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Synergistic Effect between Surfactant and Nanoparticles on the Stability of Methane Foam in EOR Processes

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Synergistic Effect between Surfactant and Nanoparticles on the Stability of Methane Foam in
EOR Processes

by

Chen Qian

A THESIS

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Abstract

This thesis investigates the enhanced oil recovery (EOR) potential of nanoparticles stabilized methane foam to improve the performance of conventional gas injection methods for oil reservoirs. This work conducts static and dynamic tests that help in understanding the sodium fatty alcohol polyoxyethylene ether sulfate surfactant (AES) and silica nanoparticles with alumina coating (SNOWTEX-AK) interaction mechanisms and in designing foam injection processes. With a carefully designed mixture of surfactant and nanoparticles at certain concentration ratios in the foaming solutions, the generated foam can overcome the challenges such as surfactant adsorption, effects of crude oil and oil saturation, and salinity in reservoir conditions.

The extent to which nanoparticles surface is covered with surfactant governs the foam stability both in static and dynamic conditions, with both heavy oil and brine present. In particular, when the nanoparticle surface is covered by a partial monolayer of surfactant molecules, foam stabilized by the partially covered nanoparticles provides a step-change improvement in performance for EOR due to its high dynamic stability. In contrast, foam stabilized by nanoparticles covered by a bilayer of surfactant has performance comparable to a surfactant-only foam, and both are ineffective for EOR due to their poor dynamic stability when contacting reservoir fluids.

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Dedication

To my parents, for their unconditional love and encouragement.

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Nomenclature

Symbol	Definition
θ	Contact angle
γ	Surface tension, MLT^{-2}
PV	Pore volume, L^3
PVI	Pore volume of injection, L^3

Chapter 1 : Introduction

1.1 Introduction

An oil recovery process can be divided into three classes: primary, secondary and tertiary or enhanced oil recovery (EOR). Primary recovery exploits the natural energy present in the reservoir without supplemental energy from the surface. Typical primary oil recovery process includes solution gas drive, water drive, gas cap drive, gravity drainage, fluid expansion and rock compaction (Green and Willhite, 1998). Secondary oil recovery refers to additional oil obtained by injecting water or immiscible gas back to the reservoir. Water flooding and gas flooding are common secondary oil recovery processes. EOR methods target the residual oil after the secondary processes. EOR uses more advanced techniques such as mobility control, chemical flooding, miscible gas flooding and thermal methods. Chemicals used in EOR include surfactants, polymers, and alkali. Surfactant flooding aims to reduce the interfacial tension between oil and liquids. It can also alter the wettability of the rock surface or cause spontaneous emulsification. Large molecular weight polymers increase the viscosity of displacing fluid and can improve the volumetric sweep efficiency. Alkali reacts with the organic acid components inside the crude oil, generating surfactant or emulsion in-situ. Miscible flooding involves injecting a fluid that can mix into oil as a single phase, thus eliminating interfacial tension and capillary forces. There are two types of miscible flooding, namely first contact miscible (FCM) and multiple contact miscible (MCM). In FCM, the injected fluid will mix with crude oil under the reservoir condition as soon as contacting, and in MCM, the injected fluid is not totally miscible with crude oil at first contact, but the composition of crude oil or the injected fluid will change after multiple contacts. The density and viscosity of injected fluid are usually much lower than that of crude oil, thus viscous fingering and

gravity segregation are the major concerns in miscible gas flooding. Thermal recovery usually involves the injection of steam to reduce the viscosity of heavy oil. SAGD (steam-assisted gravity drainage), CSS (cyclic steam stimulation) and steam flooding are the main thermal recovery methods.

Gas flooding has multiple usages in the oil recovery process. Methane and other hydrocarbon gas are commonly used in miscible flooding, supercritical CO₂ injection aims to create a miscible zone of oil to move the oil more easily to the production well, steam injection aims to increase the reservoir temperature and reduce the oil viscosity dramatically and improve its mobility. The major challenge in the gas flooding is the poor volumetric sweep efficiency, and there are two reasons for this; the first reason is the high mobility of injected gas, and the second reason is the reservoir heterogeneity. Gas has low viscosity and can easily go through the high permeable layers. After the early breakthrough of the gas at a production well, a short cut has formed, and the following injected gas get recycled while most of the reservoir remains untouched. The early breakthrough of gas happens to most of the gas injection during the EOR process: steam, air, nitrogen, carbon dioxide, and hydrocarbon gases.

Foam flooding is an improved enhanced oil recovery method (EOR) for gas flooding, in that foam acts as a more viscous fluid in the reservoir to resist gas flow. The main advantage of foam is fluid diversion. Foam can divert fluid from the high permeability layers to the low permeable layers, and thus form a uniform displacing front to enhance volumetric sweep efficiency.

1.2 Fundamentals of foam in porous media

Foam is defined as a dispersion of gas in a continuous liquid phase, or some part of the gas phase is made discontinuous by thin liquid films called lamellae (Hirasaki, 1989). In porous media, foam

is an improved EOR method for gas injection, in that foam acts as a more viscous fluid in the reservoir. Foam can reduce gas mobility by reducing gas relative permeability and increasing the apparent viscosity of the gas phase. Foam can effectively divert fluid from high permeable zones to low permeable zones and establish a uniform displacing front in the reservoir to enhance sweep efficiency and increase oil recovery. The schematic of foam improving sweep efficiency is shown in **Figure 1-1**. The ability of the foam to resist gas flow depends on the texture of foam, such as bubble size, or the number of lamellas per unit volume of gas. Small bubbles or greater number of lamellas mean more resistance to gas flow and are considered as strong or stable foams to enhance sweep efficiency and increase oil recovery.

Figure 1-1 Schematic of foam (bottom panel) improving volumetric sweep efficiency compared to gas injection (top panel), which creates channels between injection and production wells.

1.2.1 Surfactant

Conventional foam generation methods use surfactant alone as the stabilizer. Surfactants can stabilize the foam by reducing the interfacial tension between gas and liquid phases (Hirasaki 1989) as shown in Figure 1-2. However, foam stabilized by surfactant alone is unstable based on three reasons, namely chemical loss due to surfactant adsorption, precipitation or partitioning into the oil and degradation under high temperature and high salinity reservoir environment (Grigg and Mikhalin, 2007). Surfactant loss due to adsorption is important on common reservoir minerals, and the total amount of adsorption depends on the temperature of the reservoir, pH, salinity and ion exchange (Lau and O'Brien, 1988). Crude oil destabilizes foam by spreading and/or bridging along the gas/water interfaces (Lau and O'Brien, 1988; Garrett, 1992). Salinity plays different roles in foam stability. In some cases, salt could decrease the CMC (critical micelle concentration) and enhance interfacial shear viscosity, while in other cases, salt destabilized foam by reducing the electrostatic repulsion (Dilgren and Owens, 1982). High temperature could increase CMC and lead to a reduction of total micelles number in the liquid, and even if the high temperature could reduce surfactant adsorption, it still reduces the interfacial viscosity and hastens the thinning of lamella.

Figure 1-2 Foam structure in bulk phase and surfactant adsorption to the gas/liquid interface in conventional surfactant stabilized foams (adapted from Schramm 2000).

1.2.2 Foam generation mechanism

There are three foam generation mechanisms in the porous media, namely leave-behind, lamella division, and snap-off. Ransohoff and Radke (1988) identified these three mechanisms in homogeneous bead packs test, and investigate the effect of bead size, flow velocity, gas/liquid ration and permeability on the foam generation process.

The first mechanism is leave-behind. In the leave-behind mechanism, the pore body and pore throat are saturated with a surfactant solution first, and then gas fingers invade the pore throat from different directions. The liquid inside the pore throat is squeezed into a lamella. The procedure is shown in **Figure 1-3**. The lamella generated under this mechanism is usually parallel to the gas flow direction, and it cannot efficiently block or bridge the gas phase (Schramm, 2000). If there are enough surfactants present in the liquid phase, the lamella may be stable, or else the lamella

collapses very fast. After the lamella collapses, another lamella cannot be generated spontaneously under this mechanism, unless sufficient liquid enters the pore throat again.

Figure 1-3 Schematic of leave-behind mechanism. (a) gas finger invades the pore throat; (b) liquid in undrained pore throat is squeezed into a lamella between volumes of gas occupying adjacent pores (adapted from Ransohoff and Radke, 1988).

The second mechanism is snap-off. In the snap-off mechanism, the pore body and pore throat are saturated with surfactant solution, and then a gas finger penetrates the pore throat and jumps out of the site as shown in **Figure 1-4**. The gas bubble keeps expanding, and the curvature of the bubble decreases, and based on the relationship between capillary pressure and interface curvature, the capillary pressure across the gas-liquid interface decreases while the pressure in the surrounding liquid remains almost the same. Thus the pressure difference between the surrounding liquid and the interface will drive the surrounding liquid into the pore throat, and the liquid accumulates there, blocking the subsequent gas flow. If the gas bubbles continue to expand and the capillary pressure of the interface drops down to a critical value, the liquid will snap-off a gas bubble at last. There are two results of this mechanism: first, a separate gas bubble will form and

the lamella makes the gas phase discontinuous; secondly, since the flow rate is high under the snap-off mechanism, and there is enough pressure gradient between the pore throat and the surrounding liquid, the liquid will enter to the pore throat spontaneously, and the snap off mechanism can happen repeatedly at the same site in a short time. Thus Ransohoff and Radke (1988) believe it is the dominant mechanism of foam generation in the porous media at a high flow rate. There are two criteria for this mechanism to happen: first, the aspect ratio of the porous media, which is defined as the size of the pore body over the size of pore throat, must be larger than 2; second, it also requires enough wetting liquid nearby (Schramm, 1994; Chambers and Radke, 1991).

Figure 1-4 Schematic of snap-off mechanism. (a) Gas penetrates the pore throat and (b) jumps out of the site as water reconnects in the throat (Adapted from Ransohoff and Radke, 1988).

The third mechanism is lamella division. Lamella division requires a moving lamella and describes the subdivision of the existing lamella, thus it is different from the previous leave-behind and snap-off mechanism. In the lamella division mechanism, a moving gas bubble flows to a branch point, and the lamella enters the downstream pore space around the branch point. The procedure is shown

in **Figure 1-5**. In some cases, the gas bubble only enters one side of the branch point and there is no new bubble generated. In other cases, the gas bubbles enter two or more channels and then separate into two or more new bubbles as shown in Fig. The results of lamella division are similar to those of snap-off mechanism, in that: first, the gas phase is discontinuous by the new subdivided bubbles or by the original moving bubbles; and second, it could occur repeatedly at one site as long as separate gas bubbles keep flowing to the branch point. Therefore, when the gas injection rate is high, there is more possibility of more separate gas bubbles approaching the same point (Ransohoff and Radke, 1988).

Figure 1-5 Schematic of lamella division mechanism. (a) A gas bubble moving towards a branch point and (b) divided into new bubbles (Adapted from Ransohoff and Radke, 1988).

Critical capillary number Nc^* is the most important factor in determining the foam generation mechanism in porous media. Below Nc^* , there is a moderate decrease of relative permeability to the gas phase compared with pure water in the porous media, while above Nc^* , there is a sharp decrease of relative permeability to the gas phase. Thus, above the critical capillary number, snap-off and lamella division are the dominant generation mechanisms, and below this value, the foam was mainly generated by the leave-behind mechanism. Critical capillary pressure is determined by

the flow velocity and is increased by increasing gas fractional flow. Moreover, the snap-off mechanism was observed at all flow velocities from low permeable zones to high permeable zones (Ranshoff and Radke, 1988).

1.2.3 Foam stability

Chambers and Radke (1991) brought out two factors that affect foam stability in the porous media, namely capillary suction and gas diffusion.

The first factor is the capillary suction. Khatib et al. (1988) observed a sharp gas mobility increment of the system as the gas fractional flow increased to a certain value in the core flooding tests. They believed the foam in the system collapses immediately at that point and as they continued to increase the gas fraction flow, gas mobility continued to increase, and the foam was not re-formed in the system. They concluded that there is a transition of foam stability related to the capillary pressure of the system, and the capillary pressure at that certain value is called Limiting Capillary Pressure. Khatib et al. (1988) believed the capillary pressure of the porous media is increased when they increase the gas fractional flow, and as the gas fractional flow increase, liquid saturation of the system decreases correspondingly. Below the limiting capillary pressure, the system is in the stable foam region, and the increase of gas fractional flow favors foam generation in the system, and the relative gas mobility is reduced. However, above the limiting capillary pressure, the system is in the unstable foam region, where the foam collapses fast and cannot be generated again inside the porous media.

The gas/liquid interface of a bubble can be illustrated as in **Figure 1-6**. Neighboring 3 bubbles connected together and formed a plateau border with each angle at 120° . The thin liquid films are flat with larger radii, where the plateau border had a small radii. The capillary force difference will

drive the liquid flow towards the plateau border and cause the thinning of the film. Film thinning and the breaking of films are originated from the limiting capillary pressure (Schramm,1994).

Figure 1-6 Schematic of a foam system. The liquid inside thin liquid film will be driven towards the plateau border at the center by the capillary difference. This is thinning of foam film and cause the foam to collapse.

The second factor is gas diffusion. In a foam system containing different sizes of bubbles, small bubbles have small curvature and large bubbles have large curvature, and the capillary pressure of the small bubble is larger than that of the large bubble, thus the pressure difference between bubbles will drive the gas inside the small bubbles to diffuse into larger bubbles. Therefore, small bubbles will disappear eventually and more large bubbles will form. The ability of the foam to resist gas flow depends on the texture of foam. Thus more large bubbles in the system, or in other words, a smaller number of lamella per unit volume of gas, causes less flow resistance to gas flow. However, the process of non-condensable gas diffusion is slow and relatively less important in

foam flowing through porous media (Hirasaki, 1989), Capillary pressure is believed to govern foam texture in the porous media (Rossen and Zhou, 1995).

1.3 Effect of Oil in Foam Stability

Kinetic foam stability in porous media depends on the lamella stability, the presence of oil, hydrophobic particles or the combination of both effect lamella stability.

1.3.1 Surfactant depletion

It is widely believed that lamella thinning due to local fluctuation is an important mechanism in lamella stability. One driving force for the lamella movement in the porous media is capillary waves, and the movements depend on temperature and surface tension (Stockle et al. 2010). The surfactant might partition into the oil phase or adsorb to the oil/water interface and reduce the surfactant concentration at the gas/water interface consequently. On the other hand, oil might adsorb into the micelles and change the surface tension. One solution is to increase surfactant concentration in the foaming system to compensate for surfactant loss (Schramm, 1994).

1.3.2 Entering, spreading or bridging

To break a lamella, the oil droplet must first enter the gas/water interface, and then spread over the surface or bridge across the film. The process can be illustrated in **Figure 1-7**. The process can be interpreted into three coefficients, namely entering coefficient ($E_{o/w}$), spreading coefficient ($S_{o/w}$), and bridging coefficient ($B_{o/w}$) (Harkins, 1922).

$$E_{o/w} = \gamma_{wg} + \gamma_{ow} - \gamma_{og} \quad (1-1)$$

$$S_{o/w} = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \quad (1-2)$$

$$B_{o/w} = \gamma_{wg}^2 + \gamma_{ow}^2 - \gamma_{og}^2 \quad (1-3)$$

Where γ_{wg} and γ_{og} are the surface tension between water/gas interface, and oil/gas interface, respectively, and γ_{ow} is the interfacial tension between the water/oil interface.

Figure 1-7 Schematic of an oil droplet breaking a lamella by first entering the gas/liquid interface, and then spreading over the interface or bridging across the film (adapted from Harkins, 1922).

As the oil droplet approaches the water/gas interface, when $E_{o/w} > 0$, the oil droplet will enter the gas/water interface, or else, it will remain in the water phase. After entering the interface, if $S_{o/w} > 0$, oil droplet will spontaneously spread along the water/gas interface. If the spreading does not occur, however, this may lead to the result of bridging. When the oil droplet remains as a lens on

the water/gas interface and the contact angle between surfactant solution and oil droplet $\theta_{ow} > 90^\circ$, the film ruptures, and the bridging coefficient $B_{o/w} > 0$. Otherwise, the lamella remains stable.

Comparing the entering coefficient with the bridging coefficient, one can conclude that:

- $B_{o/w}$ is positive when $E_{o/w}$ is positive, but a positive $E_{o/w}$ does not guarantee a positive $B_{o/w}$. Therefore, a positive $B_{o/w}$ is a sufficient condition for oil droplets to enter the water/gas interface.
- $S_{o/w}$ is negative when $B_{o/w}$ is negative. Therefore, oil droplet with negative bridging coefficient does not spread along the water/gas interface.

1.3.3 Generalized entering coefficient

Classic entering and spreading theory might fail to explain the oil-foam interaction in porous media in that it does not consider the geometry of the system or the interfacial interactions within the film. Bergeron et al. (1993) defined a generalized entering coefficient that considered the effect of porous media, thin liquid films and capillary suction in the plateau borders, and the generalized entering coefficient is defined as:

$$E_{o/w}^g = \gamma_{wg} + \gamma_{ow} - \gamma_f \quad (1-4)$$

where γ_f is the interfacial tension of the pseudoemulsion films. When the pseudoemulsion films are less curved at equilibrium, the system demonstrates a negative entering behavior and stable pseudoemulsion films that foam can remain stable when contacting crude oil (Bergeron et al., 1993).

1.3.4 Oil emulsification and lamella number

Schramm and Novosad (1990) proposed an alternative lamella rupture mechanism of oil emulsification into the foam structure. Capillary suction in the plateau border draws oil into the lamella and emulsifies oil, the capillary suction can be written as:

$$\Delta P_c = \frac{2\gamma_{wg}}{r_p} \quad (1-5)$$

where r_p is the radius of curvature of the Plateau border. Oil tends to minimize the interfacial area between the aqueous solution and the corresponding resisting force can be written as:

$$\Delta P_R = \frac{2\gamma_{ow}}{r_o} \quad (1-6)$$

where r_o is the radius of curvature of the oil droplet. Lamella number (L) is defined as the ratio between capillary suction and resisting force across the interfacial area:

$$L = \frac{\Delta P_c}{\Delta P_R} = \frac{r_o \gamma_{wg}}{r_p \gamma_{ow}} \quad (1-7)$$

If $L > 1$, the oil droplets are small enough to enter the lamella and cause the film to rupture, and if $L < 1$, this equation anticipates a stable lamella. Mannhardt et al. (2000) pointed out that the most stable lamella exists when L is low, and E is negative.

1.4 Benefits of Additional Nanoparticles in the Foaming System

1.4.1 Nanoparticles

Recently, solid particles have been proved to emulsify emulsions or stabilize foams, such as polymers, microparticles, and nanoparticles (Binks, 2002). Kruglyakov and Taube (1972) investigated the effects of surfactant type, particle size and concentration on solid particles stabilizing foam.

Solid particles play an important role in stabilizing foam, but there are certain differences between nanoparticles and conventional stabilizers such as surfactant. Firstly, nanoparticles do not form micelles in the aqueous phase, and there is no concern about solubility. Secondly, moving nanoparticles to the interfaces is a slow process compared with moving surfactant (Okubo, 1995). Thirdly, the adsorption of particles to the fluid/liquid interface does not change the interfacial tension like surfactant molecules do (Vignati et al, 2003). Lastly, surfactant molecules can adsorb to or desorb from the interface in a short time, but the adsorption of nanoparticles to the interfaces can be considered as an irreversible process, in that the energy required to move the nanoparticles away from the interfaces are high. This energy is defined as detachment energy (Binks, 2002)

1.4.2 Detachment energy

The detachment energy E is defined as the energy required to move the particles away from the interfaces, and E highly depends on the wettability of the nanoparticles. E is given by

$$E = \pi r^2 \gamma_{\alpha\beta} (1 \pm \cos\theta)^2 \quad (1-8)$$

where r is the radius of the nanoparticles, $\gamma_{\alpha\beta}$ is the interfacial tension between fluid α and fluid β , θ is the contact angle between the particle and the interface. The particle is adsorbed to the fluid α – fluid β interfaces, and the gravity force on nanoparticles is negligible in this case. The sign inside the bracket is positive for moving the particles into the air or oil phase and negative for moving particles into the water phase.

The contact angle θ of hydrophilic particles is normally $< 90^\circ$, and the majority of the particles tend to stay in the water phase rather than in the air or oil phase. If the particles are hydrophobic and contact angle θ is normally $> 90^\circ$, it is easier to move the particles into the air or oil phase than to the water phase.

Binks and Horozov (2005) pointed out that foam cannot be generated with pure hydrophilic or hydrophobic particles, but the foamability can be progressively improved for particles with intermediate hydrophobicity. This conclusion could be confirmed by the detachment energy equation. With extreme hydrophilic particles, the contact angle $\cos \theta$ is approximate to 1, thus it requires a large amount of energy to move the particles to the air phase to stabilize the foam, and the energy required to move the particles back to the water phase is almost 0. Thus the nanoparticles cannot reside at the interface and stabilize foam. With extreme hydrophobic particles, particles can reside at the air phase at a low energy state, but it requires a large amount of energy to move particles to the liquid phase. Thus foam cannot be stabilized by extremely hydrophobic particles. With tuned wettability, the contact angle $\cos \theta$ is close to 0, thus it requires less energy to move the nanoparticles into the air/liquid interfaces. Moreover it requires significant energy to move the particle into the air or into the liquid, and that energy is about the same for

both phases. Consequently, nanoparticles can reside at the air/liquid interfaces and act as stabilizers to stabilize foam.

Thus, it is reasonable for us to seek a type of nanoparticles with balanced affinity for gas and water, or to modify the nanoparticles wettability with surfactant molecules, in order to stabilize foam.

1.5 Potential of Foam and Nanoparticles Stabilized Foam in EOR

1.5.1 Application of foam in EOR processes

The first successful CO₂ foam field application in history was performed in the Siggins field, Illinois, from 1964 to 1967 (Holm, 1970). Foam flood was performed after waterflooding reached a water-oil ratio (WOR) of 25:1. Foam was stabilized by a modified ammonium lauryl sulfate surfactant and was injected into the reservoir by alternate injection method. As a result, the foam was introduced into different layers more uniformly and surfactant solution mobility was reduced to 35% of its original value, and WOR was reduced to 12:1 at the production well.

Foam flooding could be integrated into thermal processes as well. In 1974, a steam foam project was performed in Midway Sunset Field, California (Fitch and Minter, 1976) to recover heavy oil with 8-16 °API gravity at 600 °F. This project was considered a success in that it contributed to increasing oil production and demonstrated surfactant stability under high temperatures.

Foam flood does not always guarantee an increment in oil recovery, and a failed case was reported in Rock creek field, Virginia (Heller et al., 1985). The rock field was operated with gas drive, water flood and thermal recovery methods, but failed due to high WOR and large heat loss. CO₂ flood was introduced in 1970 but the results indicated poor volumetric sweep efficiency due to reservoir heterogeneity and high mobility of CO₂, and CO₂ foam flood was performed then in

1981, unfortunately, there was no oil bank formed. The failure could be caused by insufficient liquid injection, less residual oil saturation in the reservoir or unfavorable reservoir conditions.

1.5.2 Nanoparticles stabilized foam in EOR

Foam flood is considered as a potential and practical solution to the technical challenge in the gas injection process (Kovscek et al. 1994). Recently, nanoparticles have shown to stabilize a variety of foam or emulsion, in which the surface of the nanoparticles has a balanced affinity to aqueous phase and other phases, in that nanoparticles have low retention on mineral surfaces and high detachment energy (Worthen et al. 2012). Firstly, unlike surfactant can freely adsorb to or desorb from the water-gas interface, the adsorption of nanoparticles to the interface is usually an irreversible process. Secondly, bubble shape of surfactant stabilized foam is usually polygonal, while nanoparticles stabilized foam generates small and round bubbles. This is because nanoparticles present at the lamella change the curvature of the lamella, form a strict barrier and minimize the contacting area between bubbles, stabilizing the foam by reducing liquid drainage and gas diffusion (Binks, 2002; Worthen et al., 2013; Doroudian Rad et al., 2018).

The generation and propagation behavior of nanoparticles stabilized foam has been investigated by several researchers recently. Binks and Horozov (2005) reported air foam stabilized solely by silica nanoparticles. In a surfactant-free system, the foam stabilized by 32% SiOH is wet and achieved maximum foam volume compared with foam stabilized by 14% SiOH, and $\geq 70\%$ SiOH. Espinoza et al. (2010) generated stable supercritical CO₂ foams in beadpacks with 5 nm hydrophilic silica nanoparticles. San et al. (2017) investigate the effects of temperature, salinity and different ions on CO₂ foam stability. In their tests, CO₂ foam was stabilized by silica nanoparticles and the diameter of nanoparticles was measured in a range of 17-20 nm. They

reported the foamability and foam stability were increased when increasing NaCl concentration in a certain range, but further increment in NaCl concentration led to particle aggregation and core blockage. Divalent ions demonstrated the best stability compared with monovalent ions and multivalent ions. Temperature displayed a negative effect on foam stability, however, it showed a positive effect on foamability. Emrani and Nasr-El-Din (2017) investigate the effect of pressure, temperature and salinity on silica nanoparticles stabilized CO₂ foam. They included an anionic surfactant in their system. Their research proves that nanoparticles changed the contact angle through the aqueous phase and resulted in a tuned wettability of particles from completely hydrophilic to intermediate hydrophobic, and they evaluated the relationship between contact angle and detachment energy. However, their tests showed pressure and temperature had a negative effect on foam stability, which is infeasible in the EOR processes, and they failed to show the effect of oil on foam stability. Singh and Mohanty (2016) proved to generate stable foam with alumina coated silica nanoparticles and nonionic surfactant in both static and coreflood tests, they demonstrated surfactant tuned wettability of nanoparticles in stabilizing foam and investigated the foam stability with the presence of oil in the coreflood tests. However, the oil viscosity in the coreflood test was only 30 cp and the coreflood tests were performed at residual oil saturation. Here we report foam behavior at much larger oil viscosity and higher oil saturation.

1.5.3 Surfactant and nanoparticles characterization

After screening and trying more than 20 types of nanoparticles and surfactant combination in generating and stabilizing foam in static condition, Xu et al. (2018) proved that there existed a synergistic effect exists between one type of positively charged nanoparticles (SNOWTEX-AK) and one type of anionic surfactant molecules (Sodium fatty alcohol polyoxyethylene ether sulfate).

The oppositely charged nanoparticles and surfactants demonstrated the best stabilities under high temperature (50 °C) and high salinity (10.0 wt% NaCl or 10.0 wt% CaCl₂ solution) environment in the static tests, and the mixture had a better performance (foam height in static tests and flow resistance in flowing tests) than surfactant or nanoparticles alone in stabilizing the methane foam. Xu et al. (2018) contributed the synergistic effect to two reasons: first, nanoparticles with surfactant molecules moving to the gas/liquid interface and improving the interfacial dilatational elasticity, and second, enhancing the foam lamella structure.

Doroudian Rad et al. (2018) continued the previous research by Xu et al. (2018) and demonstrated that the interaction between ST-AK and AES would enhance the methane foam stability and bubble structure by involving the surfactant molecules adsorption stages on nanoparticles surface. There are five adsorption stages in her research depending on the surfactant/nanoparticles concentration ratio in a foaming solution. Stage 1 has the largest surfactant/nanoparticles ratio (≥ 0.42), where all nanoparticles surface are completely covered by a bilayer of surfactant molecules, and no nanoparticle surface exposed to the bulk liquid phase. When the concentration ratio is 0.21, the nanoparticles surface are exactly covered by a monolayer of surfactant molecules. This coverage regime is denoted stage 3. Surfactant/nanoparticles concentration ratio ≤ 0.01 represents stage 5, where nanoparticles surface are partially covered by a monolayer of surfactant molecules. The concentration boundaries were defined based on foaming solution characterization such as surface tension, zeta potential, particles size and aggregation. Aggregation leads to sedimentation of the nanoparticles to different degrees in stage 2, 3 and 4 foaming solution, However, stage 5 (partial monolayer coverage) foam and stage 1 (bilayer coverage) foam demonstrated good

foamability and stability compared with surfactant foam (nanoparticles-free) in the static foam height tests (Doroudian Rad et al., 2018).

Figure 1-8 Surfactant molecules adsorption stages on nanoparticle surface based on concentration ratio in the foaming solution. Stage 1: bilayer coverage, stage 2: partial monolayer coverage, stage 3: complete monolayer coverage, stage 4: mixture of complete monolayer and partial monolayer coverage and stage 5: partial monolayer coverage. This work compares stability of stage 1 foam and stage 5 foam with a nanoparticles-free foam, in that there is no sediment in foaming solutions of these three systems. (Adapted from Doroudian Rad et al., 2018)

1.6 Statement of the Problems

The difficulties during enhanced oil recovery (EOR) processes include unfavorable mobility ratios, inadequate sweep, gravity segregation, and reservoir heterogeneity.

- Primary recovery methods for heavy oil reservoirs use water and gas injections due to its low cost. These methods can be successful in light oil reservoirs without severe

heterogeneity, the major drawbacks are high mobility ratio, poor volumetric sweep efficiency, and pre-mature water/gas breakthrough.

- Chemical floods are common non-thermal EOR methods after waterflood. Sweep efficiency in heterogeneous reservoirs is the main concern in polymer flooding and surfactant flooding. Ion exchange with bottom water or clays cause precipitation and alkaline consumption in alkaline flooding.
- Hydrocarbon solvent injection will reduce heavy oil viscosity, however, slow rate diffusion, asphaltene precipitation, and deposition can cause formation damage and reduce fluid mobility, resulting in ineffective hydrocarbon production.

A comprehensive study of methane foam in EOR processes should be investigated from the laboratory to the field scale. This work aims to bring the innovation of nanoparticles to conventional foam systems. Foam has the potential to divert fluid in heterogeneous reservoirs, they can be integrated into other EOR methods to improve the performance and efficiency of current heavy oil recovery processes.

1.7 Objective

This research aims to investigate the potential of methane foam and nanoparticles stabilized methane foam in EOR processes to improve the performance of conventional gas injection methods for heavy oil reservoirs. Synergy effect here refers to the situation in which the foam stabilized by the mixture of surfactant and nanoparticles at certain concentration ratios demonstrates better foam stability than each stabilizer alone. The focus of this research is conducting static and flow tests which would help in understanding mechanisms and in the design of miscible flooding or gas injection process. Different challenges for foam stability occur at the

reservoir conditions, such as heterogeneity, surfactant adsorption, effects of crude oil, oil viscosity, oil saturation, and wettability. The major advantage of foam is mobility control in that foam can effectively divert fluid from high permeable zone to low permeable zone. It does this by increasing the viscosity of the displacing fluid and reducing the capillary forces due to the presence of surfactant. Therefore, the objective of this research is to evaluate the benefits of stabilizing methane foam with nanoparticles mixed with surfactants compared with conventional foam stabilized with surfactants only, and to investigate the interaction of nanoparticles stabilized foam with crude oil and salinity in static and dynamic conditions. Static tests and pore-scale studies are conducted to achieve this goal. The main objectives of this research are presented as follow:

- Evaluate the foam stability in the static condition, foam generated by shaking method with negatively charged surfactant, and effect of positively charged silica nanoparticles with alumina coating addition on foam structure and stability with or without the presence of heavy oil/salinity.
- Perform the flow test (pore-scale mechanisms of methane foams stabilized by surfactant alone and methane foam stabilized with nanoparticles) to improve conventional foam flooding performance in unconsolidated sandpacks.
- Study the nanoparticles stabilized foam flow behavior in the presence of waterflood residual oil, mobile oil and investigate the mechanisms of oil recovery by foam and the criteria for generation and propagation of a stable foam.
- Study the nanoparticles stabilized foam flow behavior when contacting a high salinity solution in the porous media and investigate the foam stability when contacting both an oil phase and a high salinity environment.

1.8 Thesis Structure

The organization of this dissertation is as follows:

Chapter 1 includes the general introduction, literature review, and objectives of the thesis.

Chapter 2 summarizes materials, experimental methods and procedures of and foam flooding tests set up.

In Chapter 3, static foam stability in aqueous condition, or contacting monovalent ions brine and crude oil were presented, bubble structure and size were monitored as well as the foam height; in the dynamic tests, foam flow resistance and apparent viscosity were presented to discuss the foam stability in porous media when contacting an oil phase in high salinity environment. At the end of this chapter, the foam oil interaction theory and cumulative oil recovery curve were presented and discussed.

In Chapter 4, additional effects of the gas phase, contact angle of the porous media, and divalent ions were investigated in the same foaming system, to test the compatibility of the existing foaming system. Confocal images were presented to discuss foam stability with nanoparticles.

Chapter 5 presents conclusions and recommendations for future works.

Chapter 2 : Materials and Procedure

2.1 Materials

2.1.1 Nanoparticles

After screening tests of the foam static stability for different types of nanoparticles and surfactants, synergy effect was observed between a positively-charged nanoparticle (ST-AK) and an anionic surfactant (AES). That is, the mixture demonstrated better foamability and foam stability than other pairs, and the performance was better than each stabilizer on its own (Xu et al., 2018).

Alumina-coated silica nanoparticles, SNOWTEX-AK (ST-AK), were supplied by Nissan Chemical Industries Co., Japan. **Table 2-1** summarizes the specification of the ST-AK dispersion as received.

Table 2-1 Specification of ST-AK

Description	Alumina coated silica particle
Particle size(nm)	10-15
SiO ₂ , solid %	17.8
Al ₂ O ₃ , solid %	2
Specific gravity (20 °C)	1.141
pH	4-5

2.1.2 Surfactant

Sodium fatty alcohol polyoxyethylene ether sulfate (AES) contains 70% active contents, was used as the negatively charged anionic surfactant in the tests. The surfactant was purchased from Chengdu Aike Chemical Technology Co., China. The chemical formula of AES is written as $\text{CH}_3(\text{CH}_2)_{11}\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{SO}_3\text{Na}$, and the molecular structure was shown in Figure 2-1.

Figure 2-1 Anionic surfactant molecular structure: sodium fatty alcohol polyoxyethylene ether sulfate (AES).

2.1.3 Methane and nitrogen

99.97% purity methane gas purchased from PRAXAIR CANADA was used as received. Methane gas was used for foam flowing tests.

99.999% purity nitrogen gas purchased from PRAXAIR CANADA was used as received. Nitrogen gas was used in one set of the foam flowing tests.

2.1.4 Water

Water was purified by Milli-Q Advantage A10 system and the purified water was used for preparing foaming solutions and flowing tests. The purified water will be referred to as Milli-Q water throughout this thesis.

2.1.5 Mineral oil

Mineral oil purchased from Fluke Corporation was used as the light oil in the flowing tests. Oil viscosity as received was 9 cp at 20 °C, and the mineral oil was dyed with perylene to be visually different from the foaming solution. The dyed oil viscosity was 18 cp at 20 °C.

2.1.6 Heavy oil

Heavy oil received from an oil company was diluted with mineral oil (mentioned above), and the mixed oil viscosity at 20 °C was 508 cp.

2.2 Experimental Methods and Setup

2.2.1 Preparation of foaming solution

First, the diluted nanoparticles dispersion and diluted surfactant solution were prepared with Milli-Q water separately, and the nanoparticles solution was bath sonicated (Branson M2800) and the surfactant solution was magnetically stirred for 10 minutes to ensure a homogeneous dispersion/solution. Then the surfactant solution was poured slowly to the nanoparticles dispersion at once. To avoid nanoparticles aggregation, the mixed surfactant and nanoparticles were probe sonicated (QSonica Q700). The sonication was done in an ice water bath to prevent the overheating of the solution. For mixture in high concentration or large volume, the sonication process lasted

for 15 minutes, else elapsed time was set at 8 minutes. In the surfactant alone stabilized foaming system, the foaming solution contained surfactant only with the same volume, and the surfactant solution was probe sonicated as well to ensure the consistency of the tests. The sonication method ensures surfactant molecules attached evenly to the nanoparticles surface and there were no sediments observed in foaming solution after preparation, or leftover inside the transfer cylinder after each test.

The concentration of surfactant and nanoparticles all are referred to mass percent. For instance, to make 200 g of the mixed surfactant and nanoparticles (0.1 wt% AES and 1.5 wt% ST-AK) dispersion, the mass of nanoparticles dispersion is calculated as $200 \text{ g} \times 1.5 \text{ wt\%} / 17.8 \text{ wt\%} = 16.85 \text{ g}$.

In the salinity test, 10.0 wt% NaCl brine was used to dilute surfactant solutions instead of Milli-Q water. The rest of the pouring and sonicating processes were the same.

All the foaming solutions were prepared right before the tests and left for 1 hour to reach equilibrium in room conditions. The pH was not adjusted.

2.2.2 Static foam test

Before the dynamic tests, preliminary static foam tests were performed to screen the synergistic pairs. Static foam was generated by a Bartsch shaking method (Bikerman, 1973). 10 ml of foaming solution was shaken continuously for 20 seconds in a 35 ml capped glass vial. Static foam stability indicators like foam height and the macroscopic bubble structure (bubble size and shape) were monitored for the following 120 minutes. The gas phase in the preliminary static test was air. All the static tests were conducted at 20 °C and ambient pressure conditions. The table was cleared for

the static foam tests, and there was no operation of pumps or other equipment that could cause vibration or disturbance to the static foam system.

2.2.3 Static foam test with oil

Static foam was generated by Bartsch shaking method first. 4 ml of foaming solution in a 15 ml plastic vial with a rubber cap was shaken with the same process. Then, 1 ml of heavy oil (508 cp) was injected slowly into the liquid/foam interface by a needle syringe. The injected liquid should not touch the pre-generated foam at this time but flowing up through the bottom liquid phase with buoyancy until it reached the interface, and the monitoring process started at this moment; in the control test, 1 ml of the same foaming solution was injected into the interface by the same process. The foam structure monitored in the control pairs can rule out the influence of the injection process itself. A schematic representation of the injection process is shown in **Figure 2-2**. Last, the bubble structure after contacting the heavy oil was monitored with time.

Figure 2-2 Schematic of injecting heavy oil into foam/liquid interface by a syringe. (a) pre-generated foam by shaking method. (b) injecting heavy oil into the interface without touching the foam. (c) heavy oil flowed up and touched the foam, the monitor process started.

2.2.4 Foam flow test

Figure 2-3 presents the schematic of apparatus for dynamic foam tests. Methane gas and the foaming solution were co-injected into a foam generator at a higher shear rate; foam exiting the generator flowed through tubing (0.175 cm ID) then into a sandpack. Two types of sand were used in this work to achieve different permeability in the flowing tests. The parameter and properties of the foam generator and the sandpack were summarized in **Table 2-2**. The foam generator and the sandpack was packed before each flooding test. The sandpack was dry-packed with a vibration method. The whole flooding system was vacuumed (CPS VP2D) and then saturated with Milli-Q water to measure the permeability and porosity.

The porosity was calculated as the ratio of pore volume over the total sandpack volume. Pore volume was measured by the weight difference between a dry sandpack and a water saturated sandpack after vacuuming, and the water weight was converted to water volume at given density; total sandpack volume was measured as the inner cross-sectional area multiply by the length. Shear rate was calculated by the following equation:

$$\text{superficial velocity} = \frac{\text{flow rate}}{\text{cross - sectional area}} \quad (2-1)$$

$$\text{pore radius} = \left(\frac{8 * \text{permeability}}{\text{porosity}} \right)^{0.5} \quad (2-2)$$

$$\text{shear rate} = 1.7 * 4 * \frac{\text{superficial velocity}}{\text{pore radius}} * 10000 \quad (2-3)$$

where superficial velocity is in cm/s, permeability is in darcy, pore radius is in μm and shear rate is in s^{-1} . The porosity, shear rate (calculated at the flow rate of 1 ml/min) of sandpack were 38% and $20 \pm 2 \text{ s}^{-1}$, respectively.

Table 2-2 Parameters of porous media used in flow tests

	Foam Generator	Sandpack
Inner Diameter (ID)/cm	0.46	1.57
Length/cm	15	30
Sand provider	US Silica	US Silica
Sand size/mesh	100-140	40-70

Pore volume of injection (PVI) is calculated as $PVI = \text{total injection rate} \times \text{injection time} / \text{pore volume}$. For instance, $1 \text{ ml/min} \times 22 \text{ min} / 22.0 \text{ cm}^3 = 1 \text{ PVI}$.

The flooding tests were operated under room temperature and with a backpressure of 4 MPa (580 psi). To facilitate the foam generation process, the foam generator was pre-flushed with the same surfactant solution for 5 PVs before co-injection of methane gas and foaming solution. Two syringe pumps (Teledyne ISCO, 500D) provided precise flow rate control, ranging from 1 ml/min and up to 204 ml/min at pressures up to 259 bar (3750 psi). Transfer cylinders were used to hold the foaming solution and the methane gas and made the system compatible with the most type of gas and nanoparticles dispersions. The vacuum pump could bring the whole system down to -85 kPa to remove the air.

Methane gas and the foaming solution were co-injected into the foam generator at a total injection rate of 5 ml/min during the pre-generation process. The large flow rate hastened the foam generation process. Then the total injection rate was reduced to 1 ml/min (24.56 ft/day), and the gas/liquid ratio was set at 4/1 at the inlet of the foam generator. Since the whole system was operated at elevated pressure, the gas/liquid ratio throughout the thesis referred to the gas/liquid volume ratio at the inlet of the foam generator. After foam inside the foam generator reached a steady-state (constant pressure drop) for at least 30 PVs, the generated foam was directed into the sandpack to investigate the foam propagation behavior inside the porous media. This research used the same pre-generation method to investigate the foam-oil/salinity interaction in dynamic conditions. The purpose of pre-generation method is to rule out the possibility that foam cannot be generated. That is, if pressure gradient across the sandpack is small during foam injection, the cause must be instability of the foam upon contact with oil or brine.

The downstream pressure was maintained by a backpressure regulator (BPR) (Equilibar U6L) set at 4 MPa for all tests. The fluctuation range of this BPR with multi-phase flow was within 200 kPa. Three pressure transducers (Omega PX409) were installed at the inlet of the foam generator, between the foam generator and the sandpack, and the outlet of the sandpack. The transducers recorded the absolute pressures every second. This allowed for the generation of high-resolution flowing resistance curve. Experimental data were shown at a moving average of 100 period in Excel for visualization. Section 4.4 compares the data fluctuation of different foaming systems at original resolution. The pressure differences across the foam generator and across the sandpack were the simplest indicators of foam stability inside the porous media. The automated data acquisition system (provided with the transducer from Omega) allowed the consistency of the raw data.

After 8 PVs of foam injection (equal to 1.6 PVs of liquid injection) through the sandpack, water flood was performed at a flow rate of 4 mL/min immediately after foam flooding for another 4-6 PVs to determine whether any permeability reduction occurred during foam injection. The thesis only presents the foam flow behavior for the first 5 PVs of foam injection (equals to 1 PV of liquid injection).

Two tests were conducted to investigate the effect of surfactant adsorption on foam generation and propagation. In a “pre-flush” test, the whole system was pre-flushed with the same foaming solution at 1 ml/min for 3 PVs. The intent was to fill the surfactant adsorption capacity of the sand grains, so as to avoid surfactant loss while injecting gas and foaming solution. In the “no pre-flush” test, the sandpack was only saturated with Milli-Q water before the foam generation.

In the salinity test, 5.0 wt% NaCl solution was first held in transfer cylinders and used to saturate the whole system for 5 PVs. The rest of the procedures were the same as above.

Figure 2-3 Foam flow test apparatus. Foam was pre-generated by co-injection of methane and foaming solution at a higher shear rate. After foam generator producing a stable foam, it was then directed into the sandpack at a lower shear rate. The sandpack contained either Milli-Q water, foaming solution, oil and/or salinity.

2.2.5 Oil displacement experiments

There were three types of oil interaction tests with different oil viscosities and saturations in the sandpack: 1) displacing mineral oil at residual oil saturation, 2) displacing mineral oil at a mobile oil saturation corresponding to the irreducible water saturation, and 3) displacing the heavy oil at residual oil saturation. Residual oil saturation was established by 3 PVs of waterflood at 1 ml/min and 4 MPa backpressure. There was no oil inside the foam generator, and the foam generation processes were the same as above.

Oil displacement experiments investigated foam flow behavior of foams at different surfactant coverage stages (Doroudian Rad, et al., 2018), namely partial mono-layer coverage (stage 5), fully bi-layer coverage (stage 1), surfactant-only foam and simultaneous water-gas injection (no foam stabilizers, same gas/liquid ratio, referred as baseline throughout the thesis).

First of all, the permeability and porosity of the porous media was measured by vacuum and Milli-Q water saturation method. Then the sandpack was removed from the system and held in a vertical position, oil was injected from the bottom of the sandpack at a flow rate of 1 ml/min until there was no water produced at the top outlet, and effluent samples were collected at the outlet each 0.3 PV of injection. The sandpack with mobile oil was placed back into the setup in a horizontal position and aged overnight (17 hours) to reach an equilibrium state.

For experiments conducted at mobile oil saturation, foam flow tests were performed directly and effluent samples were collected each 0.5 PV of injection. For experiments conducted at residual oil saturation, waterflood was performed at 1ml/min before the foam flow tests, effluent samples were collected each 0.5 PV of injection. Waterflood was continued until the oil volume collected in each sample was small. The waterflood continued for 3 PVs of injection for all the residual oil tests for consistency of the results. In the salinity test, 5.0 wt% NaCl solution was used to displace mobile oil and the rest of the procedures were the same as the other tests.

Table 2-3 Properties of the sandpack used in flowing tests in Chapter 3.

Flow test Number	AES concentration /wt%	ST-AK concentration /wt%	Stage (1 = bilayer 5 = partial monolayer)	Permeability /d	NaCl Concentration / wt%	Oil viscosity /cp	Initial oil saturation (S _{oi})/%	Waterflood residual oil saturation (S _{or})/%
1	0.01	-	-	37.43	-	-	-	-
2	0.01	-	-	40.11	-	-	-	-
3	0.01	4	5	39.01	-	-	-	-
4	0.1	-	-	37.47	-	-	-	-
5	0.1	0.1	1	43.19	-	-	-	-
6	0.1	1.5	5	31.85	-	-	-	-
7	-	1.5	-	43.93	-	-	-	-
8	0.1	-	-	37.13	5.0	-	-	-
9	0.1	1.5	5	32.19	5.0	-	-	-
10	0.1	-	-	38.42	-	18	74	18
11	0.1	0.1	1	41.07	-	18	68	8
12	0.1	1.5	5	35.18	-	18	68	19
13	0.1	1.0	5	36.68	-	18	66	8
14	0.1	0.1	1	36.86	-	18	91	-
15	0.1	1.5	5	34.16	-	18	91	-
16	0.1	-	-	37.25	-	508	76	35
17	0.1	0.1	1	36.46	-	508	72	45
18	0.1	1.5	5	39.21	-	508	75	36
19	0.1	-	-	33.78	5.0	508	-	-
20	0.1	1.5	5	33.41	5.0	508	-	-

- Not applicable

Table 2-4 List of equipment used in flowing tests.

Equipment	Type
Tubing and Valves	Swagelok stainless steel, 1/8 inch
Syringe Pump	Teledyne Instruments, Inc. Model ISCO 500D.
Vacuum Pump	CPS 2 CFM Vacuum Pump with CPS VG200 pressure gauge.
Pressure Transducer	Omega Engineering Canada, Model/Part No.: PX409-1.5KGUSBH (0-1500 PSIG).
Data Acquisition System	Omega Engineering Canada,
Transfer Cylinder	500 ml stainless steel cylinder with brass floating piston. Manufactured by Machine shop, University of Calgary.
Backpressure Regulator	Equilibar LLC. Model/Port size: U6L – 1/8 inch (0-5000 psig), with series 3000 high pressure reducing regulator (0-6000 psig).

2.5 Surfactant Retention and Oil Recovery Analysis

2.5.1 Surfactant concentration analysis

Sulfur elemental analysis was performed with an Agilent 7800/7900 Inductively Coupled Plasma Mass Spectrometer (ICP-MS), to measure and calculate the AES content in the effluent samples at room temperature and ambient pressure. Prior to ICP-MS measurement, the collected effluent samples were bath sonicated (Branson M2800) for 30 minutes. Samples were diluted with Milli-Q water to meet the measurement accuracy of the equipment. Diluted samples were vortex (Fisher Scientific 9454F1HDUSA) mixed right before the measurement. A minimum of three calibration tests were performed for sulfur standard solutions before the effluent sample measurements.

ICP-MS results gave the amount of surfactant retention in the porous media, by measuring the AES concentration in the initial sample (foaming solution sample) and effluent samples. Retention was indicated by c/c_0 , where c is the AES concentration in the effluent samples, and c_0 is the AES concentration in the initial sample. If c/c_0 was 1, then that sample experienced no retention of surfactant as it traveled through the porous media. If c/c_0 was 0, then all the surfactant molecules present in the corresponding volume of injected fluid got adsorbed to the sand grains as that volume flowed through the porous media. Because adsorbed surfactant is not available to generate foam, these data help interpret foam propagation tests.

2.5.2 Oil recovery analysis

Pore volume (PV) of the sandpack was measured by weighing the difference between dry sandpack and sandpack after vacuuming and saturation. During the mobile oil saturation process, effluent samples were collected each 0.3 PV of injection, for a total of 6 samples. Water volume was analyzed in each sample, and original oil in place (OOIP) in the sandpack was the difference between PV and sum of water volume in effluent samples.

In the flowing tests with oil, effluent samples were collected each 0.5 PV of injection at the outlet of BPR in a graduated plastic cylinder, with a cap to seal after collection. Samples were centrifuged (Eppendorf 5810) at 4000 rpm for 50 minutes, then the aqueous phase and oil phase volume was read separately. Oil recovery was calculated based on the cumulative oil recovery as a fraction of the OOIP.

2.6 Sand Surface Treatment

Silica sand (40-70 mesh, provided by US Silica) was soaked in a mixture of 10.0 wt% Surfasil Siliconizing fluid (Thermo Scientific) and 90.0 wt% heptane (Fisher Scientific) solution for 2 hours in room temperature and ambient pressure conditions. Then the sand was flushed with methanol (Fisher Scientific) solution for 3 times. Finally, the sand was heated in the oven at 100 °C for 10 hours to evaporate the liquid then allowed to cool to room temperature before sandpack packing. All the surface treated sand was prepared one day before the flooding test and discarded after each flowing test.

2.7 Surface tension and interfacial tension measurements

2.7.1 Surface tension measurement

The surface tension of foaming solution were measured based on plate method using DCAT 21 – Dynamic Contact Angle measuring devices and Tensiometer (Folio Instruments Inc.), with a Wilhelmy plate 11 (Platinum – Iridium, length: 10 mm, width: 19.9 mm, thickness: 0.2 mm, DataPhysics Instruments Group). Surface tension was measured for surfactant foaming solution and stage 5 (partial monolayer coverage) foaming solution with various brine concentration.

To start the measuring procedure, the Wilhelmy plate was burned with a butane lighter for 5 seconds to remove any chemical residual on it. The foaming solution was poured into the beaker slowly to avoid generating foam. The machine requires a minimum of 7.5 mm solution height in the beaker. Measurement was taken by dipping the plate into the solution and removed the plate automatically. The automated data acquisition system provided with the DCAT 21 allowed the consistency of the results. For each sample, an average value of 3 measurements is presented.

2.7.2 Interfacial Tension Measurement

The interfacial tension measurement used the same DCAT 21 machine and the data acquisition system. The interfacial tension measurement procedure requires to measure the separate oil or water phase surface tension separately at first, and then pouring the light density phase (oil in this work) on top of the heavy density phase (foaming solution) slowly, to avoid generating bubbles in the light phase. The measurement required a minimum of 7.5 mm solution height of the heavy phase but a maximum of 17 mm solution height in total.

Oil/foaming solution interfacial tension was measured for surfactant foam, stage 1 (bilayer coverage) and stage 5 (partial monolayer coverage) foaming system, and the oil phase is the heavy oil mentioned in section 2.1.6, with a viscosity of 508 cp at ambient conditions.

Surface tension and interfacial tension were measured to first, demonstrate the consequence of different adsorption stages of surfactant on nanoparticles surface, and secondly, support classic foam-oil interaction theory or propose a new theory if not applicable.

2.8 Nanoparticles affinity to gas/liquid interface analysis

Nanoparticles affinity to the gas/liquid interface analysis was performed with a confocal reflectance microscopy (Leica TCS SP8), to capture the bubble structure and nanoparticle location in static foam at room temperature and ambient pressure.

Foam was generated right before the confocal observation by the shaking method, and the foam was carefully transferred to a microscope slide with a dropper. To prevent liquid evaporation during the image capture process, a lid was placed on top of the foam.

The Leica TCS SP8 confocal reflectance microscope sends laser at 88 nm wavelength and captures the bubble/liquid interface based on the reflection. The solid nanoparticles, gas and liquid reflect light differently at the interface, and the microscope detects the different refractive index at the interface to show the shape of the interface and the location of nanoparticles. By changing the focal length, the microscope scanned the sample layer by layer and put all the images together for visualization. In this study, 100 2-D images were scanned and then stacked together for a final 3-D image. It provides imaging at super-resolution down to 300 nm.

The microscope cannot detect surfactant molecules, and both liquid and gas phases appear black. Nanoparticles and gas/liquid interface are highlighted in green in the images.

Chapter 3 : Static and Dynamic Foam Behavior

3.1 Introduction

This chapter presents the nanoparticles stabilized methane foam stability in both static and flowing tests with heavy oil and salinity in the system. The work was based on the screening results of surfactant molecules and nanoparticles, and the adsorption theory of surfactant to the nanoparticles surface (Doroudian Rad et al., 2018, Xu et al., 2018).

Previous research focused on material selection and the theoretical explanation of the synergistic interaction between surfactant and nanoparticle of adsorption stages in static conditions (Doroudian Rad et al., 2018, Xu et al., 2018). This thesis builds on previous research results to show, for the first time, the performance of nanoparticles/surfactant mixture stabilized methane foam in conditions of oil and high salinity while flowing into a porous media. The results enable the engineering design of surfactant and nanoparticles foaming system to achieve a highly and uniquely stable foam in porous media in the presence of typical reservoir fluids.

This thesis compares three foaming systems, including stage 1 and stage 5 foaming systems, with a nanoparticles-free, surfactant-only system as a comparison. Details are presented in **Table 3-1**. The nanoparticles-free system is referred to as “surfactant foam” throughout the thesis. The three systems were studied at two surfactant concentrations. In low surfactant concentration tests, the surfactant foam contains 0.01 wt% AES solution, and stage 5 foam contains a mixture of 0.01 wt% AES and 4.00 wt% ST-AK solution. No stage 1 foam was studied at low surfactant concentration. In high surfactant concentration tests, the surfactant foam contains 0.1 wt% AES solution, stage 1 foam contains a mixture of 0.1 wt% AES and 0.1 wt% ST-AK solution, and stage 5 foam contains

a mixture of 0.1 wt% AES and 1.5 wt% ST-AK solution. In the salinity test, the foaming solution contains 5.0 wt% NaCl brine.

Table 3-1 Table of surfactant and nanoparticles concentration and coverage region in the flowing tests

Foaming system	Coverage region	Surfactant	Nanoparticles	Comments
		concentration/ wt%	concentration/ wt%	
Surfactant foam	-	0.01	-	Low surfactant concentration tests
Stage 5 foam	Partial monolayer	0.01	4.00	
Surfactant foam	-	0.1	-	High surfactant concentration tests
Stage 1 foam	Bilayer	0.1	0.1	
Stage 5 foam	Partial monolayer	0.1	1.5	

Bubble size and shape, and foam height decay with time are indicators of foam stability in the static tests. The gas composition in the low-pressure static tests had little effect on the results. Zeng et al. (2016) proved that methane and N₂ have similar mole fraction solubility (of order 10⁻⁵ at 20 °C, 1 bar), and comparable film permeability (0.13 m/s and 0.3 m/s, respectively) (Farajzadeh et al. 2014). These observations of similar lamella stability and film strength justify using air as the gas phase in static tests. Moreover, previous researches used methane and the same surfactant and nanoparticle sample (Xu et al. 2018) to generate foam in static tests, and there was no significant

difference observed between air foam and methane foam in bulk. In this study, the air replaced methane in static tests for ease of experimental condition.

In the flowing tests, normalized pressure difference and apparent viscosity are the indicators of foam stability in the porous media. Normalized pressure difference is the ratio of absolute pressure difference across the sandpack of different foaming system to the pressure difference of the baseline test (same ratio of gas and liquid but without stabilizers.) The non-dimensional pressure differences make different foaming systems comparable with each other. In the foam flowing test in the absence of oil, baseline refers to simultaneously water and gas injection at the same gas/liquid ratio. In the oil displacing test, baseline refers to water and gas injection to displace residual heavy oil. Normalized pressure difference reflects the improved flow resistance provided by foam. Foam is considered as a homogeneous phase in the porous media and the apparent viscosity of foam is calculated based on Darcy's Equation. Raw data were collected per second and a moving average of 100 period were presented.

3.2 Static Foam Stability

3.2.1 Static foam test without oil nor salinity

Foam half-life is defined as the time took for foam to decay to half of its initial height. Foam half-life less than 120 minutes, or bubble size expanded by a factor of two, or the shape changed from spherical to polyhedral within 120 minutes are considered as unstable, otherwise, the foam is stable. All the tests were conducted at 20 °C and ambient pressure conditions.

Figure 3-1 demonstrated the bubble shape and size as time increased to 120 minutes after foam generation. In vial A, surfactant foam showed the best foamability in that the initial foam height

was the highest among all the samples. Even if the foam height remained almost unchanged after 120 minutes, the bubble expanded, and the structure changed from spherical to polyhedral within 120 minutes. Thus the surfactant stabilized foam was unstable in the static test. In vial B, stage 1 foam demonstrated similar behavior to surfactant foam. It was no surprise in that the nanoparticles are fully covered with a bilayer of surfactant. Vial D contains only nanoparticles solution, and the nanoparticles showed no foamability at all. Only Stage 5 foam in vial C showed both foamability and high stability in the static test. The bubble remained small and round for more than 120 minutes. In fact, the synergy effect between these two nanoparticles and surfactants can survive more than 24 hours in the static tests.

Figure 3-1 Top row: Static foam structure and bubble size at 0 min and 120 min (left to right) after generation. Bottom row: close-up of foam structure at location indicated by red ovals. Surfactant-only foam (A) and stage 1 foam (B) bubbles expanded, and structure changed from spherical to polyhedral, while stage 5 bubbles (C) remained small and round after 120 minutes. Nanoparticles alone (D) cannot generate foam.

Surfactant molecules can stabilize foam by reducing the surface tension at gas/liquid interphase. Lamella thickness is controlled by surfactant concentration, and higher surfactant concentration can generate thicker and more stable foams (Emrani and Nasr-EI-Din 2017). However, surfactant-formed lamella cannot effectively prevent liquid drainage or gas diffusion, which can result in thinner lamella and foam breakage. Foams with a wide range of bubble sizes can easily break when gas in the small bubbles diffused into neighboring larger bubbles or lamella are thinned (Eren 2004) driven by capillary force, and as a result, small bubbles disappear eventually (Hirasaki

1989). The polyhedral bubble structure provides more contacting areas among bubbles in the bulk phase and facilitates gas diffusion and bubble expansion. The behavior of surfactant foam in **Figure 3-1** is consistent with classical theories.

Stage 1 (bilayer coverage) foam showed similar behavior to the surfactant foam, which is expected given that nanoparticles are fully covered by surfactant molecules. However, stage 5 foam with partial monolayer coverage is highly stable in that the nanoparticles can be attached strongly to the gas/liquid interface. As shown in **Figure 3-1**, stage 5 foam structure is small and round, and most importantly, the structure does not change as time increased. This stable behavior can be proven from previous research, e.g. nanoparticles present in the lamella can effectively reduce gas diffusion and liquid drainage (Pugh, 2005), and nanoparticles with intermediate hydrophobicity, here in this work due to nanoparticles surface partially covered by hydrophobic surfactant tails and uncovered surface regions exposing hydrophilic metal oxide/hydroxyl groups, provide optimal foamability and stability (Binks and Horozov, 2005).

3.2.2 Effect of crude oil and no salinity

Figure 3-2 compares the static foam stabilities for surfactant foam (top row), stage 5 foam (bottom row), without (left column) and with (right column) the presence of heavy oil up to 120 minutes after oil or foaming solution injection. Control tests (left column) proved the injection of foaming solution into the pre-generated foam/liquid interface would not affect foam stability or foam structure. In the control pair, surfactant foam and nanoparticles stabilized foam were both stable for more than 120 minutes as long as there was no oil. However, in the test pair, oil entered the lamella and covered the bubbles immediately in the surfactant foam. Small bubbles broke and collapsed in the center of the tube once it touched the oil, leaving bubbles only near the tube wall

after about 30 minutes. After 120 minutes, the foam broke completely after touching heavy oil. In contrast, partially covered nanoparticles present in the lamella can effectively prevent oil from entering the foam structure. The foam was stable for more than 120 minutes, and the bubble size and structure did not change with the time.

Figure 3-2 Static surfactant foam (top row) and stage 5 foam (bottom row) stability without (left column) and with (right column) the presence of heavy oil at 0 min, 30 min and 120 min (left to right) after solution/oil injection. Oil entered surfactant foam lamella and caused the bubbles to break, while stage 5 foam prevented oil from entering the lamella and was stable for 120 minutes. Control tests (left) demonstrated both foams were stable without oil.

3.2.3 Effect of salinity and no oil

Figure 3-3 demonstrated static foam stability in a high salinity environment. Surfactant foam and stage 5 foam both have good foamability with brine. However, in a surfactant foam system, foam

bubbles expanded within 120 minutes while stage 5 foam bubbles remained small and round. Stage 5 foam remained stable up to 24 hours after generation while the surfactant foam breaks completely. The behavior is similar to that in freshwater (**Figure 3-1**), indicating that the salinity has little effect on static foam stability.

Figure 3-3 Static surfactant foam with 5.0 wt% NaCl (top row) and stage 5 foam with 5.0 wt% NaCl (bottom row) at 0 min and 120 min (left to right) after generation. Surfactant foam expanded and changed into polyhedron shape while stage 5 bubbles remained small and round. The same behavior occurred in freshwater (Figure 3-1, samples A and C), indicating that salinity had little effect on stability.

3.2.4 Effect of oil and salinity

Figure 3-4 shows the static foam stability with the presence of heavy oil in a high salinity environment. Compare the static salinity foam stability in **Figure 3-2**, one can conclude that salinity improves the surfactant foam stability with the presence of oil, in that the surfactant foam

did not collapse completely within the 120 minutes following oil injection. Stage 5 foam demonstrated good oil tolerance in high salinity as well as Milli-Q water. Even if salinity improved the surfactant foam stability, stage 5 foam was substantially more stable.

Figure 3-4 Static surfactant foam with 5.0 wt% NaCl (top row) and stage 5 foam with 5.0 wt% NaCl (bottom row) stability without and with the presence of heavy oil (508 cp) at 0 min, 30 min and 120 min (left to right) after oil/solution injection. Surfactant foam with 5.0 wt% NaCl solution demonstrated better oil tolerance compared with a salt-free system (Figure 3-2). Stage 5 foam with 5.0 wt% NaCl was stable in the presence of oil, just as in the absence of salt.

3.3 Foam Flow in Porous Media in the Absence of Oil

3.3.1 Synergy effect at low surfactant concentration and no salinity

As shown in **Figure 3-5**, at low surfactant concentration (0.01 wt %AES solution), surfactant foam could not propagate through a water-saturated sandpack. This is attributed to surfactant foam flow in porous media being a process of break and reform, and that the low concentration did not provide sufficient free surfactant molecules in bulk phase to re-generate the foam at the lower shear rate in the sandpack. (The foam generator operates at much higher shear rate, and the low surfactant concentration is sufficient to maintain foam at high shear conditions.) Low surfactant concentration can also destabilize foams by chemical loss due to surfactant molecules adsorption to sand grains.

Another flowing test was conducted where the sandpack had been pre-flushed with a surfactant solution at the same concentration. The blue line in **Figure 3-5** shows that the pre-flush did not fully saturate the sand surface, or else the low concentration is insufficient to propagate foam either could not enable foam propagation successfully in the porous media.

In contrast to surfactant foam, when nanoparticles are present (green line) at a partial monolayer coverage region (stage 5, 0.01 wt% AES and 4.00 wt% ST-AK), foam could propagate successfully, building to substantial flow resistance within 2 PVs of injection. The successful foam propagation at stage 5 was attributed to the strong attachment of the surfactant to the nanoparticle surfaces. This has two consequences: it reduces the loss of surfactant to sand grains, and it may stabilize bubbles so strongly that there is less need to regenerate bubbles during flow. In other words, nanoparticles present in the foaming solution can replace conventional pre-flush or

sacrificial agents methods to mitigate chemical loss. Moreover, the nanoparticles can enable foam propagation at low surfactant concentrations, reducing surfactant costs and reducing payback time.

Figure 3-5 At low surfactant concentration (0.01 wt% AES), surfactant foam cannot propagate through the porous media with (blue line) or without (orange line) a surfactant pre-flush, while partially surfactant covered nanoparticles (stage 5) foam propagated successfully. Flowing test #1: surf foam without pre-flush; flowing test #2: surf foam with 3 PVs of pre-flush; flowing test #3: stage 5 foam with 3 PVs of pre-flush (flowing tests referred to **Table 2-3**).

Effluent samples of stage 5 foaming solution during pre-flush were collected at the outlet of BPR each 0.5 PV and shown in **Figure 3-6**. The initial sample here referred to the foaming solution before injection into the porous media. Vial S1 to S6 were samples collected during 3 PVs of pre-flush. Since the sandpack was originally saturated with Milli-Q water, and assuming the pre-flush

at 1 ml/min was piston-like displacement, the foaming solution was expected to come out after 1 PV of injection and vial S3 should have the same appearance as initial sample if there was no chemical loss. However, the arrival of foaming solution was delayed due to the surfactant loss of sand grains.

Figure 3-6 initial and effluent samples collected each 0.5 PV during the pre-flush. 0.01 wt% AES and 4.00 wt% ST-AK mixture. Vial S3 would have the same appearance as the initial sample if there was no adsorption of stabilizers to sand grains. The arrival of injected concentrations (based on visual appearance) was delayed until vial S4, indicating loss of chemicals to sand grains during pre-flush.

The surfactant concentrations in effluent samples in the pre-flush process and in the foam injection process were compared with initial surfactant concentration in foaming solutions as shown in **Figure 3-7**. All the concentration results are the average surfactant concentration in the corresponding vial containing 0.5 PV of effluent (shown in **Figure 3-6**). The surfactant concentration ratio increased from 0 to 0.75 after 3 PVs of pre-flush, and it means the pre-flush of 3 PVs was not sufficient when surfactant concentration was low at 0.01 wt%. During the foam

injection process, there was still chemical loss during the first 2 PVs of injection, and it corresponded to the pressure profile in **Figure 3-5**: Pressure difference started to build up after 2 PVs of injection, when the sand grains were fully saturated with surfactant molecules, and the following injection surfactant molecules were free to re-generate foam in the porous media.

Figure 3-7 Averaged effluent surfactant concentration normalized to injected concentration during 3 PVs of pre-flush followed by 4 PVs of continuous foam injection. Surfactant concentration increased to 75% of injected concentration by the end of the pre-flush, indicating that adsorption capacity of the sand grains was almost filled. After another 2 PVs of foam injection, c/c_0 reached 1 and it means no more surfactant adsorption in the porous media. Recall in the pressure profile in **Figure 3-6**, after 2 PVs of foam injection, the system started to build up pressure difference, which proved the delay in pressure difference build up was caused by chemical loss to sand grains.

In the initial condition, the sandpack was saturated with Milli-Q water, where the surfactant concentration is 0. The surfactant concentration in S2 vial (corresponds to 0.5 PVI in **Figure 3-7**)

does not equal to 0, which means the pre-flush was not a piston-like displacement process, and the surfactant front breaks through early. This is attributed to preferential flow of liquid through regions where foam has destabilized, leading to early arrival of diluted surfactant.

The pressure and concentration profiles indicated chemical loss is the major challenge in foam flooding at low surfactant concentrations, and one possible solution is to pre-flush the porous media with a foaming solution. In the oil field application, pre-flush consumes a large amount of time and money. This thesis proposed an optimized surfactant and nanoparticles concentration at stage 5, by increasing surfactant concentration to overcome chemical loss and decreasing nanoparticles concentration to reduce the cost.

3.3.2 Synergy effect at high surfactant concentration and no salinity

The high surfactant concentration was set at 0.1 wt%. This is an economically feasible concentration. It is also operationally feasible, because at surfactant concentration lower than 0.1 wt%, overcoming chemical loss would require large pre-flush volumes and/or long delay in pressure build up during flow. This concentration is also optimal, in that when the surfactant concentration was higher than 0.1 wt%, increasing the surfactant concentration increase the flow resistance. **Figure 3-8** shows 4 different coreflood tests at increased surfactant concentration. All showed the same flow behavior in the porous media: an immediate build up in pressure difference and the same pressure difference at steady state. Therefore, all subsequent flow tests were conducted at 0.1 wt% surfactant concentration with varied nanoparticle concentration.

Figure 3-8 Absolute pressure difference during foam flow in water-saturated sandpacks. The optimal surfactant concentration is 0.1 wt%. Above this concentration, additional surfactant added no benefit to the flow resistance. Lower than 0.1 wt%, the system had slower pressure difference build-up and chemical loss was a major challenge in the foaming system.

Figure 3-9 shows the foam propagation behavior of different foaming systems, all at higher surfactant concentration (0.1 wt% AES), in water-saturated sandpacks and no pre-flush used in these tests. The apparent viscosity of surfactant foam after 5 PVs of injection reached 1600cp. This surfactant foaming solution demonstrated good foamability in the static tests (**Figure 3-1**), and clearly, the higher concentration (compared to **Figure 3-5**) enabled better propagation of the foam. In contrast, injecting a nanoparticle solution and gas at the same gas/liquid ratio yielded a normalized pressure drop of approximately 1, which indicates no foam propagating through the porous media and no flow resistance improvement in this case. This result was consistent with no foam generated in the static test (**Figure 3-1**). The flow behavior of foam stabilized by a mixture of surfactant and nanoparticles at bilayer coverage (stage 1) was similar to that of surfactant foam.

A mixture of surfactant and nanoparticles corresponding to partial monolayer coverage (stage 5) also generated a high-viscosity foam that propagated successfully through the sandpack. Thus, when surfactant concentration is set at 0.1 wt%, the static foam stability are good indicators of the dynamic tests.

Figure 3-9 Normalized pressure across the sandpack saturated with water of different foaming systems compared with averaged pressure drop of baseline. Baseline is water and gas injection without foam stabilizers. The dynamic flowing test results match with the static test results.

Flowing test #4: surf foam; flowing test #5: stage 1 foam; flowing test #6: stage 5 foam; flowing test #7: NP and gas (flowing tests referred to **Table 2-3**).

Stage 5 foam provided large resistance to flow in sandpacks saturated with fresh water, though not as large as stage 1 or surfactant only. In this case, there is no synergistic effect, because the nanoparticles alone do not stabilize foam, but the surfactant alone does stabilize foam.

3.3.3 Foam flow in porous media in a high salinity environment and no oil

Flowing tests were performed by adding 5.0 wt% NaCl in Milli-Q water to investigate the foam propagation behavior in a high salinity environment. **Figure 3-10** compares the apparent viscosity of each foaming system with salt present to that without salt present. If the ratio is 1, then salinity had no effect on foam stability; if the ratio is larger than 1, then salinity increased foam flow resistance; otherwise, salinity decreased foam flow resistance, presumably by partially destabilizing the foam. The apparent viscosity profile here in **Figure 3-10** showed additional NaCl had a negative effect on surfactant foam, in that the flow resistance and apparent viscosity was less than that of salt-free system, especially during the first pore volume of foam injection. In contrast, stage 5 foam exhibited larger flow resistance in the presence of salt. The flowing test results were consistent with static results.

Figure 3-10 Ratio of the apparent viscosity of foam in a high salinity environment to foam in a salt-free system. Stage 5 foam (green curve) demonstrated larger flow resistance with 5.0 wt% NaCl solution. In contrast, salinity reduced the apparent viscosity of surfactant foam (blue curve). Flowing test #8: surf foam + 5.0 wt% NaCl; flowing test #9: stage 5 foam + 5.0 wt% NaCl (flowing tests referred to **Table 2-3**).

Adding salt weakens the stability of surfactant foam in this research. Salt can reduce the electrostatic repulsion (Dilgren and Owens, 1982) and results in faster foam collapsing as observed in **Figure 3-3**. Adding salt to the nanoparticle stabilized foam (stage 5) not only does not destroy the foam texture (**Figure 3-3**) but also enhanced the foam flow resistance as shown in **Figure 3-10**. One contribution from salt is higher ionic strength in the liquid phase reducing the solvation of nanoparticles, and in return, it increases the nanoparticles' affinity to the gas-liquid interface. The greater affinity would increase the foam stability. Another contribution is that additional salinity in stage 5 foaming solution decreases the surface tension by 10% (to 33.1 mN/m from 36.55 mN/m) but does not change the surface tension of the surfactant foaming solution significantly.

3.4 Foam Flow in Porous Media in the Presence of Oil: EOR Potential

3.4.1 Mineral oil at residual oil saturation and no salinity

As shown in **Figure 3-11**, surfactant foam broke when it touched mineral oil, and despite continued injection, it could not regenerate spontaneously inside the porous media. The apparent viscosity of surfactant foam was less than 10 cp. Stage 1 foam also broke once contacting mineral oil. In contrast, the apparent viscosity of stage 5 foam reached up to 280 cp at steady state, which proved a stable foam with the presence of residual oil. Moreover, apparent viscosity of stage 5 foam at lower nanoparticle concentration (0.1 wt% AES and 1.0 wt% ST-AK) was 150 cp. This shows the apparent viscosity of foam can be tuned while maintaining stability in the presence of oil as long as the coverage region was set at stage 5, partial monolayer coverage. These results are consistent with the static observations in **Figure 3-2**. In the presence of residual oil, the synergistic interaction of nanoparticles and surfactants provides a qualitative increase in foam performance, as neither surfactant nor nanoparticles alone can stabilize foam.

Figure 3-11 Normalized pressure drop and apparent viscosity across the sandpack containing mineral oil at residual oil saturation (18 cp, $S_{or} = 10\%$) to baseline. The baseline is water and gas injection without stabilizers into sandpacks containing mineral oil at residual oil saturation (18 cp, 10%). Surfactant foam (red) and stage 1 foam (dark blue) collapsed when they encountered residual mineral oil and never built up significant pressure drop. Stage 5 foam (green, light blue) is the only stable system in the presence of mineral oil, and foam viscosity can be tuned based on nanoparticles concentration at stage 5. Flowing test #10: surf foam; flowing test #11: stage 1 foam; flowing test #12: stage 5 with high NP concentration; flowing test #13: stage 5 with low NP concentration (flowing tests referred to **Table 2-3**).

3.4.2 Mineral oil at mobile oil saturation and no salinity

Stage 1 foam and stage 5 foam were selected to flow through porous media containing mineral oil at irreducible water saturation as shown in **Figure 3-12**. The results again proved stage 5 foam was the only stable system with the presence of mineral oil, in this case while displacing an oil bank.

The apparent viscosity of stage 5 foam and stage 1 foam at the end of 5 PV of injection was about 650 cp and 50 cp, respectively.

Figure 3-12 Injecting foam into sandpack saturated with mineral oil (18 cp, $S_{oi} = 90\%$) shows that only stage 5 foam (green) remains stable. Flowing test #14: stage 1 foam; flowing test #15: stage 5 foam (flowing tests referred to **Table 2-3**).

3.4.3 Heavy oil at residual oil saturation and no salinity

The residual saturation of heavy oil was much larger than that with mineral oil, in that most of the heavy oil was bypassed during the waterflood. Foam flows through or past larger connected volumes of oil in these experiments than in those with mineral oil. As shown in Figure 3-13, surfactant foam and stage 1 foam broke immediately after touching the heavy oil in the sandpack, while stage 5 foam demonstrated good stability. One can conclude that the morphology of the oil phase, whether small droplets trapped by capillary forces, as in the case of residual mineral oil saturation, or large blobs bypassed by preferential flow as in the case of heavy oil, does not

influence the stability of foams. Instead, only the extent of coverage of nanoparticle by surfactant governs foam stability. As with mineral oil, the synergistic interaction occurs when the nanoparticles have a partial monolayer of surfactant.

Figure 3-13 Stage 5 foam (green) was the only stable system in the presence of residual heavy oil (508 cp, $S_{or}=40\%$). Stage 1 foam (red) and surfactant foam (blue, hidden by red curve) broke upon contact with heavy oil and never developed significant viscosity. Flowing test #16: surf foam; flowing test #17: stage 1 foam; flowing test #18: stage 5 foam (flowing tests referred to **Table 2-3**).

3.4.4 Foam stability in a high salinity and heavy oil environment

Figure 3-13 shows the results of stage 5 foam and surfactant foam flow behavior with residual oil and high salinity aqueous phase. The flow behavior was consistent with the static test results. Both systems showed good foamability inside the foam generator when there was no oil, but once the foam contacted heavy oil inside the sandpack, the surfactant stabilized foam broke, while the stage

5 foam showed good oil tolerance and salt tolerance. Salinity increased surfactant foam flow resistance in the presence of heavy oil, consistent with the static results, though its flow resistance was nevertheless much smaller than that of stage 5 foam.

Figure 3-14 Stage 5 foam demonstrated both good oil tolerance (508 cp, $S_{or} = 40\%$) and salinity tolerance (5.0 wt% NaCl) in the porous media. Surfactant foam demonstrated good tolerance to residual oil in the high-salinity environment; as shown in figure 3-13 this foam collapsed upon encountering residual oil in the salt-free system. These results matched with the static test results. Flowing test #19: surf foam + 5.0 wt% NaCl ; flowing test #20: stage 5 foam + 5.0 wt% NaCl (flowing tests referred to **Table 2-3**).

3.5 Oil Recovery Analysis

3.5.1 Entering, spreading and bridging coefficients

The entering, spreading and bridging coefficients of surfactant foam, stage 1 foam and stage 5 foam are indicated in **Table 3-2**. The entering coefficients of the three foaming systems all

exceeded 0, which means the oil can enter the gas/liquid interface easily. The spreading coefficients were all less than 0, which implies the spreading of oil droplets to the surface was unfavorable. The bridging coefficient was less than 0 for the surfactant foaming system, which means the bridge was stable, while the bridging coefficients for stage 1 and stage 5 foaming systems both exceed 0, which means the bridge was unstable and lamella would break. Thus the classic theory would expect the surfactant foam to be stable in the presence of oil while stage 5 nanoparticle stabilized foam to be unstable. However, the observation of static tests from **Figure 3-2** contradicted the theory. In the static tests, oil droplets spread over the surfactant foam surface and caused surfactant foam to break in a short time, as shown in **Figure 3-2**, while the spreading and bridging of stage 5 foam was unfavorable. The observations of surfactant foam and stage 5 foam in this work contradict with the classic theory and the inconsistent coefficients were highlighted with * in **Table 3-2**.

Table 3-2 Interfacial tension and Entering, Spreading and Bridging coefficients of surfactant foam, stage 1 foam, and stage 5 foam with heavy oil (508 cp). Interfacial tensions are measured; coefficients are calculated from **Equations 1-1, 1-2 and 1-3**. Coefficients that do not meet the theoretical expectation were highlighted with *.

Foam type	γ_{ow} (mN/m)	γ_{wg} (mN/m)	γ_{og} (mN/m)	E (mN/m)	S (mN/m)	B (mN/m)	Predicted stability with oil	Observed stability with oil
Surfactant	5.49	29.87	31.52	3.84	-7.14*	-131.44*	Stable	Unstable
Stage 1	6.12	34.21	31.52	8.81	-3.43*	139.46	Unstable	Unstable
Stage 5	9.72	36.55	31.52	14.75*	-4.69	247.91*	Unstable	Stable

To propose a new theory of foam-oil interaction in supporting the synergistic effect between the oppositely charged surfactant and nanoparticles at partial monolayer coverage region, while surfactant alone or bilayer coverage region cannot stabilize the foam, further work must be done to measure contact angle of the three foams on oil surface. In this oppositely charged surfactant and nanoparticles foaming system, the surface charge of the surfactant – nanoparticles mixture influences the balance of repulsion and attraction between particles, and also determines the particle sizes and their stability at the oil/liquid interface. Contact angle measurement can reveal the hydrophobicity of nanoparticles at different adsorption stages, and hence tuning the detachment energy from the gas/liquid interface. These results can provide insight into nanoparticles stabilized foam theory with oil and are highly recommended in future work.

3.5.2 Oil recovery

Cumulative oil recovery was calculated based on OOIP after oil injection into the sandpack and a fraction of OOIP was reported in the figure. OOIP referred to the initial oil saturated in the sandpack. After 3 PVs of waterflood, foam was injected into the system to recover residual oil. In **Figure 3-15**, waterflood referred to continuous water injection without gas nor foam in the system; baseline referred to water and gas injection at the same 4/1 gas/liquid ratio. The stage 5 foaming system (blue) significantly increased oil recovery following waterflood. The largest oil recovery increment occurred in the interval of 1 to 2 PVs of foam injection and increased oil recovery by 25% in total. The surfactant foam showed similar oil recovery with baseline. This is attributed to surfactant foam being unstable in the presence of oil, so that the gas and water from collapsed foam simply continued to move through the shortcut path previously established during the water flood.

Figure 3-15 Cumulative heavy oil (508 cp) recovery of waterflood, baseline, surfactant foam and stage 5 foam, first 3 PVs of waterflood following foam injection. Cumulative oil recovery referred to oil recovered as a fraction of initial oil saturation in the sandpack. Waterflood referred to continuous water injection without gas nor foam in the system. Baseline referred to water and gas injection at the same 4/1 gas/liquid ratio. Stage 5 foam significantly increased oil recovery after 1 PV of injection, and increased oil recovery by 25% compared with waterflood in total.

Surfactant foam showed no significant benefits of increased oil recovery compared with waterflood and baseline. Flowing test #16: surf foam; flowing test #18: stage 5 foam (flowing tests referred to **Table 2-3**).

Figure 3-16 Tertiary oil recovery (heavy oil, 508 cp) of waterflood, baseline, surfactant foam and stage 5 foam. Tertiary oil recovery referred to oil recovered as a fraction of ROIP after waterflood. Stage 5 foam significantly increased oil recovery after 1 PV of injection, and increased oil recovery by 25% compared with waterflood in total. Surfactant foam showed no significant benefits of increased oil recovery compared with waterflood and baseline. Flowing test #16: surf foam; flowing test #18: stage 5 foam (flowing tests referred to **Table 2-3**).

3.6 Confocal images of static foams

3.6.1 Stage 5 foam

To understand the role of silica nanoparticles in stabilizing foams, bubble structure and nanoparticles location was captured by a confocal microscope. **Figure 3-17** display stage 5 foam bubble structure and nanoparticles location in the static test. As shown in **Figure 3-17 (upper row)**, the bubble was small and round with a diameter of less than $250\ \mu\text{m}$. More than 80% of the bubbles exhibited similar size and structure. **Figure 3-17 (lower row)** proves that nanoparticles preferentially attach to the gas/liquid interface. The bubble images were scanned layer by layer.

Obtaining a well defined 3D image of the bubble/liquid interface, as observed here, thus indicates that the bubble is essentially motionless during the scanning process.

Figure 3-17 Confocal images of static stage 5 foam: (upper row) top and perspective views of bubble between several other bubbles; (lower row) perspective and top view of lamella between two bubbles. Nanoparticles appear green. Stage 5 foam bubbles were small and round with nanoparticles concentrated at the bubble surface (arrow). The well-defined interfaces are visible because the bubble remained static during image acquisition, which is consistent with the high stability of Stage 5 foam.

3.6.2 Stage 1 foam.

In contrast, bubbles in the stage 1 foam system moved around the scanning area and were unable to stay in one place for more than a millisecond. Consequently constructing a 3D image similar to those of the stable bubbles in Figure 3-16 was impossible. Instead, movies consisting of 2D images at a fixed depth were recorded. Screenshots selected from these frames are presented in **Figure 3-18** and **Figure 3-19**.

In **Figure 3-18**, only one discrete (highlighted in red circle) nanoparticle was observed within the liquid between two bubbles. This is consistent with the fact that at stage 1, the silica nanoparticles were fully covered by a double layer of surfactant molecules. The double-layer coating gives the nanoparticles some affinity for the bubble/liquid interface but prevents the nanoparticles from attaching to the gas/liquid interface strongly. Instead, they tend to attach and detach rapidly. This situation contrasts with the stage 5 foam in Figure 3-16, where a cohesive, stationary structure of nanoparticles is evident. The absence of such a structure in Figure 3-18 explains why the stage 1 foam showed no improvement of foam stability and flow resistance in the tests.

Figure 3-19 shows the same gas/liquid interface at six different times (at 8, 9, 10, 11, 21, 35 second). During a 35-second time interval, only one nanoparticle appeared, and it remained visible and in the same location for one second (red circles in the images taken at 9 seconds and at 10 seconds). No more nanoparticles observed at the interface. The large radius of curvature of the gas/liquid interface showed the stage 1 foam bubble expanded. In the sample, the bubble structure changed from spherical to polyhedral within 30 minutes.

Figure 3-18 Screenshot of stage 1 foam under confocal microscopes. Stage 1 foam was unstable and moved too fast to generate a clear 3D image. Nanoparticles have a double-layer coating of surfactant and thus do not attach to the gas/liquid interface strongly. Only one nanoparticle (highlighted in red circle) attached long enough to be visible, the rest of the nanoparticles moved rapidly between interface and the bulk phase liquid.

Figure 3-19 Six screenshots of stage 1 foam under confocal microscope at 8, 9, 10, 11, 21, 35 seconds (time shown on top right of each screenshot). The only nanoparticle (same in Figure 3-18) appeared once for one second, in a 35 seconds time interval. Only one nanoparticle (highlighted in red circles at 9 and 10 seconds) attached long enough to be visible, the rest of the nanoparticles moved rapidly between interface and the bulk phase liquid.

3.7 Summary

Surfactant foam, stage 1 foam and stage 5 foam all demonstrate good foamability in the static tests, however, surfactant foam and stage 1 foam are unstable (under the convention adopted in this thesis, Page 44) in that the bubble texture changes significantly within 120 minutes. Stage 5 foam

is the only stable system in static tests that demonstrate both good oil tolerance and salinity tolerance.

Figure 3-20, Figure 3-21 and Figure 3-22 summarize the surfactant foam, stage 1 foam and stage 5 foam flow behaviors in porous media under different conditions. In a surfactant foam or stage 1 foam system, foam can survive only if it does not encounter oil in the porous medium. The highest flow resistance for surfactant or stage 1 only appeared in a water-saturated sandpack, and additional oil or salt would weaken or collapse the foam. This limits the application of surfactant foam or stage 1 foam in the oil field. Synergy effect only existed at stage 5 coverage. At high surfactant concentration (0.1 wt%) synergy occurred only in the presence of oil, salinity or both. At low concentration (0.01 wt%) synergy also occurred while displacing fresh water. For both mineral oil and heavy oil, stage 5 was the only stable system at mobile and residual oil saturations or high salinity. Salinity (up to 5.0 wt%, monovalent ion) enhanced foam stability with or without oil in the porous media.

Figure 3-20 Surfactant foam was most stable when there was no oil or no salt in the systems. The presence of oil or salt had a detrimental effect on foam stability and flow behavior in the porous media, sometimes causing complete destabilization.

Figure 3-21 Stage 1 foam was only stable when there was no oil or salt in the system. Additional nanoparticles at this stage have no contribution to the foam stability.

Figure 3-22 Stage 5 foam was the only system that demonstrated good foamability and stability in the presence of oil and salt.

The location of the nanoparticles strongly affects the bubble structure and foam stability in both static and dynamic tests. When the nanoparticles were partially covered by a single-layer of surfactant molecules, the nanoparticles with intermediate hydrophobicity can strongly attach to the gas/liquid interface and hold the bubble in small and round shape for a long time; when the particles were fully covered by a double-layer of surfactant molecules, the mixture cannot remain at the interface, thus showed no benefits in stabilizing the foam.

This work presents the foam development and flow behavior in the porous media up to 5 PVI, where in the field application, the foam behavior at later PVI (more than 1 PV) represents the foam properties near the injection end, and the foam behavior at early PVI (less than 1 PV) represents the foam properties near the production end.

The results in this work indicated the foam needs more than 1 PV of injection to build up pressure difference, which might be a concern in the field application. However, the sandpack used in this research is on a much smaller scale compared with a real reservoir, thus the absolute length that requires to develop foam in this study was significantly small.

3.8 Conclusions

Synergy effect existed between the oppositely charged surfactant (AES) and nanoparticles (ST-AK) in stabilizing methane foam in both static and dynamic conditions. This type of surfactant demonstrated good foamability but lack of stability with oil and brine present. This type of nanoparticles cannot generate or stabilize foam. The extent to which nanoparticles are covered with surfactant governs foam stability for the combined nanoparticle/surfactant system. In the presence of oil foam is only stable when the nanoparticles surface are partially covered by a monolayer of surfactant molecules (stage 5 foam). The foam apparent viscosity can reach to 200 cp while flowing in 5.0 wt% NaCl past residual heavy oil (viscosity of 508 cp and waterflood $S_{or} = 40\%$). In contrast, when nanoparticles are fully covered by a bilayer of surfactant molecules (stage 1 foam), the generated foam showed no oil or salinity tolerance neither in static nor dynamic conditions. Similarly, surfactant-only stabilized foam showed little or no tolerance to oil or salinity.

Besides the scale comparison, foam injection technique optimization could also make this concept for reservoir-stable foam feasible in the field. The results demonstrated that stage 5 (partial monolayer coverage) foam is highly and uniquely stable with the presence of heavy oil and high salinity in reservoir conditions. This foam could in principle be generated in-situ. Once the foam is fully developed inside the porous media, efficiently blocking already swept zones and diverting

subsequently injected fluid to un-swept zones, the operation can switch back to whatever technique costs less. This means the mobility ratio can be optimized with a stage 5 foam displacing front, rather than a continuous stage 5 foam generation and injection process.

Chapter 4 : Foaming System Compatibility Tests

In the previous chapter, the methane foam generation and propagation behavior in static and dynamic tests of three different foaming systems were compared, and nanoparticles stabilized methane foam at a partial monolayer coverage demonstrated uniquely high stability when contacting heavy oil in a high salinity environment. In this chapter, the effect of gas type, sand surface treatment, and divalent ions are discussed. The foam flowing tests was conducted with Nitrogen in regular porous media, and methane foam flowing tests in the porous media with sand surface treatment. Properties of sandpack used in Chapter 4 are presented in **Table 4-1**.

Table 4-1 Flowing tests properties in Chapter 4.

Flow test Number	AES concentration /wt%	ST-AK concentration /wt%	Stage (1 = bilayer 5 = partial monolayer)	Permeability /d	Gas	NaCl Concentration / wt%	CaCl ₂ Concentration / wt%	Wettability
21	0.1	-	-	39.65	N ₂	-	-	hydrophilic
22	0.1	0.1	1	42.70	N ₂	-	-	hydrophilic
23	0.1	1.5	5	40.61	N ₂	-	-	hydrophilic
24	0.1	-	-	31.34	CH ₄	-	-	hydrophobic
25	0.1	0.1	1	37.75	CH ₄	-	-	hydrophobic
26	0.1	1.5	5	39.99	CH ₄	-	-	hydrophobic
27	0.1	1.5	5	36.21	CH ₄	5.0	0.5	hydrophilic

- Not applicable

4.1 Effect of Gas Type

Figure 4-1 shows the foam stability and flows behavior of the three foaming systems flowing in initially water-saturated sandpacks when the gas phase was nitrogen. All the foaming system

showed immediate pressure difference built up, which means stable foam could be propagated when the gas phase is nitrogen. This is consistent with the fact that static tests using air indicated stable foam. The apparent viscosity of surfactant foam after 5 PVs injection reached 1000 cp, which was 40% less than that of methane foam. Stage 1 foam and stage 5 foam demonstrated similar flow resistance with nitrogen. This work shows the foaming system was compatible with both methane gas and nitrogen.

Figure 4-1 Pressure difference across the sandpack saturated with water of different foaming systems with nitrogen normalized by the averaged pressure difference for the baseline (water and gas injection without foam stabilizers). The foaming system was compatible with Nitrogen and methane. Flowing test #21: surf foam; flowing test #22: stage 1 foam; flowing test #23: stage 5 foam (flowing tests referred to **Table 4-1**).

4.2 Effect of Wettability of Porous Medium

4.2.1 Sand after surface treatment

Figure 4-2 compares the sand before and after surface treatment. Before surface treatment, the silica sand was recognized as hydrophilic as received, and Milli-Q water drops imbibed immediately into the sand; after surface treatment, Milli-Q water drops stayed on top of the sand surface and do not imbibe. This observation indicates that the surface treatment increases the hydrophobicity of the sand, but it was not possible to quantify the change by measuring the contact angle. Thus this work refers simply to “sand after surface treatment,” and compares the foam generation and propagation behavior of different foaming systems in the “porous media with surface treatment” to the behavior in untreated sand.

Figure 4-2 Comparison of sand before(left) and after (right) surface treatment. Before surface treatment, the sand is recognized as hydrophilic, water drops imbibed into sand immediately. After surface treatment, water drops do not imbibe.

Contact angle measurement is recommended in future work to make the hydrophobicity nature of treated sand more quantitatively.

4.2.2 Effect of sand after surface treatment

Figure 4-3 shows the foam generation and propagation behavior of the three different foaming systems in a porous media with surface treatment. Apparent viscosity of stage 1 foam and surfactant foam were substantially lower than the untreated porous media, refer to **Figure 3-9**. The three tests were conducted with pre-flush of 0.1 wt% AES solution for 5 PVs before foam injection. Stage 5 foam, however, demonstrated larger flow resistance. Recall that in the untreated porous media, the apparent viscosity of stage 5 was approximately 1000 cp after 5 PVs of injection, and here in a surface treated porous media, the apparent viscosity reached up to 1500 cp. The summary of wettability effect on foam stability are shown in **Figure 4-4**, where foam flow behavior in hydrophilic sandpacks are plotted in blue and in hydrophobic sandpacks are plotted in orange.

Figure 4-3 Normalized pressure of three different foaming systems in porous media with surface treatment. The porous media are initially saturated with 0.1 wt% AES solution. Stage 5 demonstrated better stability and flow resistance in treated porous media than other systems, as well as the stage 5 foam in untreated porous media. Stage 1 foam and surfactant foam suffered from late pressure difference built up, which limits the further application of surfactant foam or stage 1 foam in hydrophobic reservoirs. Flowing test #24: surf foam; flowing test #25: stage 1 foam; flowing test #26: stage 5 foam (flowing tests referred to **Table 4-1**).

Surfactant foam had poor performance in a treated porous media while stage 1 foam demonstrated moderate stability, but none of the systems could compare with the large flow resistance brought by the stage 5 in a treated porous media. This shows stage 5 foam has a potential application into hydrophobic reservoirs as well as hydrophilic reservoirs.

Stage 1 foam or stage 5 foam all showed larger pressure difference built up within first 3 PVs of injection, thus surfactant concentration analysis in the effluent samples are recommended, to investigate the effect of chemical loss in a hydrophobic porous media on foam stability.

Figure 4-4 Changing wettability from hydrophilic (blue) to hydrophobic (orange) weakens surfactant foam greatly (left); weakens stage 1 foam moderately (middle); and strengthens stage 5 foam (right).

4.3 Effect of Divalent Ions – Ca^{2+}

To investigate the stage 5 foam stability with the presence of field water and heavy oil, this work presents foam flow behavior at residual heavy oil condition with both monovalent ions Na^+ and divalent ions Ca^{2+} present in the foaming solution and porous media. Surfactant foam stability test with Na^+ and Ca^{2+} are recommended for future work.

The foaming solution was prepared with a mixture of 5.0 wt% NaCl and 0.5 wt% CaCl_2 solution, and the rest of the procedures were the same with heavy oil and salinity tests.

Figure 4-5 compares the surfactant and stage 5 foams in residual heavy oil conditions at different salinity environment. Stage 5 foam demonstrated larger flow resistance than surfactant foam in a monovalent ion environment (green line vs blue line). The presence of Ca^{2+} had a negative effect on the stage 5 foam stability (grey line).

Figure 4-5 Normalized pressure difference of two different foaming systems in residual heavy oil condition. Stage 5 demonstrated the largest flow resistance with Na^+ present; the presence of Ca^{2+} with Na^+ had a negative effect on foam stability. However, the flow resistance was still larger than the surfactant foam system with only Na^+ present. Flowing test #8: surf foam Na; flowing test #9: NP foam stage 5 Na+Ca; flowing test #27: NP foam stage 5 Na+Ca (flowing tests referred to **Table 2-3** and **Table 4-1**).

The surface tension measurement of surfactant foam and stage 5 foaming system with monovalent ions and divalent ions were indicated in **Table 4-2**. Na^+ or a mixture of Na^+ and Ca^{2+} cannot reduce the surface tension of surfactant foaming solution, and the results difference were in the reasonable measurement error range. However, Na^+ can reduce stage 5 foam surface tension by 10%, and the mixture of Ca^{2+} and Na^+ can reduce the surface tension of stage 5 by an additional 10%.

Table 4-2 Surface tension of surfactant foam and stage 5 foam systems. Ions cannot reduce the surface tension of surfactant stabilized foam, while the mixture of Ca^{2+} and Na^+ can reduce the largest surface tension by 20%.

Foam type	Foaming solution prepared with		
	Milli-Q water	5.0 wt% NaCl	5.0 wt% NaCl and 0.5 wt% CaCl_2
surfactant	29.87	29.55	29.22
Stage 5	36.55	33.11	30.11

Divalent ions may have similar interaction with silica nanoparticles methane foam as monovalent ions, in that the presence of a background electrolyte could modify the surface energy of nanoparticles and the gas/water interface. Binks et al. (2007) reported an increment of contact angle in nano-silica dispersions as they increase the NaCl concentration in the solution. San et al. (2017) reported higher NaCl solution concentration can reduce CO_2 foam bubble size and change the foam color from gray to milky white. They also observed similar behaviors when the brine was switched to the CaCl_2 solution. The divalent ions present in the solution can increase the hydrophobicity of particles, and as a result, the adsorption energy at CO_2 /brine interface is increased and foam stability is improved. By comparing the grey line (stage 5 foam with Na^+ and Ca^{2+}) and the green line (stage 5 foam with Na^+), one can conclude that the increased stage 5 foam stability with NaCl present is not simply caused by the presence of a electrolyte background, but probably a specific interaction between NaCl and the nanoparticles interface (Binks et al., 2007).

4.4 Fluctuation analysis

The flowing data were collected every second and presented at 100 period moving average. The raw data were presented in **Figure 4-6** without the 100-point moving average smoothing presented in all other figures. Nanoparticles flooding (orange line) shows when there was no foam in the system, there was less fluctuation in the system. Surfactant foam, stage 1 foam and stage 5 foam show periodical fluctuations, this attributed to the lamella breakage and reform in the porous media. Especially when nanoparticles present, the amplitude of fluctuation is larger than that of the surfactant foam in absolute terms, and is much larger relative to the magnitude of the pressure drop. Y-axis shows the minimum of -5 kPa due to the accuracy of the data acquisition system.

Figure 4-6 Fluctuation analysis of stage 5 foam, surfactant foam and nanoparticles flooding. In Nanoparticles flooding, 1.5 wt% ST-AK dispersion was co-injected into the sandpack with methane at 4/1 gas/liquid ratio. Surfactant alone or nanoparticles alone injecting into the sandpack could cause some fluctuation, but the combination of surfactant and nanoparticles gives largest flow fluctuation in the sandpack. Flowing test #6: NP foam stage 5; flowing test #5: NP foam stage 1; flowing test #4: surf foam; flowing test #7: NP flooding (flowing tests referred to **Table 2-3**).

4.5 Conclusion

The preliminary results of stage 5 foam and surfactant foam stability with nitrogen, divalent ions and in a hydrophobic porous media show that stage 5 foam are more compatible with various reservoir conditions. To prove the synergistic effect and potential EOR application of stage 5 foam uniquely, it is recommended to conduct all the tests with heavy oil (508 cp) present.

Chapter 5 : Conclusions and Future Work

5.1 Summary and conclusions

In a mixture of oppositely charged nanoparticles and surfactant, the coverage of surfactant to the surface of the nanoparticles determines the properties of foam stabilized by the mixture. This thesis compares the two limiting stages (out of five stages of coverage, ranging from full bilayer through complete monolayer to partial monolayer). Mixtures of ST-AK (positively charged silica nanoparticles with alumina coating) and AES (negatively charged anionic surfactant) are used to investigate static foam structure (bubble size and shape) and dynamic foam generation and propagation behavior in the porous media. Stage 1 and stage 5 refer to nanoparticles fully covered by a double-layer of surfactant molecules and nanoparticles partial covered by a single-layer of surfactant molecules respectively.

When the interaction between surfactant molecules and nanoparticles is sufficiently strong, the generated foam can remain stable while flowing through porous media which contains oil and brine and overcome chemical loss or crude oil partition. Partially covered nanoparticles (stage 5) can strongly attach to the gas/liquid interface, producing foam with superior and unique stability in both static and flowing tests.

Table 5-1 summarizes the foam stability factors and their effect on foam stability. In the static tests, unstable foam is defined as foam half-life less than 120 minutes, or bubble structure changed, and size doubled within 120 minutes. In the dynamic test, unstable foam is defined as foam apparent viscosity less than 200 cp after 5 PVs of foam injection. Otherwise, the foam was considered as stable.

Table 5-1 Foam stability factors summary; U=unstable, S=stable

Factors	Surfactant foam	NP foam at stage	NP foam at stage	Synergy effect
		1	5	
Surfactant conc.<1000 ppm	U	U	S	yes
Surfactant conc.>1000 ppm	S	S	S	no
Adsorption	U	S	S	yes
Mineral oil, 18 cp, S_{or}	U	U	S	yes
Mineral oil, 18 cp, S_{oi}	U	U	S	yes
Heavy oil, 508 cp, S_{or}	U	U	S	yes
Na^+	U	U	S	yes
Na^+ and Ca^{2+}	U	U	S	yes
Na^+ , heavy oil, 508 cp, S_{or}	U	U	S	yes
N_2	S	S	S	no
Hydrophobic porous media	U	U	S	yes

- At a low surfactant concentration (<1000 ppm), the synergistic interaction between surfactant and nanoparticles provides a step-change in flowing tests: the stage 5 foam successfully propagated through porous media, whereas surfactant foam failed due to large

amount of chemical loss to sand grains. Surfactant molecules had a strong affinity to the surface of the nanoparticles which results in less surfactant adsorption to the sand grains and favors foam generation and propagation process in the porous media by providing more free surfactant molecules in the solution.

- At a high surfactant concentration (>1000 ppm) and in a bilayer coverage (stage 1) system, nanoparticles are fully covered by surfactant molecules and had a very low affinity to the gas/liquid interface. Nanoparticles at this stage cannot prevent liquid drainage or bubble expansion, and the foam generated by such a mixture thus behaves similarly to surfactant alone stabilized foam. Nanoparticles at this stage contribute no benefits to the foaming system.
- Foam is highly stable at partial monolayer coverage (stage 5), and uniquely stable when contacting an oil phase. Nanoparticles at this coverage stage demonstrated low surface tension and strong adsorption to the gas/liquid interface in stabilizing the foam. The synergy effect provides the robustness of the foam in both static and dynamic conditions.
- Flow resistance (apparent viscosity) of the foam can be tuned by changing the nanoparticle concentration as long as coverage remains at stage 5. This provides customized mobility control in EOR processes with gas injection.
- Salinity increased the stability of stage 5 foam but decreased the stability of surfactant foam. The synergy effect between nanoparticles and surfactant molecules is responsible for this improvement.

The extension of stage 5 systems demonstrated the foaming system is compatible with nitrogen as gas phase, or hydrophobic porous media, and different types of ions (Na^+ and Ca^{2+}) in the formation water.

The adsorption stages provide insight into designing the foam injection and EOR processes. Stage 5 foam provides robust foam in reservoir conditions to sweep more oil; the foam can be killed easily by varying the concentration ratio of surfactant and nanoparticles and have less flow resistance at the production end.

5.2 Recommendations and future work

- It is suggested to repeat all the tests in high temperature (50 °C, 100 °C, and 150 °C) conditions. This is to demonstrate the temperature tolerance of the existing foaming system and explore the thermal oil recovery potential.
- To have a better insight into how far the foam can travel inside the porous media, pressure taps are recommended to install along the sandpacks (at distances 1/3 and 2/3 of sandpack length from the inlet). This way we can specify foam stability by the absolute distance it traveled. This will be useful for future long slim tube (6-meter-long with 4 pressure taps) tests.
- To investigate the foam stability and flow behavior in a hydrophobic reservoir conditions, contact angle measurement of surface treated sand are recommended, to quantify the hydrophobic nature of the treated sand.
- It is suggested to investigate the effect of similarly (both negatively and positively) charged nanoparticles and surfactant molecules in stabilizing the foam and see if a synergistic effect could occur in a similarly charged surfactant and nanoparticles system.
- It is suggested to conduct the nitrogen, divalent ions and hydrophobic porous media tests with heavy oil (508 cp) present in the system.

- Stage 1 foam at 1.5 wt% AES and 1.5 wt% ST-AK combination is recommended for confocal reflectance microscopy test. This work can rule out the effect of nanoparticles concentration on nanoparticles affinity to the gas/liquid interface, and prove the strong attachment of nanoparticles to the gas/liquid interface is only due to the partial monolayer surfactant coverage.

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