gas within the foam bank and gravity effect on foam flow behavior in porous media. We performed a comprehensive series of foam injection experiments in both horizontal and vertical orientations in a micromodel porous media in the presence of oil. The porous media was designed with the Rhinoceros CAD software package and printed with an acrylic-based material (acrylic oligomer) using a high-resolution Polyjet 3D printer (Objet 30 pro, Stratasys, United Kingdom). A high-resolution camera was used to visualize the dynamics of foam flow in porous media as a function of time. The recorded images were analyzed using in-house codes developed in MATLAB and ImageJ software. The findings of this research suggest flow rate and gravity segregation influences the dynamics of foam front displacement.

In horizontal orientation, lamella generation and mobilization were too low at the capillary number below $10^{-6}$. However, increasing the flow rate improved the rate of foam generation and displacement efficiency, but gas fingering into the oil bank had an adverse effect on the displacement efficiency at a very high flow rate. In vertical orientation, segregation of gas and surfactant was dominant at a gravity number higher than $10^{-2}$. Increasing flow rate led to increasing foam generation in the mixed zone and addressed gravity segregation, but gas fingering appeared to have a negative effect on displacement efficiency at high flow rate likewise to horizontal orientation. These findings delineate the significant adverse impact of gas fingering and gravity segregation on the foam performance, which is a step towards understanding the foam flow behavior in porous media.
Foam flow investigation in 3D printed porous media: Fingering and gravitational effects

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2.1 Abstract

Flow in porous media investigations have shown foam injection have a higher sweep efficiency compare to gas injection. However, fingering of highly mobile gas into the foam bank and separation of fluids (gas and surfactant) resulted by gravity segregation can influence the performance of foam injection project. To the best of our knowledge, this phenomenon has not been investigated experimentally in the literature. In this study, foam injection experiments have been performed in a model oriented in a horizontal and perpendicular orientation with respect to gravity using also different flow rates. High resolution imaging tools were utilized to record displacement process of oil by gas/surfactant/foam. The recorded images enabled us to monitor gas fingering and foam flow dynamics at pore scale. The obtained results highlighted the adverse effect of fingering of highly mobile gas into the foam bank and fluids separation by gravity segregation in the performance of foam project.

**KEYWORDS:** Foam flow in porous media, Gas Fingering, Gravity segregation, 3D printing technology, Pore-scale visualization
2.2 Introduction

Displacement of fluids with gas and water is a common practice in many industrial applications such as soil remediation, enhanced oil recovery (EOR) and CO2 sequestration. Gravity segregation due to the density difference between displaced and displacing fluids divides the porous medium into three zones I) override zone where only the phase with the lower density exists, II) underride zone where only the phase with the higher density exists and III) the mixed zone where both phases exist simultaneously\textsuperscript{1}. This selective movement of fluids inside the porous media causes unstable displacement that influences the reservoir performance\textsuperscript{2,3}. Foam which is a discontinuous gas phase separated by thin liquid films called lamellae can decrease mobility ratio between displacing and displaced fluids and address gravity segregation\textsuperscript{4-6}. Foam modifies mobility ratio in two ways: first, the relative permeability of the displacing fluid ($K_{rD}$) decreases by trapping gas in porous media, and second, by increasing the effective shear viscosity of the displacing fluid ($\mu_{rD}$)\textsuperscript{7}. Increase in apparent viscosity by foam comes from three contributions: (1) surface tension gradient created when surfactant foaming agent migrates from the front of the bubbles and accumulates at their back, (2) the thin liquid slugs between bubbles, and wall and bubbles, and (3) resistance to deformation of air bubbles pass through the porous media that have smaller size than foam bubbles\textsuperscript{8}. Foam forms inside the porous media by three mechanisms leave behind, snap-off, and lamellae division. Leave behind is the dominant mechanism of foam generation at lower flow rates. As gas invades into a media saturated with surfactant, the lamellae are left behind the gas\textsuperscript{9}. Snap off mechanism is more important at high flow rate and can reduce the mobility of foam more significantly in comparison to the leave behind mechanism. Gas bubble expands as it moves through a pore throat to a pore body causing a decrease in capillary pressure and a pressure gradient in the liquid phase. Consequently, liquid accumulates in the pore throat and if the capillary pressure
is large enough the liquid finally snaps off the gas bubble\textsuperscript{10}. Lamellae division is similar to
snap off and occurs at high flow rates. As a pre-existing lamellae approaches a branch point in
porous media it divides into several lamellae\textsuperscript{11}. Foam flows in porous media as a continuous
phase or discontinuous phase\textsuperscript{12}. Continuous flow occurs when gas goes through porous media
without interruption by lamella. In discontinuous mode, gas is transferred as a chain of gas
bubbles that are separated by lamella.

Foam can be placed in the reservoir by pre-generated foam injection, co-injection of gas and
surfactant and surfactant-alternating-gas (SAG) injection. Surfactant must be used as the liquid
phase to stabilize lamellae. Researches showed SAG injection in which alternating slugs of a
surfactant solution and gas are injected into the reservoir is the optimum method for foam
placing into the reservoir\textsuperscript{13-15}. It reduces the contact of gas and water in surface facilities. More
importantly, foam weakens as the gas displaces water from the near well-region and the
injectivity of gas increases and the possibility of reservoir fracturing decreases\textsuperscript{5,16}. Holt and
Vassenden\textsuperscript{6} showed foam injection resulted in higher segregation length (i.e. a longer distance
over which segregation occurs as a result of gravity) than gas and water. They showed that the
following equation which was proposed by Stone\textsuperscript{1} and Jenkins\textsuperscript{17} can be used for calculating
segregation length ($L_g$) in SAG injection process (the distance over which segregation occurs
as a result of gravity):

$$L_g = \frac{Q}{K(\rho_w-\rho_g)gD\gamma_{rt}m}$$  \hspace{1cm} (1)

where $Q$ (m$^3$/s) is the total volumetric injection rate of gas and liquid, $K$ (m$^2$) is the vertical
permeability of the porous medium, $\rho_w$ and $\rho_g$ ($kg/m^3$) are liquid and gas density respectively,
$g$ (m/s$^2$) is the gravity acceleration, $D$ (m) is the thickness of the porous medium, and $\gamma_{rt}m = \frac{K_{rw}}{\mu_w} + \frac{K_{rg}}{\mu_g} (1/ Pa.s)$ is the total relative mobility of the mixed gas-liquid zone. Here $K_{rw}$ and $K_{rg}$ are
relative permeability of water and gas respectively, and $\mu_w$ (Pa.s) and $\mu_g$ (Pa.s) are the viscosity of water and gas respectively. Shi and Rossen$^5$ indicated high value of gravity numbers (e.g. ratio between viscous and gravity forces) defined as $N_g = \frac{\Delta \rho g}{\nu_p}$ promote gravity segregation in SAG injection process. Here $\nabla p$ (Pa) is the pressure gradient, $\Delta \rho$ (kg m$^{-3}$) is the density differences between fluids and $g$ (m s$^{-2}$) is the gravity acceleration. Some other researchers studied the effect of gravity segregation in SAG injection process$^{18-22}$. However, they did not consider the effect of fingering of highly mobile gas into the foam bank in their studies. Recently, Farajzadeh et al$^{23}$ showed in a simulation study that the fingering of highly-mobile gas into the foam bank may be unavoidable and causes instabilities in a foam injection process. This fingering can also distort the foam front, even when favorable mobility control creates in foam front. To the best of our knowledge, there is no experimental study to support these findings or refute them. 

In this work, fingering of highly mobile gas into the foam bank and gravity segregation effects on fluids separation were studied in a foam injection process using a 2D micromodel system at a wide range of the injection rate.

2.3 Experimental Considerations

2.3.1 Design and fabrication of porous media

Following the procedure described by Osei-Bonsu et al.$^{24}$, the porous medium used in this research was designed with ‘Rhinoceros’ CAD software package for 3D illustrations. The pore network was created from a Voronoi diagram consisting of 660 polygons. In a polygon plane with specific number points, each polygon contains exactly one generating point, and every point in a given polygon is nearer to its generating point than to its other neighbors.
Voronoi diagrams can be used to design homogenous and heterogeneous microfluidic and micromodel network that was used in many theoretical and numerical studies in the field of porous media and also commonly used in the foams literature\textsuperscript{25-27}. The model was populated with a random length pore throat size distribution ranging from 0.3 to 0.5 mm. The pore throat size can be defined as the radius of a circle fitting in the narrowest space that connect two adjacent pore bodies together. Figures 1 (a), (b) and (c) show the top view of the porous medium, a zoomed portion of the model and the pore throat size distributions of the model, respectively. The dimension of the printed matrix was 110 mm x 50 mm x 0.25 mm. The model was oil wet and the porosity and permeability of the model were 39.4 % and 10.6 Darcy, respectively. The stereolithographic (STL) file of the CAD model was printed with an acrylic based material (acrylic oligomer) using a high resolution Polyjet 3D printer (Objet 30 pro, Stratasys, UK). The top of the model was sealed with a Plexiglas plate to prevent flow over the grains. Furthermore, two perforations (1 mm diameter) at opposite ends of the porous medium were placed to serve as the inlet and outlet.

**2.3.2 Fluid properties and experimental procedure**

In each run of the experiment, the printed porous medium was saturated with Isopar V (Brenntag, UK) referred to as ‘oil’ hereafter. The oil was stained red in order to enhance the visual contrast. The surfactant solution used for foam generation was prepared from a 1:1 blend of sodium dodecyl sulphate and cocamidopropyl betaine (2% active content) with 0.25M NaCl solution. Osei-Bonsu et al. \textsuperscript{28} showed that this surfactant combination was tolerant to the presence of oil under our experimental conditions (see Osei-Bonsu et al. \textsuperscript{28} for properties of oil and surfactant used in this study). The surfactant solution and nitrogen were injected using a syringe pump (Harvard Apparatus, PhD Ultra) and a mass flow controller (Bronkhorst, UK).
Surfactant and gas met before the model and flowed into the model as intermittent slugs of surfactant and gas.

A high-resolution digital camera (Teledyne DALSA Genie) controlled by a computer was used to acquire images of the displacement process at regular time intervals. The model porous medium was placed adjacent to a light box to improve the illumination of the captured images. The recorded images had a resolution of 2560 x 2048 pixels with 8 bit gray levels resulting in the pixel size of 40 microns.

To understand the effect of fingering of high mobile gas into the foam bank and gravity segregation on fluids separation, we conducted experiments in horizontal and vertical orientations in a printed porous medium. In all experiments, foam was generated in-situ by intermittent injection of gas and surfactant slugs at six flow rates of 1, 5, 10, 20, 40 and 80 ml/hr. The fraction of surfactant in injection fluids was 15% of the total volume injected in all experiments. Each run of the experiment was repeated at least three times to ensure the reproducibility of the data. The error bars in the following figures represent the variability in the obtained results for each kind of experiments.

### 2.3.3 Image analysis

The recorded images were analyzed using in-house codes developed in MATLAB to distinguish the oil, grains (solid phase) and the injected fluids (see Osei-Bonsu et al.24 for details of the segmentation algorithm). Additionally, Image J software was used to determine the number of oil blobs due to the fragmentation of the oil phase. Figure 1 (d) and (e) illustrate a typical recorded image and its corresponding segmented image.
Figure 1 (a) Top view of the printed model used in our study. The upper and lower part of the model is referred as Zone A and Zone B in the following analysis. (b) Magnified image of pores to better illustrate the patterns of pores/grains in the printed porous medium. (c) Pore throat size distribution of the printed porous medium. (d) A typical image recorded during oil displacement by foam. Dark grey represents oil. (e) The corresponding segmented image of the phase distributions presented in (d) with white, black and red representing foam (or escaping gas and surfactant), oil and grain respectively.
2.4 Results and discussion

2.4.1 Effects of gas fingering and gravity segregation on foam displacement efficiency

Figure 2 presents oil recovery in the case of horizontal and vertical orientations at different pore volume injected under different injection rates. The recovery factor is defined as the fraction of oil initially in place that is produced during the injection process after a given number of pore volumes have been injected.

According to the Figure 2, three distinct flow regimes are detectable in both vertical and horizontal orientations depending on the applied injection rate. The characteristics of each flow...
regime are discussed in the following. For better understanding the nature of each flow regime, phase distribution and pressure drop corresponding to each flow regime are presented in Figure 3.

![Figure 3 Phase distribution in horizontal and vertical orientations at different flow rates.](image)

Figure 3 Phase distribution in horizontal and vertical orientations at different flow rates. (a), (d) and (g) correspond to the horizontal orientation and (b), (e), and (h) corresponds to the vertical orientation. (c), (f) and (w) illustrate the measured pressures in the case of horizontal and vertical orientation at the flow rate of 1, 20 and 80 ml/hr, respectively.

### 2.4.2 Horizontal orientation

Applying low injection rate (1 ml/hr) impacted lamellae generation and mobilization and subsequently displacement efficiency. Visual inspections at this flow regime showed limited rate of lamellae generation. Lamellas were created by leave behind mechanism and snap-off and stayed stagnant. According to Rossen and Gauglitz\(^2^9\) a minimum pressure gradient required for lamellae generation and mobilization that was not achieved initially at this flow regime. It
was observed gas tended to be trapped behind lamellae in some point until the pressure drop per lamella built up and passed the threshold for mobilization. After mobilization, the pressure drop of the model decreased and lamella destruction occurred when the moving lamellae met the oil phase. The fluctuations in the recorded pressures observed in Figure 3 (c) are due to the unsteady state nature of the displacement process (i.e. lamella generation leads to increase the pressure and lamella mobilization and coalescence leads to pressure reduction). Capillary numbers (e.g. ratio between viscous and gravity forces, $Ca = \frac{\mu \cdot \text{v}}{\sigma}$) were calculated for each set of experiments in Table 1. Here $\mu$ (Pa.s) is the viscosity of the injected fluids (due to most of the injected fluids was gas, viscosity of gas was used in the calculations), $\text{v} \left(\frac{\text{m}}{\text{s}}\right)$ is the total superficial velocity of the injected fluids, and $\sigma \left(\frac{\text{N}}{\text{m}}\right)$ is the surface tension between gas and surfactant. Low value of capillary number at low flow rate in horizontal orientation is associated with low rate of lamellae generation and mobilization.

Table 1. Capillary numbers for the experiments conducted at different flow rates.

<table>
<thead>
<tr>
<th>Flow rate (ml/hr)</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4 x 10^-6</td>
</tr>
<tr>
<td>5</td>
<td>7.2 x 10^-6</td>
</tr>
<tr>
<td>10</td>
<td>1.4 x 10^-5</td>
</tr>
<tr>
<td>20</td>
<td>2.9 x 10^-5</td>
</tr>
<tr>
<td>40</td>
<td>5.8 x 10^-5</td>
</tr>
<tr>
<td>80</td>
<td>1.1 x 10^-4</td>
</tr>
</tbody>
</table>
The limited rate of lamellae generation and mobilization and the existence of lamellae destruction resulted in establishing a weak foam in the model. Figure 4 shows low value of apparent viscosity at low flow rate associated to limited rate of foam generation. Full oil recovery achieved after 10 PV injections and the residing oil displaced mostly by gas and surfactant instead of foam. High rate of lamellae generation and mobilization was observed after 6 PV of injection as the pressure gradient increased and the oil saturation decreased. After adequate fluids injection, the whole model was saturated with foam bubbles. According to table 1, this flow regime is corresponding to capillary numbers lower than about 1.0 x 10^{-6}.

Figure 4 The relationship between apparent viscosity of foam and flow rate after 4 PV of injection process.

The second flow regime occurred when the pressure gradient is large enough to produce fine textured foams generated mostly by snap-off mechanism and lamella division. The rate of lamellae generation and mobilization was large enough to make strong foam as can be seen in Figure 4. The gradual increase in the pressure drop and less pressure fluctuations in Figure 3 (f) confirmed strong foam generation. Fingering of the gas phase through the foam bank was however observed in this flow regime such that a continuous gas phase was formed inside the model. In addition, gas released from foam coalescence fingered through the oil phase in front
of it and created some isolated oil blobs as can be seen in Figure 3 (d). In this flow regime, full oil recovery from the porous medium was attained after approximately 2.5 PV of injection.

At high flow rates, the displacement efficiency of foam injection decreased again as can be seen in Figure 2 (a) and Figure 3 (g). This is due to that at higher injection flow rate, more volume of gas fingers and subsequently more escaping gas occurred as can be seen in Figure 5. Visual observations also showed the volume of foam that existed as continuous phase increases by increasing flow rate. This continuous gas phase eventually fingered through the oil phase. Fingering more volume of gas caused instability in the displacement process and decrease in displacement efficiency. It may be expected that this gas fingering is due to dry-out effect of foam at 85 foam quality. It can be said the dry-out effect is not relevant in our system with rather larger pores. Also, Kofi Osei-Bonsu et al.²⁴ used the same surfactant and a porous media quite similar to what we used in our study and found the foam quality corresponds to the critical capillary pressure was 98. Therefore, we can be sure that in our system, it is presumably the presence of oil (rather than the dry out effect) which is what helps to destabilise foam. Complete oil displacement was occurred after about 3.5 PV of injection at 80 ml/hr flow rate.

Figure 5 (a) and (b) show phase distribution for 20 and 80 ml/min gas flow rate respectively in horizontal orientation.

2.4.3 Vertical orientation
Similar to the horizontal orientation, three distinct flow regimes were observed in the case of the vertical orientation. The first flow regime includes the lower end of injection rates (from 1 ml/hr to 5 ml/hr). Complete segregation of gas and surfactant was the dominant characteristic of this flow regime as depicted in Figure 3 (b). As Shi and Rossen proposed \(^5\) large values of gravity number imply gravity segregation. Here gravity number \((N_g = \frac{\Delta \rho g}{\rho P})\) was calculated for different flow rates after 1 PV injection in Table 2 for the experiment conducted in vertical orientation.

Table 2. Calculated Gravity number for the experiments conducted at different flow rates in vertical orientation after 1 PV injection.

<table>
<thead>
<tr>
<th>Flow rate (ml/hr)</th>
<th>(N_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1.5 \times 10^{-1})</td>
</tr>
<tr>
<td>5</td>
<td>(2.7 \times 10^{-2})</td>
</tr>
<tr>
<td>10</td>
<td>(7.3 \times 10^{-3})</td>
</tr>
<tr>
<td>20</td>
<td>(4.3 \times 10^{-3})</td>
</tr>
<tr>
<td>40</td>
<td>(2.4 \times 10^{-3})</td>
</tr>
<tr>
<td>80</td>
<td>(1.45 \times 10^{-3})</td>
</tr>
</tbody>
</table>

At low flow rate, flow rate was not large enough to provide a proper mixing zone for foam generation. Upon entering the model, gravity segregation occurred resulting from the density differences between the fluids: gas flowed upward (Zone A) while the surfactant flowed downward (Zone B) in the model. Therefore, oil was displaced predominantly by gas in Zone
A and by surfactant in Zone B. The upper and lower part of the model is referred as Zone A and Zone B as depicted in Figure 1 (a). Complete oil recovery was achieved after 16 PV owing to the adverse impact of the high gravity segregation on fluids separation. Foam generation was started after 12 PV of injection mostly by leave behind mechanism. After many pore volume fluids injections, the whole model was saturated with foam. Based on Table 2, high gravity segregation occurred at gravity number more than 1.0 x 10^{-2}.

The second flow regime corresponds to the intermediate injection rates. According to equation (1), increasing flow rate leads to longer mixed zone and thus more foam generation and increase in apparent viscosity of foam as depicted in Figure 4. Segregation length $L_g$ can be estimated by combining Darcy’s law with equation (1) which leads to $L_g = \left( \frac{\Delta P_{\text{Horizontal}}}{\Delta P_{\text{Hyd}}} \right) \left( \frac{W \cdot D \cdot L}{L} \right)$ that $W$, $D$ and $L$ are the width, thickness and length of the porous medium. The hydrostatic pressure ($\Delta P_{\text{Hyd}} = \rho g W$) across the model porous medium with $W=50$ mm in height gives rise to an approximate pressure of 4 mbar. Assuming a horizontal pressure drop of 100 mbar (Figure 3 (f)), the segregation length will be in the order of 3 mm. The recorded images showed that the foam generation mostly occurred at this segregation length followed by foam propagation to other parts of the porous medium as illustrated in Figure 3 (e). Beside foam generation in the mixed zone, the movement of gas to Zone A and surfactant to Zone B was observed. The accumulation of surfactant in Zone B provided suitable condition for generating lense in Zone B by leave behind mechanism.

The third regime in the case of vertical orientation corresponds to the higher injection rates. In this flow regime, foam was generated in the mixed zone. However, similar to horizontal orientation, fingering of high volume of gas had adverse effect on foam displacement as can be seen in Figure 3 (h). Although, higher flow rates helped with addressing the effect of gravity segregation, but displacement efficiency decreases due to gas viscous fingering.
2.4.4 Quantitative analysis on foam saturation

The analysis presented above highlighted the adverse effect of gas fingering and fluids separation by gravity segregation on foam bank saturation. Our recorded images of oil displacement by foam in porous media enabled us to measure the area of porous media saturated by foam. Figure 6 (b) illustrates foam saturations at different flow rates after 1.2 PV injections for both horizontal and vertical orientations. Foam saturation was calculated by dividing the area occupied by foam to the total area of the pore space. The recorded images were segmented to calculate the area covered by the foam bubbles. A typical example of the segmented image is illustrated in Figure 6 (a). The solid blue line in Figure 6 (a) indicates the foam front. The white color to the right side of the foam front corresponds to the gas phase escaping out of foam due to gas fingering or the coalescence of foam bubbles by oil which was not included in the calculation of foam saturation.

Figure. 6 (a) A typical segmented image used for calculating the saturation of foam. Red, black and white indicate the grains, oil and foam (and escaping gas) respectively. This image
corresponds to the case of 10 ml/hr injection rate in the horizontal orientation. (b) Relationship between the flow rate and foam saturation after 1.5 PV injection of gas and surfactant solution for the horizontal and vertical orientation. The error bars indicate the standard deviation over 3 repeat measurements.

In the horizontal orientation, after 1.2 PV injection and when the injection rate is low (first flow regime), due to low rate of lamellae generation and mobilization and existence of lamellae destruction there was no foam and hence foam saturation was zero. Then foam saturation increased in the second flow regime (the intermediate stage) to about 75 percent as foam generation by snap off mechanism increased. In the third flow regime, the saturation of foam influenced by gas fingering and decreased to about 25 percent.

In the vertical orientation, the saturation of foam was zero in the first flow regime (when the injection rate is low) due to complete segregation of gas and surfactant. In the second flow regime, the effect of gravity segregation decreased by increasing flow rate leading to increasing foam saturation (around 50 percent) followed by the third flow regime (when the injection rate is high) where the saturation of foam decreases to about 15 percent resulted from gas fingering.

2.4.5 Effects of the injection rate and gravity segregation on oil entrapment

Our results indicated that gas fingering and fluids separation by gravity segregation has significant impact on the oil entrapment and spatial distribution of the oil blobs during foam flooding in porous media. Using the recorded images, we computed the number of disconnected oil phase in Zone A and Zone B (defined in Figure 1) with the results presented in Figure 7.
Figure 7 The relationship between the number of trapped oil blobs in Zone A and Zone B in (a) horizontal and (b) vertical orientation, respectively. The legend indicates the applied injection rates.

Figure 7 (a) shows the oil blob distribution through the horizontal model porous medium is almost homogenous with nearly similar number of isolated oil blobs distributed in Zone A and Zone B (defined in Figure 1). However, this is not the case when the porous medium is placed vertically with most of the blobs trapped within Zone A (i.e. the upper part of the porous medium). As already illustrated, during injection through the vertical oriented porous medium, gas and surfactant solution moved to Zone A and Zone B, respectively due to the gravity
segregation. Since the viscosity contrast between gas and oil is greater than viscosity contrast between surfactant and oil, Zone A is more prone to fingering and formation of isolated oil blobs. One can add to this the contribution of the fraction of gas escaping from Zone B toward Zone A due to the gravity.

2.4.6 Dynamics of foam displacement influenced by the gravity

In addition to the number and distribution of oil blobs, oil recovery and foam saturation, gravity segregation influences the dynamic of foam front displacement. As an example, Figure 8 qualitatively shows the patterns and dynamics of foam front displacement at 10 ml/hr injection rate in the case of horizontal and vertical porous medium.
Figure 8 The interface (white line) between invaded and uninvaded area at the equal pore volume injected intervals of 0.2 in the porous medium placed (a) horizontally and (b) vertically. The interface propagates from left to right. The first interface at the left side of the figure corresponds to 0.5 PV injected. The injection rate in both cases was fixed at 20 ml/hr. The dashed line is the boundary between Zone A and Zone B. The insets illustrate typical examples of phase distribution at upper, middle and lower parts of the porous medium.

During oil displacement in horizontal orientation, the front had a convex shape up to 1.2 PV injection followed by a gradual evolution into a concave front. The morphological evolution of
the front is likely due to variations in the foam texture along the front. The insets in Figure 8 illustrating typical phase distribution patterns at the upper, middle and lower regions of the porous medium placed horizontally shows that the bubble density in the middle region is higher than upper and lower regions. Higher bubble density decreases the mobilization of foam bubbles in the middle section of the model thus diverting the flow to the upper and lower regions which causes the change in the morphology of the front.

In vertical orientation, foam front adopted an ‘S’ shape after 1.7 PV injections. This is due to the gradual increase of the bubble density in the middle region and that a small part of Zone A caused high flow resistance (this is once again due to high bubble density) and changed flow orientations to other parts of the model. Subsequently, the foam front propagation in Zone B was faster than Zone A due to the presence of more liquid in Zone B (higher saturation) compared to Zone A as a result of the gravity segregation which led to a decrease in flow resistance in that region.

2.5 Summary and conclusions

This study set out to investigate the effects of fingering of highly mobile gas into the foam bank and gravity segregation on fluids separation on the performance of foam injection process. A comprehensive series of foam injection experiments were conducted in both horizontal and vertical orientations in a porous medium fabricated by 3D printing technology in the presence of oil. In horizontal orientation, obtained results showed lamellae generation and mobilization was not large enough at capillary number below $10^{-6}$ to generate strong foam. Increasing flow rate led to generation of fine textured foam by snap off mechanism. However, gas fingering into the oil bank influence foam injection process and had adverse effect on displacement efficiency at higher flow rate. In vertical direction, complete segregation of gas and surfactant occurred at gravity number higher than $1.0 \times 10^{-2}$. A rise in flow rate led to increase in foam
generation in the mixed zone and addressing gravity segregation. However, gas viscous fingering at high flow rates resulted in a decrease in foam sweep efficiency. These findings highlight the significant adverse impact of gas fingering and gravity segregation on foam performance echoing the necessity to include these phenomena when investigating flow displacement by foam in porous media.

Acknowledgment

We would like to acknowledge the UK Engineering and Physical Sciences Research Council (EPSRC) to provide the PhD studentship for Mohammad Javad Shojaei. We thank Mr. Andrew Evans, Mr. Ian Small and Mr. Craig Shore for their assistance with the experimental setup.
2.6 References


Chapter 3: **Foam stability influenced by displaced fluids and by pore size of porous media**

This chapter has been published on the Journal of Industrial & Engineering Chemistry Research - ACS Publications, 2019, 58, 2, 1068-1074. The specific objective of this study was to delineate the combined effect of the hydrocarbon chain length and pore size of porous media on the foam stability and its displacement efficiency. We performed a systematic set of experiments in Hele-Shaw cell and glass bead pack with different pore size. Most remarkably, our findings suggest there was no meaningful correlation between foam stability and type of oil when pore size of porous media changes. Stability of foam and displacement efficiency was lower in the presence of the lighter, less viscous oil (Isopar G) in the Hele-Shaw cell and also in the coarse and medium porous media. In contrary, foam showed to have higher displacement efficiency in the presence of the lighter oil in the fine bead pack. The finding of this study suggests that the pore size of the porous medium has a much more important influence on the foam displacement efficiency in the presence of oil than the type of oil itself.
Foam stability influenced by displaced fluids and by pore size of porous media

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3.1 Abstract

Stability of foam in the presence of hydrocarbons is a crucial factor in the success of its use in various applications in porous media, such as soil remediation and enhanced oil recovery (EOR). It is generally believed that shorter chain hydrocarbons with lower density and viscosity have more detrimental effect on foam stability than longer chain hydrocarbons. However, it is still unclear how pore size of porous media could influence this behaviour. The main objective of the present study was to investigate the combined effect of the hydrocarbon chain length and hence the hydrocarbon’s viscosity and pore size of porous media on the foam stability and its displacement efficiency. To this end, a systematic series of experiments was conducted using an empty Hele-Shaw cell and glass bead packs with different pore size. The results in the Hele-Shaw cell and with coarse and medium beads revealed that the lighter, less viscous oil (Isopar G) was more destructive to foam. However, the results in the fine glass bead pack experiments, did not correlate well with this finding. In the fine bead pack, foam appeared to have higher displacement efficiency in the presence of the lighter, less viscous oil. Generally, our results suggest that the pore size of the porous medium plays a more important role on the foam displacement efficiency compared to the type of oil.

Keywords: Foam stability, Foam–oil interaction, Hele-Shaw cell, Pore size of porous media
3.2 Introduction

Foam is a dispersion of a large volume of gas in a small volume of liquid in which gas bubbles are made discontinuous by thin liquid films called lamellae.\textsuperscript{1-3} Foam has a higher apparent viscosity compared to its constituents (gas and surfactant solution) making it a desirable mobility control agent for fluid displacements.\textsuperscript{4-8} The stability of foam is one of the key determining parameters that influences the displacement efficiency of foam flooding projects.\textsuperscript{9-12} Many studies have been conducted to investigate and describe the factors controlling foam stability. Derjaguin and Landau \textsuperscript{13} introduced the theory of film disjoining pressure ($\Pi$), dependent upon film thickness ($h$), to explain the stability of a foam film. The disjoining pressure ($\Pi$) is defined as the sum of the repulsive positive electrostatic force per unit area ($\Pi_{\text{EL}}$) and attractive negative van der Waals force per unit area ($\Pi_{\text{VW}}$) according to classical DLVO theory.\textsuperscript{14} At stable equilibrium, the disjoining pressure of a lamella film is equal to the capillary pressure, i.e., $\Pi = \Pi_{\text{EL}} + \Pi_{\text{VW}} = P_C$ which is the pressure difference across the interface of gas and surfactant (solution). Adsorption of surfactant to the gas liquid interface results in an increase of the repulsive positive electrostatic force ($\Pi_{\text{EL}}$) which stabilizes the lamellae. In contrast, attractive van der Waals forces destabilize the thin film. If $\Pi_{\text{EL}} > \left| \Pi_{\text{VW}} \right| + P_C$ foam will be stable, conversely, if the negative component is stronger ($\Pi_{\text{EL}} < \left| \Pi_{\text{VW}} \right| + P_C$), the foam will be destabilized.\textsuperscript{15,16}

The effect of oil on foam stability has been explained by three mechanisms, i.e. entry of oil droplet into gas-liquid interface\textsuperscript{17,18}, spreading of oil on the gas-liquid interface\textsuperscript{19}, or formation of an unstable bridge across the lamella which destroys it.\textsuperscript{20} So called, entry, spreading and bridging coefficients can be determined using interfacial tension and the signs of these coefficients are believed to govern stability. However, several studies showed that this theory may not be able to offer an accurate prediction of foam stability.\textsuperscript{21-25} For example, Hadjiiski et
al. 25 concluded that, no direct relation exists between the entering and spreading coefficients and the detrimental effect of oil on foam stability. Instead, they demonstrated that there is a strong correlation between the destabilising effects of oil and the magnitude of an “entry barrier” that is formed on the pseudoemulsion films between the oil droplet and the gas-liquid interface. The suppression of this oil drop entry is dictated by various surface forces (e.g. electrostatic, van der Waals) which are influenced by the physiochemical properties of the oil. The effect of oil on foam stability within porous media is still not very well-understood as the presence of the medium adds another layer of complexity with only limited data available on foam-oil interactions in porous media. Indeed, although foam stability has been generally studied using bulk foam tests, several studies have demonstrated that bulk foam stability does not necessarily correlate with the stability of that same foam during flow in porous media. Dalland et al. 26 reported there is no correlation between the stability of foam in bulk systems and porous media. Jones et al. 27 found apparent viscosity of foam in porous media is correlated to stability of foam in the bulk system in the absence of oil, but this correlation was not confirmed in the presence of oil. Osei-Bonsu et al. 28 showed stability of foam in bulk does not correlate with its effectiveness in oil displacement in porous media. Although the vast majority of research suggest that shorter chain hydrocarbons have more destabilising effect on foam than longer chain hydrocarbons with the shorter chain systems being typically less viscous 24, 29-32, it is still unclear how the combined effect of pore size and hydrocarbon chain length and viscosity of the oil influence foam stability in porous media. The primary objective of this study was therefore to investigate the influence of the bead size (i.e. pore size) on foam stability during oil displacement in porous media composed of packed bead. In addition, we investigate the influence of the viscosity of oil on foam stability during the displacement of oil by foam in a glass bead system and in a Hele-Shaw cell.
3.3 Material and methods

3.3.1 Experimental Setup and Procedures

In order to investigate the effects of the various parameters on foam stability in bulk and porous media, two types of experiment were conducted. In both experiments a transparent cell (either empty or packed with glass beads) was initially saturated fully with oil/water. Pre-generated foam was then injected at a constant rate to displace the oil/water from the cell. The resulting displacement dynamics and foam-oil interactions were recorded using a camera. In the following more details about the experiments are described.

3.3.1.1 Hele-Shaw Cell Experiments

A customised Hele-Shaw cell (32 × 20 cm dimensions) was fabricated to investigate the dynamics of oil displacement by foam in bulk scale. The Hele Shaw cell was similar to the one described in Osei-Bonsu et al.\textsuperscript{33} It consisted of two transparent glass plates fixed to a Plexiglas frame. During the experiment these glass plates were clamped together, with a gasket sandwiched in between to create a small gap (1 mm) in which the two fluids (oil and foam) could flow. This gasket dictated the size of the gap (assuming the gasket was incompressible) and prevented any leakage of fluid around the edges of the cell. The top plate/frame contained a hole with a screw fitting at either end to allow fluid to move in and out of the cell creating a flow path. A pressure transducer (Thurlby 30V-2A, with 0.3% accuracy and working range starting from 1 mbar) was installed at the inlet of the Hele-Shaw cell. The outlet of the experiments was connected to the atmosphere. Prior to each round of experiments, the surfactant solution was mixed again for 10 minutes using the magnetic stirring device, ensuring consistency between experiments. Before assembling the Hele-Shaw cell, each glass plate was cleaned thoroughly on both sides to
remove any residual oil or deposits stuck to the surfaces. Initially the plates were washed using a combination of water and laboratory detergent. A cloth was then doused in Isopropanol and used to wipe the surfaces in order to dissolve and remove any residual oil, ensuring the results could not be influenced by these residues. It was vital that care was taken when handling and cleaning the glass plates to ensure the surfaces did not become scratched, maintaining a smooth and consistent flow path for oil and foam. This was also important for obtaining clearer images of the flow. The Hele-Shaw cell was then placed over a light box and the camera positioned above it using a clamp stand. The light box was used to ensure there was sufficient light to capture clear images showing a highly defined foam network, with individual lamellae easily distinguishable. The cell was then filled with oil using a syringe connected to a tube which was temporarily attached to the entrance of the cell. A metal tap was attached to the outlet to allow fluid to flow out of the cell and into a collection beaker. During this oil injection, the Hele-Shaw cell was tilted (at the outlet end) to ensure any gas bubbles trapped in the oil escaped at the exit. Once the oil reached the collection beaker (i.e. the cell was full) the outlet tap was closed. Two identical syringes (diameter of 19.3 mm) were filled with equal measures of surfactant solution (initially filled to 20 ml mark) and placed onto the syringe pump, where they were clamped in place. The corresponding syringe diameter was programmed into the pump and the rate was set according to the desired foam quality (see later calculations). A tube was attached to each syringe and then connected to the foam generator, with the tubes arranged either side of the gas inlet. The gas cylinder was connected to the foam generator via the mass flow controller. Initially, the gas cylinder outlet pressure was turned from 0 to 1 bar to introduce a gas supply. The FlowDDE program was opened on the lab computer and communication with the mass flow controller was initiated. FlowView was then used to control the gas flow rate. Both the gas and liquid flows were switched on simultaneously to begin generating foam. In this experiment the gas flow rate was kept constant at 2 ml/min. The flow rate of the
The surfactant solution was adjusted to 0.22 ml/min and 0.35 ml/min to produce the two different foam qualities chosen for this experiment – 90% and 85% respectively before the injection of foam into the system. Foam quality was calculated based on the equation \( f_g = \frac{q_g}{q_g + q_l} \) where \( q_g \) and \( q_l \) are gas and surfactant flow rates respectively. Each experiment was repeated at least three times to ensure the repeatability.

### 3.3.1.2 Experiments with Glass Beads

The cell packed with glass beads had a similar design to the Hele-Shaw cell described above. The gap size between the plates was 2 mm. This time, however, the two plates were fixed permanently in place using a number of screws fitted around the outside of the cell. This was necessary to allow glass beads to be packed into the cell sufficiently without damaging the glass plates. The inlet to this cell was very narrow to ensure that no glass beads could escape and potentially disrupt the packing. A fine metal mesh was fixed at the inlet of the model, again this was to prevent the glass beads from escaping and potentially disrupting the packing. Three different bead diameter ranges were used in this investigation: 1.25-1.55 mm, 0.50-1.00 mm and 0.15-0.21 mm. This enabled us to analyse the effects of grain/pore size of porous media on foam-oil interactions in porous media. The porosity of these three glass bead packings was approximately the same and equal to 35%, but the permeability was different and equal to 1100, 450, and 24 D, for coarse, medium, and fine systems respectively. The permeability of the glass beads were calculated by injection of water at different flow rate using the obtained pressure data and employing Darcy equation. The glass bead was preferentially wet by surfactant. The cell contained a pressure transducer port located above the entrance of the cell to allow pressure drop to be measured. Like the Hele-Shaw cell, this bead pack design allowed us to obtain a 2D visual description of foam-oil displacement dynamics.
At the beginning of each experiment the clean, empty cell had to be packed with glass beads. Initially, the cell was fixed vertically in place on the edge of the worktop using clamps, with the inlet in a downward-facing position. The inlet and pressure transducer port were temporarily blocked to prevent any fluid exiting the cell. The plate containing the outlet holes was removed to expose the outlet end of the cell. The cell was filled with oil (or water) and glass beads were then poured in, sinking to the bottom under gravity. The glass beads were inserted in stages, with compaction carried out using a metal ruler between each stage to ensure packing was as consistent as possible. Any excess oil that overflowed at the outlet was removed using a syringe. It was important that the same packing procedure (i.e. number of bead insertion/compaction stages) was used for each experiment to ensure that the porosities/total pore volumes were roughly the same (for experiments using the same bead size distribution). This ensured that packing inconsistencies did not distort any of the results and subsequent conclusions. Once the cell was packed, the detachable plate containing the outlet tubes was clamped to the outlet end of the cell. The glass bead pack was restored to its horizontal position and placed on top of the light box. The camera, which was connected to the lab computer, was then placed above the cell using a clamp stand. The precise positioning of the camera was adjusted by looking at the live field of view displayed by its supporting software, Capture, on the lab computer. A pressure transducer was attached above the entrance of the cell. In this experiment the outlet was assumed to be at atmospheric pressure so the pressure drop was taken as the gauge pressure at the cell entrance. A collection beaker was placed beneath the outlet tubes to collect any fluid exiting the cell during the experiment. In this experiment the displacements of oils Isopar V and Isopar G were investigated in glass bead packs at three different bead sizes. Besides the detrimental effect of oil on foam stability, capillary suction influences the stability of foam in porous media\textsuperscript{34}. Water displacement experiments with foam were performed at different pore size to see how capillary pressure influences foam stability.
The experimental procedure of these experiments were exactly the same as for oil displacement and just the type of fluid was changed.

In all the glass-bead experiments, the gas flow rate was the same as that used in the Hele-Shaw cell experiment (2 ml/min) and so the surfactant solution flow rate was set accordingly to achieve 85% foam quality before injection to the system. Each experiment was repeated at least three times to check the repeatability.

### 3.3.1.3 Foam Generation and Fluid Properties

To generate foam, air and aqueous surfactant solution were pumped simultaneously, at specified and well-controlled flow rates, through a foam generator. Surfactant solution was injected by the syringe pump (Harvard Apparatus, USA with ±0.35% accuracy and working range from 0.0001 µl/hr to 100 ml/sec) while a mass flow controller (Bronkhorst, UK, with ±0.5% accuracy and working range from 1 ml/min to 100 ml/min) was used to deliver accurate and precise gas flow rates from the gas supply cylinder. 33

The same surfactant solution (which forms the aqueous phase of the foam) was used in all experiments conducted in this investigation. This solution contained a 1:1 ratio of two different surfactants; Cocamidopropyl betaine (Cocobetaine) (The Soap Kitchen, UK, with 61789-40-0 CAS Number) and Sodium dodecyl sulphate (SDS) (Sigma, UK), each at 1% concentration (mass concentration) in a 0.1M NaCl aqueous solution. Osei-Bonsu et al.24 showed that this surfactant provides more foam stability than the surfactants taken individually under our experimental conditions with the viscosity and surface tension being equal to 0.35 Pa.s and 0.13 mN/m respectively. 24 Two different oils, both belonging to the same hydrocarbon family (Isoparaffins), were used in these experiments to investigate the influence of oil properties on foam stability. It was important that these oils were of a similar type so that specific oil properties could be compared. The oils used were Isopar V and Isopar G (Sil-Mid Limited,
UK); the former being the heavier and more viscous oil. Table 1 summarises the properties of these isoparaffin oils.

Table 1. Properties of the Isoparaffin Oils Used in these Experiments.

<table>
<thead>
<tr>
<th>Isopar</th>
<th>Carbon chain</th>
<th>Dynamic viscosity 25°C (Pa.s)</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>C14-C19</td>
<td>1.08</td>
<td>25.44</td>
</tr>
<tr>
<td>G</td>
<td>C10-C12</td>
<td>0.08</td>
<td>22.57</td>
</tr>
</tbody>
</table>

3.3.2 Image Processing

An automated monochromic camera (Dalsa Genie TS-2500) with a resolution of 2560 x 2048 pixels was used to capture high quality images of the foam evolution and oil displacement process over time. The captured images were processed and analysed using Image J software. The images were segmented and analysed each image sequence at a time (one experiment provided one image sequence). Initially, an image sequence was imported into ImageJ and the scale was set, converting the image pixel dimensions to a corresponding length in mm measured during the experiments. The horizontal dimension of 2560 pixels corresponded to a length of 228 mm. This enabled the software to calculate areas in mm² which therefore allowed us to calculate volumes of oil and gas (gap depth = 1 mm). The images were then segmented using the “Process>Find Edges” function which converted the images from greyscale to black and white. This allowed the software to detect lines, curves and boundaries within the images which represented individual lamellae (foam films), oil/gas and oil/liquid interfaces and the perimeter around the cell (edge of the gasket). The contrast and brightness were adjusted using the “Adjust>Brightness/Contrast” function to allow these lines to become more distinguishable to ensure the software was able to detect them during the analysis.
The foam stability during oil displacement in the Hele-Shaw cell was quantified by calculating the volume of the released gas. It was expected that the higher the foam stability, the smaller volume of gas released from the foam network during the course of the displacement. Typical examples of the segmented images are presented in Figure 1 showing the displacement of oil by foam in the Hele-Shaw cell (in the absence of glass beads). Figure 1 qualitatively shows that as the foam progresses through the cell, the volume of the released gas from the foam increases as a result of the detrimental effect of oil on foam stability.

Once gas was released from the foam network, it either accumulated ahead of the foam front or along the walls of the Hele Shaw cell. This gas had a tendency to accumulate and form larger gas bubbles that were easily distinguishable from foam bubbles in terms of shape and size. Certain criteria were used to distinguish between foam bubbles and escaped gas as a result of destabilization. The first criterion was that the released gas bubble had to be located ahead of the foam front or along the walls of the cell. The second criterion was that the gas bubble area had to be larger than 10 mm$^2$. This value was chosen after meticulously studying numerous images from a range of image sequences. It represented a bubble size larger than that of the usual generated foam bubbles with 0.4 mm typical diameter.

![Figure 1](image)

Figure 1. Two typical images taken at 100s time intervals showing the displacement of oil (Isopar G in this case) by foam in the Hele-Shaw cell at 85 % foam quality and 2 ml/min flow rate. The white colour in the image represents the gas and oil while the grey colour represents the lamellae.
3.4 Result and discussion

3.4.1 Effect of Oil Type on Foam Stability in Hele Shaw Cell

Figure 2 shows cumulative gas volume released (mm$^3$) from the foam network over time during oil displacement in the Hele-Shaw cell (in the absence of glass beads) at two different foam qualities (85 and 90%). The pressure drop of the system during the Hele-Shaw cell experiments was modest (less than 10 mbar) so that the compressibility effect of foam can be ignored.

![Figure 2](image)

Figure 2. The cumulative volume of gas released from the foam network over time during oil displacement in the Hele-Shaw cell. V and G in the legend represent Isopar V and Isopar G respectively and the numbers represent the foam qualities in percentage. The error bars (half the length) indicate the standard deviation over 3 repeat measurements.

Figure 2 demonstrates the influence of oil chain length (hence viscosity) and foam quality on the stability of foam in the presence of oil during Hele-Shaw cell experiments. It can be inferred from Figure 2 that more gas volume is released from foam during oil displacement at the higher foam quality (90%). This resulted in a final cumulative gas volume (at foam breakthrough point) that is approximately 66% higher for the higher foam quality for the same oil; a substantial difference. The higher the volume of gas released, the more the destabilisation of the foam by the oil. This implies that lamella rupture (i.e. coalescence) is much more prevalent at higher foam qualities. The comparison between foam qualities in the presence of Isopar V
(the more viscous oil) also follows the same trend as for the less viscous Isopar G and hence supports this interpretation. These results are in agreement with previous research on the influence of foam quality on foam stability in the presence of oil.33, 35-37

There are several reasons to explain why lower quality foams exhibit a higher tolerance to the defoaming activity of oil. One of the main reasons is that both foam films and the Plateau borders between those films are thicker, relative to bubble size. At lower foam qualities, these thicker films are more capable of suppressing the penetration of oil into gas-water interfaces, a mechanism which often leads to film rupture.33 Thicker borders also ensure that there is a lower capillary suction pressure which means less liquid drainage within the films. Another possible reason for the increased stability at lower foam qualities is that the length of the foam films separating bubbles, in relation to total bubble perimeter, is lower meaning it is less probable that oil will enter the foam films in the first place and cause film rupture.

Figure 2 indicates that the lighter oil shorter carbon chain Isopar G tends to have a more detrimental effect on foam stability. In fact, the rate of foam coalescence (i.e. gas release) initially appeared to be very similar in the presence of both oils. However, as the experiments progressed and overall contact times between oil and foam increased, the rate of gas release from the foam in contact with Isopar G (lighter, less viscous) increased relative to Isopar V. A possible explanation for this is that as time progressed more of the lighter, less viscous oil was able to emulsify and form multiple smaller droplets that could be drawn up into foam films and potentially destabilise them. This can be attributed to the fact that less viscous oils emulsify more quickly which would consequently accelerate the rate of lamellas collapse in relation to the more viscous oil.38

The final cumulative volume of gas released in both experiments (85% and 90% quality) was approximately 30% higher in the presence of Isopar G than Isopar V. Comparing this to the effect of foam quality discussed in the previous section, a 5% increase in foam quality appeared
to have a much stronger influence on foam stability in the presence of oil than the differences between the two oils themselves (66% difference compared with 30%).

### 3.4.2 Effect of Type of Oil on Foam Stability in Porous Media with Different Pore Size

In contrast to the Hele-Shaw cell, it was challenging to measure the amount of gas released from the foam in the experiments with porous media. It is hypothesised that the gas released as a result of foam destruction was able to penetrate the glass bead-pack rapidly, forming gas channels connected to the outlet rather than accumulating ahead of the foam front in gas pockets. Accordingly, the area within the model occupied by foam (foam saturation) and the pressure drop across the glass bead pack were measured as an indication of foam stability and its efficiency for fluid displacement.

Figure 3 shows foam saturation, defined as the volume occupied by foam relative to total pore volume, and the pressure drop during the displacement of oil/water by foam in the porous media with different pore size. We can assume as the foam has higher stability, its saturation will be higher as the unstable foam decomposes to gas and surfactant.
Figure 3. (a), (b), (c) Foam saturation as a function of time during the displacement of water, Isopar V and Isopar G respectively (d), (e) and (f) Pressure drop vs time during the displacement of oil/water by foam at coarse, medium and fine sand pack beads respectively. The gas flow rate and foam quality were 2 ml/min and 85 % respectively at the inlet of the model. The error bars (half the length) indicate the standard deviation over 3 repeat measurements.

Figure 3 clearly demonstrates the destructive effect of oil on foam stability and its displacement efficiency in porous media. Saturation of foam and the pressure of the system are higher in the...
presence of water compared to oil when the other experimental conditions are the same. Moreover, Figure 3 (a) in the presence of water appear to show a significant difference in the behaviour of foam at different pore sizes as more time is needed to ensure that the foam saturates all the system as the pore size of the porous media decreases. This suggests that a significantly larger amount of foam was destroyed during water displacement in the finer glass bead pack due to capillary suction. In porous media, capillary pressure can be considered as the force per area required for squeezing a hydrocarbon droplet through a pore throat, working against the interfacial tension between oil and water. This capillary pressure is higher in smaller pores. Hence this increased capillary pressure have destabilised the foam to a greater extent, making foams films more susceptible to rupture as they attempt to force oil through tighter pore constrictions.\textsuperscript{34}

Figure 3 shows foam provided higher pressure drop as the pore size of the sand pack decreases. This is due to the lower permeability of finer sand pack. As the foam is in general a compressible fluid, it seems compressibility could influence the texture of the foam and its saturation. The texture of foam is generally determined by the porous medium in which it resides and the surrounding pressure. It follows that pre-generated foam (used in this investigation) is re-shaped and re-textured by the porous medium through which it is injected\textsuperscript{40}. Accordingly, we can expect foam would have higher foam quality in the upstream of the system compare to downstream as the outlet of the system is connected to atmosphere and the inlet of the system is influenced by the pressure upstream inside the porous media. Lower foam quality in the upstream has more liquid content that made it more tolerant to detrimental effect of oil and capillary suction. This help the system to increase its foam saturation as the time passed. The quality of pre-generated foam before injection into the model was 85 %. If we assume the gas phase of foam behaved as ideal gas, it can be expected that the rise in pressure could lead to the decrease in volume of gas based on the equation $\frac{P_2}{P_1} = \frac{V_1}{V_2}$. For example 500
and 1000 mbar increase in pressure, could change to 33 and 50 % change in gas volume that can decrease the foam quality to 79 and 74 % respectively.

Comparing Figure 3 (b) with (c) shows similar to the Hele-Shaw cell case, heavier oil (Isopar V) provide more foam stability in the medium and coarse bead system compared to fine beads. However, Figure 3 (b) shows the stability of foam in the presence of Isopar V is actually greater in the medium bead system compared to the coarse bead system whereas for Isopar G stability is greater in coarse bead systems compared to medium bead ones as Figure 3 (c) shows. Visual observations of displacement of oil by foam showed two fronts. The first front (further back) was the front of foam and second front (further forward) was the front of the escaped gas that resulted from foam coalescence. The second front was not effective to displace all the oil and there were some unswept oil areas. Visual inspections showed this unswept oil did not have a high detrimental effect on the foam for heavier oil in medium bead systems and the first front propagated effectively and achieved higher foam saturation. However, these unswept areas had a detrimental effect on foam for lighter oil (Isopar G) and delayed the formation of a strong foam bank in medium bead systems.

Figure 3 shows foam behaves significantly differently in fine bead packs as the type of oil changes. This difference is also manifested in the pressure drop curves in Figure 3 (f). This implies that for fine beads the foam was more effective to displace fluid in the presence of the lighter, less viscous Isopar G, which contradicts our original finding made during the foam displacement in coarse and medium beads and Hele-Shaw cell. It was observed that the released gas resulted from the detrimental effect of oil and capillary suction, fingered more in the low permeability medium. Accordingly, the subsequent injection of foam followed these preferential flow paths and produced from the outlet without propagation to the other parts of the system. As Figure 3 (b) shows foam in the fine glass bead packs was not able to propagate
across the whole of the cell during heavier oil displacement (Isopar V) due to the high level of viscous fingering.

3.5 Summary and conclusion

Oil displacement experiments were carried out in a Hele-Shaw cell and glass bead packs to investigate the combined effect of type of oil and pore size of porous media on foam stability and its displacement efficiency. The effects of foam quality studied in the Hele-Shaw cell showed conclusively that lower foam qualities result in formation of foam with an increased tolerance to the destructive effects of oil.

The type of oil appeared to have a strong influence on foam stability during oil displacement in the Hele-Shaw cell and porous media. Foam showed lower foam stability and displacement efficiency in the presence of the lighter, less viscous oil (Isopar G) in the Hele-Shaw cell and also in the coarse and medium porous media.

The effect of oil type in the fine glass bead experiment did not appear to correlate well with the trends displayed in the Hele-Shaw cell and coarser porous media. The fine bead pack actually demonstrated the opposite effect as the foam appeared to have higher displacement efficiency in the presence of lighter oil. Overall these results suggest that the geometry of the porous medium (i.e. average pore size) has a much more important influence on the foam displacement efficiency in the presence of oil than the type of oil itself.

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Notes

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3.6 References


Chapter 4: Dynamics of foam flow in a rock fracture: effects of aperture variation on apparent shear viscosity and bubble morphology

This chapter has been published in Journal of Colloid and Interface Science Volume 552, Pages 464-47. The objective of this work was to study the effect of aperture variation on dynamic of foam flow in a rock fracture. To do so, a comprehensive set of single-phase experiments was conducted in a replica of a Vosges sandstone fracture of well-characterized aperture map and a Hele-Shaw (i.e., smooth) fracture of identical hydraulic aperture. A high resolution camera was used to visualize the dynamic of foam flow and foam coarsening as a function of time. The results highlighted the strong effect of aperture variation on foam’s apparent viscosity and shear rate. Foam bubbles showed higher velocity, shear rate, bubble size and foam coarsening rate in the regions of larger aperture. These findings echo the necessity of considering fracture wall when predicting the pressure drop through the fracture and the effective viscosity, as well as in situ rheology, of the foam which could be useful in a variety of engineering applications.
Dynamics of foam flow in a rock fracture: Effects of aperture variation on apparent shear viscosity and bubble morphology

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4.1 Abstract

There has recently been renewed interest in understanding the physics of foam flow in permeable media. As for Newtonian flows in fractures, the heterogeneity of local apertures in natural fractures is expected to strongly impact the spatial distribution of foam flow. Although several experimental studies have been previously performed to study foam flow in fractured media, none of them has specifically addressed that impact for parallel flow in a realistic fracture geometry and its consequences for the foam’s in situ shear viscosity and bubble morphologies. To do so, a comprehensive series of single-phase experiments have been performed by injecting pre-generated foams with six different qualities at a constant flow rate through a replica of a Vosges sandstone fracture of well-characterized aperture map. These measurements were compared to measurements obtained in a Hele-Shaw (i.e. smooth) fracture of identical hydraulic aperture. The results show that fracture wall roughness strongly increases the foam’s apparent viscosity and shear rate. Moreover, foam bubbles traveling in regions of larger aperture exhibit larger velocity, size, a higher coarsening rate, and are subjected to a higher shear rate. This study also presents the first in situ measurement of foam bubbles velocities in fracture geometry, and provides hints towards measuring the in situ rheology of foam in a rough fracture from the velocity maps, for various imposed mean flow rates. These findings echo the necessity of considering fracture wall when predicting the pressure drop through the fracture and the effective viscosity, as well as in situ rheology, of the foam.

**Key words:** Fractured media, Foam flow, Aperture heterogeneity, Shear rheology, Bubble morphology
Fracture media are present in a wide range of geological media used for industrial applications including CO$_2$ sequestration, subsurface/soil remediation, and Enhanced Oil Recovery (EOR) [2-6]. In these applications, when injecting a displacing fluid in a reservoir containing fractures, channeling and preferential flow paths occur, which leads to low sweep efficiency [7-9]. The use of foams, which consist of gas bubbles separated by thin liquid films denoted as lamellae [10-12], has proven to be a potential solution to overcome these issues [13-16]. In particular, a high viscous pressure drop is produced through the foam-saturated fracture, diverting the flow to less permeable regions and thus improving oil recovery [17-20].

Foams are generated by three main mechanisms: snap-off, lamellae division, and leave-behind [21, 22], and can exist in either bulk or confined form [23]. “Bulk foams” are foams with individual bubbles which are considerably smaller than the characteristic length scale of the porous medium [24]. This type of foams can be classified into ball (or wet) foam and polyhedral (or dry) foam, depending on the foam bubble shape [25]. Polyhedral foam bubbles are more common at high gas volume fractions, while spherical foam bubbles form at low gas volume fraction [25, 26]. On the other hand, confined foams are produced when the characteristic length scale of individual bubbles is of the same order of magnitude or greater than, the characteristic length scale of the porous medium [27].

Predicting and controlling foam coalescence is a key factor for successful foam flooding projects. Chambers and Radke [28] proposed two main mechanisms of foam coalescence. The first one is capillary-suction, which results from the Lamellae’s expansion and contraction to conserve mass as they go out through constrictions in the porous medium. The lamellae thin and thicken in a sequence of squeezing-stretching and draining-filling events. This oscillation of the lamella thickness has a wider oscillation range at a higher gas flow rate and larger pore-
body to pore-throat aspect ratio [29], and can lead to lamella rupture. In this respect, Jimenez and Radke [29] stated that the capillary suction pressure increases with pore-body to pore-throat aspect ratio. The other mechanism stems from Ostwald ripening and occurs due to differences in gas pressure between neighboring bubbles of different sizes, due to Laplace law, which stipulates that the pressure drop across the interface is all the larger as the curvature ratio of the interface is smaller. That pressure difference results in gas diffusion from the smaller to the larger bubbles, and progressive vanishing of the smaller bubbles. According to Von Neumann’s law [30], the rate of change in bubble surface area depends on the number of neighbor bubbles, the surface tension of the liquid and the permeability of the porous medium. It is worth mentioning that whereas foam coarsening was extensively investigated in bulk systems, there is less evidence of this phenomenon in confined geometry [31], probably because the involved diffusive time scales are larger than the characteristic time of most laboratory experiments.

Foams can serve as efficient displacing fluids in porous media due to their specific rheological properties. A concept frequently used to characterize the rheology of foams is their apparent (or effective) viscosity, \( \mu_{\text{app}} \) (Pa.s). Knowing the foam’s apparent injection velocity (or specific discharge) \( q \) (m/s), defined as the ratio of the total volumetric flow rate of the foam to the cross-sectional area of the fracture \( S = w \times h_m \), with \( w \) being the width of the fracture and \( h_m \) (m) its mechanic (that is, arithmetic mean) aperture, the pressure drop \( \Delta P \) (Pa) through the fracture of length \( L \) (m), and the permeability \( K \) (m\(^2\)) of fracture, the apparent viscosity is the viscosity that must be used in order to be able to write a Darcy’s law for the foam flow [29]:

\[
\mu_{\text{app}} = \frac{K \Delta P}{qL} = \frac{h^2 \Delta P}{12qL} \tag{1}
\]

In the preceding equation, \( h = (12K)^{3/2} \) (m) is the constant aperture of a smooth fracture (parallel plate) generating the same pressure drop as the considered real fracture when a Newtonian fluid is injected at the same flow rate.
It is important to note that $\mu_{\text{app}}$ is not an intrinsic property of the foam: its value is usually observed to decrease as $q$ increases, which indicates a shear-thinning behaviour of the foam. Indeed, the foam bubbles tend to agglomerate at low flow rates, which impedes their relative movement, but are aligned and deformed in the direction of flow when the flow rate increases, resulting in a decrease in viscosity. Note however that the in-situ rheology of a foam in a porous medium whose characteristic pore size is on the same order as the typical foam bubble size, is not necessarily the same as that of the bulk flow of the same foam, since in the former case most friction occurs between the liquid films and the solid walls, while in the latter case viscous dissipation occurs mostly within liquid films between bubbles. In this regard, Hirasaki and Lawson [11] showed that the apparent viscosity of a foam is the sum of three contributions: (1) the flow resistance of slugs of liquid between gas bubbles (which results from viscous friction at the solid walls), (2) the flow resistance due to surface tension gradient between the front and rear of foam bubbles (3) and the resistance to deformation of foam bubbles as they pass through the pores. They considered both bulk foam flows and the flow of foam in porous media. They also showed that foam texture (i.e. the number of bubbles per unit area) is a key parameter controlling $\mu_{\text{app}}$. Some studies showed that foam behaves as a yield stress fluid [32-34]. After the stress passes a threshold, foam bubbles rearrange and flow like a viscous non-Newtonian fluid. Princen [35] and Hohler and Cohen-Addad [36] showed that the yield stress is inversely proportional to the bubble size in bulk and bubble scale.

The effects of aperture variations on the creeping (that is, laminar with $Re \ll 1$) flow through a rough fracture, in particular its departure from the ideal model of the flow through two perfectly smooth parallel palates [37], have been addressed extensively in the literature of the last 35 years [37-39]. Spatial variations of aperture result in flow channelling, which is all the larger as the fracture is more closed and as the correlation length between the facing fracture walls is larger [40]. Flow channelling usually coincides with a deviation of the hydraulic
conductivity of the fracture from that of the parallel plate of identical mechanical (mean) aperture. Surprisingly, this effect has up to now been largely ignored in most studies dealing with foam flow in rock fractures, with a few striking exceptions, which we present below. Indeed, relatively few studies on foam flows in fractured media are reported in the literature, and several of them neglect fracture wall roughness, considering Hele-Shaw cell fractures which consist of the space between two parallel plane walls. For example, Yan et al. [41] studied the flow of an aqueous foam in a Hele-Shaw cell fracture at ambient conditions, and showed how the gas fraction, mean bubbles size and ratio between the latter and the fracture aperture control foam displacement efficiency. They also showed experimentally, and evidenced theoretically, a diversion mechanism in which the foam tends to flow in thinner fractures rather than thicker fractures within a fractured medium. Osei-Bonsu et al. [42] also used a Hele-Shaw cell set-up analogous to a smooth fractures and investigated the link between foam quality, mean bubble size, mean flow behaviour and the foam’s apparent viscosity; they also measured the recovery factor of a silicon oil. The experimental and theoretical study by Jones et al. [43] provides detailed insight into how pressure drops develop in such smooth channels when the foam can be considered two-dimensional (a feature observed by Kovscek et al. in natural fractures [27], see below) due to friction at the Plateau border between the lamella separating bubbles and wall films The effect of surface roughness was also confirmed by Polden et al [45]. Buchgraber et al. [44] went one step further in addressing geometrical complexity, by considering both a constant aperture (Hele-Shaw) fracture, a checkerboard-like fracture with two different apertures of 20 and 40 micrometers, and a fracture possessing a three-level synthetic roughness, to study the effect of aperture variations on foam flow. They found that the geometry of the fracture can greatly impact foam generation mechanisms and foam texture. They visualize and analysed quantitatively the size distribution of bubbles in situ, but did not measure their velocities.
To our knowledge the first study to address foam flows in a realistic fracture geometry is that by Kovscek et al. [27], who studied the radial flow of an aqueous foam through a transparent replica of a natural rough-walled fracture at ambient conditions, and measured the pressure drop for various global flow rates and foam qualities [27]. They could characterize qualitatively the morphology of the bubbles in the fracture plane and in planes perpendicular to the fracture plane, evidencing the two-dimensionality of the foam under these conditions. But they did not obtain quantitative characterization of the flow from the visualization of the bubbles. Very recently, AlQuaimi and Rosen [46] performed very detailed flow experiments at ambient conditions in synthetic fractures made of roughened glass plates to study foam generation mechanisms and propagation, and found that fracture-wall roughness geometry played a major role in controlling the mechanisms of foam generation as well as the foam’s mobility. Note however that the geometries which they consider (roughened plates) does not correspond to the known geometry of fractures, i.e., geometries obtained from the fracturing of solid materials (rocks, metals, ceramics); in particular, AlQuaimi and Rossen’s geometries exhibit different spatial correlation properties than those of walls resulting from a fracturing process, and are much more akin to two-dimensional porous media than the latter.

Other studies have addressed fractured media at a scale larger than the scale of a single fracture. Haugen et al. [47] studied foam flow in a carbonate rock cores cut along a plane containing their axis with a saw, at ambient conditions, and found that using pre-generated foam greatly enhanced oil recovery by diverting the injected fluid from fracture to matrix. . Fernø et al. [48] performed foam flow experiments at ambient conditions in fracture networks consisting of fractured marble tiles. They measured the global rheology of the foam and performed qualitative analysis of bubble geometries some of the fracture. They also found that that foam improved sweep efficiency significantly and delayed gas breakthrough. Using a synthetic porous two-dimensional micromodel containing a parallel plate fracture in its middle,
Telmadarreie and Trivedi [49] examined the pore-scale phenomenology of heavy oil displacement by foam in fractured carbonate reservoirs at ambient conditions [49]. Their mostly qualitative analysis revealed that foam not only acts as a mobility enhancement agent, but also significantly increase heavy oil recovery from the oil-wet matrix. Gauteplass et al. [50] studied the mechanisms of foam generation in a porous microfluidic micromodel mimicking a sandstone geometry and characterized the role of snap off, evidencing that it also occurs at the boundary between fractures and the porous matrix.

In all the preceding studies addressing foam flow at the fracture scale, the only one to consider a realistic fracture geometry is the seminal paper by Kovscek et al. [27], but it addresses a radial flow (i.e., a point injection) for which the velocity decreases as the inverse of the distance to the injection point. The prime objective of the present research was to provide insight into the role of aperture spatial variations on the shear rheology of the foam, the foam bubbles size, and foam coarsening in a realistic fracture geometry under parallel flow conditions, with the additional knowledge of the bubble velocity field (following recent studies of foam flows in two-dimensional porous media [51, 52]), which has been measured in none of the earlier studies on foam flows in fractures. To do so, single-phase foam flow experiments were carried out using a replica of a Vosges sandstone fracture with well-characterised aperture map at several flow rates and different foam qualities. The results were compared with those performed by Osei-Bonsu et al. [42] in a Hele-Shaw cell of constant aperture equal to the hydraulic aperture of the Vosges fracture.

4.3 Materials and Methods

4.3.1 Experimental Setups and Procedure

The experiments were conducted by injecting pre-generated foam in a replica of a Vosges sandstone fracture with a length $L$ of 26.0 cm, a width $w$ of 14.8 cm, a mechanical (mean)
aperture $h_m$ of 0.86 mm and a hydraulic aperture $h$ of $0.500 \pm 0.005$ mm. The details about the fabrication of the replica can be consulted elsewhere [53, 54]. The aperture map of the fracture replica, which was obtained by Nowamooz et al. [55] by using an image processing procedure based on the attenuation law of Beer-Lambert, is presented in FIGURE 1(a). The minimum aperture is 0 (closed regions) and the maximum aperture 2.294 mm. This figure shows that the smallest apertures are located in the centre of the model, while the largest apertures are close to the inlet and the outlet. The probability density function (PDF) of the fracture apertures, shown in FIGURE 1(b), is peaked around 0.71 mm but not symmetrical, as a second smaller peak is seen around 1.13 mm. The power spectrum of one-dimensional profiles of the aperture map parallel to x (FIGURE 1(c)) exhibits a power law behaviour with a global exponent -1.6, which indicates long range spatial correlations along the aperture field. This so-called self-affine behaviour is characterized by the exponent of self-affinity (the so-called Hurst exponent $H$), such that the exponent of the Fourier power spectrum should be $-(2H + 1)$ [56]. Hence $H = 0.3$ here. The properties of aperture field of geological fractures are in large part inherited from those of the facing fracture walls which define them. In particular, the Fourier spectrum of the aperture field is expected to be self-affine with a Hurst exponent characteristic of the fracture surface topographies (which, for sandstone, is 0.5 [57]) at scales smaller than the correlation length between the two fracture walls, and to exhibit a lesser decrease at larger scales due to matching of the two walls at these scales [58, 59]. The measured aperture field is consistent with such behaviour if one considers that the correlation length is on the order of the fracture’s length. In addition, an inflection of the spectrum towards a -2 exponent is visible at the largest probed wave numbers (see FIGURE 1(c)). Similarly, the PDF of fracture wall topographies has been measured to be Gaussian [60], from which it follows that the aperture field should have a PDF that is not very different from a Gaussian. In our data (FIGURE 1(b)), a log-normal distribution which may be suggested by the asymmetry of the curve has been
ruled out by plotting the PDF of $\log(a)$, and so the hypothesis of a Gaussian distribution with an additional secondary peak is the most likely. The secondary peak could be due to chemical weathering of the minerals over long times.

FIGURE 1. (a) Aperture map of the fracture used in the present experiments (data obtained from Nowamooz et al. [55]). (b) Probability density function (PDF) of the aperture map. (c) The Fourier power spectrum of 1D profiles parallel to $x$, averaged over all profiles, exhibits a power law behaviour.

The foam was generated by simultaneous injection of gas and surfactant solution into a customised foam generator containing a sintered glass disc (Glass Scientific, UK) with a pore size distribution comprised between 16 and 40 µm. The foaming agent was prepared by adding a 1:1 blend of Sodium Dodecyl Sulphate and Cocamidopropyl betaine (2% active content) to
a 0.25M NaCl aqueous solution. A dual piston pump (Prep Digital HPCL pump, A.I.T., France) was used to inject the surfactant solution at controlled flow rate. The gas phase was air, injected from a pressurized cylinder in series with a mass flow rate regulator (Brooks Instrument 5850S, Serv’ Instrumentation, France). The generated foam was transferred to the models by means of a tube with 4 mm internal diameter and then injected through four ports regularly spaced across the width of the inlet to ensure uniform foam injection. A membrane-type differential pressure sensor (DP15 Variable Reluctance Pressure Sensor, Validyne, USA) was used to measure the steady-state pressure drop through the model during foam injection. The outlet of the model was connected to the atmosphere. A digital camera with a resolution of 2045 × 2048 pixels was used to capture the dynamics of the process. A light box was placed under the flow cells to improve the illumination of the captured images.

Two different series of fracture flow experiments were conducted in this study. First, pre-generated foams with different qualities were injected at a constant gas flow rate of 10 ml/min through the real fracture. The qualities of the injected foams were of 98, 95, 90, 85, 80 and 75% in each case. The fracture was saturated with air before injection of each foam. In these first series of experiments, the foam quality was varied by setting a different liquid flow rate while keeping the gas flow rate constant. Therefore, the total flow rate decreased with increasing foam quality. The second type of experiments aimed at assessing the effects of flow rate by injecting a single foam with a constant quality of 85% through the Vosges sandstone fracture at different gas flow rates: 10, 20, 30, 40, 50 and 60 ml/min. Each experiment was repeated three times to ensure reproducibility and possibly evaluate the uncertainty of the measurements. Error bars represent the standard deviation of the measurements over the three experimental runs performed under identical experimental conditions.

The results were compared to those obtained by Osei-Bonsu et al. [42] using a Hele-Shaw cell with uniform aperture of 0.5 mm size (equal to the hydraulic aperture of the real fracture) and
smooth surface. This allowed the identification of the impact of aperture variations on the foam flow. A customised Hele-Shaw cell with dimensions of $31 \times 20 \times 0.5$ cm was used by the latter authors, and the foam was generated by simultaneously pumping air and aqueous surfactant solution through a foam generator similar to the one used in the present experiments. The pre-generated foam was then delivered to the cell through a tube connected to a metal pipe junction, which was screwed to the inlet of the medium. Pressure transducers were also connected to the inlet and the outlet so as to measure the pressure drop throughout the Hele-Shaw cell.

At the end of the foam flood experiments in the real fracture, after the injection had been interrupted and once the pressure gradient along the fracture could be considered to have approached zero and foam bubbles to have become stagnant, the evolution over time of the size of the bubbles was recorded in different zones in order to assess the impact of the local aperture on foam coarsening.

Finally, another type of flow cell was used to characterize the bubble size distribution of the foams. Indeed, foams obtained with the same foam generator as in the rough fracture flow experiments were flown through a Hele-Shaw cell, that is, a parallelepipedal tank of thickness much 1 mm much smaller than its two other dimensions, and pictures of the foams were taken.

4.3.2 Image processing & segmentation

A combination of the open source image-processing program ImageJ [61], and of either custom-written MATLAB scripts or available MATLAB functions were used to segment and analyse the image sequences captured during the experiments. Two types of analyses were performed.

Firstly, the foams images taken in the 1mm Hele-Shaw cell were treated in order to measure the bubble size distribution of the foams, for the various foam qualities. The images were first thresholded and transformed into black and white pictures were the bubbles appeared white on
a black background (see figure 2(a)), then the equivalent diameter of all connected white regions in the images was measured as $d = (A/\pi)^{1/2}$ from their area $A$. We thus obtained the probability density functions for the bubbles’ apparent diameters. There are power laws (see figure 2(b)), except for the largest foam quality (0.98) for which we obtained an exponential distribution. The foam image appeared very different in the latter case, as compared to the others, so obtaining a different type of bubble size distribution was not surprising. For all images a range of small apparent diameters that were outside of the functional trend and corresponding to connected white regions with shapes very different from the circular shapes, were discarded in the analysis.

![Figure 2](image_url)

**FIGURE 2.** (a) Image of a foam of quality 85% in the Hele-Shaw cell (with 12535 bubbles). (b) Corresponding PDF for the apparent diameters of bubbles in (a), fitted with a power law of exponent -2.63. The smallest connected white regions, which fell outside of this distribution and had very non-spherical shapes, were removed from (a).

The bubbles whose apparent diameter is smaller than the HS cell’s thickness ($e = 1$ mm) can be considered to have real diameter equal to the measured apparent diameter, while those with an apparent diameter larger than 1 mm are squeezed between the top and bottom glass plates, so their real diameter (when unconstrained) is different from the measured apparent diameter. We have considered that the bubbles of apparent diameter three times larger than the confining
cell thickness had a cylindrical shape, and that their real diameter could therefore be estimated from the apparent diameter as $d_{\text{real}} = \left( \frac{3}{4} e \left( \frac{d}{2} \right)^2 \right)^{1/3}$. In the range of apparent bubble diameters between 1 and 3 mm we have considered a smooth monotonic transition based on a nonlinear combination between these two regimes. The obtained results do not depend much on the functional form taken for that nonlinear combination. Finally the average diameter for the foam bubbles was computed from the distribution. Given the fact that the distribution is a power law, it was obviously important to perform the measurement on a large population of bubbles.

Secondly, pictures or the foams flowing inside the rough fracture, taken at regular time intervals, were used to obtain maps of velocity vectors of the foam bubbles inside the fracture using PIV (Particle Image Velocimetry) analyses, which estimates local velocity by cross-correlating sub-regions of the images between two successive time steps. We used package PIVLab [62] in MATLAB, with a single interrogation size of 128×18 on the first pass, and 64×64 pixels on the second pass. The raw images were first applied a high pass filter of size 15 pixels (see figure 3(a-b)). The horizontal dimension of 2048 pixels corresponded to a length of 260 mm, hence one pixel corresponded to 127 µm in real space, about one order of magnitude smaller than the typical bubble size, but the PIV procedure provided a horizontal resolution of the velocity map of 16 mm. Note that the bubbles whose velocities were measured in this manner belonged to the top layer of bubbles, in contact with the upper wall of the fracture. For some subparts of the image, the filtered image did not contain any significant “dots” to be traced, so no velocity was measured in these regions (see figure 3(b-d)). It is in particular the case for four circular regions along the center line of the flow cell, where pressure sensors were installed.
FIGURE 3. (a) Raw image of the foam flowing through the fracture (flow rate 10 ml/min, quality 85%). (b) Filtered image (high-pass filter). (c) Velocity field obtained with a window size of 128 for the first pass, and 64 for the second pass. (d) Corresponding map of the velocity magnitude. The white regions in (c) are regions where the image contrast was not good image for the PIV to be successful. In (d) they have been filled by linear interpolation to the surrounding measured values, and the velocity map has been interpolated to match the original resolution.

4.4 Results and discussion

4.4.1 Dependence of the initial mean bubble size on the foam quality

From analyzing images of the foams in the Hele-Shaw cell as explained in section 2.2, we obtain the mean bubble size for the freshly-generated foams, that is, the initial bubble size for the foams that are being injected in the rough fracture. This initial mean bubble size increases monotonically with the foam quality (see figure 4 (a)) but only varies by 25% when the foam
quality varies between 80% and 95%. Between 95% and 98% the foam structure changes sharply and consequently the increase in mean bubble size is much more abrupt.

**4.4.2 Bubble velocity fields**

For Newtonian fluids it is well known that the presence of in a real fracture of spatially-correlated regions of large (respectively, low) apertures results in the creation of tortuous preferential flow paths [37-39, 63]. This flow channelling impacts the fracture’s permeability (or transmissivity), but is also responsible for the anomalous (non-Fickian) transport [55]. According to the results of Tsang [64] for Newtonian fluids, this mechanism can generate pressure drops one or two orders of magnitude higher as compared to the case of a smooth Hele-Shaw cell. In the present experiments, tracing the trajectory of bubbles in the fracture plane shows that the bubbles do not follow an extremely tortuous path that avoids the low-aperture region in the central part of the fracture (see for example figure 3), but their velocity varies significantly along their trajectories, decreasing sharply in this central region. One should remember that such a foam flow is overall incompressible, so if the overall flux for this layer of bubbles varies longitudinal, it must be compensated by an antagonist change in the flux of other bubble layers which we do not measure. In any case, the aperture heterogeneities impact the velocity field significantly, and, therefore, the values of $\mu_{\text{app}}$ are expected to be higher in the rough fracture than in a smooth fracture of identical mean aperture.

**4.4.3 Dependence of the apparent shear viscosity of the foams on their quality**

The relationship between foam quality and $\mu_{\text{app}}$ for both the real fracture and the Hele-Shaw cell was calculated from the experimental measurements using Eq. (1). The results are presented in FIGURE 4 (b). It can be noticed that $\mu_{\text{app}}$ is much higher in the real fracture than in the Hele-Shaw cell for all investigated foam qualities at the considered flow rate, which is consistent
with the increase in pressure drop resulting flow channelling which is responsible for changes in hydraulic conductivity. Note that the pressure loss sensitivity to aperture fluctuations is expected to be higher in the case of shear-thinning fluids and yield stress fluids as foams (shear viscosity depends on the local aperture) [65], as compared to Newtonian fluids.

FIGURE 4. (a) Dependence of the mean initial size of the generated bubble on the foam quality. (b) Relationship between the quality and the apparent viscosity of the injected foams in the real fracture and in the Hele-Shaw cell [42]. (c) Relationship between the quality and mean velocity, computed from the volumetric flow rate. (d) Relationship between the quality and the aperture threshold. The gas flow rate \( q_g \) is 10 ml/min.

It can be also observed from FIGURE 4 (b) that the relationship between the foam’s apparent viscosity and its quality in the Vosges fracture is monotonically decreasing whereas this dependency is monotonically increasing in the Hele-Shaw cell. In their work, Osei-Bonsu et al [42] stated that the bubbles of a foam with a higher quality offer more resistance against interface deformation and hence exhibit lower mobility in the Hele-Shaw cell. In contrast, \( \mu_{app} \) is all the larger as the foam quality is smaller in the present case of realistic fracture geometry,
which is in agreement with some previous studies [44, 66, 67]. Note however that foam was mainly generated by snap off in a foam generator. As we increased the flow rate of surfactant to decrease the foam quality, more surfactant solution was available for foam generation, leading to an increased rate of foam generation and a decrease in the size of the mean bubble size of the foam at the inlet of the fracture (i.e., mean initial bubble size), as shown in FIGURE 4 (a). This also explains the decreasing dependence of the apparent viscosity $\mu_{\text{app}}$ on the foam quality (FIGURE 4 (b)). Note however that in the data of FIGURE 4(c) the foam quality is not varied independently of all other parameters. Part of the dependence of $\mu_{\text{app}}$ on the foam quality is due to the slight increase in mean velocity observed as the foam quality is decreased, which clearly appears in FIGURE 4 (c).

Visual observations (which will be discussed in more details in section 3.4) revealed that foam bubbles were stagnant in some parts of the fracture, which means (not surprisingly) that the foam behaved as a yield stress fluid. These observations also showed, in agreement with previous studies [35, 36], that the extension of the stagnant area in the rough fracture become smaller as the foam quality was decreased and smaller foam bubbles were generated. The apertures encountered in these areas where bubbles were stagnant were smaller than a threshold value. This threshold value was observed to vary with the foam quality, as shown in FIGURE 4(d), due to the dependence of the bubbles size on the foam quality (FIGURE 4(a)).

4.4.4 Shear rate distribution in the rough fracture
A remarkable feature of the flow patterns in the real fracture is that bubbles were stagnant in the lowest aperture regions. As expected, the foam behaved as a yield stress fluid which does not flow when the applied shear stress is below a threshold value. In the present case, the local shear stress in the low-aperture area fell below the yield stress as the pressure gradient was not high enough at the lowest flow rates. The required pressure gradient to exceed this threshold is obtained by increasing the flow rate. This phenomenon can be seen by comparing velocity map at 10 and 20 ml/min in FIGURE 5. As the flow rate increased, a larger area of the fracture plane was occupied by flowing foam bubbles.

4.4.5 Shear rate distribution in the fracture plane

Given that the foam is a shear thinning fluid, the variation in velocity leads to different viscosity values in different regions of the fracture. The equivalent Newtonian wall shear rate \( \dot{\gamma}_N \) was calculated from the aperture and velocity magnitude maps using the following expression [68].

\[
\dot{\gamma}_N = \frac{6v}{a}
\]  

FIGURE 5. Maps of velocity magnitude and wall shear rate at 85% foam quality for the rough fracture (a, c) at 10 ml/min gas flow rate and (c, d) at 20 ml/min gas flow rate.
In the preceding equation, \( v \) is the local velocity magnitude, i.e. the average value of the velocity profile between both surfaces of the fracture. Here we assume that the local velocity magnitude which we measure and is represented in FIGURE 5 can be assimilated to \( v \) in Eq. (2). In the same equation, \( a \) is the local aperture value as represented in the aperture map of Figure 1. Eq. (2) applies to the 2-D flow of a constant viscosity liquid between two infinite parallel planes (the plane Poiseuille configuration). However, for flows of liquids with a shear-rate-dependent viscosity, the calculation of shear rate is more complex as the velocity profile is no longer parabolic [69]. In this case, the true wall shear rate can be found using the Weissenberg–Rabinowitsch–Mooney equation [69]:

\[
\dot{\gamma} = \frac{\dot{\gamma}_N}{3} \left[ 2 + \frac{d(\ln \dot{\gamma}_N)}{d(\ln \tau)} \right],
\]

with \( \tau \) the wall shear stress. It must be noted that the rough approximation \( \dot{\gamma} \approx \dot{\gamma}_N \) has been made in the present analysis. Improved accuracy can be achieved by calculating \( \frac{d(\ln \dot{\gamma}_N)}{d(\ln \tau)} \), which is needed as input in Eq. (3). However, the experimental pressure distribution throughout the fracture would be required for the calculation of \( \tau \), which was not available in the present experiments.

The results in terms of wall shear rate distribution are shown in FIGURE 5, for foams of quality 85% and flow rates of 10 and 20 ml/min. This figure shows that the shear rate in the rough fracture is strongly impacted by the spatial variations of the aperture field, as expected from its definition. In contrast, it would be uniform within the Hele-Shaw cell of [42]. The zero shear rate regions are simply the regions where the velocity of the foam is zero, which exist due to the fact that the foam is a yield stress fluid. The extension of these regions of stagnant bubbles became smaller as the flow rate was increased (see Figure 5).
The steady-state shear flow of bulk foams has been proved to be well described by the Herschel–Bulkley law [70] in previous works [71-73]. This empirical law can be written as follows:

\[
\begin{align*}
\tau &= \tau_0 + \alpha \dot{\gamma}^n \quad \text{for} \quad \tau > \tau_0 \\
\dot{\gamma} &= 0 \quad \text{for} \quad \tau \leq \tau_0
\end{align*}
\]

(4)

Where \(\tau_0\) is the yield stress, \(\alpha\) is the consistency and \(n\) is the flow index of the fluid. In the case of shear-thinning yield stress fluids, \(n\) is inferior to unity. For bulk foams it is usually in the range \([0.2; 0.4]\) (see for example[74]). The three parameters are generally calculated by fitting the data obtained by measuring the shear rate \(\dot{\gamma}\) as a function of the applied shear stress \(\tau\) using a rheometer, which is particularly challenging in the case of foams. For a foam flowing through a porous medium, the rheology is also expected to follow a similar Herschel-Bulkley rheology, but with values of the yield stress, consistency and yield stress that are different from those exhibited in bulk foam flow. Our present study provides hints towards a method to measure the in situ rheology of the foam flowing through the porous medium.

The apparent shear rate of the complex fluid flowing through the real fracture \(\dot{\gamma}_{app}\) can be obtained from the ratio of the characteristic pore velocity \(q\) (obtained by dividing the total flow rate by the cross-sectional area) and the characteristic microscopic length usually taken as \(\sqrt{K}\):

\[
\dot{\gamma}_{app} = \alpha \frac{q}{\sqrt{K}}
\]

(5)

where \(K = \frac{h^2}{12}\) for a fracture and \(\alpha\) is an empirical shift factor known to be a function of both the bulk rheology of the fluid and the porous media [75-78]. \(\dot{\gamma}_{app}\) is commonly used as an input in the rheological model (Eq. 4) in order to predict the viscosity of the fluid in the porous medium. Nevertheless, \(\tau_0, \alpha\) and \(n\) are unknown in the case of foams, so the preceding approach is hardly applicable. Also, it has been traditionally assumed that \(\alpha\) is independent of \(q\). However, Rodríguez de Castro and Radilla [79] recently showed, using flow experiments of
polymer solutions in rough fractures, that this assumption is no longer valid in the presence of a yield stress.

The average wall shear rate $\dot{\gamma}_{av}$ throughout the media, obtained from averaging the shear rate maps such as those shown in FIGURE 5 is plotted as a function of the foam quality for a flow rate of 10 ml/min in Figure 6(a). FIGURE 6(a) shows that the average shear rate is not monotonic as a function of the foam quality in the real fracture. It is reminded here that foam quality was varied by setting a different liquid flow rate while keeping the gas flow rate constant. Therefore, decreasing foam quality leads to increased rate of foam generation with finer texture (smaller bubbles). According to Princen [35] and Hohler and Cohen-Addad [36], the yield stress is inversely proportional to the size of the bubbles. Finer foam bubbles at lower foam quality have lower yield stress that lead to the flow of foam bubbles to a wider area of the fracture (FIGURE 4 (b-d)), which tends to increase the average shear rate. On the contrary, decreasing the foam quality means decreasing the average flow velocity (see Figure 4(c)) to some extent, which tends to promote a lower mean shear rate. These two competing effects may explain the non-monotonicity of the plot in Figure 6(a).

The average shear rate was also computed for the series of experiments at constant foam quality 85% and various flow rates ranging between 10 and 60 ml/min, but the acquisition frequency of 1 Hz allowed obtaining meaningful velocity fields only for the data recorded at 10 and 20 ml/min (at 11.5 and 22.6 m/s, respectively), with an increase when increasing the flow rate, as expected. In contrast the dependence of the apparent viscosity could be obtained from Eq. (1)) for all flow rates. Figure 6(b) shows apparent viscosity decreases with flow rate in both fracture and Hele-Shaw cell as expected due to shear thinning behaviour of foam. It is shown in Figure 6(c) and seems consistent with a power law behaviour, of exponent -0.41, to be compared to the exponent -0.27 for the Hele-Shaw cell data of Osuei-Bonsu et al. Since only two measurements of the average shear rate were available, we could not check that the dependence
of the apparent viscosity on the average shear rate was consistent with a power law behaviour, but we propose that a method based on such “apparent rheograms” could be used to measure the in situ rheology of the foam in the porous medium.

FIGURE 6. (a) Dependence of the average shear rate on the foam quality at a 10 ml/min gas flow rate. (b) and (c) Apparent viscosity $\mu_{app}$ vs. the mean flow velocity $q$ for foams of quality $f_g = 85\%$.
85% in linear and log-log plot respectively. The same is also shown for the Hele-Shaw cell of identical transmissivity, for comparison.

Similarly, the shift factor \( \alpha = \dot{\gamma}_{av} \sqrt{K/q} \) assuming \( \dot{\gamma}_{av} \sim \dot{\gamma}_{app} \) in Eq. (5) could be computed for the two flow rates 10 and 20 ml/min, to 1.30 and 1.26, respectively.

### 4.4.6 Correlations between foam coarsening and aperture distribution

The nature of foams is dynamic; their structure changes with time due to foam coalescence by liquid drainage, film rupture and gas diffusion across the films separating neighbouring bubbles [36]. It is interesting to observe how the local fracture aperture influences the coarsening dynamics the foam after the flow has been stopped. To this end, closed views of the foam’s structure were recorded in sub-windows of the entire fracture plane positioned at different positions in that plane. All these sub-windows corresponded to different mean apertures (computed over the sub-window). The evolution of the mean bubble sizes was monitored for a total duration of 15 hours. FIGURE 7(a) shows pictures taken for three sub-windows for which the mean aperture was respectively 0.2, 0.5 and 1.5 mm, at three different times after the flow has been stopped: 0 s, 3000 s, and 15 h. The coarsening in time of the foam is clearly visible in all image, and appears to be all the faster as the mean aperture is larger. FIGURE 7(b) shows the corresponding dependence of the mean bubble size \( \langle d \rangle_{sw} \) on the mean aperture \( \langle a \rangle_{sw} \), at times 0 s and 15 h after the flow has been stopped. The gas diffusion rate through the films is expected to be higher at earlier times as smaller foam bubbles with higher internal pressure exist in the system. Gas diffuses from smaller to larger bubbles with a rate that is proportional to the pressure difference between them, eventually leading to the vanishing of the smallest bubbles and continuous coarsening of the foam. The mean bubble size \( \langle d \rangle_{sw} \) is indeed observed increase in time, for a given \( \langle a \rangle_{sw} \), as expected, but as we only have measurements at two different times we cannot quantify the changes in coarsening rates. More interestingly, at a
given time the mean bubble size appears to be highly correlated to the mean aperture in the sub-windows, following a monotonically increasing dependence.

It is interesting to note that mean apertures for which the plots are above the $\langle d \rangle_{sw} = \langle a \rangle_{sw}$ line correspond to regions in which the mean horizontal size of the bubbles is larger than the aperture that confines them vertically. Consequently, it is very likely that there is only one layer of bubbles in these regions of the fracture planes. In contrast, as the mean aperture is larger than the mean horizontal bubble size, the bubbles are expected to be pseudo-spherical as they are not confined between the two fracture walls. Therefore, more than one layer of bubbles can exist in these regions. The plot obtained for the initial time (after the flow has been stopped) is particularly interesting as it shows the structural state of the foam resulting from its flow in the fracture. This means that smaller bubbles flow in smaller aperture regions, while larger bubbles flow in larger aperture regions. Furthermore, only bubbles present in low aperture regions (or mean aperture smaller than 0.5 mm) are confined vertically (despite being smaller than in regions of larger aperture). On the contrary, at $t = 15$ h after the flow has been stopped, the local mean bubble size is larger than the local mean aperture in all sub-windows, and so the foam can be expected to be confined vertically in all of them. In other words, at $t = 15$ h the foam is two-dimensional in the entire fracture plane (i.e., there is a monolayer of bubbles everywhere).
FIGURE 7. (a) Bubbles observed in different sub-windows of the aperture plane, at successive times 0 s, 3000 s and 15 h after the flow has been stopped. The mean fracture aperture in the sub-window in question is denoted $\langle a \rangle_{sw}$. (b) Dependence of the mean bubble size in the sub-window as a function of the mean aperture $\langle a \rangle_{sw}$. 
As Cohen-Addad [80] showed, the foam’s apparent viscosity decreases during foam coarsening process. Accordingly, we can expect deterioration of the sweep efficiency when using coarsened foam as displacing fluid, given the decrease in $\mu_{\text{app}}$.

4.5 Conclusions

As for the creeping flow of a Newtonian fluid [81, 82], spatial variations of the aperture field of a rough fracture with a realistic geometry strongly impacts the flow of an aqueous foam. To the best of our knowledge, all previous experimental studies addressing foam flow in fractured media had only been conducted on fractured media manufactured by glass plates [41, 42, 44, 83], with unrealistic fracture geometries, or real fracture media but with no quantitative characterization of the aperture field [47, 84-86]. In additional, though several of these previous studies featured local visualization of bubble morphologies [26], and in some cases the measurement of bubble size distributions [40, 44], none of them reported bubble velocity measurements nor tried to link local bubble velocities to the in situ rheology of the foam. This study set out to provide an understanding of the effects of spatial aperture variations on the flow patterns, shear rheology, and bubble morphology during the flow of foams through a realistic fracture geometry, that is, a geometry that possesses the right spatial correlation properties which are known to be typical of fracture surfaces and the gap between them [86, 87]. To do so, a comprehensive series of single-phase flow experiments were conducted in a replica of natural rough-walled fracture (Vosges sandstone), and confronted to similar measurement performed in a Hele-Shaw cell fracture of identical hydraulic aperture. Based on theses measurements, the following observations and conclusions can be drawn:

- The aperture variation strongly affects the apparent viscosity of foam. In particular, the existence of spatially-correlated low- and high-aperture areas increases flow tortuosity and the velocity contrast between preferential flow channels and stagnant zones, as is
the case for the flow of a Newtonian fluid. By modifying the velocity field and, consequently, the shear rate distribution, it controls the in situ rheology of the foam.

- Foam is a yield stress fluid and exhibits shear-thinning behaviour when flowing through a porous medium, but the rheology is not necessarily the same as that of the bulk foam. Here we could not obtain a complete “in situ” rheogram for the 85% foam from foam bubble velocity measurements, but we propose to use this method to measure the in situ rheology of the foam. In this case the measurements that could be made point to a power law of exponent -0.41.

- The foam’s bubble size inside the fracture is correlated to the local fracture aperture, and is all the larger as the local aperture is larger. The transition from bulk foam to a vertically-confined two-dimensional foam occurs in the fracture plane along the equip-aperture lines \( a=0.5 \text{ mm} \) in our setup.

- The dynamics of foam coarsening inside the fracture is correlated to the local aperture and is all the faster as the local aperture is larger.

A replica of a Vosges sandstone fracture with a given Hurst exponent was considered in the present study to investigate the effect of spatial distribution on apparent shear viscosity and bubble morphology. In future studies, it would be interesting to consider similar geometries with various Hurst (\( H \)) exponent values as well as, possibly, different matching (i.e., correlation) scales between the two fractures walls, and correlate the flow properties of the foam to these stochastic geometrical parameters.
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4.6 References


manuscript


Chapter 5: Synergy between nanoparticles and surfactants on foam stability at bubble and bulk-scale

This chapter is a draft of a manuscript to be submitted to RSC Advances for possible publication. The main objective of this paper is to study the synergy between nanoparticles and surfactant. To do so, a comprehensive set of foam stability experiments have been conducted at bubble and bulk-scale with three different surfactants of different surface charges and silica nanoparticle. Our findings showed nanoparticles do not have always a positive effect on foam stability and that depends on the type of surfactant and nanoparticles. For example for the case of DTAB, the interaction between surfactant and nanoparticles led to the precipitation of surfactant that harmed the stability of foam. Moreover, we found the concentration of surfactant plays a major effect in stabilizing of foam with nanoparticles. Our results extend the understanding of foam stability in the presence of nanoparticles which could be useful in a variety of engineering applications.
Synergy between Nanoparticles and Surfactants in Controoling Foam Stability at Bubble and Bulk-scale

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Abstract

In this work, we investigate the effect of surfactants with different charges (anionic, cationic, and non-ionic) on foam stability in the presence of charge-stabilized silica (SiO$_2$) nanoparticles. Toward this aim, a comprehensive series of experiments on a Hele-Shaw cell and a foam column is conducted at bubble and bulk-scale respectively, that is, investigating separately the phenomenologies of foam coarsening by gas diffusion and gravitational drainage. Our results show that nanoparticles do not necessarily have a positive effect on foam stability, and that stability strongly depends on the nature of the surfactant, its concentration and the concentration of nanoparticles. For anionic surfactants (SDS), an optimal concentration of silica nanoparticles was found to generate a foam with the highest stability, due to the accumulation of nanoparticles at the gas-liquid interface. In the case of the surfactant DTAB (cationic), the interaction between DTAB and the SiO$_2$ nanoparticles led to that gravitational drainage plays a more dominant role that influence on foam coarsening. Therefore, different impact of nanoparticles depending upon whether gravitational drainage or foam coarsening is considered. This finding suggests that compatibility experiments are pre-requisite to foam stability experiments to test the compatibility between surfactants and nanoparticles. Nevertheless, with DTAB as surfactant we observed less stable foams in bubble-scale experiments due to the interaction between DTAB and the SiO$_2$ nanoparticles, which led to precipitation of the latter and to reduction of the amount of free surfactant available to generate foam. Similarly, the presence of nanoparticles harmed foam stability for Triton X100 (nonionic) at its CMC concentration. However, a positive effect was observed at concentrations beyond the CMC. This suggests that surface tension alone is not the only parameter that influences foam stability and that other parameters such as the viscosity of the surfactant solution and the permeability of the nanoparticle-laden foam lamellas play an important role in foam stability. Our results extend the understanding of foam stability in the presence of
nanoparticles which is a step towards understanding the behaviour of foam in a more complex system.

**Keywords:** Gas diffusion, Gravitational drainage, Foam stability, Nanoparticle, Surfactant, Bubble-scale, Bulk-scale,
Introduction

Gas injection into subsurface reservoirs is a common practice in many industrial and engineering processes such as enhanced oil recovery (EOR), CO$_2$ sequestration and soil remediation [1-3]. In most cases, viscous fingering and gravity override due to unfavourable viscosity and density ratios between the gas and the resident liquid(s), and preferential flow of gas due to reservoirs heterogeneity are responsible for low sweep efficiency [4, 5]. Foams, which are dispersions of a large volume of gas in a liquid such that the gas phase is made discontinuous by films of the liquid phase denoted lamellae [6, 7], are a promising potential remedy to these complications [8, 9]. The apparent viscosity of foam can be up to 1000 times higher than that of its constituents, which makes foams ideal for fluid displacement [10, 11].

In general, foams are classified into two categories, which are typically known as *bulk foam* and *confined foam* [12], based on the size of bubbles relative to the typical length scale of the confined media (e.g., the average pore size or channel width). Foam can be considered a *bulk foam* when the dimension of the confining space is significantly larger than the typical bubble size. On the other hand, the foam is *confined foam* when the bubbles have the same size or are larger than the typical length scale of the confining space. Foams exhibit two different geometries depending on their quality, i.e., their gas content [13, 14]. In wet systems (i.e., at low foam qualities), the lamellae are thick, the foam bubbles have a quasi-spherical shape, and the foams are fine-textured, whereas, at higher foam quality, the lamellae are thinner and foam bubbles tend to have a more polyhedral shape.

The stability of foam is its capacity to retain its geometry/topology over a significant amount of time despite not being stable from a thermodynamically point of view. The foam's texture evolves irreversibly in time as a consequence of four different processes (1) gas diffusion (2), liquid drainage (3), interaction with oil and (4) capillary suction [12, 15].
Adjacent foam bubbles do not have exactly the same size, and hence the gas is at different pressures inside the bubbles. The gas in smaller foam bubbles is at a higher pressure than the gas in coarser ones. Indeed, the bubble radius controls the pressure inside the bubbles as a consequence of the Young–Laplace equation, which relates the pressure difference $\Delta P$ across a fluid interface to the surface tension coefficient $\sigma$ and the principal radii of curvature $r_1$ and $r_2$ according to $\Delta P = 2\sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$ [16]. Gas thus diffuses from the small bubbles with higher pressure to larger bubbles with lower pressure, which eventually causes the disappearance of neighboring small bubbles [17-19]. This phenomenon is called gas diffusion coarsening.

Liquid drainage is a multistage process consisting of (a) liquid flow from the lamellae to the Plateau border (which are the lamellae’s intersections) due to capillary suction, (b) liquid release from the coalescence of foam bubbles, and (c) downward liquid drainage along Plateau borders under the effect of gravity, resulting in accumulation of liquid in the lower layer of the foam [20]. The entire process is mainly controlled by gravity and capillary suction and eventually leads to film ruptures as the thickness of lamellae falls below a certain value [21].

Another major challenge to the effective utilization of foam application in oil displacement is the adverse effect of oil on foam stability as a result of direct surface interactions between oil and foam, which leads to aqueous film thinning and rupture [22-24]. The negative effect of oil on foam stability depends on the properties of the surfactant and oil. Light oil (small hydrocarbon chains) was found to be more detrimental to foam stability than heavier oil (long hydrocarbon chains) [25, 26].

Moreover, in capillary suction mechanism, when the capillary pressure (the pressure across the interface of gas and surfactant solution) increases, the lamellae thickness decreases and after a threshold, it breaks.

In view of the above-mentioned challenges to foam stability, in recent years, there has been a growing interest in conjunction using nanoparticles with surfactant to stabilize foam [19, 27,
28, 29]. The effective contribution of nanoparticles to foam stability is attributed to the adsorption and accumulation of nanoparticles at the gas-liquid interfaces of foam bubbles and Plateau borders [27]. Nanoparticles reduce the direct contact between the fluids, which decelerates the gas diffusion rate and bubble bursting [19, 28, 29], film drainage is slowed as well due to the presence of the nanoparticles. The lower tendency of nanoparticles compared to the surfactant to adsorb on reservoir rocks is another reason that makes them a desirable foam stabilizer [27]. Nanoparticles are otherwise well suited to subsurface applications. Their small size limits the possibility of pore plugging as they pass through the pore throats in porous media [29]. Their solid nature also makes them highly resistant to the harsh condition of reservoirs such as high pressure and temperature, high salinity and the presence of oil [30, 31]. Also, nanoparticles can be functionalized with different chemical groups to improve their aqueous stability and tune the wettability of the solutions, or coated for different purposes such as increasing their CO$_2$ solvation capability and capability to adhere to the fluid-gas interface, which contributes to improving the foam’s stability [32, 33].

In addition to the decrease in gas diffusion and liquid drainage, the main proposed causes for the increase in foam stability when using nanoparticles are an increase in particle detachment energy and the maximum capillary pressure of coalescence [27]. The particle detachment energy is the energy required for the removal of the nanoparticles from the lamellae [34]. The adsorption of nanoparticles at the interface is thus considered irreversible due to their large adsorption energy, while other conventional foaming agents can easily adsorb and desorb from the gas-liquid interface of foam bubbles. As the capillary pressure increases, the lamellae thin, and after passing a threshold called the maximum capillary pressure of coalescence, foam collapses. The presence of nanoparticles however as alluded to above increases the maximum capillary pressure of coalescence [27].
The presence of nanoparticles at the gas-liquid interface decreases the interfacial tension and increases the curvature radius of foam bubbles with respect to conventional foams [35], and hence decreases the capillary pressure. Consequently, the pressure differences between adjacent bubbles decrease in the presence of nanoparticle and gas diffusion decreases accordingly as well as decreasing the permeability of film to gas. Moreover, it was reported that the maximum capillary pressure for foam coalescence increases in the presence of nanoparticles [36]. The increase in maximum capillary pressure depends on nanoparticle concentration and on how they agglomerate at the gas-liquid interface.

Indeed, nanoparticles can be arranged at the gas-liquid interface as a monolayer, bilayer, or a network of particles based on their surface wettability [37]. The resistance of nanoparticles to exit the interface controls the stability of a monolayer nanoparticle arrangement [38], while the stability of a bilayer and network of nanoparticles arrangement is influenced by interfacial rheological properties and by the capillary pressure [39]. Generally, a network of nanoparticles provides higher stability by forming thick solid lamellae that prevent film thinning and gas diffusion more effectively by increasing the surfactant solution viscosity and here decreasing gas diffusivity. In addition, liquid drainage and gravitational drainage is decelerated in the presence of nanoparticles. Hence the rearrangement of nanoparticles at the interface during liquid drainage is a key control parameter in foam stability enhancement by nanoparticles.

Some researchers have stated, based on experimental data that in any given system, there is an optimal concentration of nanoparticles that improves foam stability to the largest extent [40]. At low concentration, the presence of nanoparticles at the gas-liquid interface is not enough to achieve high stability. As the nanoparticle concentration is increased, more nanoparticles find themselves at the gas-liquid interfaces which enhances foam stability by reducing foam drainage and liquid film thinning. However, foam stability either remains constant or decreases when the concentration passes a critical value [41, 42]. It has been established that
nanoparticles, irrespective of the type, have an effective influence on static and dynamic stability of foam [27]. What is not yet clearly understood is how the nature of the surfactant affects foam stability in the presence of nanoparticles. To improve our physical understanding of the synergy between nanoparticles and surfactants on foam stability, we investigate in this study the impact of nanoparticles in the presence of surfactants with varying charges (anionic, cationic, and non-ionic) on foam stability using column experiments and Hele-Shaw cell experiments. The Hele-Shaw experiments provide information about foam coarsening in the absence of gravity drainage, while the column experiments allow quantifying the magnitude of gravitational drainage. It is worth mentioning, that in particular we study for the first time the synergy between non-ionic surfactant and nanoparticles in this research.

5.1 Materials and Methods

5.1.1 Foaming suspensions:

All of the foam experiments were prepared using deionized water in ambient conditions (T~23°C, RH~36%). We used deionise water to keep the chemistry as simple as possible. Although, the real reservoir condition could be saline. Three surfactants of different natures (respectively anionic, cationic, and non-ionic) were used in this study; sodium dodecyl sulfate (SDS) (Sigma, UK), dodecyl trimethyl ammonium bromide (DTAB) (Sigma, UK) and Triton X100 (Sigma, UK), respectively. The properties of theses surfactants used in this work are summarised in Table 1. The surfactants were used at their CMC, (unless otherwise specified). Spherical charge-stabilized dispersions of colloidal silica particles (Ludox HS, Grace) with a diameter of 16 nm were added to the surfactant solutions.
Table 1 Properties of the surfactants [43, 44], including the critical micellar concentration (CMC).

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Charge</th>
<th>CMC (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulphate (SDS) at CMC</td>
<td>Anionic</td>
<td>8</td>
</tr>
<tr>
<td>Dodecyl trimethyl ammonium bromide (DTAB) at CMC</td>
<td>Cationic</td>
<td>11</td>
</tr>
<tr>
<td>Triton X100 at CMC</td>
<td>Non-ionic</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The interaction of the surfactants with the silica particles was characterized qualitatively using ultraviolet-visible (UV-vis) spectroscopy, with an analysis based on the method described by Desarnaud et al. [45]. It is based on measuring the decolorization of a dye solution (here a cationic dye: methylene blue (MB)) due to the adsorption of the dye on the oppositely charged surface (i.e., the silica particles). Here, one would expect that the formation of a silica-surfactant complex, due to charged interactions, would reduce the decolorisation of the MB solution as the surface of the silica particles are essentially covered due to surfactant adsorption. To confirm this, silica particles were mixed in each of the prepared surfactant solutions. The solutions were then filtered and left to dry. The obtained dried particles were then placed in an MB solution and using UV/Vis-spectrometer, the decolorisation of each dye solution was measured.
Figure 1. UV-vis absorption spectra of methylene blue solution (MB) after the addition of silica beads and silica beads treated in SDS, DTAB, and Triton X100 solution.

In the case of the negatively charged SDS surfactant, the measurements show that the anionic surfactant hardly adsorbs onto the negatively charged surface of the silica particles, presented in Figure 1, since the reduction of absorbance (indicative of the decolorization of the solution) is nearly identical when silica particles and silica particles treated in SDS solution are added to the methylene blue solution. This observation is consistent with the recent work of Osman et al. [46]. Conversely, in the case of silica particles treated in DTAB solutions, the decolorization is measured to be significantly less intense due to adsorption of the cationic surfactants onto the oppositely charged silica surfaces, which minimize the interactions between the MB dye and silica. Similarly, but to a lesser extent, adsorption of Triton X100 onto the silica particles also occurs, as seen in Figure 1. Figure 2 shows an image of the solutions containing silica nanoparticles. In the case of DTAB (Figure 2b), precipitation occurs due to the strong interaction of the cationic surfactants with the anionic silica particles. The adsorption of DTAB onto the surface of the particles tunes the DLVO barrier, which describes the balance between charge-induced repulsive forces together with the attraction induced by van der Waals forces at a short-range [47, 48]. In such a case, adsorption leads to a decrease in the electrostatic repulsion between the nanoparticles, and consequently, the van der Waals attraction become dominant, thus contributing to flocculation of the suspension.
Figure 2. Visual aspect of surfactant solutions (a) Triton X100 (b) DTAB and (c) SDS containing silica particles (1%).

The rheology of the foaming suspensions was measured using a rheometer (Rotational DV3T Rheometer, Brookfield) in the plate-plate configuration.

Figure 3 presents the viscosity-shear rate for surfactant solutions at different nanoparticle concentrations.

Figure 3. Viscosity vs shear rate of the different foaming suspensions at different silica nanoparticles concentration. All the surfactants are at their CMC in (a). The concentration of Triton X100 in (b) is 1% (6.7 times more than its CMC). The vertical axis is log scale. As the DTAB precipitated and we had two phases, we did not present its related data in (a).

Figure 3 shows that the addition of silica nanoparticle increases the viscosity of the solution. This effect is especially significant for Triton X100 as its concentration increase from CMC to
1 %. This can be due to the interaction between nanoparticles and surfactants at high concentration of Triton X100.

The contact angle of the foaming suspensions was measured from images of droplets resting on a glass substrate, for the different surfactants and different concentrations in surfactant and silica nanoparticles (see Figure 4). The second fluid was air.

<table>
<thead>
<tr>
<th></th>
<th>SDS (at CMC)</th>
<th>Triton (at CMC)</th>
<th>Triton (at 1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2 (0%)</td>
<td>Θ=24.0 °</td>
<td>Θ=22.5 °</td>
<td>Θ=19.5 °</td>
</tr>
<tr>
<td>SiO2 (0.5 %)</td>
<td>Θ=33.8 °</td>
<td>Θ=38.2 °</td>
<td>Θ=34.5 °</td>
</tr>
<tr>
<td>SiO2 (1 %)</td>
<td>Θ=40.5 °</td>
<td>Θ=43.1 °</td>
<td>Θ=41.2 °</td>
</tr>
</tbody>
</table>

Figure 4. Photographic images of the surface of a foaming suspension droplet resting on a glass substrate, for different surfactants and different concentrations in surfactant and silica nanoparticles.

Figure 4 shows that the surface is water-wet for all the prepared foaming suspensions and also the silica nanoparticles increase the contact angle of the solutions.

All the measurements were repeated at least three times, and the reported results are the average of all.
5.2 Experimental Setup and Procedure

A series of foam stability experiments were conducted using a Hele-Shaw cell (Figure 5) and a column cell (Figure 6) to investigate the synergy between nanoparticles and surfactants in impacting foam stability at bubble and bulk-scale, respectively.

**Bubble-scale experiments:** The Hele-Shaw cell consisted of two plexiglass plates of dimensions 30 × 17 × 0.5 cm³. The plexiglass plates were tightened using medium-duty clamps in all experiments. A gasket of thickness 1 mm was clamped between the two plates to impose a constant distance between them and prevent leakage. Two holes (1 mm diameter) were drilled on opposite sides on the top of the plexiglass plate to act as inlet and outlet channels for the flow of foam through the Hele-Shaw cell. Foam was generated by injecting both compressed air and the surfactant solution simultaneously into a foam generator fitted with a sintered glass disc (Scientific Glass, UK) with a pore size distribution between 40 and 60 µm. The flows of gas and surfactant were set to 10 ml/min and 1.11 ml/min respectively to achieve a 90 % foam quality for all the foam displacement experiments. The pressure was measured at the inlet of the Hele-Shaw cell via a pressure transducer while the outlet was connected to the atmosphere. The Hele-Shaw cell was initially fully saturated by air.
A high-resolution camera (Teledyne DALSA genie) was placed on top of the micro model and captured a snapshot of the aging process every 30 minutes for a total of 6 hrs. The images produced were 8-bit grey levels with a resolution of 2560 x 2048 pixels. The contrast of the images was improved by the use of a lightbox placed underneath the model. The images were imported into ImageJ software for further segmentation and analyses. Firstly, the contrast and brightness were adjusted using the “Adjust > Brightness/Contrast” function. Then after that, the number of bubbles at the initial time (Ni) and later times (N(t)) were calculated using “Analyze>Analyze Particles” function.

**Bulk-scale experiments:** The column experiments were conducted in a chromatography column (Scientific glass, UK) with an inner diameter and a height of 4 cm and 80 cm, respectively. Figure 6 shows a schematic diagram of the column used in this study. A sintered glass disc with a pore size distribution between 40 and 60 µm was placed at the bottom of the column as a foam generator. The liquid phase for each surfactant was prepared by adding the surfactants to deionized water at their CMC (Table 1) and then mixing using a stirrer (Fisher
Scientific, UK) for 2 hours. Silica nanoparticles were added to the solution at various concentrations (0-1%) and mixed for an additional 30 minutes. The experiments were conducted immediately after the solution was prepared to prevent hydrolysis of the surfactants. Air was injected through a tube with an inner diameter of 0.5 cm into the column via the sintered glass using a mass flow controller at 100 ml/min flow rate. The gas flow rate was adjusted using the Flow View and Flow DDE (Bronkhorst, UK) software. Flow View provides an interface between the computer and the mass flow controller while Flow DDE provides the user with manual control of the desired flow rate. The injection was stopped when the column had completely filled with foam, that is when the foam inside the column had reached an 80 cm. The liquid then drained from the column by gravity. The drained mass of liquid was recorded every minute for each experiment with a balance.

Figure 6. A schematic diagram of the bulk-scale experiment set-up.

Each experiment was repeated three times to check the reproducibility. The results presented in the next section will thus be an average of all three tests unless specified otherwise.

5.3 Results and discussion

5.3.1 Synergistic effect of nanoparticles and surfactants on foam stability at bubble scale
A series of Hele-Shaw cell experiments were conducted to investigate the synergy between nanoparticles and surfactants in impacting foam properties at bubble scale. In these experiments foam drainage was very slow since we were working with a quasi-two-dimensional model positioned horizontally.

Figure 7 shows the pressure drop measured during foam flooding of the Hele-Shaw cell at different experimental conditions. The pressure drop enables us to determine the apparent viscosity of the foam based on the Darcy law \( \mu_{app} = \frac{KA \Delta P}{qL} \), where \( K \) is the permeability of the Hele-Shaw cell, \( q \) is the flow rate, \( A \) is the cross-sectional area and \( L \) is the length of the system.

Figure 7. Measured pressure drop versus time during foam injecting at different experimental conditions in the Hele-Shaw cell. The legends indicate nanoparticle concentrations.

Figure 7 (a) shows the pressure drop (foam apparent viscosity) for the SDS surfactant in the presence of silica nanoparticles. It can be seen that an increase in silica concentration leads to a larger pressure drop, which can be interpreted as the generation of a stronger foam. We stopped the injection of gas and liquid solution at the end of the experiments, and the structural evolution of foam bubbles was then monitored in time over the Hele-Shaw cell. Figure 8
qualitatively shows foam coarsening in the Hele-Shaw cell for six different foaming suspensions, prepared with the three different types surfactants at a concentration equal to their CMC and with two different concentrations of nanoparticles (0 and 1%). The pictures taken at T=0 after the end of the injection show the foam structure at the end of foam generation, while comparing the picture at T=0 and T=6 h provides information about foam coarsening. Comparing Figure 8 (a) with Figure 8 (g), show that the SDS foam has a finer texture in the presence of silica nanoparticles. A finer textured foam provides a higher pressure drop and hence results in a higher apparent viscosity of the foam. The other possible reason for finer texture foam could be related to an increase in the maximum capillary pressure of coalescence due to the presence of silica nanoparticles.

In the case of the DTAB surfactant, on the contrary, the presence of nanoparticle results in a decrease of the foam’s apparent viscosity, as shown in Figure 8 (b). This is due to the adsorption of the cationic surfactants onto the silica nanoparticles, which promotes flocculation of the suspension, that is, phase separation of the solution between the flocculated/sedimented phase and the liquid phase, as seen in Figure 2 (b). Consequently, less surfactant will be available in the solution for strong foam generation. Figure 8 (b) with Figure 8 (h) shows coarser foam bubbles were generated in the presence of SiO$_2$. High fluctuation in pressure drop curves is also an indication of instability of foam in the presence of nanoparticles.

Figure 8 (c) indicates that the foam is generally unstable in the absence and presence of nanoparticles for Triton X100. This might be due to the low molar concentration of Triton X100 at its CMC (Table 1). To validate this point, we performed experiments at a higher concentration (1.0 %) of Triton X100 with varying concentrations of silica nanoparticles. The corresponding temporal evolution of the pressure drop across the flow cell is presented in Figure 8 (d). Comparisons between Figure 8(c) and (d), with the plots in Figure. 8(d) exhibiting appearing much smoother than those in Figure. 8(c), shows that an increase in the surfactant
concentration improved foam stability. These findings suggest that surface tension is not the only physical quantity controlling foam stability and foam generation and that CMC may not be the optimal concentration to generate the most stable foams in the case of surfactants with an extremely low CMC.

Figure 8. Bubbles observed for six different foaming suspensions, corresponding to the three types of surfactants and two different SiO$_2$ concentrations of 0 and 1%, at two successive times 0 hr and 6 hr after the flow has been stopped in the Hele-Shaw cell. All surfactants are at a concentration equal to their CMC.
As expected, the ratio $N_i/N(t)$ of the initial number of bubbles $N_i$ to the number of bubbles at time ($t$), which is plotted as a function of time in Figure 9, grows monotonically in time for all foaming suspensions, which is the signature of both diffusive coarsening of the foam at the bubble scale and bubble bursting.

Figure 9. The ratio of the initial number of bubbles, $N_i$, to the number at time $t$, $N(t)$ plotted as a function of time for different foaming suspensions, prepared with the three types of surfactant and different concentrations of SiO$_2$ nanoparticles, as presented in the legends.

Figure 9 (a) shows that foam coarsening is limited by the presence of nanoparticles (0.5%) for SDS surfactant. However, a further increase in silica concentration showed no further changes. This suggests that a concentration of 0.5% of nanoparticles was sufficient to saturate the gas-liquid interface, thus reducing direct contact between the fluids and as a result slowing down gas diffusion and bubble bursting, as explained in the Introduction. In this case, once the optimal concentration of nanoparticles allowing the gas-liquid interface to be saturated has been reached, a further increase in nanoparticle concentration does not influence foam coarsening.
In contrast, according to Figure 9 (b), foam coarsening becomes faster in DTAB-based suspensions as the concentration in silica nanoparticles is larger. This is likely due to the interaction between DTAB and SiO$_2$ which results in flocculation of the suspensions, as discussed earlier. In the case of Triton X100, Figure 9 (c) reveals that foam coarsening is also faster as the nanoparticle concentration is larger. This is believed to be associated with the joint effects of the extremely low CMC value of Triton X100 and of its interaction with the silica nanoparticles. Indeed, at low concentration of Triton X100, most of the surfactants adsorb onto the surface of the silica particles, leaving little surfactant deposition at the gas-liquid interface. This is detrimental both to foam stability and foam generation. This is consistent with the captured images shown in Figure 9 (c) and (i) which reveal that the number of generated foam bubbles decreases with increasing nanoparticle concentration. Figure 9 (d) shows the temporal evolution of the ratio of the initial bubble number to the current bubble number at for Triton X100 at a concentration above the CMC, i.e. at 1%. Here foam coarsening is observed to be all the slower as the SiO$_2$ nanoparticle concentration is increased. Similarly to SDS surfactant, an optimum concentration of silica nanoparticles exists for Triton X100 at a concentration above its CMC.

5.3.2 Synergistic impact of Nanoparticles and Surfactants on Liquid Drainage

The duration of the column experiments is between 15 min and 1h (see Figure 10). This duration is nearly one order of magnitude smaller than the time scales, which are characteristic of foam coarsening, as probed by the Hele-Shaw experiments. Hence the column experiments investigate mostly the effect of gravitational drainage on foam stability. Figure 10 presents the mass of drained liquid measured at the bottom of the column for 11 different foaming suspensions.
Figure 10. Liquid drainage over time for different based on SDS, DTAB, and Triton X100 surfactants (the latter at two different concentrations). The legends indicate nanoparticles concentration. Foam did not generate for Triton X100 at its CMC and 1% concentration of SiO2.

Figure 10 (a) for SDS shows that the drained liquid mass at any given time decreases with the addition of the SiO2 nanoparticles at 0.5 wt% compared to the same surfactant solution devoid of nanoparticles. This is consistent with the expected role of nanoparticles, which position themselves at the gas-liquid interface, thus decelerating liquid drainage. However, a further increase in nanoparticle concentration from 0.5 to 1% results in no significant changes in the liquid drainage rate. This is very similar to what was observed for foam coarsening in the Hele-Shaw cell, which confirms that the effect must be related to the occupation of the gas-liquid interfaces by the nanoparticles.
In the case of DTAB, on the contrary, the foam instability resulting from liquid drainage does not follow the same trend as that resulting from coarsening. Indeed, contrary to what was observed for coarsening in the Hele-Shaw cell experiments, liquid drainage is always slower as the concentration in silica nanoparticles is larger. This is due to the adsorption of DTAB surfactants on the silica particles, as shown in Figure 1, which leads to a decrease in the electrostatic repulsion between the nanoparticles, thus resulting in their flocculation. After the solution was poured into the column, the particle-surfactant complex precipitated at the bottom of the column on the foam generator. This interaction between DTAB and silica nanoparticle influences the liquid viscosity and increases it. The addition of nanoparticles to the DTAB solution provides a more viscous suspension compared to the suspensions prepared with other surfactants. The flocculated part of the mixture (which has a high viscosity) contributes to the largest part of the foam generation since it is where air first contacts the solution. This highly viscous solution present in the lamellae and Plateau borders decelerates liquid drainage. In general, these findings SiO2 suggest that doing compatibility experiments between the nanoparticle and surfactants used is prerequisite to foam stability experiments. When the DTAB surfactant is used, adding SiO2 nanoparticles is positive for suppressing gravitational drainage, but negative for suppressing foam coarsening, so the impact on global foam stability may depend on the time scales considered. At shorter time scales (less than 30 min here), the use of nanoparticles is likely to have a positive impact on foam stability.

In the case of Triton X100, Figure 10 (c) and (d) suggest that the effectiveness of silica nanoparticle to generate foams which are less prone to collapse under gravitational drainage depends on the concentration of the surfactant, similar to the Hele-Shaw cell experiments. Figure 10 (c) shows that the drained liquid mass measured at any given time increases with concentration of nanoparticles. For the 1% SiO2 concentration, foam generation hardly occurred so that the foam did not fill the column; hence we have not included the corresponding
data in Figure 10 (c). This result could be due to the extremely low critical micelle concentration (CMC) of Triton X100, coupled to its adsorption on nanoparticles, as previously discussed for the Hele-Shaw cell experiments. To confirm this, we performed column experiments at a concentration in Triton X100 of 1%. Figure 10 (d) suggests that at this concentration in Triton, which is larger than the CMC, a 0.5 % concentration in nanoparticles provide higher stability against gravitational drainage than 0 and 1% concentrations. This means that a further increase in silica nanoparticle concentration from 0.5% led to faster liquid drainage, possibly due to a larger density of the suspension.

5.4 Summary and conclusion

We have presented an investigation of foam stability using surfactants with different charges (anionic, cationic and non-ionic) in the presence of charge-stabilized silica nanoparticles. A comprehensive series of experiments were conducted using a horizontal Hele-Shaw cell and columnar flow cells. Hele-Shaw cell experiments are typically termed ‘bubble scale’ experiments in the literature [7]; in our study they mostly probed the foam’s instability by coarsening through gas diffusion and bubble bursting. Columns experiments are typically termed ‘bulk scale’ experiments; more importantly they mostly probe the foam instability by gravitational drainage.

The presence of nanoparticles increased foam stability (whether against foam coarsening or gravitational drainage) for the foam comprised of anionic (SDS) surfactants. This is due to both the surfactant and nanoparticles having surface charges of the same sign; hence adsorption of surfactant on nanoparticles did not occur, and therefore these free nanoparticles could deposit them at the gas-liquid interface. In the case of a foaming suspension prepared with cationic surfactant (DTAB), the presence of oppositely charged nanoparticles led to precipitation of particles taking surfactant adsorbed by the particle out of solution and consequently resulting
in the formation of a less stable foam. Accordingly, compatibility experiments between surfactant and nanoparticle are pre-requisite to foam stability experiments. For foaming suspensions prepared with the surfactant Triton X100, our findings suggest that the effectiveness of nanoparticles to stabilize foam depends on the concentration of surfactant, and the CMC value alone is not an accurate criterion to choose the optimal surfactant concentration for generating stable foam. The presence of SiO$_2$ nanoparticles harmed foam stability due to the extremely low CMC value of Triton X100. Adsorption of the surfactant onto the nanoparticles decreases the amount of free surfactants present in bulk, which negatively impacts foam generation. However, at a concentration above CMC, foam with higher stability towards coarsening and drainage than that prepared with the CMC was generated, and an optimal concentration of nanoparticle for stabilizing the foam was found. Our results extend the understanding of foam stability in the presence of nanoparticles. The prospects of this study include similar experiments performed with porous media. The effect of salinity and high temperature would be interesting to consider in the future study.
5.5 References


Chapter 6: **Summary and conclusions**

This thesis was in the so-called “alternative thesis format,” which includes three published papers and one more under review.

In the first paper (i.e. chapter 2), we looked into the effect of gas viscous fingering into oil bank and gravitational effect on foam flow behavior. This is relevant in processes related to use foam for soil remediation, CO2 sequestration, and Enhanced Oil Recovery (EOR) applications. In this regard, foam flooding experiments were conducted with varying flow rates at vertical and horizontal orientations. We tracked, for example, the temporal development of oil displacement by foam and oil blob distributions. We combined all the experimental data to show foam flow behaviour inside porous media is dependent on both flow rate and gravitational effect. This resulted in proposing an optimum flow rate to maximize displacement efficiency in both orientations. Our results extend the fundamental understanding of the factors controlling foam flow in porous media.

In chapter 3, the effect of type of oil and pore size of porous media on the foam stability and its displacement efficiency was investigated. We showed that there is no meaningful relationship between type of oil and foam stability when size of porous media changed. In general, pore size of porous media appeared to have a higher influence on foam displacement efficiency compared to the type of oil itself.

In chapter 4, the effect of the aperture variation on foam flow behaviour in a rock fracture was investigated. Single phase flow experiments of pre-generated foam was injected through a replica of a Vosges sandstone fracture of well-characterized aperture map and a Hele-Shaw cell with identical hydraulic aperture. Our analysis suggests that the aperture variation of fracture has strong influence on foam apparent shear viscosity and bubble morphology. The results revealed foam bubbles has higher shear rate, velocity, bubble size and foam coarsening
rate in the area with larger aperture. This research provides insight into the importance of the role of the aperture variation on foam flow dynamics in fractured media which is useful in soil remediation, CO2 sequestration and EOR application technologies.

In chapter 4, the synergy between nanoparticle and surfactant was investigated on foam stability at bubble and bulk-scale. To do so, a comprehensive set of experiments have been performed in Hele-Shaw cell and column with three different surfactant with different surface charge and silica nanoparticles. Our results showed the nanoparticles do not have necessary positive effect on foam stability and that depends on the type of surfactants and nanoparticle and their concentrations. Also, this results suggest the compatibility experiments between surfactants and nanoparticles should be pre-requisite to foam stability experiments.

**Applicability of this research**

Foam flow in porous media is ubiquitous in industry and is observed over a wide variety of processes such as in the soil remediation, CO2 sequestration, enhanced oil recovery (EOR) pharmaceutical applications, and food technology, etc. This thesis contributes to the fundamental aspects of the mechanism that determines the behavior of foam in porous media and the stabilization of the foam bubble. We highlight the importance of the properties of the solutions, properties of porous media, and additive particles such as nanoparticle on foam flow behavior. The information is useful in controlling accurately the dynamic of foam flow, and foam coalescence in porous media, which has a direct influence on the efficiency of using foam for soil remediation and EOR.

Another relevant application is the pharmaceutical industry, for example, in using foam for drug delivery purposes. In general, having a higher stable foam would provide a better vehicle for drug delivery by foam.
Besides, an important aspect of foam flow in fractured porous media in this thesis is how the properties of the fracture, such as aperture variation influence the dynamics of foam in porous media. Here we showed that the shear viscosity and bubble morphology of foam is affected by changes in the aperture of the fracture. We showed that the foam stability are strongly influenced by several parameters such as flow rate, gravity, and type of surfactants and nanoparticles. This highlights the importance of the role of the surfactant and nanoparticle surface charges on foam stability. These fundamental parameters associated with other factors described in chapter 2 and chapter 4 is not only important in soil remediation and EOR, but also very relevant in applications such as CO2 sequestration and drug delivery purposes.

**Future work**

This thesis revealed the importance of several parameters on the overall foam stability and foam flow behavior in porous media. More investigation is required to quantify exactly how each parameter influences the dynamics of foam flow. Modeling and simulation of the experimental conditions could be implemented to investigate this relationship. This will be very useful in developing reliable models to predict behavior foam at different condition. Another possible extension of this work could be to investigate the effect of the environmental condition, such as the temperature, pressure, salinity, PH on the stability and behaviour of foam in porous media. This feature was not studied in the present work.