Comparative Study of CO$_2$ and N$_2$ Foams in Porous Media at Low and High Pressure—Temperatures

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We report an experimental study of the behavior of CO$_2$ and N$_2$ foams in granular porous media using X-ray computed tomography. In the experiments either CO$_2$ or N$_2$ gas is forced through natural porous media initially saturated with a surfactant solution, a process known as surfactant-alternating-gas or SAG. The CO$_2$ was either under sub- or supercritical conditions, whereas N$_2$ remained under subcritical conditions at all experimental conditions. We found that CO$_2$ injection following a slug of surfactant can considerably reduce its mobility and promote higher liquid recovery at the experimental conditions investigated. Foaming of CO$_2$ builds-up a lower pressure drop over the core at both low and high pressures than N$_2$. Both gases require space to develop into foam. The space is longer for N$_2$ (larger entrance effect) and increases with increasing gas velocity. Moreover, the ultimate liquid recovery by CO$_2$ foam is always lower than by N$_2$ foam. The possible mechanisms explaining the observed differences in foaming behavior of the two gases are discussed in detail.

1. Introduction

The growing concern about global warming and shortage of energy supply has increased the interest in combined geological CO$_2$ storage and CO$_2$ flooding to enhance oil recovery (EOR).1–3 Favorable characteristics of CO$_2$ include miscibility with oil, swelling, and the ensuing lowering of viscosity.4–6 Even at immiscible conditions CO$_2$ can considerably reduce the oil viscosity and swell the oil volume leading to a significant improvement of oil recovery.4–6 Nevertheless, due to its low viscosity and density, CO$_2$ segregates upwards, thus, overriding water (and eventually oil) and channels through high permeability streaks.5,7 Foaming of CO$_2$ reduces its mobility and can potentially overcome these drawbacks.5,8–10 Foam in porous media is a gas−liquid mixture with a continuous liquid phase wetting the rock, whereas a part or all of the gas is made discontinuous by thin liquid films called lamellae.9,11,12 The mobility reduction of gas will result in a more favorable macroscopic sweep efficiency.5,9,13 Even if the recovery is not improved the costs of handling of the gas will be reduced.14

Although the geological storage of CO$_2$ is considered as an attractive solution for global warming, the efficiency (or even feasibility) of the process is not yet established.15 One major problem is the leakage of the injected CO$_2$ through the walls of abandoned wells or through the cap rock.16 In this case foaming of CO$_2$ may temporarily hamper the leakage while other actions are considered.

There are two main injection strategies in EOR-field projects related to foam. These include co-injection of gas and liquid, and surfactant alternating gas (SAG) injection. In the first strategy the gas and the liquid are co-injected at a fixed ratio. The ratio between the gas flowrate and the sum of the gas and the liquid flowrates (total flowrate) determines the foam quality. The foam can also be generated outside the porous medium before injection; however, we categorize this strategy under the co-injection scheme. In the SAG scheme alternating slugs of surfactant solution and gas are injected and therefore foam is generated inside the porous medium (in situ generation)9,17,18 The SAG foam is sometimes called drainage foam in the literature.19 In a recent EOR application of the foam in the Norwegian Snorre field the SAG phase operations were conducted without any major problem while the co-injection was hampered by operational problems that resulted in unstable injectivity.20,21 Moreover, the SAG process is similar to water alternating gas process (WAG) and requires little additional effort.5,17–22 SAG injection minimizes contact between water and gas in surface facilities and piping which can be important when the gas, e.g., CO$_2$, forms an acid upon contact with water.23,24 The laboratory study of Huh and Handy25 also revealed that the gas-surfactant co-injection foam can completely block the porous medium under certain conditions, while this never occurs with the SAG foam. It was also shown that the mobility reduction factor is higher for co-injection foam than for SAG foam with the same gas flowrate.

While the co-injection foam has been the center of attention of many experiments [e.g., refs 26–31] there is only a little data on SAG foam.18,32–34 Moreover, in most of the previous studies on foam flow in porous media the measured pressure drop became stationary only after 10−100 pore volumes of the injected fluids (liquid and gas). In these experiments the pressure drop does not increase significantly until the gas phase reaches the end of the initially surfactant saturated porous medium, a phenomenon that cannot be explained by the existing models.35 Possibly, this happens due to the high gas flowrates or short length of porous media used in experiments. Indeed, the injected gas needs to travel inside the porous medium before it mixes with the available surfactant and foams. However, when the gas flowrate is high or the porous medium is short, the gas will breakthrough before making a strong foam. The gas will only start to form a strong foam if many pore volumes are injected in the laboratory setup and therefore the obtained results can only be representative of the initial stages of the injection process. It has been also observed that different gases behave differently, both in bulk36–38 and porous media18,39–42 experiments. Recently, Du et al.27 experimentally showed that there is essential difference between CO$_2$ and N$_2$ foams in porous

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media. In their experiments the gases were co-injected with sodium dodecyl sulfate (SDS) solution with high gas flowrates. The differences were attributed to the dissimilar physical properties of the gases, mainly higher CO2 solubility in water than N2.

The choice of surfactant with respect to the injected gas, type of the porous medium, and chemical/physical properties of the fluids in the porous medium, for example, oil is an important key in the success of a foam injection process. A suitable surfactant should be capable of generating ample and stable foam in the presence of reservoir rock and oil at high pressures and temperatures. Furthermore, a successful surfactant should have low adsorption on the rock. Adsorption of the surfactant on the rock surface decreases the surfactant concentration and therefore shortens the distance that the surfactant will propagate into the oil reservoir before its concentration becomes too low to be effective in generating the foam.43 The stability of foam in the presence of oil (often regarded as antifoam) is another challenge in the application of foam as an enhanced oil recovery (EOR) method. In general, the selected surfactant in EOR foam has to balance chemical costs against the expected gas mobility reduction, taking into account surfactant adsorption and foam-oil interaction.44

Alpha olefin sulfonate (AOS) surfactants have comparatively low adsorption on sandstones.45 Moreover, AOS surfactants provide outstanding detergency, high compatibility with hard water, and good wetting and foaming properties with CO2 even when the porous medium is partially saturated with oil. These properties make AOS surfactants an excellent candidate for (CO2)-foam applications, for example, EOR projects that aim to produce more oil from underground reservoirs.

The purpose of this paper is two-fold. First we aim to add (high P−T) experimental data to the currently small database of SAG in the literature. Second, our goal is to study the effect of the gas type on the behavior of foam in porous media, at both low and high pressure—temperatures. Therefore, this paper focuses on describing the experiments when CO2 or N2 is injected into a porous medium that is initially saturated with a surfactant solution (SAG foam). Section 2 describes the experimental setup and the experimental procedures. Section 3 presents the experimental results for two sets of experiments. The first set of the experiments is performed at atmospheric pressure and a room temperature of T = 20 °C. The second set of experiments is conducted at P = 90 bar and T = 50 °C. This condition is well above the critical point of CO2. Section 4 provides detailed explanations of the differences observed in the experiments and investigates the relevant physical/chemical properties of gases affecting the foam behavior in the porous medium. Finally, we draw the main conclusions of this study.

2. Experimental Details

2.1. CT Imaging. The values of the CT scanner are measured in Hounsfield units (HU). The relationship between attenuation coefficient and HU is

\[
H_{U_m} = 1000 \left( \frac{\mu_m}{\mu_w} - 1 \right)
\]

where \(\mu_m\) displays the water attenuation coefficient: we obtain \(H_{U_m} = 0\) for water and \(H_{U_m} = -1000\) for air. The following equation is used to compute the liquid saturation, \(S_w\), from the measured HU, eliminating the contribution of the rock by the subtraction:

\[
S_w = \frac{H_{U_{\text{foam}}} - H_{U_{\text{dry}}}}{H_{U_{\text{wet}}} - H_{U_{\text{dry}}}}
\]

where the subscripts foam, wet, and dry stand for the foam flow, solution saturated, and dry core conditions, respectively.

2.2. Materials, Chemicals. The surfactant used was alpha-olefin sulfonate, AOS (Stepan Company). This surfactant is anionic and was used as received without any further purification. The general structure of olefin surfactants is \(R = SO_2Na^+\), where R represents the hydrophobic group. In our case, the number of carbon atoms in the surfactant structure is 12 and the molecular weight of the surfactant is \(M_w \approx 273\) g/mol. A fixed active surfactant concentration of \(c_{\text{AOS}} = 0.50\) wt % was used in our experiments. Sodium chloride (NaCl) was used to make the brine. The concentration of NaCl was a fixed value of 0.5 M (~3 wt %) in all experiments reported here. All solutions were prepared with deionized water (pH = 6.8 ± 0.1). To increase the CT attenuation of the solutions, 10 wt % of sodium wolframate (Aldrich, 99% purity) was added to the solutions.

Gases. The gases used to carry out the experiments were 99.98% pure CO2 and N2. The solubility of CO2 in water is about 55 times higher than that of nitrogen.46

2. Porous Media. The porous medium used was consolidated, quasi-homogeneous, and quartz-rich Bentheimer sandstone. The main properties of the porous medium are presented in Table 1. The permeability was calculated from the pressure data of a single-phase (brine) flow (with a known flowrate) through the core and the porosity was determined from the CT data. The radius of the pore throats are mainly in the range of 10−30 μm.

2.3. Experimental Setup. The schematic of the experimental setup is schematically shown in Figure 1. It consists of four parts: injection unit (IU), test unit (TU), pressure controlling unit (PCU) and data acquisition system (DAS).

Injection Unit. To ensure the supply of the gas at a stable rate, the gas flow rate is controlled by using a high precision needle valve (for low-pressure experiments) and an ISCO pump (for high pressure experiments) and it is monitored by using a gas flow meter. A high precision double-effect piston displacement pump (Pharmacia P 500) is used to inject the brine and the surfactant solution at a constant rate.

Test Unit. In the test unit, the sample core is placed inside a cylindrical coreholder. The coreholder is made of poly(ethylene ether ketone) (PEEK) that combines good mechanical properties to a low X-ray attenuation. The geometry and structure of the core holder were designed to minimize beam hardening and scattering artifacts.47 The core holder was placed vertically on the platform of the CT scanner apparatus and kept in place using a polymethyl methacrylate (PMMA) stand. The foam is introduced from the injection tube, and the liquid production is collected in a glass cup on an electronic mass balance. Two high precision pressure transducers locate at the inlet and the outlet to monitor the pressure drop along the core.

Pressure Control Unit. The pressure control part connects to the outlet of the core. By using a backpressure regulator and a manometer we can measure different pressures in the system. The data acquisition system records gas and liquid injection rates, pressures, and the liquid production data automatically. All experiments are conducted under isothermal conditions. The low pressure experiments are done at room temperature of \(T = 20\) °C and the high pressure experiments are performed at a constant temperature of \(T = 50\) °C.

Most of the core-flood setup is positioned on the table of the CT scanner. The PEEK core holder is vertically placed,
perpendicular to the length of the table, to control the gravity segregation effects. The third generation SAMATOM Volume Zoom Quad slice scanner is used in our work. The main technical information about this machine has been provided elsewhere and the imaging settings in our experiments are listed in Table 2. The X-ray tube of the CT scanner is operated at the voltage of 140 kV and the current of 250 mA. The thickness of CT slice is 3 mm, and one series of scan includes four slices. In the calculations the slice corresponding to the center of the core was used.

2.4. Experimental Procedure. Core Preparation. The cores were drilled from a large block and sawed to the dimensions specified in Table 1 using a diamond saw cooled with water. The cores were dried in an oven at 60°C for at least 48 h. Then the cores were molded in Araldite glue to avoid production from the axial core sides. The core was then placed in a PEEK core holder. For pressure measurements inside the core, the pressure gauges were connected through a small hole drilled in the glue to the surface of the core. The connectors were also made of PEEK to reduce the beam-hardening effects of X-ray beam.

Before starting the experiments all of the connections in the setup were checked for possible leakages by keeping the setup under high pressure and monitoring the measured pressures.

Core Saturation. The core was flushed with CO₂ for at least 30 min to replace the air in the system. Afterward, at least 20 pore volumes of brine with the flowrate of \( q_w = 2 \) ml/min were injected to the system while the backpressure was set \( P_b = 20 \) bar. Therefore, all CO₂ present in the core is dissolved into the brine and carried away. This is confirmed by CT images.

Surfactant Injection. After the core was saturated with the brine, 1 pore volume of the surfactant was injected (\( q_s \approx 2 \) ml/min) to the porous medium. The adsorption of AOS surfactant on Bentheimer sandstone is very low. Moreover, 1 wt % of AOS is well above its CMC value and therefore, injection of 1 PV of surfactant would be sufficient to satisfy the rock adsorption.

Foam (Gas) Injection. The gas is injected into the core previously saturated with the surfactant solution (SAG foam).

3. Results

3.1. Low Pressure Foam Development. a. CT Scan Images. Figure 2 presents the CT images of the central part of the CO₂ and N₂ experiments, respectively. The time of each image is also shown in terms of the dimensionless time of pore volumes, \( PV \), which is the ratio of the cumulative volume of injected fluids (in these experiments only gas) to the volume of the pore space in the porous medium. In these experiments the gas (CO₂ or N₂) was injected with a flowrate of 0.5 mL/min to the core initially saturated with 1–2 PV of the surfactant solution (SAG scheme). The blue and red colors represent the gas and the liquid phases, respectively. The general features of these experiments (foam advance) are similar to foam experiments in which the surfactant solution and the gas are co-injected into the porous medium. For both CO₂ and N₂, the images show a front-like displacement of the aqueous phase by foam. Three regions can be distinguished in both experiments along the flow direction: (1) an upstream region which is characterized by low liquid saturation, (2) a region downstream of the foam front where the liquid saturation is still unchanged and equals unity, and (3) a frontal region characterized by a mixing of flowing foam and liquid and exhibits fine fingering effects. The extent of the fingering behavior is caused by the local rock

Table 1. Properties of Sandstone Cores (Porous Media)

<table>
<thead>
<tr>
<th>name</th>
<th>permeability [mD]</th>
<th>porosity [%]</th>
<th>diameter [mm]</th>
<th>length [mm]</th>
<th>pore volume [ml]</th>
<th>main composition</th>
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<tbody>
<tr>
<td>long core</td>
<td>1100 ± 100</td>
<td>22 ± 0.2</td>
<td>40 ± 1</td>
<td>170 ± 2</td>
<td>42.5 ± 0.5</td>
<td>quartz</td>
</tr>
<tr>
<td>short core</td>
<td>1100 ± 100</td>
<td>22 ± 0.2</td>
<td>40 ± 1</td>
<td>90 ± 2</td>
<td>22.5 ± 0.5</td>
<td>quartz</td>
</tr>
</tbody>
</table>

Table 2. Settings of the CT Scan Measurements

<table>
<thead>
<tr>
<th>parameters</th>
<th>CT-scan settings</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>current [mA]</td>
<td>250</td>
</tr>
<tr>
<td>slice thickness [mm]</td>
<td>3</td>
</tr>
<tr>
<td>number of slices</td>
<td>4</td>
</tr>
<tr>
<td>filter</td>
<td>B40-medium</td>
</tr>
</tbody>
</table>

Figure 1. Schematic of the foam setup: It consists of four major units: injection unit (pumps), test unit (the porous medium), pressure controlling unit, and data acquisition system (not shown in this Figure).
heterogeneity and apparently depends on the type of the foamed gas (foam strength).

Nevertheless, a closer examination of the images reveals the considerable differences between CO₂ and N₂ foams. About 0.30 PV of CO₂ is injected before the gas penetrates the core and becomes visible in the images while N₂ becomes visible much more rapidly as the gas penetrates the core immediately displacing the liquid. This is possibly due to the higher solubility of CO₂ in water. The upstream region of CO₂ foam front is less blue indicating higher water content compared to the upstream region of N₂ foam. However, similar to N₂ foam, as the foam front progresses in the core, the gas sweeps parts of the remaining liquid from the upstream region toward the outlet. In the frontal region, N₂ foam is sharper than CO₂. Finally, the higher solubility of CO₂ in the aqueous phase results in its substantially delayed breakthrough. The gas breakthrough takes places at a time between 1.30 and 1.70 PV for N₂ foam while the foamed CO₂ breaks through at a time slightly larger than 2.20 PV.

The amount of CO₂ that can be dissolved in water can be estimated by Henry’s law. The solubility of CO₂ in water is ∼38.4 mol/m³ at our experimental condition. Using the CT images the volume of water that gas has met was estimated at each PV and then the amount of dissolvable CO₂ was calculated. The results are summarized in Table 3. In these calculations the possible effect of surfactant micelles on CO₂ solubility is disregarded. It turns out that the amount of dissolved CO₂ is considerable and therefore the effect of water solubility cannot be neglected. Indeed, considering also some dead volume in the system, more than 1 PV of the injected CO₂ is required to saturate the liquid before it can form foam.

b. Saturation Profiles. To quantify the evolution of the liquid saturations, S_w, over the entire core, the CT data of the obtained images were converted to water saturation profiles using eq 2. The results are shown in Figure 3a,b at various times for CO₂ and N₂, respectively. Note that every point on these figures is the averaged water saturation over a disk of the core with ∼8 mm thickness. These figures show that foamed CO₂ and N₂ displace the liquid, that is, the surfactant solution from the porous medium. Prior to the gas breakthrough the saturation profiles along the core show a steep increase of S_w at the foam front, which indicates an effective front-like displacement of the initial liquid for both foams. In the case of CO₂ foam due to more fingering in the foam front, revealed by the CT images, the front is not as sharp as for the N₂ foam.

Another difference in the saturation profiles of these experiments (SAG scheme) with experiments reported in refs 26, 48 is the absence of so-called secondary liquid desaturation (SLD) stage in our experiments. The secondary liquid desaturation is driven by gas expansion and to be controlled by the competition between viscous and capillary forces. Considering the differ-
In the experimental conditions, it seems that SLD is a phenomenon that happens in the experiments with high gas flowrates (and/or short cores).

The high values of liquid saturation at the region close to the core inlet indicates the capillary end effect where the porous medium retains the liquid in an attempt to maintain equilibrium across the outlet where the capillary pressure is zero or near zero. After about 2 PV of gas injection, CO₂ foam removes about 50% of the liquid while N₂ removes more than 70% of the liquid. Further injection of N₂ after (foam) breakthrough removes the liquid retained at the inlet and outlet of the porous medium while further injection of CO₂ produces the liquid from the whole core as the liquid content is still high after foam breakthrough. Finally, comparing the water saturation profiles of two gases at the same pore volumes, one can conclude that the foamed N₂ displaces more liquid than foamed CO₂. Indeed, the foamed N₂ produces more than 82% of the initial liquid in the porous medium while the foamed CO₂ sweeps less than 65% of the initial liquid after more than 11 PV of gas injection.

c. Pressure Profiles. Figure 4 compares the measured pressure drops versus dimensionless time (PV) of the two experiments. It appears that the foamed N₂ builds up larger pressures over the core than foamed CO₂. The high liquid saturation and the small pressure drop indicate that CO₂ is in the form of relatively weak foam. Although this foam is relatively weak, it does produce a pressure drop higher than expected for the steady state pressure drop with the gas injection to a core initially saturated with water. In both experiments the pressure drop across the core reaches a maximum and then declines slowly. The maximum point corresponds to the foam breakthrough at the outlet. The pressure decreases after breakthrough because of the coalescence of the bubbles due to diffusion or breaking of the foam films.

For a detailed explanation of foam progress in the core the pressure drop measurements at different sections of the core are plotted for the N₂ experiments in Figure 5. At early times, until 0.50 PV, the pressure drop is quite small. This means that foam is still weak. From time 0.50 PV to 0.70 PV there is a sharp increase in the pressure drop across the beginning of the core. This is confirmed by the saturation profile in Figure 3b. After 0.50 PV of gas injection, the foam front moves relatively slower along the core, nevertheless, it produces more water from the upstream region. Comparing the saturation profiles of two gases, this effect is more pronounced in the CO₂ foam, possibly because (i) CO₂ foam is weaker and (ii) unlike N₂ foam, the transition from weak to strong foam does not happen for CO₂.

The low pressure drop and relatively high liquid saturation at the core inlet at early experimental times is referred to as the *entrance effect* in the literature. Apparently gas needs time and space before it develops into foam. The pressure drop continues to increase as gas moves forward along the core. Again due to the capillary end effect the pressure drop at the last section of the core is low (water saturation is high). The pressure drop reaches maximum of 0.42 bar, which is equal to the overall pressure drop across the core. This means that foam in the last section is weaker than foam in the first half of the core. However, as it is seen from Figure 5 the pressure drop at the last section of the core increases with time indicating that foam becomes stronger with increasing amounts of injected gas. After foam breakthrough the pressure drop decreases due to the destruction of foam films as mentioned previously.

3.2. High Pressure Experiments. The second set of experiments were done at P = 90 bar and T = 50 °C. This P–T condition is well above the critical point of CO₂. The density of CO₂ is 286 kg/m³ at this condition calculated from the Span and Wagner EoS. Moreover, at this pressure and temperature, a water-rich liquid phase coexists with a CO₂-rich liquid, where a distinction between the vapor and liquid phases of CO₂ disappears. Note that foams formed with dense CO₂ as the internal phase are strictly emulsions, sometimes referred to as *foamulsion*. However, for the sake of consistency we use the term foam here as well.

a. CT Images. Figure 6 presents the central CT images of CO₂ gas, CO₂ foam, and N₂ foam flow at P = 90 bar and T = 50 °C. The time of each image is also shown in the dimensionless time of pore volumes, PV. The gas flowrate in these experiments was set to 1 mL/min. In the CO₂ gas experiment the core was initially saturated with brine, and CO₂ was injected into the core afterward. The images reveal the remarkable effect of the surfactant solution in the porous medium. When CO₂ is injected to the core initially saturated with the brine, there is no (clear) sharp interface between the gas and the brine. CO₂ forms channels through the brine and breaks through in less than 0.20 PV. When CO₂ is injected into the core initially saturated with the surfactant solution a clear interface between the moving gas and the liquid appears and CO₂ breakthrough is delayed until a time between 0.45 PV and 0.50 PV. The breakthrough time for N₂ foam is longer than 1.2 PV. Similar to the low pressure foam experiments the three regions are again present at high pressure foam experiments. In the CO₂ foam,
the gas bypasses part of the porous medium and therefore the brine content is high at regions near the core inlet and outlet. In the N₂ foam, the foam front moves a lot slower after 0.40 PV which is an indication that the foam has become stronger.

b. Pressure Profiles. Figure 7 shows the pressure history for CO₂ gas and CO₂ foam experiments while Figure 8 compares the pressure drop of CO₂ and N₂ foams. The pressure drop along the core follows a similar trend; it reaches a maximum at gas breakthrough and then declines with time. The maximum value of the pressure in CO₂ foam is about two times larger than that of CO₂ gas. Compared to the low pressure experiment, the pressure peak is higher at the high pressure CO₂ (and N₂) foam because (i) the gas flowrate is higher and (ii) CO₂ has a higher density (and viscosity) in the latter case. One interesting feature is that after 1.0 PV of CO₂ injection, the pressure drop of the CO₂ foam experiment is comparable to that of CO₂ gas experiment, meaning that after breakthrough there is almost no foam (or emulsion) present in the porous medium due to the shortage of the surfactant. The pressure drop for the N₂ foam is again larger than the CO₂ foam (see Figure 8). In the N₂ foam the pressure drop over the core is low until 0.40 PV, confirming the idea that gas should invade some part of the core before it develops into foam. This effect appears to be less significant for CO₂ than N₂ and as can be seen from Figures 2 and 6, the higher the gas flowrate the larger the entrance effect is.

c. Saturation Profiles. The calculated liquid saturation profiles, $S_w$, for the three experiments are shown in Figure 9. In all three experiments gas displaces the liquid, although when gas is foamed inside the porous medium the amount of the liquid that remains inside the core is less than when the gas is not foamed. Moreover, in the gas injection there is no steep increase of $S_w$ at the gas front while in foam experiments an effective front-like displacement of the initial liquid by foam takes place. The capillary end effect is present in the experiments as the

Figure 6. CT images of (a) CO₂ gas, (b) CO₂ foam, and (c) N₂ foam flow in a porous medium initially saturated with surfactant solution (red) at $P = 90$ bar and $T = 50$ °C ($q_g = 1$ mL/min). The time of each image is shown in pore volumes of the injected gas.
liquid saturations are high near the core outlet. A detailed analysis of the N2 foam experiments reveals that when the foam becomes stronger (after 0.40 PV of gas injection), the liquid saturation is reduced to a value as low as 8%; nonetheless due to the capillary end effects the saturation starts to increase to maintain the pressure equilibrium near the core outlet (This would have happened later if the core was longer). The SLD is present in this experiment because of the significance of the capillary end effects. After about 1.5 PV of gas injection, CO2 gas produces about 40% of the initial liquid. Foaming of CO2 increases the recovery by 25% and brings out more than 65% of the liquid. The N2 foam removes more than 80% of the liquid.

4. General Discussion

The experiments in previous sections have clearly demonstrated that under a SAG scheme CO2 foams are weaker than N2 foams at both low and high pressures. Foam in porous media is considered weak when the number of the lamella is not large enough to resist the gas flow.56,57 To interpret these observations we need to recall that foams are thermodynamically meta-stable. They evolve irreversibly over time because the interfacial area in the lamella diminishes in order to minimize interfacial free energy.58 The longevity of foam in porous media essentially relies on the stability of single foam films or lamellae. The stability of foam films depends on quantities and processes like surfactant concentration, salt concentration, adsorption kinetics, gravitational drainage, gas diffusion through foam films, surface forces (or capillary pressure) and fluctuations.59,60 Before we assert the dominant factor responsible for the difference between CO2 and N2 foams it is worth reviewing how individual mechanisms could affect foam stability.

Coalescence and Drainage. These two processes are responsible for the changes in degree of dispersion of gas bubbles in foam as they cause (i) the diffusion of gas through the lamellae and (ii) collapse of liquid lamellae and subsequent coalescence of contiguous gas bubbles.61
between bubbles of unequal size induces gas-transfer from small to larger bubbles. Even in the ideal situation of an initially perfectly ordered foam, comprising uniform bubbles with a uniform gas pressure, finite size perturbation in bubble shape (e.g., due to irregularities and heterogeneity in porous media) would lead to an irreversible growth of the larger bubbles at the expense of the smaller.\textsuperscript{56} This foam coarsening, the Oswald ripening, is unavoidable.\textsuperscript{37}

The mass-transfer rate of gas through foam films can be characterized by the film permeability $k$. Following Princen and Mason\textsuperscript{62} gas permeability depends on physical coefficients according to equation

$$k = \frac{k_{hi}D}{h_w + 2D/k_{ml}} \quad (3)$$

where $D$ is the diffusion coefficient of the gas in the liquid phase, $k_{hi}$ is the Henry’s coefficient, $k_{ml}$ is the permeability of the surfactant monolayer to gas, and $h_w$ is the thickness of the liquid film. Equation 3 shows that the permeation rate for thick foam films, $(2D/k_{ml} \ll h_w)$, is mainly controlled by the liquid layer via $D$ and $k_{hi}$ ($k \sim k_{hi}D$), while for thin foam films $(2D/k_{ml} \gg h_w)$ the permeability of the monolayer ($k = k_{hi}k_{ml}/2$) is the limiting factor.

The rather good agreement between the two ratios (solubility and film permeability ratio) suggests that coalescence rate of CO$_2$ foam bubbles must be much higher than that of N$_2$ foam bubbles. Therefore this could be why CO$_2$ foam is weaker than N$_2$ foam. This is analogous to the situation of steam foam where water vapor can pass through lamellae by condensing on one side and evaporating on the other side.\textsuperscript{68} A small amount of nitrogen is added to reduce this effect in steam foam\textsuperscript{69} and in the beer industry.\textsuperscript{37,70} The higher solubility of CO$_2$ could also explain why in CO$_2$ foam more pore volumes of gas are needed before the gas becomes visible in the core and also why the speed of the foam front is lower for CO$_2$ than for N$_2$.\textsuperscript{66} In the only published data, the transfer rate of CO$_2$ through the foam films stabilized by hexadecyltrimethylammonium bromide (HDTAB) in the presence of NaBr was measured to be about 60 times larger than that of N$_2$.\textsuperscript{62,67}

The interfacial tension of the N$_2$-water binary system does not change and is constant in the range of our experimental pressures. \textsuperscript{73,74} The interfacial tensions of the CO$_2$-water and the N$_2$-water systems exhibit different behavior. Initially both foams show similar behavior, that is, while the gas displaces the liquid the pressure drop remains low (weak foam). However, as time passes for similar gas fractions (above $S_g \approx 0.30$), N$_2$ foam exhibits higher pressure drop over the core. This implies that (1) while a transition from weak foam to strong foam occurs in N$_2$ foam, CO$_2$ foam always remains weak, and (2) CO$_2$ foam is coarser than N$_2$ foam in porous media due to more intense rupture of the foam films (lamellae), as discussed previously. Figure 11 provides a similar plot for high pressure experiments. Again in this case there is a gas saturation in which the transition from weak foam to strong foam occurs in N$_2$ foam ($S_g \sim 0.35$). This saturation is higher than that of the low pressure N$_2$ foam presumably due to the differences in the flowrates. Seemingly, CO$_2$ continues to flow as a weak foam (or more accurately foamulsion) in the core.

**Role of Interfacial Tension.** The interfacial tensions of the CO$_2$-water and the N$_2$-water systems exhibit different behavior. The interfacial tension of the N$_2$-water binary system does not vary considerably with pressure such that it can be assumed constant in the range of our experimental pressures.\textsuperscript{73,74} Nevertheless, the interfacial tension between CO$_2$ and water...
depends strongly on pressure for pressures smaller than 10 MPa,
decreasing as the pressure increases (from 72 to about 20 mN/m),
and displays an asymptotic behavior toward a constant value
for higher pressures.65–67 Even at low pressure of 1 bar the
presence of CO2 above a surfactant solution may lower the
interfacial tension possibly due to the surface hydrolysis of
the surfactant.78 The resistance to flow of the individual lamella
in porous media is proportional to the surface tension.79 It is
interesting to mention that decrease in the interfacial tension
leads to higher permeation of the gas molecules through the
foam films and therefore may decrease the stability of foam.80
Moreover, it has been observed that the relative permeability
of CO2 increases as the interfacial tension of the CO2-water
system decreases.77

Wettability Alteration Effects. Part of the observed differences
in CO2 and N2 foam experiments may be attributed to both,
differences in the interfacial tension and differences in the
wetting angles of the two gases, that is, the value of \( \sigma \cos \theta \),
where \( \sigma \) is the gas–water interfacial tension and \( \theta \) is the contact
angle. Hildenbrand et al.81 stated that for the N2-water system
the product of \( \sigma \cos \theta \) exceeds the corresponding product for
the CO2-water system by a factor of 1.3–2.0. This suggests
that wettability of the clay part of the rock may change with
injecting CO2. Foam is more stable in water-wet rock than in
intermediate (or oil) wet porous media.82–84 If the medium is
not water-wet the walls may cause the lamellae to detach and
collapse.85 Our experiments are done in Bentheimer sandstone
that contains 1–4 wt % of clay.85 Therefore, injection of CO2
affects the wettability of the cores. When the lamella moves
across a nonwetting spot of the pores it ruptures by the pinch-off
mechanism86 lowering the resistance of foam to flow. It is
important to remark that wettability and interfacial tension forces
at the interface between liquid and rock may also affect bubble
formation.86 Hence, it is possible that the rate of foam generation
in CO2 foam is different than N2 foam due to wettability effects.

pH Effects. Another factor that may affect the foam stability
is the pH of the aqueous phase. When CO2 is injected into a
reservoir, CO2 reacts with water and forms carbonic acid. This
reaction may lower the pH of the brine down to 4.0.87 The value
of pH may influence the foam film stability by affecting the
disjoining pressure through screening of the van der Waals
and electrostatic forces.86 The pH changes could also influence
the surfactant performance in porous media.87 The pH effects can be
related to the differences in their nature, mainly solubility in water,
interfacial tensions, pH effects, type of surfactant, and the possible
wettability effects. From these properties for CO2 and N2 are
the same, the local gas velocities will be different, that is,
cause (1) part of the gas is dissolved in the aqueous
phase and, therefore, when volumetric flowrates of two gases
are the same, the local gas velocities will be different, that is,
the amount of available CO2 for foaming will be lower than of
N2 at similar PVs, and (2) it significantly affects the gas
permeability coefficient and, thus, the foam stability.

Type of Surfactant. Different gases may show different
foaming behavior with different surfactants. Although AOS
surfactants have been previously used in CO2 foam projects, it
is possible that type of surfactant is responsible for the
differences observed in the experiments.

Temperature Effects. Temperature is another parameter that
controls the foam stability by influencing the diffusion rate and
adsorption of the surfactant molecules at the gas–water interface
and rock surface. CO2 dissolution in water is exothermic. The
solution heat of CO2 is given by

\[
-(d \ln k_f d(1/T))_{CO2} = \Delta H_{CO2} / R = \frac{2400 \text{ K} \rightarrow \Delta H_{CO2}}{\frac{3400 \times 4.2 \times 10^6}{2.0 \times 10^4 \text{ J/mol}}} 
\]

This implies that CO2 dissolution can cause a temperature increase of

\[
\Delta T_{CO2} = \frac{\Delta H_{CO2}}{k_f \rho_w c_p} = \frac{2 \times 10^4}{3400 \times 4.2 \times 10^6} \approx 0.15 \text{ K/bar}
\]

A similar calculation for N2 reads \( \Delta T_{N2} \approx 0.00015 \text{ K/bar} \). Therefore, the temperature rise in the water due to CO2
dissolution is more significant, especially at higher pressures.
The increase in temperature can reduce the foam stability in
porous media because (i) it can initiate the interbubble diffusion
process by causing infinitesimal perturbation and thus disturbing
the equilibrium and (ii) it increases the mass transfer rate through
the bubbles. However, it should be noted that the temperature
effects cannot completely be responsible for the differences in
foaming behavior of CO2 and N2 since at low pressure the
temperature effect will not be significant.

5. Conclusions

The foaming behavior of CO2 and N2 were comparatively
studied in a sandstone core by the means of a CT scanner (X-
ray). (C14-C16) Alpha Olefin Sulfonate (AOS) was used as
surfactant. It has been shown that injection of a slug of surfactant
prior to CO2 injection can reduce the CO2 mobility, below and
above its critical point. The two investigated gases exhibit
different behavior in the porous medium. Foaming of CO2 builds
up lower pressure drop over the core at both low and high
pressures when compared to N2. Both gases require space to
develop into foam. The space is longer for N2 (larger entrance
effect) and increases with increasing gas velocity. The CT
images and calculated water saturation profiles reveal that N2
foam displaces the liquid in a front-like manner (sharp-vertical
interface) while the propagation front for CO2 foam is not the
exact front-like displacement at low pressure. Moreover, the
ultimate production by N2 foam is always higher than by CO2
foam. The observed differences in the foaming behavior of two
gases can be related to the differences in their nature, mainly
solubility in water, interfacial tensions, pH effects, type of
surfactant, and the possible wettability effects. From these
various factor solubility is likely the most critical one be-
cause (1) part of the gas is dissolved in the aqueous
phase and, therefore, when volumetric flowrates of two gases
are the same, the local gas velocities will be different, that is,
the amount of available CO2 for foaming will be lower than of
N2 at similar PVs, and (2) it significantly affects the gas
permeability coefficient and, thus, the foam stability.

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