RICE UNIVERSITY

A Multiscale Study of Foam: the Phase Behavior, Transport, and Rheology of Foam in Porous Media

by

Yongchao Zeng

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE

George S. Hirasaki, co-Chair
A.J. Hartsook Professor Emeritus, Department of Chemical and Biomolecular Engineering
Member of National Academy of Engineering

Sibani L. Biswal, co-Chair
Associate Professor, Department of Chemical and Biomolecular Engineering
Associate Department Chair

Clarence A. Miller
Louis Calder Professor Emeritus, Department of Chemical and Biomolecular Engineering

Andrew J. Meade
Professor, Department of Mechanical Engineering

HOUSTON, TEXAS

November 2017
ABSTRACT

A Multiscale Study of Foam: the Phase Behavior, Transport, and Rheology of Foam in Porous Media

by

Yongchao Zeng

This dissertation provides an in-depth multiscale understanding of the foam flow in porous media for subsurface applications such as gas mobility control, aquifer remediation, CO₂ sequestration, water production control etc. In enhanced oil recovery (EOR), gas flooding has superior crude oil displacement efficiency where the gas sweeps. However, the overall oil recovery is often not much better than that of water flooding because of viscous fingering, gravity override, and reservoir heterogeneity. Using surfactant to generate foam in situ the porous media offer promise to simultaneously address all the three issues mentioned. Yet, the successful design of foam projects requires insightful understanding of the phase behavior, transport and rheology of foam in porous media.

My research investigates the dependence of foam transport on its constituent components: the effect of gas types and surfactant structures. An experimental investigation of the effect of gas type and surfactant structure is presented. The effects of gas solubility, the stability of lamellae, the surfactant Gibbs adsorption, and the gas diffusion rate across the lamellae were examined. Our experimental results showed that the steady-state foam strength is inversely correlated with the gas permeability across a liquid lamella, a parameter that characterizes the rate of mass transport. We also calculated the limiting capillary pressure for different foaming surfactants and found that foam stability is correlated with the Gibbs surface excess concentration.
My research also advances the understanding of “smart” foam rheology that can improve the sweep efficiency of gas flooding in porous media. Laboratory research work was conducted to capture the effect of heterogeneity on foam using actual reservoir rocks of varied permeabilities. It is observed that foam is more stable in high permeability cores compared to low permeability cores. Such smart rheology was also visualized in a 3-layered heterogeneous micromodel at the pore-level. Foam was shown to respond to the porous media heterogeneity by separating into a relatively dry and wet regime in the high- and low-perm regions respectively. Due to the capillary continuity between the layers of different permeability, the saturation step change induced a phase separation between the layers which resulted in responsive flow resistance.

In addition, understanding the foam-oil interaction is crucial to the success of foam EOR projects. In this thesis, foam strength dependence on oil was probed using nuclear magnetic resonance (NMR) imaging technique. Manganese (II) was doped into the surfactant solution to reduce the $T_2$ relaxation time of water in order to differentiate the NMR response from the oil. The measured apparent viscosity was mapped out with respect to different oil fractional flows and oil saturations. It is found out that the presence of oil can not only weaken the foam strength by promoting bubble coalescence but also strengthen the apparent viscosity by emulsifying in the surfactant solution. Unlike the bulk foam column test with oil, the overall apparent viscosity is found to be dependent on both oil saturation (oil fractional flow) and oil composition.

Moreover, an improved numerical algorithm is developed to estimate foam model parameters based on laboratory-scale experiment for field-scale reservoir simulation. Both dry-out effect and shear-thinning rheology of foam were considered. The algorithm reduced the five-parameter estimation to a few simpler steps, such as linear regression and single-variable optimization, and successfully avoided the sensitivities of initial estimates and the non-uniqueness
solution issues. Our improved algorithm was also compared with others reported in literature. The robustness of the algorithm was validated by varied foam systems.

Last but not least, the idea of injecting the surfactant with the gas phase (WAG+S, water-alternating-gas-plus-surfactant-in-gas process) has been conceptualized for the next generation CO₂ foam EOR. Some novel nonionic or switchable surfactants are CO₂ soluble, thus making it possible to inject the surfactant with CO₂ slugs. Since the surfactant can be present in both the CO₂ and aqueous phases, it is important to understand how the surfactant partitioning between the phases influences foam transport in porous media. Foam simulations were conducted in both 1-D and 2-D systems respectively. We conclude that when surfactant has approximately equal affinity to both the CO₂ and the water, the transport of surfactant is in line with the gas propagation and therefore the sweep efficiency is maximized.
Acknowledgments

To my most admirable and respectful advisors Dr. George J. Hirasaki and Dr. Sibani L. Biswal who I have always looked up to in life as my role models. I am most appreciative to Dr. Biswal who always had faith in me and allowed me the freedom to pursue the research interest of my own. I am deeply indebted to Dr. Hirasaki for teaching me not only his authoritative knowledge in chemical engineering but also his professional expertise in windsurfing. I could not have imagined having better advisors than Dr. Hirasaki and Dr. Biswal.

Many thanks go to Dr. Clarence A. Miller and Dr. Andrew J. Meade for serving on my thesis committee. I am grateful to all the helpful discussions during my Ph.D. study.

I owe my sincere thankfulness to Maura Puerto, an unofficial mentor who constantly offered help and took care of me in lab.

I thank Dr. Kun Ma, Dr. José Lopez Salinas, and Dr. Leyu Cui for enlightening me the first glance of research when I joined the group.

I would like to thank Prof. Arne Graue and Prof. Martin Fernø for inviting me to University of Bergen for a short-term exchange program in Norway.

I am grateful to Dr. Rouhi Farajzadeh and Dr. Sebastien Vincent-Bonnieu from Shell Rijswijk who invited me to the Deft University of Technology (TU Delft) for a whole semester and guided me through my research in Netherlands. I would like to acknowledge Prof. William Rossen, Dr. Ali Akbar Eftekhari for insightful discussions and Mr. Michel Slob for tremendous help in lab.
Many thanks to Pauziyah Abdul hamid, Arif Azhan B A Manap, Siti Rohaida Bt M Shafian, and Ridhwan Zhafri B Kamarul Bahrim for inviting me to Petronas Research Sdn Bhd (PRSB) in Malaysia. I am deeply touched by your cordial hospitality. I am also grateful to all the friends I met at PRSB Ahmad Amirhilmi, Kessler Sendeli, Sarveen Mahendran, and Ivy Chai.

To all my current and former group members Dr. Di (Daniel) Du, Dr. Peng He, Dr. Qing Wang, Dr. Charles Conn, Dr. Julie Byrom, Dr. Kung-Po Chao, Dr. Jinghui Wang, Dr. Anulekha Haridas, Dr. Ying (Annie) Wang, Elaa Hilou, Jingjing Zhao, Yu-Jiun (Nate) Lin, Pengfei (Patrick) Dong, Guoqing (Michael) Jian, Leilei Zhang, Botao (Farren) Song, Steve Kuei, Quan Nguyen, Sunny Niu, Dan Vecchiolla, Tao Deng, etc., thank you all for making our research group like a big happy family.

With a special mention to Mr. Eric D. Vavra who is my unofficial English tutor and Mr. Reza Amirmoshiri who continues my project and did most of the experiments for me when I was interning at Shell.

I also thank all my undergraduate interns Chang (Carson) Da, Xindi Duan, Jeffrey Joyce etc. who have supported my Ph.D. research throughout the years.

Many thanks go to all my friends at Rice: Xiao Tan, Xiaoyi (Tracy) Li, Hao (Roy) Mei, Zhuqing Zhang, Siyang (Sean) Xiao, Yi-Lin Chen, Eva Jin, and all others. You make my journey to Ph.D. full of laughter and happiness.

To my very best Indian cheerleader Dr. Aarthi “Buddha” Muthuswamy, a loyal friend, a wonderful travel companion, and an inspirational artist: we have had so much fun together in the exploration of science, art, and Europe.
My sincere thankfulness goes to Qiqi (Scarlet) Xiang: it is of great joy to have met her and I wish her all the very best in all her endeavors in life.

Special thanks to Jin Song who makes my life beyond ordinary: I am grateful to all the memorable moments we shared.

Most importantly, to my dearest parents, who raised me up and allowed me to pursue my dream, I owe my deepest gratefulness to them. Their love is the greatest gift I have ever had in life.
Contents

Acknowledgments ....................................................................................................................... v

Contents ...................................................................................................................................... viii

List of Figures .............................................................................................................................. xii

List of Tables ............................................................................................................................... xix

Nomenclature ............................................................................................................................. xxi

Chapter 1 Introduction .................................................................................................................. 1
  1.1. Scope of Study: Improved Oil Recovery (IOR) ................................................................. 1
  1.2. Object of Study: Foam Flow in Porous Media ................................................................. 8
  1.3. Technical Background Part I: Fluid Mechanics in Porous Media .............................. 17
  1.4. Technical Background Part II: Foam Modeling Techniques ......................................... 19
  1.5. Thesis Structure .................................................................................................................. 21

Chapter 2 Dependence of Foam Transport on Its Constituent Component Part I: Role of Gas Type and Composition .............................................................................................................. 22
  2.1. Background ....................................................................................................................... 22
  2.2. Materials and Methods ................................................................................................. 25
  2.3. Results and Discussions ............................................................................................... 26
    2.3.1. Hypothesis I: Gas Solubility .................................................................................... 28
    2.3.2. Hypothesis II: Stability of the Lamella ................................................................. 29
    2.3.3. Hypothesis III: Diffusion Coarsening .................................................................. 33
  2.4. Conclusion ....................................................................................................................... 36

Chapter 3 Dependence of Foam Transport on Its Constituent Component Part II: Effect of Surfactant Partitioning .................................................................................................................. 38
  3.1. Background ....................................................................................................................... 38
  3.2. Model Description .......................................................................................................... 41
  3.3. Results and Discussions ............................................................................................... 51
    3.3.1. Case I: CO₂ Displacing Water ............................................................................... 51
    3.3.2. Case II: Single Slug of CO₂ Followed by Water .................................................. 53
    3.3.3. Case III: Water-Alternating-Gas-Plus-Surfactant (WAG+S) ............................... 55
3.3.4. Simulation v.s. Fractional Flow Theory .......................................................... 56
3.4. Conclusion ............................................................................................................. 59

Chapter 4 Dependence of Foam Transport on the Rock Permeability: The Smart Foam Rheology ................................................................. 60
4.1. Background ........................................................................................................... 60
4.2. Experiment Section .............................................................................................. 61
   4.2.1. Materials ......................................................................................................... 61
   4.2.2. Setup ............................................................................................................... 63
   4.2.3. Procedure ....................................................................................................... 65
4.3. Modeling Section .................................................................................................. 67
4.4. Results and Discussions ...................................................................................... 69
4.5. Conclusions .......................................................................................................... 75

Chapter 5 Foam-Oil Interaction in Porous Media Part I: Microfluidic Visualization at the Pore-level ................................................................. 77
5.1. Background ........................................................................................................... 77
5.2. Materials and Methods ......................................................................................... 80
5.3. Results and Discussions ...................................................................................... 86
   5.3.1. The Displacement Front Zone: Foam Destabilization ....................................... 86
   5.3.2. The Transition Zone: Surface Wettability Alteration from Oil-wet to Water-wet ................................................................. 90
   5.3.3. The Foam Bank: In-Situ Lamella Generation in Water-wet Conditions ................. 94
   5.3.4. The Smart Rheology of Foam ........................................................................... 99
5.4. Conclusion ........................................................................................................... 104

Chapter 6 Foam-Oil Interaction in Porous Media Part II: Core-level Investigation with NMR Imaging ................................................................. 106
6.1. Background ........................................................................................................... 106
6.2. Methods and Materials ........................................................................................ 109
   6.2.1. Chemicals and Materials ............................................................................... 109
   6.2.2. Core Flooding Apparatus ............................................................................... 110
   6.2.3. Experiment Procedure .................................................................................... 111
      6.2.3.1. Saturation Measurement with NMR ............................................................ 111
      6.2.3.2. Core Preparation ....................................................................................... 112
9.1.2. Dependence of Foam Transport on Rock Permeability: Smart Foam Rheology ................................................................. 173
9.1.3. Foam-Oil Interactions in Porous Media at Multiple Scales ....................... 174
9.1.4. Improvement in Model Parameterization Algorithms ............................. 175
9.1.5. Development of the Foam Flooding Process with CO₂ Soluble Surfactant... 175
9.2. Future Recommendations ........................................................................ 176

References ........................................................................................................ 180

Appendix ............................................................................................................. 201
List of Figures

Figure 1-1 The maturity and development of various IOR technologies (Adapted from Lake L.) ................................................................. 2

Figure 1-2 Number of IOR projects till 2014 worldwide 2 ................................. 3

Figure 1-3 The favorable reservoir conditions for different IOR technologies (Adapted from Lake L.) ................................................................. 4

Figure 1-4 Displacement fronts for different mobility ratios and injected pore volumes 6 ................................................................................. 5

Figure 1-5 Schematic of capillary desaturation curve for carbonate formation, sandstone formation and sandpack system 3 ........................................... 6

Figure 1-6 Projected CO2-IOR U.S. regional oil production 10 ................................. 8

Figure 1-7 Foam generation by snap-off mechanism .............................................. 12

Figure 1-8 Foam generation by lamella-division mechanism ................................ 13

Figure 1-9 Foam generation by leave-behind mechanism ...................................... 13

Figure 1-10 Foam generation by pinch-off mechanism: the blue bubble is pinched off against the constriction structure by its neighbors ........................................... 14

Figure 1-11 Schematics of foam structure: capillary drainage drives liquid flow to Plateau borders and nodes. The arrows show the flow direction 17 ......................... 15

Figure 1-12 Schematic of capillary pressure in porous media and the limiting capillary pressure above which lamellae are no longer stable and foam starts to coalesce 18 ........................................................................................................ 16

Figure 1-13 Henry Darcy’s experiment setup in 1856 19 ........................................... 17

Figure 2-1 Gibbs dividing surfaces for foam film .................................................. 24

Figure 2-2 Foam strength as a function of foam quality for various gases: nitrogen (diamond), methane (circles), and carbon dioxide (triangles) ......................... 27

Figure 2-3 Foam quality scans for CO2 under various conditions. Increasing the CO2 flow rate compensates for dissolved CO2 in the aqueous phase (dashed line) or
saturating the aqueous solution with CO₂ (dotted line) results in stronger foam at lower foam qualities compared to CO₂ gas (solid line). An increase in foam apparent viscosity is observed once the CO₂ is saturated in the aqueous phase.

Figure 2-4 Quality scans for N₂, CH₄, CO₂, and their binary mixtures. Nitrogen (solid diamond) had the strongest foam strength, followed by flue (80 mol% N₂ and 20 mol% CO₂) gas (dashed diamond), 50 mol% CH₄ and 50 mol% CO₂ (dotted triangle), CH₄ (square); and CO₂ (solid triangle). The strength of the mixed gas foams corresponds with foams of the least soluble gas.

Figure 2-5 Relative foam strengths to N₂ as a function of the film permeability. Different symbols represent various foam qualities ranging from 40-90%.

Figure 3-1 The relationship between $F_{surfactant}$ and $C_{sw}$ ($f_{msurf} = 2 \text{ g/L}$, $e_{psurf} = 1$).

Figure 3-2 The relationship between $F_{water}$ and $S_{w}$ ($f_{mdry} = 0.25$, $e_{pdry} = 50, 500, 5000$).

Figure 3-3 Relative permeability with foam in STARS.

Figure 3-4 Scheme for numerical 1-D CO₂ foam core-flood experiment.

Figure 3-5 Case I: CO₂ displacing water.

Figure 3-6 Case II: Single slug of CO₂ followed by water.

Figure 3-7 Case III: Water-alternating-gas-plus-surfactant (WAG+S).

Figure 3-8 Contour of apparent viscosity as a function of $f_{mdry}$ and $K_{sgw}$.

Figure 3-9 CO₂ displacing water with modified form of $F_{surfactant}$ to reproduce the results given by fractional flow theory.

Figure 4-1 Leverett-j function measured from mercury primary drainage experiment.

Figure 4-2 Schematic diagram of the core-flooding system.

Figure 4-3 Foam flooding experiment results (dots) and model fittings (line) with respect to reservoir cores of varied permeabilities. (a) Foam-quality-scan experiment at fixed superficial velocity of 4 ft/day and (b) flow-rate-scan experiment at transition foam qualities.
Figure 4-4 Limiting capillary as a function of rock permeability ............................. 73

Figure 4-5 Comparing maximum mobility reduction as a function of rock permeability: the value of \( \text{fmmob} \cdot \text{fmcapepcap} \) increases exponentially as a function of rock permeability ................................................................. 75

Figure 5-1 Optical microscopy image highlighting the various zones that appear as foam displaces crude oil in a heterogeneous porous media. Scale bar: 500\( \mu \)m. ....... 80

Figure 5-2(a) Photograph of microfluidic device used for experiments and 3-D CAD generated view of the micromodel illustrating permeability contrast. Scale bar: 1 cm. (b) Schematic of the microfluidic device illustrating port placements. Data is captured at the entrance of the porous media as indicated by the optical microscopy images depicting 100% crude oil saturation initially followed by images upon foam injection. Microscopy images are image processed using Matlab where oil, surfactant solution, and gas are colored red, blue, and green, respectively. Scale bar: 500 \( \mu \)m ............. 82

Figure 5-3 Optical microscopy images comparing foam displacement of (a) paraffin oil, which is not significantly detrimental to foam and (b) crude oil, which destabilizes the foam by rupturing the liquid lamella. Scale bar: 500 \( \mu \)m ..................... 87

Figure 5-4 (a) An oil droplet stays in the aqueous phase if \( E < 0 \) and (b) enters the gas-water interface if \( E > 0 \). Paraffin oil has a positive entering coefficient but does not readily destabilize the foam lamella interface. (c) An oil droplet spreads on gas/water interface if \( E > 0 \) and \( S > 0 \). Crude oil has both a positive entering and spreading coefficient, which destabilizes the gas-liquid lamella of foam ............. 89

Figure 5-5 Optical microscope images of initial stage of foam displacement of (a) paraffin oil and (b) crude oil. The zoomed in highlighted region at the displacement from illustrate oil lamellae connecting pore throats, indicative of an oil-wet condition. Optical microscope images at a later time of foam displacement in the (c) paraffin oil and (d) crude oil) shows aqueous lamella bridges between pore throats, indicative of a transition to a water-wet system. Scale bar: 500\( \mu \)m ......................... 92

Figure 5-6 Optical microscopy images of (a) paraffin oil and (b) crude oil being emulsified and transported in the fracture region Scale bar: 500 \( \mu \)m .................. 94

Figure 5-7 Time series of microscopy images taken to illustrate mechanisms by which new liquid lamellae is formed in the water-wet foam bank region. (a) Lamella division was observed as a gas bubble invades a pore throat and divides to generate new liquid lamellae. (b) Neighbor-bubble- pinch-off was observed to generate new liquid lamellae. Scale bar: 200\( \mu \)m. ......................................................... 97
Figure 5-8 Characteristic bubble size and oil recovery efficiency with respect to total injected pore volumes (PV) as dimensionless time. The bubble size increased dramatically in the displacement front zone and started to decrease in the transition zone. The average bubble size leveled off in the foam bank zone where most oil was displaced.

Figure 5-9 Optical microscopy images comparing crude oil displacement after injecting (a) N₂ gas, (b) water, and (c) foam after breakthrough. (d) Graph depicting crude oil saturation (%) versus pore volume injected, a nondimensional measure of injected fluid volume. Scale bar: 500μm.

Figure 5-10 (a) Evolution of the foam gas-fraction in the high-perm and low-perm regions. Gas enters the high-perm region first followed by the low-perm region. At steady-state, the gas content in the high-perm region is significantly greater than that in the low-perm region; (b) Capillary pressure schematic in the high- and low-perm regions. The differences in capillary entry pressure and equilibrium water saturations are responsible for the smart rheological properties of foam.

Figure 6-1 Schematic of the oil saturation profile in foam EOR: foam completely collapses in the red region whereas it preserves its full strength in the green region. Our research interest is the yellow region in which foam strength is dependent on oil saturation.

Figure 6-2 Schematic of the core-flood apparatus, (Vinci model CFS 700)

Figure 6-3 NMR measurement of the bulk brine-hexadecane system in a glass vial: the actual water content was 44.9%, whereas the NMR measured value was 45.3%. The error was less than 1%.

Figure 6-4 Foam quality scan experiment in the absence and presence of remaining hexadecane (C16) in Berea Sandstone at 94°C. The numbers represent the order in which the data points were measured in lab.

Figure 6-5 NMR saturation measurement of Core Sample B (A): at initial 100% water saturation; (B) after oil drainage experiment; (C) after 4 PV of water flooding to mimic the secondary recovery in the reservoir.

Figure 6-6 NMR measurement after the foam quality scan experiment with the water flooded residual hexadecane (C16). The yellow circle corresponds to the inlet area with no detectable oil as a result of the micellar solubilization by the AOS surfactant.
Figure 6-7 Comparison between the residual oil saturations in our experiment and the CDC curve schematics proposed by Lake et al. Foam recovered most of the oil by increasing the capillary number by 3 orders of magnitude. 120

Figure 6-8 Oil recovery mechanism comparison between water flooding, foam flooding, and surfactant micellar solubilization under our experimental condition; the oil recovery percentage was calculated based on original oil in place (OOIP) ....... 121

Figure 6-9 Foam-hexadecane co-injection experiment (a) pressure drop history for 10% hexadecane fractional flow; (b) 3-phase saturation profile of core sample E from NMR imaging after co-inject foam with 10% hexadecane fractional flow (c) pressure drop history for 15% hexadecane fractional flow; (d) 3-phase saturation profile of core sample F from NMR imaging after co-inject foam with 15% hexadecane fractional flow.................................................................................................................. 122

Figure 6-10 Shear rate scan for hexadecane-AOS emulsion. The co-injected emulsion exhibits Newtonian rheology below 10 ft/day interstitial velocity. The emulsion viscosity increased sharply and finally exceeded the pressure transducer limit when the total interstitial velocity reached 20 ft/day............................................. 123

Figure 6-11 Foam-hexadecane co-injection experiment (a) pressure drop history for 5% octane fractional flow; (b) 3-phase saturation profile of core sample C from NMR imaging after co-inject foam with 10% octane fractional flow (c) pressure drop history for 15% octane fractional flow; (d) 3-phase saturation profile of core sample D from NMR imaging after co-inject foam with 15% octane fractional flow........ 125

Figure 6-12 Apparent viscosity as a function of oil fractional flow and oil saturation: the apparent viscosity trend is governed by foam destabilization and oil emulsification. At low oil fractional flow, the apparent viscosity decreased with increasing oil saturation; whereas at high oil fractional flow, the apparent viscosity increased with oil saturation. The octane is more detrimental to foam stability whereas the hexadecane emulsion is more viscous than that of octane .......................................... 126

Figure 7-1. Schematic of foam flood experimental setup ........................................... 136

Figure 7-2 System A: N₂ and surfactant solutions were co-injected into a 6.7-inch Bentheimer sandstone (0.65 Darcy) core at ambient temperature. A quality-scan experiment at a fixed flow rate of 4.2 ft/day is on the left, and a flow-rate-scan experiment with a fixed foam quality of 0.78 is on the right................................................. 138

Figure 7-3 Quality-scan experiment for System A: the transition quality must fall within the interval of \((fg, imax - 1exp, fg, imax + 1exp)\) .................................................. 140
Figure 7-4 Flowchart outlining numerical scheme used for the estimation of $f_{m\text{mob}}, e_{p\text{dry}},$ and $f_{md\text{ry}}$ ................................................................. 141

Figure 7-5 The objective function $f_{mm\text{mob}}$ vs. $f_{mm\text{mob}}$ ........................................... 142

Figure 7-6 The linear regression between $tan(1 FM - 1 f_{mm\text{mob}} - 0.5\pi)$ and $Sw$ . 142

Figure 7-7 Quality-scan experimental data fit to the STARS™ model ................. 143

Figure 7-8 Flow-rate-scan experimental data fit to STARS™ model ................. 144

Figure 7-9 Data fit to STARS™ model for different gas type experiments ........ 146

Figure 7-10 Transition foam strength for different gas types as a function of limiting capillary pressure estimated from $f_{md\text{ry}}$ ................................................................. 147

Figure 7-11 Experimental data and STARS™ model fit for 0.5 wt% AOS1416, LB and LS foams ................................................................. 148

Figure 7-12 Surface tension measurement for different surfactant types (AOS1416, LB and LS).................................................................................................. 149

Figure 7-13 Gibbs surface excess adsorption on air-water interface for different surfactant types .................................................................................. 151

Figure 8-1 Schematic of the linear iso-perm relative permeability to oil in 3-phase region .......................................................................................... 158

Figure 8-2 Case I: Continuous CO$_2$ (with dissolved surfactant) injection to displace water with small partition coefficient $K_{sgw} = 0.01$ (A) Saturation profile indicating that the gas overrides the reservoir and prematurely breaks through; (B) Surfactant concentration profile indicating that the surfactant is highly concentrated near the well and the transport is retarded ................................................................. 162

Figure 8-3 Case II: Continuous CO$_2$ (with dissolved surfactant) injection to displace water with unity partition coefficient $K_{sgw} = 1.00$ (A) Saturation profile indicating that the sweep of CO$_2$ is greatly improved; (B) Surfactant concentration profile indicating that the surfactant transport is synchronized with the CO$_2$ propagation .................................................................................................. 163

Figure 8-4 Case III: Continuous CO$_2$ (with dissolved surfactant) injection to displace water with unity partition coefficient of $K_{sgw} = 50.0$ (A) Saturation profile indicating that the foam strength is insufficient to keep CO$_2$ from overriding the
reservoir; (B) Surfactant concentration profile indicating that the surfactant concentration in the aqueous phase is highly diluted ................................................. 164

Figure 8-5 Water recovery efficiency comparison between cases of varied surfactant partition coefficients. Unity partition coefficient is superior to either too small or too large partition coefficient in terms of water recovery efficiency .................... 165

Figure 8-6 Case A: Water-Alternating-Gas. The 3-phase saturation profile indicating that WAG mode has very limited improvement in oil recovery compared to waterflooding................................................................. 166

Figure 8-7 Case B: Surfactant-Alternating-Gas. (A) 3-phase saturation profile indicating that the gas mobility is reduced by foam in presence of surfactant and the sweep efficiency is greatly improved from WAG injection. (B) Surfactant concentration profile indicating that significant surfactant drains by gravity before the CO2 slug catches up. ........................................................................................................ 167

Figure 8-8 Case C: Water-Alternating-Gas-plus-Surfactant-in-Gas. (A) 3-phase saturation profile indicating that a larger oil bank is formed and the oil recovery is further improved from SAG mode. (B) Surfactant concentration profile indicating that the surfactant transport is synchronized with the gas phase propagation ...... 168

Figure 8-9 (a) Oil recovery efficiency comparison between WAG, SAG, and WAG+S with varied partition coefficient. (b) Sensitivity of surfactant partition coefficient on WAG+S oil recovery efficiency........................................................................................................ 169

Figure 9-1 Foam flow in water-wet and oil-wet conditions........................................ 177

Figure 9-2 Schematics of wet foam and dry foam morphology ............................... 178
List of Tables

Table 1-1 Mature IOR field application worldwide. Adapted from Nwidee et al.\(^2\) .... 3
Table 1-2 Examples of the four different surfactant categories ........................................... 9
Table 2-1 Gas Properties for N\(_2\), CH\(_4\), and CO\(_2\) ............................................................ 23
Table 2-2 van der Waals Coefficients \(a\) and \(b\), van der Waals Diameter \(\sigma_{vw}\), and Pair Potential Coefficient \(c\) for Different Types of Gases ........................................... 31
Table 2-3 Hamaker Constant for Parallel Surfaces Interacting between Pure Water .......................................................... 32
Table 3-1 Parameters in STARS foam model ................................................................. 45
Table 3-2 Parameters in Corey relative permeability model ........................................... 45
Table 3-3 Parameters for 1-D CO\(_2\) foam simulator ......................................................... 50
Table 3-4 Characteristic values for surfactant partition coefficient \(K_{sgw}\) ....... 51
Table 3-5 Effect of different partition coefficient on foam transport ......................... 59
Table 4-1 Core sample analysis under hydrostatic confinement ........................................ 62
Table 4-2 Corey relative permeability parameters for the reservoir core samples .. 62
Table 4-3 Estimated foam model parameters based on the core-flooding experiments .......................................................... 70
Table 5-1 Properties of oil samples used in experiments ............................................... 81
Table 5-2 Dimensions of the heterogeneous micromodel device ............................... 83
Table 5-3 Entering and Spreading coefficients for paraffin and crude oil ............ 88
Table 5-4 Water receding contact angle measurement with water and surfactant solution .......................................................... 93
Table 6-1 The list of salts with their concentrations in the synthetic sea water...... 110
Table 6-2 Properties of the core samples and their corresponding experiments .... 113
Table 7-1 Foam flooding systems examined in this study .................................. 136
Table 7-2 Relative permeability data of Bentheimer sandstone$^{87,154}$ .................. 137
Table 7-3 Quality-scan experimental data fit to the STARS$^{\text{TM}}$ model .............. 143
Table 7-4 Flow rate-scan experimental data fit to the STARS$^{\text{TM}}$ model .......... 144
Table 7-5 STARS$^{\text{TM}}$ model parameters fitted for experiments with different types of gas ......................................................................................................................... 145
Table 7-6 STARS$^{\text{TM}}$ model fitted for experiments with two different zwitterionic surfactants ........................................................................................................................................... 148
Table 7-7 Limiting capillary pressure for foams with different surfactants types . 149
Table 8-1 STARS$^{\text{TM}}$ foam model parameters .................................................. 157
Table 8-2 Three-phase relative permeability parameters to water, oil, and gas (no foam) .................................................................................................................................................. 159
Table 8-3 Characteristic values for surfactant partition coefficient $K_{sgw}$ for the case studies in both Section 8.3.1 and Section 8.3.2 ................................................................. 160
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{sg}$</td>
<td>Surfactant concentration in the gaseous phase</td>
</tr>
<tr>
<td>$C_{sw}$</td>
<td>Surfactant concentration in the aqueous phase</td>
</tr>
<tr>
<td>$e_{	ext{dry}}$</td>
<td>Foam model parameter that regulates how abruptly foam dries out at limiting water saturation</td>
</tr>
<tr>
<td>$e_{	ext{surf}}$</td>
<td>Foam model parameter, the exponent in $F_{	ext{surfactant}}$ function</td>
</tr>
<tr>
<td>$e_{	ext{oil}}$</td>
<td>Foam model parameter, the exponent in $F_{	ext{oil}}$ function</td>
</tr>
<tr>
<td>$F_{	ext{oil}}$</td>
<td>Oil dependent function in foam model</td>
</tr>
<tr>
<td>$F_{	ext{surfactant}}$</td>
<td>Surfactant dependent function in foam model</td>
</tr>
<tr>
<td>$F_{	ext{water}}$</td>
<td>Water saturation dependent function in foam model</td>
</tr>
<tr>
<td>$f_{	ext{oil}}$</td>
<td>Foam model parameter that sets the maximum oil saturation below which the oil has no impact on foam</td>
</tr>
<tr>
<td>$f_{	ext{moil}}$</td>
<td>Foam model parameter that sets the minimum oil saturation above which the oil kills the foam completely</td>
</tr>
<tr>
<td>$F_{	ext{M}}$</td>
<td>Correction factor for gas phase mobility reduction by foam</td>
</tr>
<tr>
<td>$f_{	ext{mmob}}$</td>
<td>Foam model parameter that sets the maximum gas mobility reduction</td>
</tr>
<tr>
<td>$f_{	ext{msurf}}$</td>
<td>Foam model parameter that sets the minimal surfactant concentration above which foam strength is no longer dependent on surfactant concentration</td>
</tr>
<tr>
<td>$k_{rg}^f$</td>
<td>Relative permeability to gas (foam)</td>
</tr>
<tr>
<td>$k_{rg}^{nf}$</td>
<td>Relative permeability to gas (no foam)</td>
</tr>
<tr>
<td>$k_{rg}^o$</td>
<td>End-point relative permeability to gas</td>
</tr>
<tr>
<td>$k_{ro}$</td>
<td>Relative permeability to oil</td>
</tr>
<tr>
<td>$k_{ro}^g$</td>
<td>End-point relative permeability to oil with respect to gas</td>
</tr>
<tr>
<td>$k_{row}$</td>
<td>End-point relative permeability to oil with respect to water</td>
</tr>
<tr>
<td>$k_{rw}$</td>
<td>Relative permeability to water</td>
</tr>
<tr>
<td>$k_{rw}^o$</td>
<td>End-point relative permeability to water</td>
</tr>
<tr>
<td>$K_{sgw}$</td>
<td>Surfactant partition coefficient between gaseous phase and aqueous phase</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>$n_g$</td>
<td>Corey exponent for gas</td>
</tr>
<tr>
<td>$n_{og}$</td>
<td>Corey exponent for oil with respect to gas</td>
</tr>
<tr>
<td>$n_{ow}$</td>
<td>Corey exponent for oil with respect to water</td>
</tr>
<tr>
<td>$n_w$</td>
<td>Corey exponent for water</td>
</tr>
<tr>
<td>$PV$</td>
<td>Pore volumes injected</td>
</tr>
<tr>
<td>$S_g$</td>
<td>Gas Saturation</td>
</tr>
<tr>
<td>$S_{gr}$</td>
<td>Residual gas saturation</td>
</tr>
<tr>
<td>$S_o$</td>
<td>Oil Saturation</td>
</tr>
<tr>
<td>$S_{org}$</td>
<td>Residual oil saturation to gas</td>
</tr>
<tr>
<td>$S_{orw}$</td>
<td>Residual oil saturation to water</td>
</tr>
<tr>
<td>$S_w$</td>
<td>Water Saturation</td>
</tr>
<tr>
<td>$S_{wc}$</td>
<td>Connate Water Saturation</td>
</tr>
<tr>
<td>$\lambda_{r , g}$</td>
<td>Mobility of the gas phase in presence of foam</td>
</tr>
<tr>
<td>$\lambda_{r , g}^n$</td>
<td>Mobility of the gas phase in absence of foam</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1. Scope of Study: Improved Oil Recovery (IOR)

A typical oil reservoir undergoes three producing phases: primary recovery, secondary recovery and tertiary recovery. During the primary recovery phase, the pressure difference within the reservoir is sufficient to drive the hydrocarbons to the production well. Approximately 10% to 15% of the original oil in place (OOIP) is recovered at this stage. Secondary recovery begins when the oil production rate falls significantly due to the reservoir pressure depletion. At this stage, water is injected into the reservoir to maintain the pressure and keep driving the oil to the production well. Another 25% OOIP can be produced. After primary and secondary recovery, about 60% to 65% OOIP remains trapped in the reservoir, which makes it a huge target for the tertiary oil recovery, otherwise known as improved oil recovery (IOR).\(^1\)

A variety of IOR processes have been developed to enhance the oil production worldwide as shown in Figure 1-1. The processes in red are the proven mature IOR technologies that have
been repeatedly applied in the field. The processes in green are technologies that have been tested at different scales. Many successful pilots have shown the technical feasibility and several small commercial projects have been completed. The processes in blue are the most recent developed IOR technologies that have not seen large scale production. Yet, some pilot tests have shown promising results. According to the U.S. Department of Energy (DOE), miscible gas flooding (mainly CO₂ injection) accounts for nearly 60% of IOR oil production nationwide; and around 40% comes from the thermal methods (mainly steam injection). Chemical injection only accounts for less than 1% of the U.S. IOR oil production. Table 1-1 summarizes different mature IOR field technologies and Figure 1-2 enumerates the worldwide number of IOR projects growth till 2014.

![Diagram](image)

**Figure 1-1** The maturity and development of various IOR technologies (Adapted from Lake L.)
Table 1-1 Mature IOR field application worldwide. Adapted from Nwidee et al.²

<table>
<thead>
<tr>
<th>Category</th>
<th>IOR Method</th>
<th>Field Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>CO₂</td>
<td>U.S., Canada</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>U.S. Mexico</td>
</tr>
<tr>
<td></td>
<td>Hydrocarbon</td>
<td>U.S. Venezuela, Libya, Canada</td>
</tr>
<tr>
<td>Thermal</td>
<td>In Situ Combustion</td>
<td>India, Romania, Canada, U.S.</td>
</tr>
<tr>
<td></td>
<td>Steam</td>
<td>Brazil, Venezuela, U.S., Indonesia,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trinidad, Oman, China, Tobago, Canada</td>
</tr>
<tr>
<td>Chemical</td>
<td>Alkaline</td>
<td>Hungary, India, U.S., Russia</td>
</tr>
<tr>
<td></td>
<td>Alkaline-Surfactant-Polymer</td>
<td>China, U.S., India, Venezuela</td>
</tr>
</tbody>
</table>

Figure 1-2 Number of IOR projects till 2014 worldwide²

The selection of IOR technologies depends on various factors including the reservoir geology, temperature, pressure, and crude oil properties, among others. Figure 1-3 shows the
favorable characteristics for different IOR technologies based on crude oil viscosity and the reservoir permeability.

![Figure 1-3 The favorable reservoir conditions for different IOR technologies (Adapted from Lake L.)](image)

Though a variety of fluids can be injected into the reservoir for incremental oil production, these chemicals/fluids operate by two principles\(^2^ - ^4\): (i) lowering the mobility ratio \(M\) and/or (ii) increasing the capillary number \(N_{Ca}\).

Mobility ratio \(M\) between the displacing phase (injecting fluid) and the displaced phase (crude oil) is defined in Equation 1-1, where \(\lambda_{Displacing}\) and \(\lambda_{Displaced}\) are the mobility of the displacing and displaced phase; \(k_{r,Displacing}\) and \(k_{r,Displaced}\) are the relative permeability of the two phases; \(\mu_{Displacing}\) and \(\mu_{Displaced}\) are the viscosity of the two phases.

\[
M = \frac{\lambda_{Displacing}}{\lambda_{Displaced}} = \frac{k_{r,Displacing}}{k_{r,Displaced}} \cdot \frac{\mu_{Displaced}}{\mu_{Displacing}}
\]

**Equation 1-1**
If the mobility ratio $M$ is greater than 1 (unfavorable mobility ratio), which is usually the case for gas, steam, or even water injection, the displacing fluid is more likely to finger through preferential pathways of least flow resistance due to the viscous instability and the reservoir heterogeneity. By lowering the value of $M$ to less than 1 (favorable mobility), better volumetric sweep efficiency can be expected as shown in Figure 1-4. Polymer injection, foam flooding and thermal IOR (steam) can be categorized to this principle. The primary goal of polymer injection and foam flooding is to decrease the mobility of the displacing fluid whereas the thermal IOR (steam) method aims to increase the mobility of the crude oil.

![Figure 1-4 Displacement fronts for different mobility ratios and injected pore volumes](image)

The second principle of IOR is to increase the capillary number $N_{Ca}$. Yet there are different forms of the capillary number definition in literature, they all quantify the relative effect of the viscous force and the capillary force. As shown in Equation 1-2 and Equation 1-3, $k$ is the rock permeability, $\nabla p$ is the local pressure gradient, $\mu$ is the viscosity, $u$ is the superficial velocity, and
σ is the interfacial tension (IFT). Though lowering the mobility ratio improves the sweep efficiency of the injected fluids; the residual oil saturation is governed by the capillary number. Figure 1-5 illustrates how the residual saturation of the non-wetting phase decreases with increasing capillary number for different porous media.

\[ N_{Ca} = \frac{-k\nabla p}{\sigma} \]  

**Equation 1-2**

\[ N_{Ca} = \frac{\mu \times u}{\sigma} \]  

**Equation 1-3**

![Figure 1-5 Schematic of capillary desaturation curve for carbonate formation, sandstone formation and sandpack system](image)

A characteristic \( N_{Ca} \) value for waterflooding is in the order of \( 10^{-6} \). As shown in Figure 1-5, the residual oil saturation does not decrease significantly until the \( N_{Ca} \) increases by at least 2-3 orders of magnitude. Yet, it is not realistic to increase the pressure gradient by orders of magnitude.
A better alternative is to reduce the IFT using surfactant. A surfactant is defined as “a substance that is energetically favorable to adsorb onto the surface or interfaces between phases”\(^8\). A good tailored surfactant formulation\(^9\) can dramatically reduce the IFT by 3–4 orders of magnitude, which in turn increasing the \(N_{Ca}\) and therefore considerably enhancing the oil displacement efficiency. A more detailed discussion on the surfactant formulation will be provided in the next section. At other times, alkaline (NaOH, Na\(_2\)CO\(_3\), Na\(_4\)O\(_4\)Si) is injected to react with the acid content in the crude oil to form soaps, a natural surfactant, in order to reduce the IFT. Alkaline flooding is more effective with high acid number (AN) crude oil.

In addition, gas injection (CO\(_2\), N\(_2\), and hydrocarbon etc.) also has superior displacement efficiency especially when the reservoir is above the minimal miscibility pressure (MMP). The miscibility is generated and developed in situ the reservoir through a composition change between the phases and results in high ultimate oil displacement efficiency. CO\(_2\) injection is the most popular gas injection projects among other gases due to its low MMP. Figure 1-6 shows the U.S. regional CO\(_2\)-IOR oil production projection estimated by the DOE and the National Energy Technology Laboratory (NETL). With the increasing awareness of the global climate change, CO\(_2\) IOR is also an ideal candidate for the utilization and sequestration of CO\(_2\) captured from natural gas processing plants and other industrial sources. Other gas candidates include the N\(_2\) gas, produced hydrocarbons, and the flue gas from the power plants.
1.2. Object of Study: Foam Flow in Porous Media

Admittedly, gas injection has superior crude oil displacement efficiency especially when the pressure is above the MMP. However, the overall oil recovery is often not much better than that of water flooding because of viscous fingering, gravity override, and reservoir heterogeneity. Using surfactant to generate foam in situ within the porous media offers promise to simultaneously address all aforementioned three issues. Yet, the successful design of foam projects requires insightful understanding of the phase/component transport and the rheology of foam flow in porous media. Therefore, the objective of my thesis is to provide an in-depth multiscale understanding of the foam flow for subsurface applications including gas mobility control, aquifer remediation, CO$_2$ sequestration, water production control, and energized-fluid fracturing etc.

Foam in porous media is defined as a dispersion of gas in liquid such that the liquid phase is continuous and at least some part of the gas is made discontinuous by thin liquid films called
lamellae\textsuperscript{11}. It is a thermodynamically metastable system which requires surfactants to preferentially adsorb onto the gas-liquid interface to lower the surface energy and therefore stabilize the lamellae. Surfactants usually are molecules that have an amphipathic structure consisting of a hydrophilic head and a hydrophobic tail (alkyl, alkene and alkyl benzene, etc.). There are 4 categories of surfactant based on the charge in the hydrophilic head: anionic, cationic, nonionic, and zwitterionic surfactant as shown in Table 1-2. The common head groups of anionic surfactants are sulfate, sulfonate and carboxylate; the common head groups of cationic surfactants are amine, quaternary ammonium, pyridinium and quaternary pyridinium; the common head groups of nonionic surfactants are ethoxylate (EO) group; and the common head groups for zwitterionic surfactants are betaine and sulfobetaine groups.

<table>
<thead>
<tr>
<th>Category</th>
<th>Chemistry of Surfactant</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>Carboxylic acids and salts</td>
<td><img src="image" alt="Carboxylic acids and salts" /></td>
</tr>
<tr>
<td></td>
<td>Sulfonic acids and salts</td>
<td><img src="image" alt="Sulfonic acids and salts" /></td>
</tr>
<tr>
<td></td>
<td>Sulfuric acids and salts</td>
<td><img src="image" alt="Sulfuric acids and salts" /></td>
</tr>
<tr>
<td></td>
<td>Alkyl xanthic acids</td>
<td><img src="image" alt="Alkyl xanthic acids" /></td>
</tr>
<tr>
<td></td>
<td>Alkyl or aryl dithiophosphoric acids</td>
<td><img src="image" alt="Alkyl or aryl dithiophosphoric acids" /></td>
</tr>
<tr>
<td></td>
<td>Polymeric anionics (repeated carboxyl acid functionality)</td>
<td><img src="image" alt="Polymeric anionics (repeated carboxyl acid functionality)" /></td>
</tr>
<tr>
<td></td>
<td>Long chain amines</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>Diamines and polyamines</td>
<td><img src="image1" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Tertiary amine</td>
<td><img src="image2" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Polyoxalkylenated long chain amines</td>
<td><img src="image3" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Amine oxides</td>
<td><img src="image4" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Nonionic</td>
<td>Polyoxymethylenated alcohols, alkyl phenols, alcohol ethoxylates</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image5" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alkanolamine condensates with carboxylic acids</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image6" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyoxalkylenated mercaptans</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image7" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Zwitterionic</td>
<td>Acrylic acid derivatives with amine functionality</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image8" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Substituted alkylamides</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image9" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-Alkyl betaines</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image10" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-Alkyl sulfobetaine</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image11" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thio alkyl amines and amides</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image12" alt="Structure" /></td>
<td></td>
</tr>
</tbody>
</table>
Surfactant adsorption, also known as surfactant depletion, is a major economic concern in the use of surfactant for subsurface applications. The governing force for the adsorption of charged surfactants is electrostatic interactions: anionic surfactants usually have low adsorption to negative charged silica formations and negative sites of clays whereas they have high adsorption on the positive sites of clays and on carbonate formations\(^\text{12}\); alternatively, cationic surfactants have low adsorption on calcite formations whereas have high adsorption on silica formation and negative sites of clays. The governing force for the adsorption of nonionic surfactants is typically the hydrogen bonding. Nonionic surfactants usually have low adsorption on carbonate formation whereas have high adsorption on silica-like layers of clays where the oxygen atom on EO groups can hydrogen bond with hydroxyl groups.

Commonly used foaming surfactants are either anionic or cationic in class. These charged surfactants are insoluble in the gaseous phase and can only be injected with water. However, some novel designed nonionic or switchable surfactants are CO\(_2\) soluble, thus making it possible to be injected with the CO\(_2\) phase (either in high density gaseous state or in supercritical state). For these CO\(_2\) soluble surfactants, it is important to understand the impact of surfactant partitioning between the two phases on foam transport in porous media.

Due to the constraint of well injectivity, direct injection of pre-generated foam is impracticable at the pilot/field scale. Instead, surfactant solution and gas slugs are injected alternatively (SAG, surfactant-alternating-gas). Therefore, the success of foam projects completely depends on the in-situ foam generation within the porous media. For clarity, foam generation, in this thesis, refers to either the formation of bubbles or the creation of lamellae. Kovscek and Radke summarized three classic pore-level foam generation mechanisms: snap-off, lamella division, and leave behind\(^\text{11,13,14}\).
The first mechanism, snap-off, is similar to the formation of the residual oil in the reservoir. As shown in Figure 1-7, when the gas thread approaches a pore throat, the curvature at the gas front is reduced. The pressure originating from the curvature gradient draws the liquid back to the pore throat and forms a ring around. As the liquid ring grows, the bubble snaps off. The occurrence of snap-off requires (1) sufficient liquid in the pores; (2) the capillary pressure $P_{cgw}$ to be less than one half of the capillary entry pressure $P_{g,entry}$; and (3) the pore body-throat ratio to be greater than 2. A general accepted consensus is that snap-off is more readily to occur in the presence of a sharp permeability increase in the direction of flow.

![Figure 1-7 Foam generation by snap-off mechanism](image)

The second mechanism, called lamella-division (shown in Figure 1-8), occurs when a single lamella divides into two new lamellae because the local pressure gradient pushes a single lamella through a branching point. Lamella-division is a secondary foam generation mechanism and requires the pre-existence of foam bubbles. The occurrence of the lamella-division requires (1) a relatively large bubble size; and (2) the local pressure gradient to exceed a threshold value called the minimum pressure gradient $\nabla p_{foam}^{min}$. Both snap-off and lamella-division mechanisms create lamellae perpendicular to the direction of flow that offers high resistance to fluid flow, resulting in strong foams.
The third foam generation mechanism is called leave-behind. As shown in Figure 1-9, when gas invades two adjacent pores, a liquid lens connecting the two grains is left behind. The lamella orientation is parallel to the direction of flow, therefore resulting in continuous-gas foam, known as weak foam\textsuperscript{11,13}.

Besides the three classic generation mechanisms described above, the fourth in situ foam generation mechanism, discovered by Liotas et al., is called neighbor-induced pinch-off\textsuperscript{16}. It was first identified and introduced in a smooth capillary microfluidic device with a constriction point as shown in Figure 1-10. This mechanism refers a bubble-bubble interaction that occurs when two or more bubbles squeeze through a constriction in the direction of flow.
Figure 1-10 Foam generation by pinch-off mechanism: the blue bubble is pinched off against the constriction structure by its neighbors

As being said, foam is thermodynamically metastable. The high surface free energy provokes processes that lead to foam coalescence. These processes include capillary drainage, diffusion coarsening, and mechanical fluctuation (lamella stretching and squeezing), etc.\textsuperscript{13} Figure 1-11 shows a schematic of the 3-D foam structure. Due to the curved interface, capillary pressure $P_c$ arises to drain the liquid flow to Plateau borders and junction nodes and therefore thins the lamellae.
In porous media, the capillary pressure $P_c$ is a function of the liquid saturation as shown in Figure 1-12. As the gas fractional flow $f_g$ increases, the liquid saturation decreases and the $P_c$ increases. The capillary pressure which attempts to rupture the lamellae by liquid drainage as described above is counterbalanced by the disjoining pressure $\Pi$ (shown in Equation 1-4) until it reaches a critical value called the limiting capillary pressure $P^*_c$. Above the $P^*_c$, foam is no longer stable and starts to coalesce, known as “dry-out” effect.

$$P_c = p_g - p_w = \Pi(h)$$

Equation 1-4
Diffusion coarsening is another major foam coalescence mechanism. According to the Young-Laplace Equation, the pressure difference across curved interfaces is proportional to the mean interfacial curvature $H$ and the interfacial tension $\sigma$. Therefore, the gas will diffuse from small bubbles to neighboring large bubbles. As shown in Equation 1-5, the rate of gas molecules diffusing across the liquid lamella $\frac{dN}{dt}$ is proportional to the gas concentration difference $\Delta C$ and the area of the lamella $A$. The constant of proportionality $k_{filtm}$, also known as the gas permeability is a transport property that varies with the gas type.

$$\frac{dN}{dt} = -k_{filtm}A\Delta C$$ \hspace{1cm} \textbf{Equation 1-5}$$

As foam flows through porous media, lamellae stretch and squeeze periodically when passing through pore bodies and pore throats. Therefore, mechanical fluctuation plays a crucial role in the lamella destruction. The foam resistance to these mechanical dilations and compressions

![Figure 1-12 Schematic of capillary pressure in porous media and the limiting capillary pressure above which lamellae are no longer stable and foam starts to coalesce](image)
is measured by film elasticity $E_f$ which is simply twice the value of the Gibbs surface elasticity $E_G$.

As shown in Equation 1-6, $\sigma$ is the surface tension and $A$ is the surface area.

$$E_f = 2E_G = 2 \frac{d\sigma}{d\ln A}$$

Equation 1-6

1.3. Technical Background Part I: Fluid Mechanics in Porous Media

According to Henry Darcy’s experiment in 1856 (shown in Figure 1-13), the volumetric flow rate of a single phase is proportional to the cross-sectional area and the hydraulic head across the porous media and is inversely proportional to the length of the vertical sand filters$^{19}$. Darcy’s 1-D experimental results can be generalized in three dimensions as shown in Equation 1-7 in which $\mathbf{u}$ is the volumetric flux vector; $k$ is the absolute rock permeability which is a second order symmetric tensor; $\mu$ is the viscosity of the fluid; $D$ is the elevation; and $\Phi$ is the flow potential defined in Equation 1-8. The 3-D Darcy’s law can be further generalized to describe multiphase flows by introducing the concept of relative permeability $k_r$ to each phase. For example, the Darcy’s Law for a phase $j$ is shown in Equation 1-9

![Figure 1-13 Henry Darcy’s experiment setup in 1856]$^{19}$
\[ u = -\frac{k}{\mu} \cdot \nabla \phi \] \text{Equation 1-7}

\[ \phi = p - g \int_{D_0}^{D} \rho dD' \approx p - \rho g(D - D_0) \] \text{Equation 1-8}

\[ u_j = -\frac{k k_{rj}}{\mu_j} \cdot \nabla \phi_j = -\frac{k k_{rj}}{\mu_j} \cdot (\nabla p_j - \rho_j g \nabla D) \] \text{Equation 1-9}

There are different models to correlate relative permeability \( k_r \) to the phase saturation. A commonly used relative permeability model for water gas two-phase flow is called Corey Model as shown in Equation 1-10 and Equation 1-11.

\[ k_{rw} = k_{rw}^o \left( \frac{S_w - S_{wc}}{1 - S_{gr} - S_{wc}} \right)^{n_w} \] \text{Equation 1-10}

\[ k_{rg} = k_{rg}^o \left( \frac{1 - S_w - S_{wc}}{1 - S_{gr} - S_{wc}} \right)^{n_g} \] \text{Equation 1-11}

The parameters \( k_{rw}^o \) and \( k_{rg}^o \) are called the end point relative permeability to water and gas. The saturation is normalized with the connate water saturation \( S_{wc} \) and the residual gas saturation \( S_{gr} \). The parameters \( n_w \) and \( n_g \) are called the Corey exponent. The Corey exponent for the wetting phase is around 4 whereas for the non-wetting phase is around 2.

For 3-phase (oil, water, and gas) flows in porous media, a three-phase relative permeability model is needed to calculate the relative permeability to the third phase. Assuming strict water-wet condition for simplicity, the \( k_{rw} \) is then only a function of the water saturation \( S_w \) and the \( k_{rg} \).
is only a function of the gas saturation $S_g$. There are various ways to estimate the relative permeability to the intermediate wet phase ($k_{ro}$), among which the linear-isoperm model, the Stone’s I, and the Stone’s II models$^{20-23}$ are most commonly used.

1.4. Technical Background Part II: Foam Modeling Techniques

Foam can reduce the gas mobility in two ways: one is to decrease the $k_{rg}$ by reducing the flowing fraction of the gas pathways; and the other is to increase the effect gas viscosity due to the capillary resistance of the lamellae that trap/disperse the continuous gas flow into separate bubbles. In the presence of foam, gas mobility can be reduced by orders of magnitude. However, it has been observed that the relative mobility to water for a given water saturation remains the same$^{24}$. The reason behind is that the lamellae formed in the porous media only make a fairly small portion of the total liquid content. Most of the liquid (as the wetting phase) still flows through the small pores or next to the solid as if there is no foam$^{11}$. Therefore, most commonly used foam models only address the reduction in the gas mobility.

There are two fundamental approaches to simulate the foam transport in porous media$^{25-27}$: the texture-explicit population-balance model and the texture-implicit local-equilibrium model.

It is observed that the reduction in gas mobility is highly dependent on the foam texture, which is defined as the bubble/lamella density. Texture-explicit population-balance models correlate the effective viscosity of the gas phase $\mu_{g,eff}$ directly with foam texture. Different correlations between the gas effective viscosity and the foam texture can be found in the literature$^{26}$. Because foam texture is an independent variable in the texture-explicit population-balance model, an additional conservation equation is introduced to describe the transport of the lamellae as shown
in Equation 1-12. The variable $n_f$ is the foam texture in the flowing gas; $n_t$ is the foam texture in the trapped gas; $S_{gf}$ is the flowing gas saturation; and $S_{gt}$ is the trapped gas saturation. The bubble generation term $R_{generation}$ and the bubble coalescence term $R_{coalescence}$ vary among different versions of the population balance model. The pioneering work of applying a population balance model to foam flow in porous media dates back to 1980s. Falls, Hirasaki et al.\textsuperscript{11} proposed a mechanistic foam simulator assuming that the snap-off mechanism dominates the bubble generation $R_{generation}$. Other models\textsuperscript{28-31} assume lamella-division is the major bubble generation mechanism and $R_{generation}$ is directly described as a function of either the local pressure gradient $\nabla p$ or the velocity $u$. For the foam coalescence term $R_{coalescence}$, it is mostly expressed as a function of local capillary pressure.

$$\frac{\partial (\phi (n_f S_{gf} + n_t S_{gt}))}{\partial t} + \nabla \cdot (n_f u_g) = \phi S_g (R_{generation} - R_{coalescence}) \quad \text{Equation 1-12}$$

The texture-implicit population-balance models have very clear physics. Yet, the additional partial differential equation (PDE) makes the reservoir simulation computationally costly. Another restriction for the application of population-balance model to the field is the difficulty to estimate and determine a number of kinetic parameters in $R_{generation}$ and $R_{coalescence}$ terms.

However, the characteristic time for the bubble dynamics is considerably shorter than the time scale for foam propagation. Therefore, it is justifiable to hypothesize that the bubble generation and coalescence are in local equilibrium. The second approach, texture-implicit local-equilibrium model, directly correlates the foam strength (reduction in gas mobility) to different local conditions of interest such as the surfactant concentration, water saturation, oil saturation,
shear rate and etc. A good example of local-equilibrium model is the STARS\textsuperscript{TM} Foam Model and will be elaborately discussed in the following chapters.

1.5. Thesis Outline

The thesis is organized as follows:

Chapter 2 presents the first part of the dependence of foam transport on its constituent components: the role of gas type and composition\textsuperscript{32}.

Chapter 3 presents the second part of the dependence of foam transport on its constituent components: the effect of surfactant partitioning\textsuperscript{33}.

Chapter 4 discusses the dependence of foam transport on rock permeability\textsuperscript{34}.

Chapter 5 visualizes the foam-oil interaction at the pore-level with a 3-layered heterogeneous micromodel\textsuperscript{35}.

Chapter 6 probes the foam-oil interaction in Berea sandstones using nuclear magnetic resonance (NMR) imaging techniques

Chapter 7 introduces an improved parameter estimation algorithm for a texture-implicit local-equilibrium foam model based on various laboratory results\textsuperscript{7}.

Chapter 8 conceptualizes the idea of using CO\textsubscript{2} soluble surfactant for the next generation foam flooding technology during which the surfactant is injected with the gas phase.

Chapter 9 concludes the thesis and provides recommendations for future work.
Chapter 2

Dependence of Foam Transport on Its Constituent Component Part I: Role of Gas Type and Composition

2.1. Background

Depending on the local availability and gas type, CO$_2$, CH$_4$, steam, and inert gases like N$_2$ can be injected into subsurface formations$^{36-40}$. Gas mixtures, such as flue gas and light hydrocarbons, can also be injected to avoid the cost of separating these gases into pure gas feeds. The mechanism of how the gas type affects foam transport in porous media remains poorly understood. In this study, we systematically compared steady-state foam strengths in porous media with respect to gas type and composition.

The gas phase can affect foam strength in several ways. First, different gases have varying solubilities in the aqueous phase, as shown in Table 2-1. The ratio of the gas and aqueous phase in foam can be varied, as defined by foam quality: $f_g = \frac{q_g}{q_g + q_w}$, where $q_g$ is the volumetric gas flow.
rate and $q_w$ is the volumetric liquid flow rate. Injection of a gas with high solubility in the aqueous phase at the same flow rate as injection of a less water-soluble gas results in a lower foam quality. Thus, the foam strength for gases with different solubilities can vary significantly.

| Gas Type | Mole Fraction | Measured Film Permeability $k_{film}$  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>1.2E-5</td>
<td>0.13</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2.8E-5</td>
<td>0.30</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>70.7E-5</td>
<td>7.85</td>
</tr>
</tbody>
</table>

Table 2-1 Gas Properties for N$_2$, CH$_4$, and CO$_2$

Second, different gases may impact the stability of a single lamella$^{45-48}$. Aronson et al.$^{49}$ demonstrated with sodium dodecyl sulfate (SDS) in NaCl solution that a larger repulsive disjoining pressure ($II$) results in greater flow resistance for foam in porous media. Disjoining pressure arises from the typically repulsive interaction between two surfaces, which balances the capillary pressure and prevents the liquid lamella from rupturing$^{49-51}$. Thermodynamically, the disjoining pressure $II$ can be calculated as the derivative of the surface energy per unit area with respect to distance between the pair of interfaces ($h$). If a liquid lamella in foam is considered to be two Gibbs dividing surfaces, as shown in Figure 2-1, the surface energy can be expressed as the sum of two surface tensions ($\sigma^{\alpha\gamma}$ and $\sigma^{\beta\gamma}$), as shown in Equation 2-1$^{52}$. The partial derivative is defined at constant temperature ($T$), chemical potential ($\eta_i$), and gravitational potential ($\phi_{gravity}$). The $O(Hh)$ in Equation 2-1 denotes the term that is proportional to the product of the mean curvature of the film ($H$) and the thickness ($h$), and is equal to zero for a flat
lamella when $H$ is negligible. Different gas types can result in varied disjoining pressures because of the differences in intermolecular interactions.

Figure 2-1 Gibbs dividing surfaces for foam film

\[
\Pi = \left[ \frac{\partial (\sigma^\alpha \gamma + \sigma^\beta \gamma)}{\partial h} \right]_{T, \eta_i, \Phi_{gravity}} + O(Hh) \tag{Equation 2-1}
\]

Lastly, gas type affects the coarsening of the foam due to the differences in gas diffusion across the liquid lamella. As shown in Equation 2-2, the rate of gas molecules diffusing across the liquid lamella ($\frac{dN}{dt}$), is proportional to the gas concentration difference ($\Delta C$) and the area of the lamella ($A$). The gas permeability ($k_{film}$) is a transport property that varies with gas type. Thus, different gases have different rates of mass transport from small to large bubbles. The measured film permeability to different gases is given in Table 2-1.

\[
\frac{dN}{dt} = -k_{film} A \Delta C \tag{Equation 2-2}
\]

It has been suggested that mass transfer is the main mechanism responsible for coarsening in steam foams, where water condenses on one side and evaporates from the other side of the
lamella. Such mass transfer is faster than simple diffusion, where gas molecules need to first dissolve and then diffuse through the liquid film. More recently, Farajzadeh et al. found that bulk foam stability is very well correlated with the rate of gas diffusion through the lamellae. However, the role of gas diffusion within foam inside porous media is not clearly understood. Nonnekes et al. found that bubbles smaller than pore space will quickly coarsen to approximately the pore size, indicating that gas diffusion is not the only mechanism responsible for foam stability.

### 2.2. Materials and Methods

Alpha olefin sulfonate C14-16 (AOS\textsubscript{C14-16}, Stepan) was chosen as the foaming agent. The properties of the solution and single foam films stabilized by this surfactant have been previously described. AOS\textsubscript{C14-16} was diluted to 1 wt% in synthetic seawater, which had a composition of 0.67 g/L KCl, 10.15 g/L MgCl\textsubscript{2}·6H\textsubscript{2}O, 1.47 g/L CaCl\textsubscript{2}·2H\textsubscript{2}O, 3.83 g/L Na\textsubscript{2}SO\textsubscript{4}, and 25.21 g/L NaCl. All aqueous solutions were prepared in deionized water. Gases used in the experiments were N\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2}, flue gas (80 mol% N\textsubscript{2} and 20 mol% CO\textsubscript{2}), and CH\textsubscript{4}-CO\textsubscript{2} mixtures (50 mol% CH\textsubscript{4} and 50 mol% CO\textsubscript{2}). Bentheimer sandstone, which is mainly composed of quartz, was used as the core material. It is a homogeneous porous medium with a measured absolute permeability of 2.3 Darcy with respect to water. The core was coated with a 2-mm layer of Araldite resin to prevent bypassing. Next, the core was mounted to a cylindrical PEEK (polyether ether ketone) core holder. Gas was injected into the inlet of the core through a mass flow controller. The surfactant solution was injected in parallel through a Quizix pump (Vindum QX6000HC-0-0-C-L-0). A back pressure regulator (Eigen merk CTS MB420) was connected to the outlet of the core holder.

The experimental protocol was to first inject CO\textsubscript{2} gas at 5 bar to displace air inside the core. Next, the pressure was raised to 25 bar and at least 10 pore volumes (PVs) of water were injected
to dissolve all the CO$_2$. Then, 5 PVs of surfactant solution were injected to saturate the core and satisfy the adsorption capacity of the rock. Finally, the back pressure was set to 21 bar and surfactant solution was co-injected with gas until a steady-state foam strength was obtained. The total pressure drop across the core was recorded during the experiment. During the foam-flooding experiment, the total superficial velocity was held at 4 ft/day and back pressure at 21 bar. Experiments were conducted at ambient temperature. To eliminate the effect of permeability differences, the same core was utilized when switching the gas type. To remove the previous gas, 5 PVs of isopropanol were injected to destroy the foam, then 20 PVs of water were injected to displace the alcohol, and then CO$_2$ was re-injected to displace the remaining gas. Permeability was re-measured each time with water to ensure the system was fully saturated with liquid.

2.3. Results and Discussions

In our study, the strength of foam in porous media was quantified by apparent viscosity ($\mu_{app}$) as defined in Equation 2-3$^{63}$. Apparent viscosity can be interpreted as flow resistance that is measured as pressure gradient ($\nabla p$) and normalized with permeability ($k_{rock}$) and total superficial velocity ($u_{total}$). Higher $k_{rock}$ leads to stronger foam, due to the lower capillary pressure between gas and liquid phases, and reduces the likelihood of rupturing the foam film. Higher $u_{total}$ leads to less strong foam due to the shear-thinning rheological property of foam flow.

$$\mu_{app} = \frac{k_{rock}}{u_{total}} \nabla p$$

Equation 2-3
Representative experimental results for the pure gas systems are shown in Figure 2-2. The apparent viscosity and pressure gradient are shown as a function of foam quality, which allows comparison of the effects of flow resistance for different gas types on foam with varying gas fractions while keeping total superficial velocity constant. The gas volumetric flow rate is calculated from the back pressure measurement. Because of the compressibility of the gas, the foam quality at the inlet is somewhat lower than the calculated value.

![Figure 2-2](image.png)

Figure 2-2 Foam strength as a function of foam quality for various gases: nitrogen (diamond), methane (circles), and carbon dioxide (triangles)

We observed both low- and high-quality regimes for each gas, which were separated by the transition foam quality at the point of maximum apparent viscosity. In the low-quality regime, the resistance to flow was determined by bubble trapping and mobilization, and foam strength was
observed to increase as foam quality increased. In the high-quality regime, foam strength decreased as the foam quality increased due to constraints of limiting capillary pressure and bubble coalescence. For a fixed foam quality, we found that N₂ foam had the maximum steady-state foam strength, followed by CH₄ foam and CO₂ foam. Three hypotheses are discussed below to probe the underlying mechanism that explains the observed effects of gas type on steady-state foam strength.

### 2.3.1. Hypothesis I: Gas Solubility

Given that different types of gases have different solubilities in the aqueous phase, one hypothesis is that the actual foam quality is lower than the injected quality for a gas with high solubility. Thus, steady-state foam strengths are different. Control experiments were performed with CO₂ because CO₂ has the maximum solubility in water (almost 60 times higher than N₂ and 30 times higher than CH₄). The amount of dissolved gas was compensated by either saturating the surfactant solution with CO₂ or by increasing gas flow rate ($Q_g$) in the control steady-state experiments.

The solid curve in Figure 2-3 shows that as foam quality (or gas fractional flow) decreases, a larger fraction of injected CO₂ is dissolved in the aqueous phase. When the foam quality is reduced to 40% or less, the injected CO₂ would dissolve completely if the surfactant solution was not pre-saturated with CO₂ or the gas flow rate was not increased to compensate. Therefore there would be no gas flowing at all. However, both dashed curves in Figure 2-3 show that the gas solubility has a negligible effect in the high-quality regime. Compensating CO₂ dissolved in the aqueous phase failed to generate CO₂ foam that is as strong as N₂ or CH₄ at steady state.
Figure 2-3 Foam quality scans for CO\textsubscript{2} under various conditions. Increasing the CO\textsubscript{2} flow rate compensates for dissolved CO\textsubscript{2} in the aqueous phase (dashed line) or saturating the aqueous solution with CO\textsubscript{2} (dotted line) results in stronger foam at lower foam qualities compared to CO\textsubscript{2} gas (solid line). An increase in foam apparent viscosity is observed once the CO\textsubscript{2} is saturated in the aqueous phase.

2.3.2. Hypothesis II: Stability of the Lamella

We hypothesized that the steady-state foam strength is influenced by the effect of gas type on the stability of the liquid lamella, which is related to the disjoining pressure. Excluding non-DLVO forces\textsuperscript{65}, disjoining pressure can be decomposed into two parts, electrostatic repulsion ($\Pi_{el}$) and van der Waals attraction ($\Pi_{v\text{w}}$), as shown in Equation 2-4.
\[\Pi = \Pi_{el} + \Pi_{vw}\]  \hspace{1cm} \text{Equation 2-4}

The electrostatic contribution to the disjoining pressure arises from charged surfactant molecules packing the two neighboring gas-liquid interfaces and is mainly a function of surfactant packing density and the salinity of the liquid phase\textsuperscript{59,66}. Tighter packing of the surfactant molecules will result in stronger repulsive interactions between the two interfaces, thus better stabilizing the foam film against rupture. The salinity in the liquid phase determines the Debye length and directly influences the packing density at the interface. There is no direct evidence that different gas molecules can significantly affect either the surfactant packing or the salinity of the liquid phase. Therefore, we investigated only the variation in \(\Pi_{vw}\) due to the difference in intermolecular forces in the gas phases.

We can roughly estimate the van der Waals contribution by assuming that all the gases obey the van der Waals equation of state as shown in Equation Equation 2-5\textsuperscript{36}. Thus, the pair potential between two molecules \([w(r)]\) can be expressed as shown in Equation 2-6\textsuperscript{37}. The pair potential coefficient \((c)\) can be calculated from the attraction coefficient \((a)\) and the van der Waals diameter \((\sigma_{vw})\) as shown in Equation 2-7\textsuperscript{67}.

\[(p + \frac{a}{V_m^2})(V_m - b) = RT\]  \hspace{1cm} \text{Equation 2-5}

\[w(r) = -\frac{c}{r^6}\]  \hspace{1cm} \text{Equation 2-6}
\[ c = \frac{3a\sigma_{vw}^3}{2\pi N_A} \]  \hspace{1cm} \text{Equation 2-7}

Table 2-2 van der Waals Coefficients \(a\) and \(b\), van der Waals Diameter \(\sigma_{vw}\), and Pair Potential Coefficient \(c\) for Different Types of Gases

<table>
<thead>
<tr>
<th>Gas Type</th>
<th>(a^{68,69}) Pa.m(^6).mol(^{-2})</th>
<th>(b^{68,69}) m(^3)/mol</th>
<th>(\sigma_{vw}) (Calculated from (b)) (\text{Å})</th>
<th>(c) (Calculated from Equation 2-7) (J.m^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>0.141</td>
<td>3.91E-5</td>
<td>4.99</td>
<td>2.3E-77</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.228</td>
<td>4.28E-5</td>
<td>5.14</td>
<td>4.1E-77</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.364</td>
<td>4.27E-5</td>
<td>5.14</td>
<td>6.5E-77</td>
</tr>
</tbody>
</table>

We further assume that the pair potential is non-retarded and additive. The “two-body” potential for two semi-infinite materials interacting in a vacuum is described by Equation 2-8\(^{68}\), where \(W_{vw}(h)\) is van der Waals interaction potential between the two parallel semi-infinite materials across a vacuum and \(A_{11}\) is the Hamaker constant. As shown in Equation 2-9\(^{68}\), \(A_{11}\) can be correlated with van der Waals pair potential coefficient \((c)\) and the number density of molecules \((\rho_1)\), which can be determined from the van der Waals equation of state.

\[ W_{vw}(h) = -\frac{A_{11}}{12\pi h^2} \]  \hspace{1cm} \text{Equation 2-8}

\[ A_{11} = \pi^2 c\rho_1^2 \]  \hspace{1cm} \text{Equation 2-9}
To calculate $A_{11}$ for two parallel surfaces with an aqueous phase sandwiched in between, we applied the combining relation$^{68}$ by assuming $A_{13}$ equals the geometric mean of $A_{11}$ and $A_{33}$ as shown in Equation 2-10. Here we neglect the effect of dissolved electrolytes on the $A_{11}$ for water.

$$A_{131} \approx A_{11} + A_{33} - 2A_{13} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})^2$$  \hspace{1cm} \text{Equation 2-10}

<table>
<thead>
<tr>
<th>Material</th>
<th>$A_{11}$ (J) 21 bar 20 °C</th>
<th>$A_{131}$ (J) 21 bar 20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>Water</td>
<td>$N_2$</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>Water</td>
<td>$CH_4$</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>Water</td>
<td>$CO_2$</td>
</tr>
<tr>
<td>Water$^{68}$</td>
<td>370.0E-22</td>
<td></td>
</tr>
</tbody>
</table>

The van der Waals force contribution to the disjoining pressure can be calculated by taking the derivative of the van der Waals potential ($\Pi_{vw}$) with respect to film thickness, as shown in Equation 2-11.

$$\Pi_{vw} = -\frac{dW_{vw}(h)}{dh}$$  \hspace{1cm} \text{Equation 2-11}

For a given film thickness $h$, a larger Hamaker constant $A_{131}$ indicates stronger van der Waals forces, which can more easily destabilize foam lamellae. As a result, the small difference in the Hamaker constant cannot be the controlling factor in the foam strength. In addition, the calculated Hamaker constants indicate that $CO_2$ should have the most stable foam, whereas $N_2$
should have the least stable foam. This conclusion agrees with Kibodeaux’s dissertation\textsuperscript{69}, but is contrary to our experimental observation.

### 2.3.3. Hypothesis III: Diffusion Coarsening

Our third hypothesis argues that steady-state foam strength is determined by the rate of gas transfer across a foam lamella. Different gases have varied permeabilities $k_{\text{film},i}$ through the lamella, thereby changing the rate of mass transfer between small and large bubbles. As a result, bubbles coalesce at different rates. Because our experimental observation revealed that N$_2$ foam has the maximum steady-state foam strength, we realize that such change in apparent viscosity is in accordance with the change in film permeability listed in Table 2-1. To further test this hypothesis, two more sets of experiments were performed with binary gas mixtures. The first mixture was a flue gas with N$_2$ and CO$_2$ in an 8:2 mol\% ratio and the second was a CO$_2$ and CH$_4$ gas mixture in a 1:1 mol\% ratio.
Figure 2-4 Quality scans for N₂, CH₄, CO₂, and their binary mixtures. Nitrogen (solid diamond) had the strongest foam strength, followed by flue (80 mol% N₂ and 20 mol% CO₂) gas (dashed diamond), 50 mol% CH₄ and 50 mol% CO₂ (dotted triangle), CH₄ (square); and CO₂ (solid triangle). The strength of the mixed gas foams corresponds with foams of the least soluble gas.

As shown in Figure 2-4, the mixture of 50 mol% CH₄ and 50 mol% CO₂ has approximately the same foam strength as the less soluble gas CH₄. Similarly, the flue gas curve overlaps the N₂ curve for qualities higher than 90% in the N₂ and CO₂ mixture in the high-quality regime. The mixture has slightly lower foam strength than N₂ in the low-quality regime. This result is in agreement with the industrial practice to add a small amount of non-condensable gases, such as N₂, to boost the strength of steam foam⁵⁶. Princen and Mason proposed that the film permeability of a mixed gas \( k_{film,mixture} \) can be approximated as the harmonic mean permeability of its constitutive components \( k_{film,i} \) as shown in Equation 2-12⁴², where \( x_i \) is the mole fraction of
component \( i \) in the gas phase. We define relative foam strength here in Equation 2-13 as normalized foam apparent viscosity with respect to N\(_2\) foam at constant absolute permeability \((k_{rock})\), foam quality, total flux, temperature, and pressure. The relative foam strength is significantly correlated with film permeability to different gases \((k_{film,i})\). As shown in Figure 2-5, foam strength decays with increasing film permeability. Though gas solubility is not the determining factor as discussed in the section 2.3.2, gas solubility is directly proportional to the film permeability \(k_{film}^{42}\).

\[
\overline{k}_{film,mixture} = \frac{1}{\sum_{i=1}^{n} \frac{x_i}{k_{film,i}}}
\]  \hspace{1cm}\text{Equation 2-12}

\[
\text{Relative Foam Strength} = \left( \frac{\mu_{app,i}}{\mu_{app,N_2}} \right)_{k_{rock},f,g,u,T,p}
\]  \hspace{1cm}\text{Equation 2-13}
2.4. Conclusion

Steady-state foam experiments through porous media using N\(_2\), CH\(_4\), CO\(_2\), and two binary gas mixtures were conducted using Bentheimer sandstone at ambient temperature and 21 bar. Under these conditions, we observed that foam apparent viscosity decreases in the order of N\(_2\), flue gas, CH\(_4\), CH\(_4\)/CO\(_2\) mixture, and CO\(_2\). The differences in gas solubility, lamella stability, and film permeability were examined. Firstly, we confirmed that gas solubility is not the main cause accounting for the difference in foam strength in porous media. Secondly, we found that the van der Waals force contribution to disjoining pressure gives a contradicting prediction of lamella stability to explain the role of gas type on foam apparent viscosity. Thirdly, we discovered a strong correlation between foam strength in porous media and the measured film permeability to different...
types of gas $k_{film,i}$. Further investigation is needed to experimentally determine the exact nature of this correlation.
3.1. Background

Foam is a thermodynamically metastable system, which requires surfactants to adsorb preferentially onto the gas-liquid interface to lower the interfacial energy and stabilize lamella. Commonly used ionic and zwitterionic surfactants such as alpha olefin sulfonate (AOS), dodecyltrimethylammonium bromide (DTAB) and lauryl betaine (LB) are insoluble in gas phase and can only be injected with water. However some nonionic surfactants, mainly ethoxylated alcohols, are CO₂ soluble thus making it possible to inject surfactants with gas phase. Besides nonionic surfactants, some novel designed smart surfactants (ethoxylated amines) are also CO₂ soluble. These smart ethoxylated amines can switch from nonionic to cationic by protonating the amine group according to the pH in solutions and exhibit preferable adsorption
characteristics. Injected in CO₂, the surfactant will automatically dissolve into the aqueous phase and foam.

Injecting surfactant in CO₂ shows some major advantages over injecting surfactant in water. Because of operational constraints and injectivity limitations, gas and liquid co-injection is not an option for foam processes at the reservoir scale. What is commonly applied is alternating injection of gas and water slugs that is here described either as (1) a Surfactant-Alternating-Gas (SAG) process when the surfactant is injected into the aqueous phase or as (2) a Water-Alternating-Gas-Plus-Surfactant-in-Gas (WAG+S) process when the surfactant is injected in gas phase. If surfactant is injected in water, a large amount of surfactant could be wasted if the surfactant quickly falls with the water phase by gravity segregation before interacting with the gas slugs. It might be a more severe issue if the slug size is large and the reservoir is highly heterogeneous in vertical direction. On the contrary, when surfactant is injected in gaseous phase and flows with the CO₂, it can generate foam when gas-containing surfactant comes in contact with the formation brine or injection water left behind from secondary recovery. Thus, it can enlarge the gas-water mixture (foam) zone before complete phase segregation happens.

Since CO₂ soluble surfactants can partition between gas phase and aqueous phase, it is of great importance to understand the effect of partition coefficient $K_{sgw}$ on foam transport in the reservoir. Partition coefficient is defined as the surfactant concentration ratio between gaseous phase and aqueous phase at equilibrium condition:

$$K_{sgw} = \frac{C_{sg}}{C_{sw}}$$

Equation 3-1
Because of the amphiphilicity of the molecular structure, CO$_2$ soluble surfactants may be either more hydrophilic (small partition coefficient) or more CO$_2$-philic (large partition coefficient). Partition coefficient reported in$^{77,78}$ also indicates that even for a specific surfactant, it may change with varied reservoir conditions. A reasonable value for partition coefficient $K_{sgw}$ can be expected in the range of 0.01 and 5.00.

A series of interesting experimental observations were reported by Ren et al.$^{78}$ regarding the effect of surfactant partitioning between the CO$_2$ and the water. Core-scale CO$_2$ foam flooding experiment was conducted with 4 different types of surfactants with different partition coefficients by co-injecting CO$_2$ and surfactant solution (that is to say surfactant was injected in water). It was concluded that there is an optimal partition coefficient for fastest foam propagation.

Another intuitive analysis, described by Aschoori et al.$^{79}$, utilized fractional flow theory to conceptualize the first-contact-miscible gas flood with surfactant dissolved in CO$_2$. This theoretical work sheds light upon the effect of surfactant partitioning on foam propagation. Other variables such as surfactant foamability and adsorption were held constant when surfactant partition coefficient was varied. It was concluded that weaker surfactant partitioning from CO$_2$ to water (larger partition coefficient $K_{sgw}$) is advantageous to accelerate foam propagation velocity.

In this chapter, a more generalized 1-D foam simulator is developed to investigate foam transport with respect to different surfactant partition coefficients. Different foam models have been proposed in literature to simulate foam transport in porous media$^{80}$. Most of the foam models have been developed based on the fact that gas relative permeability in presence of foam is greatly reduced (which is equivalent to viscosifying the gas) whereas the relative permeability for a given saturation of water remains unchanged$^{27}$. 
Embedded in our 1-D reservoir simulator is STARS\textsuperscript{TM} foam model which assumes lamella generation and coalescence rates are locally at equilibrium\textsuperscript{27,80,81}. Then the reduction of gas mobility is expressed as a function depending on variables such as surfactant concentration, water saturation, and capillary number etc.

### 3.2. Model Description

A local-equilibrium texture-implicit model proposed in the STARS\textsuperscript{TM} is used for foam simulation. The gas relative permeability with the presence of foam $k_{rg}^f$ is obtained by multiplying the gas relative permeability without foam $k_{rg}^{nf}$ at a given water saturation with a mobility reduction factor $FM$.

\[
    k_{rg}^f = k_{rg}^{nf} \times FM \tag{3-2}
\]

$FM$ is inversely related to the product of different functions, which account for the foam dependences on different factors (surfactant concentration, water saturation, oil saturation and capillary number etc.).

\[
    FM = \frac{1}{1 + f_{mmob} \times \prod_i F_i} \tag{3-3}
\]

$f_{mmob}$ sets a reference to the maximum gas mobility reduction that can be achieved by foam. $F_i$ functions are the different dependence functions all in the range of 0 to 1. When $F_i$ functions are all equal to 1, foam correspondingly obtains its maximum strength. This work only
considers foam dependence on surfactant concentration ($F_{\text{surfactant}}$) and water saturation ($F_{\text{water}}$). Then Equation 3-3 is reduced to Equation 3-4.

$$FM = \frac{1}{1 + f_{\text{momb}} \times F_{\text{surfactant}} \times F_{\text{water}}}$$  \hspace{1cm} \text{Equation 3-4}$$

$F_{\text{surfactant}}$ is surfactant concentration dependent function which is a function of surfactant concentration in aqueous phase $C_{sw}$ as shown in Equation 3-5. There are two parameters in $F_{\text{surfactant}}$: $f_{\text{msurf}}$ and $\epsilon_{\text{surf}}$. $f_{\text{msurf}}$ describes the critical surfactant concentration above which foam strength no longer changes. $\epsilon_{\text{surf}}$ is the power-law exponent. Empirically $f_{\text{msurf}}$ is always a lot higher than the critical micelle concentration (CMC). However it is not well understood how $f_{\text{msurf}}$ is correlated with critical micelle CMC yet. We find it by experiment that the surfactant hardly foams when the concentration is below CMC.

$$F_{\text{surfactant}} = \begin{cases} 
\left(\frac{C_{sw}}{f_{\text{msurf}}}ight)^{\epsilon_{\text{surf}}} & \text{for } C_{sw} < f_{\text{msurf}} \\
1 & \text{for } C_{sw} \geq f_{\text{msurf}}
\end{cases}$$  \hspace{1cm} \text{Equation 3-5}$$

It would not be difficult to fit $f_{\text{msurf}}$ and $\epsilon_{\text{surf}}$ to experiments. For the sake of simplification, we assume linearity between $F_{\text{surfactant}}$ and $C_{sw}$ by fixing $\epsilon_{\text{surf}}$ to 1. We might as well set $f_{\text{msurf}}$ to be 2 g/L (equivalent to 0.2 wt% in water) since what matters is not the absolute value of $f_{\text{msurf}}$ but the ratio between surfactant concentration $C_{sw}$ and $f_{\text{msurf}}$. The relationship between $F_{\text{surfactant}}$ and $C_{sw}$ is shown in Figure 3-1.
Figure 3-1 The relationship between $F_{surf\_actant}$ and $C_{sw}$ ($fmsurf=2\ g/L,\ epsurf=1$)

$F_{water}$ is the water saturation dependent function which is the inverse of a tangent function of water saturation $S_w$. It describes the dry-out effect when water saturation is low as shown in Equation 3-6.

$$F_{water} = 0.5 + \frac{\arctan[epdry(S_w - fmdry)]}{\pi}$$  \hspace{1cm} \text{Equation 3-6}

There are two parameters in $F_{water}$ as well: $fmdry$ and $epdry$. $fmdry$ describes the water saturation around which foam starts drying out. $epdry$ regulates how abruptly foam will dry out when water saturation decreases. Large $epdry$ indicates that foam will dry out sharply whereas small $epdry$ indicates that foam will dry out gradually as shown in Figure 3-2. Different algorithms have been proposed in literature$^{7,80-83}$ to estimate $fmdry$ and $epdry$ based on lab-scale experiments. In this work we will preset $fmdry$ to be 0.25 and $epdry$ 500.
Figure 3-2 The relationship between $F_{water}$ and $S_w$ ($fmdry=0.25$, $epdry=50, 500, 5000$)

The Corey model is applied to correlate relative permeability and saturation as shown in Equation 3-7 and Equation 3-8. Then the relative-permeability reduction of gas phase by foam can be plotted out as shown in Figure 3-3. Parameters for the foam model are listed in Table 3-1 and parameters for Corey model are listed in Table 3-2.

\[
k_{rg}^{nf} = k_{rg}^o \left( \frac{1 - S_{gr} - S_w}{1 - S_{gr} - S_{wr}} \right)^{n_g}
\]  \hspace{1cm} \text{Equation 3-7}

\[
k_{rw} = k_{rw}^o \left( \frac{S_w - S_{wr}}{1 - S_{gr} - S_{wr}} \right)^{n_w}
\]  \hspace{1cm} \text{Equation 3-8}
Table 3-1 Parameters in STARS foam model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{mob}$</td>
<td>500</td>
</tr>
<tr>
<td>$F_{surf\text{actant}}$</td>
<td>$f_{msurf}$</td>
</tr>
<tr>
<td></td>
<td>$\epsilon_{surf}$</td>
</tr>
<tr>
<td>$F_{water}$</td>
<td>$f_{mdry}$</td>
</tr>
<tr>
<td></td>
<td>$\epsilon_{dry}$</td>
</tr>
</tbody>
</table>

Table 3-2 Parameters in Corey relative permeability model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{wr}$</td>
<td>0.05</td>
<td>residual water saturation</td>
</tr>
<tr>
<td>$S_{gr}$</td>
<td>0.05</td>
<td>residual gas saturation</td>
</tr>
<tr>
<td>$k_{r\text{w}}^o$</td>
<td>0.2</td>
<td>end-point relative permeability for water</td>
</tr>
<tr>
<td>$k_{r\text{g}}^o$</td>
<td>0.94</td>
<td>end-point relative permeability for gas</td>
</tr>
<tr>
<td>$n_w$</td>
<td>4.2</td>
<td>Corey exponent for water (wetting) phase</td>
</tr>
<tr>
<td>$n_g$</td>
<td>1.3</td>
<td>Corey exponent for gas (non-wetting) phase</td>
</tr>
</tbody>
</table>
A general form for conservation equation of mass is given by Equation 3-9.

\[
\frac{\partial W_i}{\partial t} + \mathbf{V} \cdot \overrightarrow{N_i} - R_i = 0 \quad (i = w, g, s)
\]

Equation 3-9

\( W_i \) is the total concentration of \( i \) in units of mass of \( i \) per unit bulk volume. The index \( i \) can be \( w \) for water, \( g \) for gas or \( s \) for surfactant. For isothermal fluid flow in permeable media, \( W_i \) can be further expressed as shown in Equation 3-10 where \( \phi \) is the porosity, \( \rho_j \) is the density of phase \( j \), \( S_j \) is the saturation of phase \( j \), \( \omega_{ij} \) is the mass fraction of species \( i \) in phase \( j \), \( N_p \) is the number of phases and subscript \( s \) in \( \omega_{is} \) represents the mineral surface. \( \overrightarrow{N_i} \) is the flux of species \( i \) which can be further divided to a convection term and a dispersion term as shown in Equation 3-11. \( \mathbf{u}_j \) is the superficial velocity vector of phase \( j \) and \( K_{ij}^* \) is the dispersion tensor of species \( i \) in phase \( j \).
\[ W_l = \phi \sum_{j=1}^{N_p} \rho_j S_j \omega_{lj} + (1 - \phi) \rho_s \omega_{ls} \]  \hspace{1cm} \text{Equation 3-10}

\[ \bar{N}_l = \sum_{j=1}^{N_p} \rho_j \omega_{lj} \bar{u}_j - \phi \rho_j S_j K_{ij} \cdot \nabla \omega_{ij} \]  \hspace{1cm} \text{Equation 3-11}

In this work, there is no net production of species, thus the source term \( R_l \) in Equation 3-9 is equal to zero for all water, gas and surfactant. Assumptions made include: foam is a two-phase (gaseous phase and aqueous phase) three-component (gas, water, and surfactant) incompressible fluid; gas and water are immiscible; the reservoir is a 1-D homogeneous porous medium; surfactant partitioning is at local equilibrium.

For gas and water:

\[ W_g = \phi \rho_g S_g \]  \hspace{1cm} \text{Equation 3-12}

\[ W_w = \phi \rho_w S_w \]  \hspace{1cm} \text{Equation 3-13}

\[ \bar{N}_g = \rho_g \bar{u}_g \]  \hspace{1cm} \text{Equation 3-14}
\[ \vec{N}_w = \rho_w \vec{u}_w \quad \text{Equation 3-15} \]

Thus the conservation equations for gas and water become:

\[ \phi \frac{\partial S_g}{\partial t} + \frac{\partial u_g}{\partial x} = 0 \quad \text{Equation 3-16} \]

\[ \phi \frac{\partial S_w}{\partial t} + \frac{\partial u_w}{\partial x} = 0 \quad \text{Equation 3-17} \]

Surfactant can partition between gaseous phase and aqueous phase and be adsorbed on to the surface of the formation as well:

\[ W_s = \phi (S_w c_{sw} + S_g c_{sg}) + (1 - \phi) c_{ss} \quad \text{Equation 3-18} \]

\[ \vec{N}_s = c_{sw} \vec{u}_w + c_{sg} \vec{u}_g - \phi [S_w K_{sw}^\ast \nabla c_{sw} + S_g K_{sg}^\ast \nabla c_{sg}] \quad \text{Equation 3-19} \]

The conservation equation for surfactant becomes:

\[ \phi \frac{\partial (S_w c_{sw} + S_g c_{sg})}{\partial t} + (1 - \phi) \frac{\partial c_{ss}}{\partial t} + \frac{\partial (c_{sw} u_w + c_{sg} u_g)}{\partial x} = \phi [K_{sw}^\ast \frac{\partial}{\partial x} (S_w \cdot \nabla c_{sw}) + K_{sg}^\ast \frac{\partial}{\partial x} (S_g \cdot \nabla c_{sg})] \quad \text{Equation 3-20} \]

Additional equations include momentum balance for the two phases based on Darcy’s law:
\[ u_g = -k k_{rg} \frac{\partial p_g}{\partial x} \]  
\textit{Equation 3-21}

\[ u_w = -k k_{rw} \frac{\partial p_w}{\partial x} \]  
\textit{Equation 3-22}

For simplicity, surfactant adsorption \((C_{ss}=0)\) is neglected. The adsorption of surfactants can slow down the surfactant propagation and the retardation varies with different types of fluid rock interactions. However commonly used nonionic surfactants have a significantly lower adsorption onto the carbonate formations compared to ionic surfactants with oppositely charged surface\(^{77,78,84}\). Also smart ethoxylated amines can have a very low adsorption in most CO\(_2\) saturated carbonate reservoirs since the pH is oftentimes below the isoelectric point and thusly the rock surface is positively charged as the surfactants\(^{72,74,75}\).

Capillary pressure \((p_w = p_g)\) is also neglected in our computation. It does not cause major differences on the modeling and can be easily added to the simulation with any capillary pressure model.

The 1-D model is solved by implicit-pressure-explicit-saturation (IMPES) procedure. \textit{Equation 3-16}, \textit{Equation 3-17}, \textit{Equation 3-20}, \textit{Equation 3-21}, \textit{Equation 3-22} are solved simultaneously in a dimensionless form. The detailed numerical method can be found elsewhere\(^{85}\). Important parameters for this 1-D CO\(_2\) foam simulator are listed in Table 3-3.
### Table 3-3 Parameters for 1-D CO$_2$ foam simulator

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NX$</td>
<td>100</td>
<td>number of grid blocks</td>
</tr>
<tr>
<td>$L$</td>
<td>1.0</td>
<td>in feet, length of the 1-D formation</td>
</tr>
<tr>
<td>$\Delta t_D/\Delta x_D$</td>
<td>0.005</td>
<td>step length in dimensionless time</td>
</tr>
<tr>
<td>$k$</td>
<td>1.0</td>
<td>in Darcy, permeability of the formation</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.25</td>
<td>porosity of the formation</td>
</tr>
<tr>
<td>$v$</td>
<td>80</td>
<td>in ft/day, total interstitial velocity</td>
</tr>
<tr>
<td>$Pe_w$</td>
<td>500</td>
<td>Peclet number in aqueous phase ($Pe_w = \frac{Lv}{Ksw}$)</td>
</tr>
<tr>
<td>$Pe_g$</td>
<td>500</td>
<td>Peclet number in gas phase ($Pe_g = \frac{Lv}{Ksg}$)</td>
</tr>
<tr>
<td>$\mu_g$</td>
<td>0.045</td>
<td>in cP, viscosity of CO$_2$ (4000 psi, 120 °C)</td>
</tr>
<tr>
<td>$\mu_w$</td>
<td>0.24</td>
<td>in cP, viscosity of water (4000 psi, 120 °C)</td>
</tr>
</tbody>
</table>

With this 1-D CO$_2$ foam simulator, a series of numerical core-flood experiments were conducted to study the effect of surfactant partition coefficient on foam transport in porous media. In all cases, surfactant is injected with CO$_2$ as shown in Figure 3-4. Foam strength is quantified by apparent viscosity $\mu_{app}$, which is defined as pressure gradient normalized with respect to permeability and total flux of both gas and liquid as shown in Equation 3-23.

\[
\mu_{app} = \frac{k\nabla p}{u_g + u_w}
\]  

**Equation 3-23**
3.3. Results and Discussions

Three different test cases will be simulated to systematically illustrate the effect of surfactant partition coefficient in this 1-D system. We assign three different characteristic values to \( K_{sgw} \) to represent small, unity and large partition coefficient respectively as shown in Table 3-4.

### Table 3-4 Characteristic values for surfactant partition coefficient \( K_{sgw} \)

<table>
<thead>
<tr>
<th>Characteristic ( K_{sgw} )</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>0.05</td>
</tr>
<tr>
<td>Unity</td>
<td>1.00</td>
</tr>
<tr>
<td>Large</td>
<td>4.00</td>
</tr>
</tbody>
</table>

3.3.1. Case I: CO\(_2\) Displacing Water

In Case I, we continuously inject CO\(_2\) to displace water. Initially the 1-D formation core is fully saturated with surfactant-free water, i.e., \( S_w = 1 \). Gas is then injected from the inflow end at a superficial velocity of 20 ft/day. The pressure at the outflow end is kept constant. Surfactant is injected with the gas phase with a concentration of 2.5 g/L, which is slightly higher than \( fmsurf \).
Figure 3-5 illustrates the different situations when the surfactant partition coefficient $K_{sgw}$ is small ($K_{sgw} = 0.05$), unity ($K_{sgw} = 1.00$) and large ($K_{sgw} = 4.00$). The snapshots are taken after injecting 0.50 total pore volume (TPV) of CO$_2$ into the core. The first plot is gas-saturation profile, which demonstrates the gas front in the porous medium. The dashed line ($1-fmdry$) indicates the gas saturation around which foam starts drying out. The second plot is the profile of surfactant concentration in the aqueous phase, which indicates the surfactant transport and retardation in the aqueous phase. The dashed line indicates the critical concentration $fmsurf$ above which foam strength is no longer dependent on the surfactant concentration. The third plot is the apparent viscosity profile, which shows the position of the foam bank and foam strength inside the porous medium.

Figure 3-5 Case I: CO$_2$ displacing water
It can be seen from Figure 3-5 that for small partition coefficient ($K_{sgw} = 0.05$), surfactant and foam transport will be retarded. If surfactant is highly preferential to partition in water, even though injected in CO$_2$, the surfactant will be quickly stripped off from the gaseous phase and get highly concentrated near the wellbore region. Consequently the mobility control of CO$_2$ will be lost and an early gas breakthrough will be expected. Furthermore, the concentrated surfactant in the aqueous phase may cause precipitation issues if the nonionic surfactants have limited solubility in the aqueous phase.

For unity partition coefficient ($K_{sgw} = 1.00$), the surfactant transport is in accordance with gas front propagation. When surfactant is equally partitioned between the aqueous phase and the gaseous phase, CO$_2$ can hold the dissolved surfactant for a longer time and the gas breakthrough will be delayed. Surfactant concentration in water is kept around $fms_{surf}$. The foam front is strong enough so it displaces the water and increases the gas saturation effectively.

For a large partition coefficient ($K_{sgw} = 4.00$), surfactant transport is in accordance with the gas propagation and early gas breakthrough is avoided. However, the surfactant is highly spread out and the concentration in water drops below $fms_{surf}$. The foam front is not as strong as the unity partition coefficient. Thus foam displaces water in a less effective way. Foam bank is elongated.

3.3.2. Case II: Single Slug of CO$_2$ Followed by Water

In Case I when continuous gas is injected, foam dries out when water saturation drops below $fmdry$. In Case II, water is injected after a slug of CO$_2$ injection. In this case, the initial condition remains the same as that in Case I where the 1-D formation core is fully saturated with the surfactant-free water. The boundary condition now becomes that we first inject 0.2 TPV of
CO₂ with 2.5 g/L surfactant and then switch to continuous water injection. Snap shots are also taken at 0.5 TPV of injection as shown in Figure 3-6.

![Figure 3-6 Case II: Single slug of CO₂ followed by water](image)

As can be seen from Figure 3-6, water injection after CO₂/surfactant slug has different effects on foam and surfactant transport with respect to different partition coefficients. For small partition coefficient ($K_{sgw} = 0.05$), water injection can mix with the surfactant concentration near the injection wellbore and push the surfactant slug to move forward. However, the effect is limited and surfactant is still concentrated in a small region. The narrow distribution is a waste of surfactant and directly shortens foam bank. Foam is less strong than for unity partition coefficient. For unity partition coefficient ($K_{sgw} = 1.00$), water injection can mitigate the dry-out effect right after the foam front by quickly compensating the lost water. Thus foam bank is elongated and foam
is the strongest. For large partition coefficient \(K_{sgw} = 4.00\), water injection will further dilute the surfactant concentration in aqueous phase and weaken the foam.

### 3.3.3. Case III: Water-Alternating-Gas-Plus-Surfactant (WAG+S)

In the field, either continuous gas injection or a single slug of gas followed by water does not occur. Case III would represent a WAG+S process where slugs of gas and water are injected alternately. Surfactant is still injected with CO\(_2\) at the concentration of 2.5 g/L. Each cycle of WAGS consist of 0.20 TPV of CO\(_2\) and 0.05 TPV of water. Figure 3-7 shows the snap shots taken at 0.5 TPV after 2 cycles of gas and water have been injected. Similar conclusion can be drawn that when surfactant is equally preferential to staying between CO\(_2\) and water, we can generate the strongest foam strength and expect a relatively fast foam propagation velocity.

![Figure 3-7 Case III: Water-alternating-gas-plus-surfactant (WAG+S)](image)
If \( f_{mdry} \) and \( K_{sgw} \) are varied at the same time, we can plot out the contour of average apparent viscosity of foam after 1 TPV injection (which is equivalent to 4 cycles of CO\(_2\)/surfactant and water injection) with respect to \( f_{mdry} \) and \( K_{sgw} \) for the same WAG+S process.

![Contour of Average Apparent Viscosity](image)

**Figure 3-8 Contour of apparent viscosity as a function of \( f_{mdry} \) and \( K_{sgw} \)**

It can be seen from Figure 3-8 that in a wide range of \( f_{mdry} \), foam is of maximum strength (highest apparent viscosity) when surfactant partitions equally between gaseous phase and aqueous phase.

### 3.3.4. Simulation v.s. Fractional Flow Theory

As described in Section 1, Ashoori et al.\(^{10}\) utilized fractional-flow theory to study the effect of surfactant partitioning when surfactant was continuously injected with CO\(_2\) into a water saturated reservoir. Two fractional-flow curves were used to describe foam and CO\(_2\)/water two-
phase flow respectively. Foam front is where the CO\textsubscript{2}/water wave exceeds the foam wave and ‘Buckley-Leverett’ shock appears. Ahead of the foam front, gas will lose its mobility control and quickly break through the medium. It was concluded that greater surfactant partition from water to CO\textsubscript{2} (Large $K_{sgw}$) is favorable for foam propagation.

The 1-D simulation disclosed here can be reduced to fit the results obtained from fractional-flow theory by modifying the form of surfactant concentration dependent function $F_{\text{surfactant}}$. Ashoori et al. assumes that foam strength is only dependent on water saturation as shown in Equation 3-24. Namely, so long as surfactant exists locally, the foam fractional-flow curve governs the propagation of the saturation waves; otherwise CO\textsubscript{2}/water two-phase fractional-flow curve governs. Let’s consider adjusting $F_{\text{surfactant}}$ to a step function, as shown in Equation 3-25. $C_{\text{threshold}}$ is a threshold concentration ($C_{\text{threshold}}$ is set to be 0.5 g/L) above which foam is of full strength at a given saturation otherwise foam does not exist. As shown in Figure 3-9, a consistent result can be obtained as by fractional-flow theory that larger surfactant partition coefficient can enhance foam propagation velocity and is favorable for displacement.

$$FM = \frac{1}{1 + f_{mmob} \times F_{\text{water}}}$$  \hspace{1cm} \text{Equation 3-24}

$$F_{\text{surfactant}} = \begin{cases} 
0 & \text{for } C_{sw} < C_{\text{threshold}} \\
1 & \text{for } C_{sw} \geq C_{\text{threshold}}
\end{cases}$$  \hspace{1cm} \text{Equation 3-25}
Figure 3-9 CO$_2$ displacing water with modified form of $F_{\text{surfactant}}$ to reproduce the results given by fractional flow theory

Compared with Case I Figure 3-5, the surfactant concentration profiles are similar whereas the gas saturation profiles and foam apparent viscosity profiles are quite different. It is because the fractional flow theory and our reduced model oversimplify the foam dependence on surfactant concentration. It switches between full strength foam mode and gas-water two-phase flow model where gas mobility control is completely lost. In reality, foam strength monotonically increases with surfactant concentration until it reaches a plateau. However, if we only consider the position of the foam front in the gas-saturation profile in Figures 3-5 to 3-7, the fractional-flow analysis is also in accordance with previous simulation results in Case I, II and III. Regardless of foam strength (foam apparent viscosity), foam front travels faster when surfactant stays in and is transported with CO$_2$ (large $K_{sgw}$).
3.4. Conclusion

We have developed a more generalized 1-D foam simulator to study the effect of foam transport in porous media. The STARS™ model is utilized to describe the reduction of gas mobility by foam. The foam dependence on surfactant concentration and water saturation is accounted by two empirical functions introduced as $F_{\text{surfactant}}$ and $F_{\text{water}}$. IMPES method is applied to solve the transport equations numerically. Three different cases are fully discussed to illustrate how surfactant distribution between phases can affect the transport of foam. It is found that large partition coefficient can enhance foam propagation whereas small partition coefficient can hold surfactant in the aqueous phase to strengthen the foam. When plotting contours of the apparent viscosity with respect to a wide range of $f_{\text{mdry}}$, we clearly illustrated that a surfactant with unity partition coefficient is advantageous to foam transport in regard to foam strength and propagation speed. The effect of small, unity and large partition coefficient is listed in Table 3-5.

<table>
<thead>
<tr>
<th>$K_{sgw}$</th>
<th>Small</th>
<th>Unity</th>
<th>Large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Breakthrough</td>
<td>Early</td>
<td>Late</td>
<td>Late</td>
</tr>
<tr>
<td>Surfactant Concentration</td>
<td>Concentrated</td>
<td>Around $f_{\text{msurf}}$</td>
<td>Diluted</td>
</tr>
<tr>
<td>Surfactant Transport</td>
<td>Retarded</td>
<td>Fast</td>
<td>Fast</td>
</tr>
<tr>
<td>Foam Transport</td>
<td>Slow</td>
<td>Fast</td>
<td>Fast</td>
</tr>
<tr>
<td>Foam Bank</td>
<td>Short</td>
<td>Long</td>
<td>Long</td>
</tr>
</tbody>
</table>

This model can be modified to reproduce the results derived from fractional flow theory analysis by assuming that as long as surfactant is present, foam exists with a strength independent of surfactant concentration and then adjusting the form of surfactant concentration dependent function $F_{\text{surfactant}}$ accordingly.
4.1. Background

Previous studies on the permeability dependence of foam transport in literature have shown correlations between the rock permeability and certain foam parameters such as the apparent viscosity and the limiting capillary pressure\(^{86-88}\). However, those studies were mostly conducted under conditions that might be less representative of the actual reservoir that has higher temperatures, and with different gas compositions. In this chapter, experiments were conducted at elevated reservoir temperature (94°C) using actual reservoir cores of varied permeabilities, representative brine, methane gas (CH\(_4\)) and an in-house developed foaming surfactant

* The work was done at Petronas Research Sdn Bhd (PRSB), Malaysia. Ridhwan Zhafri B Kamarul Bahrim contributed equally to this chapter
formulation capable of withstanding high temperature and high oil saturation. The effect of rock permeability on the foam rheology and the relationship with the texture-implicit local-equilibrium foam model parameters were studied. Steady-state co-injection core flooding experiment data were fitted to foam model using Zeng et al.\textsuperscript{7} approach.

### 4.2. Experiment Section

#### 4.2.1. Materials

Porous Media: Cores from a proprietary reservoir with dimensions of 1.5 inches in diameter and 3.0 inches in length were selected. Several petrographic analyses such as X-Ray Diffraction (XRD) and scanning electron microscopy (SEM) were conducted in order to examine the mineralogy of the rocks. XRD showed that the most common clay types are chlorite (29 to 37 wt\% of total clay fraction) followed by illite (18 to 28 wt\%), mixed-layer clays (19 to 25 wt\%), kaolinite (14 to 23 wt\%), and smectite (1 to 2 wt\%). SEM analysis showed that in these sandstone rocks, quartz is the dominant mineral amongst the framework grains while feldspars are minor. Based on the CT-Scan, three plugs which show no flow barriers or laminations that could affect the fluid flow were selected. The cores were cleaned and dried by flow-through core cleaning (FTCC) and critical point drying (CPD) procedures successively to minimize the damage to the delicate mineral structures. Table 4-1 shows the characterization of the three selected core plugs. Table 4-2 shows the measured Corey relative permeability parameters. And Figure 4-1 shows the Leverett-j function measured by primary mercury drainage experiment in cores from the same reservoir with brine and crude oil.
Table 4-1 Core sample analysis under hydrostatic confinement

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Net Confining Stress psi</th>
<th>Pore Volume cc</th>
<th>Porosity %</th>
<th>Klinkenberg Permeability mD</th>
<th>Permeability to air (est.)</th>
<th>Grain Volume cm³</th>
<th>Grain Density g/cm³</th>
<th>Sample Weight G</th>
<th>Length cm</th>
<th>Diameter cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H</td>
<td>800</td>
<td>20.4</td>
<td>25.0</td>
<td>525.0</td>
<td>538</td>
<td>61.5</td>
<td>2.64</td>
<td>162</td>
<td>7.55</td>
<td>3.74</td>
</tr>
<tr>
<td></td>
<td>2900</td>
<td>19.9</td>
<td>24.4</td>
<td>493.0</td>
<td>508</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2H</td>
<td>800</td>
<td>19.0</td>
<td>23.2</td>
<td>201.0</td>
<td>213</td>
<td>63.1</td>
<td>2.65</td>
<td>167</td>
<td>7.51</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>2900</td>
<td>18.5</td>
<td>22.7</td>
<td>191.0</td>
<td>202</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3H</td>
<td>800</td>
<td>17.1</td>
<td>21.0</td>
<td>61.1</td>
<td>66.4</td>
<td>64.5</td>
<td>2.65</td>
<td>171</td>
<td>7.43</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>2900</td>
<td>16.6</td>
<td>20.5</td>
<td>57.5</td>
<td>62.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-2 Corey relative permeability parameters for the reservoir core samples

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>$k^o_{rg}$</th>
<th>$S_{gr}$</th>
<th>$n_g$</th>
<th>$k^o_{rw}$</th>
<th>$S_{wc}$</th>
<th>$n_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H</td>
<td>0.85</td>
<td>0.22</td>
<td>2.16</td>
<td>0.70</td>
<td>0.49</td>
<td>4.19</td>
</tr>
<tr>
<td>2H</td>
<td>0.90</td>
<td>0.18</td>
<td>2.16</td>
<td>0.83</td>
<td>0.37</td>
<td>4.19</td>
</tr>
<tr>
<td>3H</td>
<td>0.95</td>
<td>0.15</td>
<td>2.16</td>
<td>0.85</td>
<td>0.30</td>
<td>4.19</td>
</tr>
</tbody>
</table>

Figure 4-1 Leverett-j function measured from mercury primary drainage experiment
Chemical: an in-house foaming agent was diluted in synthetic field injection water to 0.5 wt% concentration. The formulation comprises of an anionic surfactant and an amphoteric surfactant due to the synergistic effect\(^8\). The composition of the synthetic injection water contains 10700 mg/L Na\(^+\), 395.1 mg/L Ca\(^{2+}\), 1214 mg/L Mg\(^{2+}\), 353.2 mg/L K\(^+\), and 4.9 mg/L Sr\(^{2+}\).

Gas: Methane gas of 99.97\% purity was used for the experiments. Methane was selected based on the composition of the produced gas from the target reservoir which contains 76.3 mol\% of methane. A fixed combustible gas detector, an alarm system and an emergency shut-down system were installed. The lab was equipped with two ventilation fans and two flexible fume suction arms, ensuring any released gas to be removed from the laboratory.

**4.2.2. Setup**

The experimental setup is schematically shown in Figure 4-2. It mainly consist of a data acquisition and control system, pressure measurement and control unit, a core sample unit, fluid controller and measurement unit.

Fluid controller and measurement unit: liquid injection was controlled using ISCO 260D dual pump system which ensured continuous brine and surfactant injections at high pressure and relatively low flow rates with good accuracy. Bronkhorst In-Flow series gas mass flow controllers (MFC) which were specifically designed and calibrated to deliver methane at constant mass flow rate were utilized for the gas injection. Bronkhorst Coriolis mass flow meter was installed downstream of the flow line to directly measure the mass flow rates of both liquid and gas, and indirectly measure the fluid densities. A Ritter TG Series drum type wet-test gas meter was used to measure the outflow gas volume.
Core sample unit: A reservoir core sample was mounted into a horizontally placed bi-axial 316 stainless steel core holder, located inside the oven that can reach a high temperature up to 160º C. A confining pressure was applied to prevent fluid bypass through the core. The pore pressure was simulated using the back pressure regulator. The liquid and gas were injected into the core through separate two tubing lines with multiple one-way valves to prevent backflows.

![Figure 4-2 Schematic diagram of the core-flooding system](image)

Pressure measurement and control unit: A DBR back pressure regulator (BPR) rated at 15,000 psi was used to precisely control and simulate the pore pressure for single- and multi-phase fluid flow. Six Validyne DP 303/360 differential pressure transducers with various measurement
accuracy ranges were used to ensure accurate pressure reading and recording along the core during the core flooding experiment.

Data acquisition and control system: a PC, equipped with LabVIEW program was connected to the other units to allow direct control of the systems during the test as well as to record experiment data.

4.2.3. Procedure

Calibration and equipment setup:

1. Calibrate pressure transducers, pressure gauges, flow meters, controllers and injection pumps;
2. Test the leakage of the accumulators and lines by applying a high liquid pressure loading and observe any pressure drop or signs of leakage;
3. Fill up the accumulators with test fluids and chemicals;
4. Insert the core into a suitable core sleeve type (Buna-N) and mount it into the core holder;
5. Vacuum the system for hours to remove the air;
6. Fill in differential pressure transducer lines with synthetic brine;
7. Set the confining pressure of the core holder at desired value (2900 psig);
8. Heat up the oven to specified temperature (94 °C);
9. Set up the back pressure regulator to target value (170 psig);
Core saturation with brine and permeability measurement: imbibe the core with brine and perform permeability test using at least three different flow rates. Ensure differential pressure for each of the injection rate is stable before switching to the next flow rate.

Surfactant injection: inject the surfactant solution for several pore volumes (PV) to satisfy the adsorption of the reservoir core.

Foam (surfactant and gas) co-injection: specific foam quality \( f_g \) is attained by altering the individual methane gas and surfactant solution injection rates (co-injection) at a fixed total flow rate. Once the differential pressure reaches a stable reading for at least 1 PV, steady-state is considered to be achieved. Repeat the co-injection process for several sets of different foam quality each until sufficient data is collected in order to generate the plot of differential pressure or apparent viscosity as a function of foam quality, which is also known as the foam quality-scan plot.

Gas velocity correction: two correction factors on the selected gas injection flow rate were calculated and implemented on the gas mass flow controllers namely with respect to the (i) gas compressibility factor due to the deviation from ideal-gas behavior, (ii) correction on the mass flow controllers due to the difference between factory inlet pressure calibration and the experiment inlet pressure.

Two types of experiments were conducted with each core sample: (i) foam quality-scan experiment: the total flow rate \( u_g + u_{\text{liquid}} \) was kept constant, while varying the foam quality \( f_g \); (ii) Flow-rate-scan experiment where the foam quality \( f_g \) is fixed, while the total flow rate (or superficial velocity \( u_g + u_{\text{liquid}} \)) was varied.
The foam quality-scan (apparent viscosity as a function of foam quality) and the flow-rate-scan (apparent viscosity as a function of total flow rate) plots were generated and utilized in the subsequent foam model parameter fitting process.

4.3. Modeling Section

In this chapter, a texture-implicit-local-equilibrium model was used to fit steady-state foam strength data with rocks of varied rock permeabilities. The model modifies gas phase mobility in the state of foam $\lambda_{rg}^f$ as shown in Equation 4-1:

$$\lambda_{rg}^f = \lambda_{rg}^{n_f} \times FM$$

Equation 4-1

According to the foam model, $\lambda_{rg}^f$ equals to the mobility of gas phase in absence of foam multiplied by a correction factor $FM$. The parameter $FM$ reduces the gas mobility when foam is formed. The parameter $FM$ is further correlated to a series of dependent functions $F_i$ as shown in Equation 4-2.

$$FM = \frac{1}{1 + f m m o b \times \prod_i F_i}$$

Equation 4-2

Only foam quality and total superficial velocity were the changing variables in our experiment. Thus we consider only the shear-rate dependent function $F_{shear}$ and the water-saturation function $F_{water}$. Surfactant concentration is not a variable in this chapter. The injected surfactant concentration is assumed to be high enough such that the surfactant dependent function $F_{surfactant}$ equals to 1 in the presence of surfactant.
The \( F_{\text{water}} \) function, as shown in Equation 4-3, is a monotonically increasing function of water saturation \( S_w \). It describes the dry-out effect and decreases significantly as water saturation \( S_w \) drops below the limiting water saturation \( S_w^* \). There are two parameters in the \( F_{\text{water}} \) function: \( f_{\text{mdry}} \) and \( e_{\text{pdry}} \). The parameter \( f_{\text{mdry}} \) corresponds to the limiting water saturation \( S_w^* \), low which foam experiences significant coarsening. The parameter \( e_{\text{pdry}} \) controls the collapse rate of foam. A large \( e_{\text{pdry}} \) value indicates that foam dries out sharply at \( S_w^* \), whereas small \( e_{\text{pdry}} \) indicates that foam dries out more gradually.

\[
F_{\text{water}} = 0.5 + \frac{\arctan[e_{\text{pdry}}(S_w - f_{\text{mdry})}]}{\pi}
\]  

Equation 4-3

The function \( F_{\text{shear}} \), as shown in Equation 4-4, is the shear-rate dependent function, which is a function of the local capillary number \( N_{Ca} \). The adjustable parameter \( e_{\text{pcap}} \) determines the shear-rate dependent rheology in porous media. A positive \( e_{\text{pcap}} \) corresponds to shear-thinning rheology whereas a negative \( e_{\text{pcap}} \) corresponds to shear thickening rheology. The parameter \( f_{\text{mcap}} \) is not an intrinsic foam parameter per se. In the case of shear-thinning rheology, the value is ought to set lower than the smallest capillary number in the simulation. It normalizes \( F_{\text{shear}} \) with the constraint that all dependent functions should fall within the closed interval of \([0,1]\). Capillary number \( N_{Ca} \) defined in Equation 4-5, is a dimensionless number in fluid mechanics, which characterizes the relative effect between the viscous force and the capillary force. The local capillary number is an indicator of the viscous shear rate in the system. Higher capillary number corresponds to a greater viscous shear stress at given interfacial tension. There are other forms of capillary number definition in the literature which are discussed in detail elsewhere\(^4\).
\[ F_{\text{shear}} = \begin{cases} \left( \frac{f_{m \cap}}{N_{ca}} \right)^{e_{\text{cap}}} & \text{for } N_{ca} > f_{m \cap} \\ 1 & \text{for } N_{ca} < f_{m \cap} \end{cases} \]

Equation 4-4

\[ N_{ca} = \frac{\mu_w \times (u_{\text{gas}} + u_{\text{liquid}})}{\sigma} \]

Equation 4-5

Besides the relative permeability parameters, there are five foam model parameters in total \((f_{\text{mmob}}, f_{\text{mdry}}, e_{\text{dry}}, f_{m \cap}, e_{\text{cap}})\) in the texture-implicit local-equilibrium model. A Matlab code (As shown in the Appendix) was developed to least-square fit the foam parameters to the quality-scan and flow-rate-scan experiment data. The detailed algorithm for parameter estimation will be explained in Chapter 7.

4.4. Results and Discussions

The experimental results of steady-state methane foam apparent viscosity in reservoir cores at elevated temperature \((94^\circ \text{C})\) are shown in Figure 4-3. We also fitted the texture-implicit-local-equilibrium foam model parameters to our experiments. The estimated parameters are listed in the Table 4-3.
Figure 4-3 Foam flooding experiment results (dots) and model fittings (line) with respect to reservoir cores of varied permeabilities. (a) Foam-quality-scan experiment at fixed superficial velocity of 4 ft/day and (b) flow-rate-scan experiment at transition foam qualities.

### Table 4-3 Estimated foam model parameters based on the core-flooding experiments

<table>
<thead>
<tr>
<th>Rock Permeability (mD)</th>
<th>fmmob</th>
<th>fmdry</th>
<th>epdry</th>
<th>fmcap</th>
<th>epcap</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.5</td>
<td>2.9e+5</td>
<td>0.56</td>
<td>90</td>
<td>5.8e-8</td>
<td>1.4</td>
</tr>
<tr>
<td>191.0</td>
<td>3.1e+5</td>
<td>0.45</td>
<td>46</td>
<td>6.0e-8</td>
<td>1.3</td>
</tr>
<tr>
<td>493.0</td>
<td>14.8e+5</td>
<td>0.43</td>
<td>48</td>
<td>6.4e-8</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The foam quality scan experiment result (Figure 4-3(a)) scan showed two regions in all three cores. In the low quality region, the foam apparent viscosity is monotonically increasing with
the foam quality. Once the foam quality passes the low quality region and reaches the transition point, the foam apparent viscosity starts to decrease with the increase in the foam quality. This is because in the low quality region, the bubble density (or foam texture) increases as a function of foam quality, and therefore the apparent viscosity increases. Yet, the capillary pressure between the gas phase and the aqueous phase increases as the liquid saturation decreases. When the pressure difference between the gas and the water exceeds the limiting capillary pressure value $P_c^*$, foam starts to collapse. This is why in the high quality region, apparent viscosity decreases as a function of foam quality.

It is also noticed that the measured foam strength in porous media is significantly dependent on the rock permeability. At given foam quality, the apparent viscosity is higher in the high permeability cores and lower in the low permeability cores. Such smart rheological property of foam is unique in the way that it can actively respond to the reservoir heterogeneity and improve the conformance of the displacement. Specifically, foam can induce a higher flow resistance in the high permeability regions in the reservoir and therefore divert the displacing fluids to the low permeability regions where more oil is trapped in the matrix due to high capillary forces.

It can be seen from Table 4-3 that some foam parameters show strong rock permeability dependence. For example, the parameter $f_{mdry}$ decreases as the rock permeability increases. This is in accordance with the observation that the transition foam quality at which the apparent viscosity peaks shifts to a higher value as the permeability increases. In the reservoir core with a permeability of 57.5 mD, the transition apparent viscosity is observed at a foam quality of 49.8%. The transition foam quality shifts to 62.0% in the core with a permeability of 191.0 mD. In the highest permeability core of 493.0 mD, the transition foam quality moves to an even higher quality of 66.3%. The transition foam quality is found to be positively correlated with the rock
permeability. The higher the rock permeability is, the higher the foam transition quality is, and vice versa.

The estimated $f_{mdry}$ values can be used to compare the dynamic foam film stability in rocks of different permeabilities\(^2\). The concept of limiting capillary pressure is firstly introduced by Khatib et al.\(^90\) to explain the dry-out effect at high foam qualities as described above. Due to the curved interface between the non-wetting phase and the wetting phase, there is a pressure difference called capillary pressure $P_c$ between the gas and the liquid. The capillary pressure drains the liquid content sandwiched between the two gas phases, thins the thickness of the lamellae and finally is responsible for the rupture of metastable foam films. The capillary pressure is counterbalanced by the repulsion force originating from the two adsorbed surfactant layers at the gas-liquid interfaces. The limiting capillary pressure $P_c^*$ corresponds to the maximum capillary pressure that a flowing foam film can withstand. In other words, the limiting capillary pressure of flowing foam in porous media is the equivalent of disjoining pressure in static systems. Yet, unlike the disjoining pressure, which is a thermodynamic variable for a static foam film, the limiting capillary pressure is dependent on a series of operating conditions. The higher the limiting capillary pressure $P_c^*$ is, the stronger the foam film is in porous media. The value of limiting capillary pressure $P_c^*$ can be estimated from the Leverett j function $f(J(S_w))$ as shown in Equation 4-6. The parameter $\sigma$ is the surface tension between the surfactant solution and the gas; $\phi$ is the porosity; and is $k$ the rock permeability.

$$P_c^* = J(S_w^*) \cdot \sigma \cdot \sqrt{\frac{\phi}{k}} = J(f_{mdry} - S_{wc}) \cdot \sigma \cdot \sqrt{\frac{\phi}{k}}$$  \hspace{1cm} \text{Equation 4-6}
The Figure 4-4 shows the calculated limiting capillary pressure $P_c^*$ as a function of the inverse of the square root of the rock permeability $\frac{1}{\sqrt{k}}$. It can be clearly seen that the $P_c^*$ is significantly correlated with the rock permeability. The value of $P_c^*$ decreases as the rock permeability increases. It indicates that foam film is less stable in high permeability regions whereas stronger in low permeability regions. The finding is in consistency with the observations reported in literature\textsuperscript{87} that even though lamellae are more stable in low permeability rocks, the overall apparent viscosity is still higher in high permeability rocks.

![Figure 4-4 Limiting capillary as a function of rock permeability](image)

It is also noticeable that the average value of $epdry$ in our study is considerably smaller than some literature suggested values\textsuperscript{83,91}. The small value of $epdry$ infers that foam does not
collapse abruptly once the $S_w$ hits the critical value. Instead, the foam transition between the low quality region and the high quality region occurs over a small range of water saturations.

Not all foam parameters show strong permeability dependence. As shown in Figure 4-3(b), the shear-thinning behaviors of foam are similar in cores of different permeabilities and the three lines are almost in parallel with each other. The parameter $epcap$ in shear dependent function $F_{shear}$, are all approximately equal to the value of 1. It indicates that the pressure gradient of foam flow in our experimental conditions is, to some extent, irrelevant to the total flow rate and that the foam flow in the reservoir cores exhibit Bingham-like fluid properties. It is discovered in literature\textsuperscript{92} that a large portion of gas is trapped as stationary phase when foam presents in the porous media. Our observed trend can be explained by the hypothesis that the stationary fraction of the gas decreases proportionally as a function of the total flow rate or the local capillary number. Therefore the measured pressure drop seemed to be constant over the measured flow rate range.

As introduced, the parameter $fmmob$ sets the reference to the maximum mobility reduction of gas phase. Yet, $fmmob$ cannot be used as a direct measure of foam strength because the value of $fmmob$ is dependent on the choice of $fmcap$ which is tunable and is not a foam parameter per se. A better alternative to compare the foam strength in rocks of varied permeability is to use $fmmob \cdot fmcap^{epcap}$. As shown in Figure 4-5, the value of $fmmob \cdot fmcap^{epcap}$ is linearly related to the rock permeability in a semi-log plot. In other words, the maximum mobility reduction of the gas phase increases exponentially as the permeability increases. The discovery is in accordance with the observation that foam apparent viscosity increases as the rock permeability increases.
Figure 4-5 Comparing maximum mobility reduction as a function of rock permeability: the value of $f_{mob} \cdot f_{mcap}^{e_{pcap}}$ increases exponentially as a function of rock permeability

4.5. Conclusions

A series of foam flooding experiment were conducted in actual reservoir cores of varied permeabilities (57.5 mD, 191.0 mD, and 493.0 mD) at elevated reservoir temperature (94 °C). Foam apparent viscosity was calculated from the pressure data as a function of the foam quality and the total superficial velocity. It is observed that the foam strength is significantly correlated with the rock permeability. Foam exhibits stronger apparent viscosity in cores with higher permeability and vice versa.

Experiment data then was fitted to a texture-implicit local-equilibrium foam model. It is observed that some foam model parameters show strong rock permeability dependence. The parameter $f_{mdry}$ tends to decrease as the rock permeability increases. It is also found that foam exhibits a shear thinning behavior in the flow-rate-scan experiment. It infers that in the real reservoir, foam shear-thins in the near well-bore region and restores its high apparent viscosity
when it propagates far away from the well. Nevertheless, the parameter $epcap$ is found to be around 1. Under our experiment condition, the foam shows Bingham-like rheological behavior and the flowing portion of the gas in the presence of foam depends on the total flowrate.
Chapter 5

Foam-Oil Interaction in Porous Media Part I:
Microfluidic Visualization at the Pore-level*

5.1. Background

The success of utilizing foam for these applications relies on a thorough understanding of the interaction between the foam, solid surfaces, and fluids such as crude oil and dense non-aqueous phase liquids (DNAPLs). Much research has been conducted to investigate the mechanisms of foam flow in porous media on different length scales. Traditionally, these displacement experiments have been performed in rock and sandpack systems.\textsuperscript{7,32,33,71,73,80,93} Still, little is understood about the pore-scale dynamics of these systems, and less is known about the fluid interactions between the displacing phase and displaced phase within the porous media.

* (i) Siyang (Sean) Xiao conducted the micromodel experiments and contributed equally
(ii) IFT measurements and MatLab imaging processes attributed to Eric D. Varva
Typically, the connected pore networks of porous media are on the scale of micro- or nanometers. Fluid interactions are challenging to study on this length scale due to the high resolution required to accurately visualize mechanisms of concern. Microfluidic devices have recently been shown to be a promising tool for understanding the fundamental mechanisms of foam-oil interactions in porous media\textsuperscript{16,94–97}. By combining microfluidic technology with optical microscopy and high-speed visualization\textsuperscript{92,98–100}, we are able to overcome these issues and provide detailed information about the pertinent fluid interactions at play on the pore level.

An example of using microfluidics to probe the foam flow in porous media is done by Geraud et al.\textsuperscript{92} who measured bubble velocity and size in an oil-free water-wet model porous media as a function of various control parameters (mean velocity, initial mean bubble size, surfactant used). It was found that the local intermittency of foam flow in porous media resulted in strong fluctuations of the local pressure gradient which we believe has the potential to mobilize disconnected pockets of trapped oil.

Another example was demonstrated by Conn et al.\textsuperscript{16,98}, who successfully visualized foam flow in a paraffin oil saturated heterogeneous porous media. The choice of oil and media material in these experiments resulted in several limitations. Paraffin oil did not result in significant foam destabilization, whereas the light hydrocarbon components in crude oil are thought to be detrimental to foam stability\textsuperscript{18,101,102}. Moreover, the unstable surface-wetting properties of polydimethylsiloxane (PDMS) cause the initially hydrophilic surfaces of the microfluidic device to quickly and spontaneously become hydrophobic\textsuperscript{103}. As surface wettability is thought to greatly influence foam transport in porous media\textsuperscript{104–106}, we chose to construct our micromodels from a material with a more predictable wetting profile.
With these factors in mind, we argue that the mechanisms by which foam displaces crude oil remain largely unexplored. Furthermore, the high oil-recovery efficiency observed in paraffin-oil displacement studies does not necessarily guarantee the same success in a more realistic scenario involving crude oil. This is because foam has a much higher tolerance to paraffin oil than crude oil. Also, compositional complexity in crude oil could possibly result in more intriguing interactions with the foam lamellae and the porous media surface that are not seen in presence of the paraffin oil. Therefore, our experiments aim to compare the behavior of foam in the presence of crude oil to that which has been observed with paraffin oil.

In this work, we first describe the unique transport of foam in porous media in the presence of crude oil. In particular, we compare and explain the displacement behavior of both paraffin and crude oil by foam within the novel context of the three characteristic zones that can be seen in Figure 5-1. In the first zone, the displacement front, foam is destabilized by oil and bubble coalescence is observed. We explain these observations in terms of the entering and spreading coefficients of the oil and liquid lamellae of the foam. In the second zone, the transition zone, surface wettability is altered from an oil-wet to a water-wet state. We provide validation for this transition via the water receding contact angles, and several qualitative observations are made to further define this zone. In the third and final zone, the foam bank, destroyed foam is re-generated in-situ. We describe the mechanisms of foam generation that can occur in porous media and discuss those which did and did not appear in our systems. Lastly, we highlight our updated mechanistic understanding of the “smart rheology” behavior of foam in porous media as an improved explanation for what has previously been described as “phase separation” in the literature. Our three-layered model porous media design consists of a high-permeability region, a fracture region and a low-permeability region from top to bottom. We observe that foam first enters the
fracture region then diverts fluids to the high- and low-permeability region consecutively. We discuss the driving force of this rheological behavior in terms of the capillary discontinuity between the three permeability layers.

![Diagram of foam bank zone, transition zone, and displacement front zone.](image)

Figure 5-1 Optical microscopy image highlighting the various zones that appear as foam displaces crude oil in a heterogeneous porous media. Scale bar: 500μm.

5.2. Materials and Methods

The surfactants we used were alpha olefin sulfonate C14-16 (AOS) (Stepan) and lauryl betaine (LB) (Mackam Lab). These surfactants are commonly used as strong foaming and foam boosting agents respectively\(^{59,107,108}\). Specifically, when LB is added to AOS solutions, a synergistic effect occurs in which the overall packing density of the surfactant molecules on the interfaces increases resulting in greater resistance to distortion\(^{89}\). Both surfactants were diluted to 1 wt% in deionized (DI) water. Blue food dye was added to help visualize the aqueous phase with
negligible effect on the rheological and interfacial properties. An AOS/LB mixture was prepared by blending solutions of 1wt% AOS and 1wt% LB in a 1:1 ratio.

A crude oil sample from the Middle East and a paraffin oil (BDH Chemicals, CAS: 8042-47-5) were used as the oil samples in our experiments. The dark brown crude oil is easily differentiated from other phases using optical microscopy. Paraffin oil is naturally colorless; therefore, a red dye was blended into this oil (Oil Red O, Sigma) for visualization purposes. Several pertinent properties of both the crude and paraffin oil are listed in Table 5-1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Crude Oil</th>
<th>Paraffin Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity (°)</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>5.4</td>
<td>40</td>
</tr>
<tr>
<td>Surface tension (mN/m)</td>
<td>20.4 ± 0.9</td>
<td>28.6 ± 1.5</td>
</tr>
<tr>
<td>IFT in DI water (mN/m)</td>
<td>22.2 ± 0.6</td>
<td>30.0 ± 1.1</td>
</tr>
<tr>
<td>IFT in 1 wt% AOS/LB Mixture (mN/m)</td>
<td>1.1 ± 0.1</td>
<td>11.6 ± 0.8</td>
</tr>
<tr>
<td>Saturates (wt%)</td>
<td>69.6</td>
<td>100</td>
</tr>
<tr>
<td>Aromatics (wt%)</td>
<td>22.0</td>
<td>0</td>
</tr>
<tr>
<td>Resins (wt%)</td>
<td>7.2</td>
<td>0</td>
</tr>
<tr>
<td>n-C5 Asphaltenes (wt%)</td>
<td>1.2</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 5-2(a) Photograph of microfluidic device used for experiments and 3-D CAD generated view of the micromodel illustrating permeability contrast. Scale bar: 1 cm. (b) Schematic of the microfluidic device illustrating port placements. Data is captured at the entrance of the porous media as indicated by the optical microscopy images depicting 100% crude oil saturation initially followed by images upon foam injection. Microscopy images are image processed using Matlab where oil, surfactant solution, and gas are colored red, blue, and green, respectively. Scale bar: 500 μm.

To probe the viscosifying nature of foam, the device geometry was designed with extreme heterogeneity perpendicular to the primary direction of flow. Three regions of varying permeability were incorporated into this device: a high-permeability region, a low-permeability region, and a simulated fracture between the two regions, as shown in Figure 5-2(a). The porosity of the flow spaces was achieved by designing circular posts of two different sizes to obstruct the flow. The posts in the high permeability region have a larger radius, and those in the low permeability region have a smaller radius. The pertinent dimensions of this device are given in Table 5-2, and a constant flow channel thickness of 20-μm was chosen.
### Table 5-2 Dimensions of the heterogeneous micromodel device

<table>
<thead>
<tr>
<th></th>
<th>Diameter of post (μm)</th>
<th>Pore size (μm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-perm</td>
<td>182</td>
<td>100</td>
<td>67</td>
</tr>
<tr>
<td>Low-perm</td>
<td>62</td>
<td>37</td>
<td>65</td>
</tr>
<tr>
<td>Fracture</td>
<td>0</td>
<td>398</td>
<td>100</td>
</tr>
</tbody>
</table>

Previously, Conn et al. utilized polydimethylsiloxane (PDMS) to construct the microfluidic porous media devices\(^95\); however, PDMS swells considerably in the presence of light organic solvents, which causes unpredictable deformation of the microfluidic geometry. Glass and silicon-based micromodels are usually considered superior alternatives\(^94\); however, the fabrication of these devices involves hydrofluoric acid etching and can be both expensive and time consuming. As an alternative to traditional PDMS, we cast our porous media micromodels using a UV-curable epoxy: NOA 81 (Norland Products Inc.), which has previously shown chemical resistance to light organic solvents\(^109–113\). To fabricate our micromodel, we first created a PDMS mold. This procedure is described in the literature in detail\(^16,95,103\). NOA 81 was then poured onto this mold and exposed to UV light (Novascan PSD-UV) for 25 minutes. Once the NOA 81 micromodel was fully cured, it was peeled off the PDMS mold. Then, the casting was bonded to a flat piece of NOA 81 functioning as a base after treatment with oxygen plasma for 30 seconds. Since NOA 81 is a relatively stiff material, the device was left undisturbed for 24 hours to allow the internal stresses to relax.

As shown in Figure 5-2(b), the micromodel was initially pre-saturated with crude oil by flowing from the outlet port to the drain port and then allowed to age for an additional 24 hours to allow NOA 81 to become oil-wet, which was confirmed used contact angle measurements described later in this section. A foam generator was utilized to mix the surfactant solution and gas
to obtain foam of a desired quality. The flow rate of surfactant solution was controlled with a syringe pump (Harvard® Pump 33). A long capillary tube (length: 10 m ID: 25 μm, SGE Analytical Science) was used to connect the N₂ gas tank to the foam generator. This system allows for ultra-low mass flow rates that are not achieved reliably with commonly used mass flow controllers. A pressure gauge and needle valve were set at the inlet of the capillary tube. The mass flow rate of N₂ at the outlet of the tube was precisely controlled by tuning the inlet gas pressure.

The mass flow rate was correlated with the inlet pressure by combining the ideal gas law with Darcy’s law, assuming laminar ideal gas flow, as shown in Equation 5-1 where \( \rho \) is density of the gas, \( u \) is mean velocity, \( M \) is molar weight of N₂, \( R \) is universal gas constant, \( T \) is temperature, \( k \) is capillary-tube permeability, \( \mu \) is gas viscosity, \( L \) is capillary-tube length, \( p_I \) is inlet pressure, and \( p_O \) is outlet pressure. For all experiments, \( p_I \) ranged from 100-200 psig and \( p_O \) equaled the pressure from at the inlet to the micro-model which was a maximum of 20 psig. Considering \( p_O \) was an order of magnitude smaller than \( p_I \), the mass flow rate was assumed to be a function of \( p_I \) only. A characteristic Reynolds number of 0.9 accurately described the flow in the capillary tube.

\[
\rho u = - \frac{pMk}{RT\mu} \frac{\partial p}{\partial x} = - \frac{kM}{2RT\mu} \frac{\Delta(p^2)}{L} = - \frac{kM}{2RT\mu} \frac{p_O^2 - p_I^2}{L} \tag{Equation 5-1}
\]

Foam was initially injected into the micromodel from the inlet port to the drain port until steady foam flow was achieved. Then foam was directed into the porous media by closing the drain port. Displaced oil was collected from the outlet port. A high speed camera (Phantom v4.3) connected to an inverted microscope (Olympus® IX71) recorded the foam flooding process at a capture rate of 50 frames per second. The inlet of the porous media was chosen as the region of interest to evaluate foam displacement of crude oil.
During video analysis, each frame of the experimental recording was extracted and the three fluid phases, gas, surfactant solution, and oil, were digitally identified using image processing methods. This data processing method was accomplished in MATLAB using the Image Processing Toolbox. In MATLAB, the RGB values of each pixel for every frame of a video were generated. Each pixel was assigned to a distinct phase: oil, surfactant solution, or gas. Consequently, the saturation of the micromodel flow channels by each phase was quantified in terms of the abundance of each pixel color. Microscopy images were digitally enhanced to clearly identify each phase: crude oil is red, surfactant solution is blue, and gas is green.

Contact angle measurements were performed in a transparent quartz cuvette (5 x 5 x 5 cm) using a goniometer system (KSV CAM-101). The cuvette was filled with the water or the surfactant solution. A block of NOA 81 (approximately 1 x 1 x 0.1 cm) was then immersed into the aqueous phase. A crude/paraffin oil droplet was injected from below the NOA 81 block using a hooked needle. The droplet attached to the underside of NOA 81 surface under the influence of buoyancy. Sufficient time was allowed for the contact angle to stabilize, and the final value was recorded. All measurements were performed at ambient temperature and pressure.

The surface tension and interfacial tension of different fluids were measured via the pendant drop method and/or a spinning drop tensiometer (KRÜSS SITE100). To perform the pendant drop method, a liquid (water, surfactant solution, or oil) drop was suspended in air from a vertically oriented needle. The profile was imaged using a goniometer system (KSV CAM-101) and fitted to the Young-Laplace equation to calculate the surface tension. For the interfacial tension (IFT between an aqueous phase and oil phase) measurement, an oil droplet was injected from a hooked needle into the bottom of a quartz vessel filled with the corresponding aqueous phase. The spinning drop tensiometer was used in when the IFT was on the order of 1 mN/m or less. Before
recording the final value, all the measurements were left for sufficient time such that no further changes were observed in the shape of the droplet.

5.3. Results and Discussions

5.3.1. The Displacement Front Zone: Foam Destabilization

Foam was injected into the micromodel to recover paraffin oil, Figure 5-3(a), and crude oil, Figure 5-3(b) respectively. In presence of crude oil, foam coalesced into large gas slugs at the displacement front whereas the bubbles showed greater stability in the case of paraffin oil. This coalescence resulted in the large bubbles evident in Figure 5-3(b). The difference in the foam-oil interactions can be explained by calculating the entering and spreading coefficients for the two types of oil\textsuperscript{114}. 
Figure 5-3 Optical microscopy images comparing foam displacement of (a) paraffin oil, which is not significantly detrimental to foam and (b) crude oil, which destabilizes the foam by rupturing the liquid lamella. Scale bar: 500 μm

To affect foam stability, oil must first enter the gas-water interface. The ability of oil droplets to enter the gas-water interface can be quantified via the entering coefficient $E$ in Equation 5-2 where $\sigma_{wg}$ is the water-gas surface tension, $\sigma_{ow}$ is the oil-water interfacial tension, and $\sigma_{og}$ is the oil-gas surface tension.

$$E = \sigma_{wg} + \sigma_{ow} - \sigma_{og}$$ \hspace{1cm} \text{Equation 5-2}

As shown in Figure 5-4(a), a negative entering coefficient $E$ implies that oil droplets prefer to stay in the aqueous phase to minimize the total free energy of the system. A positive entering coefficient $E$ indicates that, thermodynamically, oil droplets are inclined to enter the gas-water
interface and to increase the likelihood of rupturing lamellae. The relevant interfacial properties of the oils tested have been listed in Table 5-1. The measured surface tension is about 35.5 mN/m. Inserting these values into Equation 5-2, the calculated entering coefficients of both crude oil and paraffin oil, shown in Table 5-3, were found to be positive. This result indicates that both the crude oil and the paraffin oil droplets are inclined to enter the interface.

The relevant interfacial properties of the oils tested have been listed in Table 5-1. The measured surface tension is about 35.5 mN/m. Inserting these values into Equation 5-2, the calculated entering coefficients of both crude oil and paraffin oil, shown in Table 5-3, were found to be positive. This result indicates that both the crude oil and the paraffin oil droplets are inclined to enter the interface.

Table 5-3 Entering and Spreading coefficients for paraffin and crude oil

<table>
<thead>
<tr>
<th></th>
<th>Paraffin Oil</th>
<th>Crude Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entering Coefficient</td>
<td>18±3</td>
<td>16 ±2</td>
</tr>
<tr>
<td>Spreading Coefficient</td>
<td>-5±3</td>
<td>14 ±2</td>
</tr>
</tbody>
</table>

What makes the difference is the sign of the spreading coefficient. After entering the gas-water interface, oil droplets can either spread or stay as oil lenses. Droplet spreading over the interface is governed by the spreading coefficient\(^ {115} \) in Equation 5-3. If \( S > 0 \), the oil will spread out onto the interface, replacing a gas-water interface with an oil-water interface, as shown in Figure 5-4(c).

\[
S = \sigma_{wg} - \sigma_{ow} - \sigma_{og}
\]  

Equation 5-3

Though these two coefficients, \( E \) and \( S \), are relatively simply defined, the differences in the values of entering and spreading coefficients between paraffin oil and crude oil offer insight into the differences in the oil-foam interactions of the two systems. Paraffin oil has a negative spreading coefficient whereas this value for crude oil is positive. This case is illustrated by the cartoon in Figure 5-4(b). Simply put, paraffin oil will preferentially exist as a lens on the liquid lamella whereas crude oil will spread on the liquid lamella which tends to be more detrimental to the foam
film stability. This is because the newly formed crude oil-water-gas asymmetric film may affect the disjoining pressure that counterbalances the capillary pressure. Specifically, crude oil can alter the charge distribution from the gas-aqueous interface to the oil-aqueous interface by affecting the surfactant adsorption behavior; thus, the electrostatic repulsion between the two interfaces can be reduced\textsuperscript{18,51,116}. In addition, the van der Waals component of disjoining pressure, which is a strong function of bulk-phase density, can also be altered when one side of the lamella is replaced by oil\textsuperscript{68,117}. Also dynamic effects are involved. For example, the spreading can cause local thinning of the lamella and therefore lead to the foam destruction. Besides entering and spreading coefficient, it needs to be pointed out that the bridging coefficients $B$ for both crude oil and paraffin oil are positive. Yet, the foam destabilization by the paraffin oil was not readily observed.

Figure 5-4 (a) An oil droplet stays in the aqueous phase if $E < 0$ and (b) enters the gas-water interface if $E > 0$. Paraffin oil has a positive entering coefficient but does not readily destabilize the foam lamella interface. (c) An oil droplet spreads on gas/water interface if $E > 0$ and $S > 0$. Crude oil has both a positive entering and spreading coefficient, which destabilizes the gas-liquid lamella of foam.
Some gas bubble coalescence was observed along the displacement front in the case of the crude oil, as shown in Figure 5-3(b), but there were slightly lower coalescence rates outside of the fracture. This is because the surfactant enters the high- and low-permeability regions in advance of the gas. The surfactant solution separates the bubbles from the oil and acts to partially protect the thin liquid lamellae from contacting the oil when the gas invades the porous media. The mechanisms for this fluid diversion and redistribution are the primary topic of discussion in section 5.3.4.

5.3.2. The Transition Zone: Surface Wettability Alteration from Oil-wet to Water-wet

Since the micromodel was aged in oil before foam flooding, it was initially oil-wet. In oil-wet systems, aqueous lamellae typically de-wet from the surface leading to foam destabilization and coalescence. This phenomenon is enhanced by the surface-active components, such as asphaltenes and/or naphthenic acids, that were present in the crude oil but absent in the model paraffin oil\(^9,10,118,119\). As can be seen in Table 5-4, the crude oil system had larger water receding contact angle than the paraffin oil system in water. The more hydrophobic surface found in the crude oil system had a greater tendency to de-wet water films and rupture advancing lamellae impinging on the hydrophobic portion of the media making foam in this system less stable in the initial stages of foam flooding. However, as the flooding continued, surfactants adsorbed onto the hydrophobic surface making it more hydrophilic; thus, the foam soon became stable again. This wettability alteration has not been addressed previously in the work of Conn et al., for foam was not observed to exhibit significant coalescence. Because crude oil destabilizes the foam liquid lamellae upon initial contact, this wettability transition is a critical step in the current displacement study. All forms of in-situ foam generation require that stable aqueous films wet the porous media...
surface, and the success of foam flooding shows a strong positive correlation with the number of lamellae in the foam.

Oil lamellae appeared at the displacement front when surfactant solution from the foam contacted and mixed with oil. The oil lamellae formed via the leave-behind mechanism as surfactant solution invaded the hydrophobic NOA 81 microchannel. Comparing Figure 5-5(a) and Figure 5-5(b), the paraffinic oil lamellae were generally thicker than those of crude oil lamellae. This is likely due to the higher viscosity of paraffin oil as compared to that of crude oil, which typically slows oil drainage as the aqueous phase invades the porous media; therefore, relatively thicker paraffin oil lamellae formed. The wettability alteration is partially evidenced by paraffin and crude oil lamellae that formed at the displacement front and were replaced by aqueous lamellae films in the transition zone, as shown in Figure 5-5(c) and Figure 5-5(d). The aqueous lamellae that span across the pore throats indicate removal of the oil that initially wetted the NOA 81 surface, likely due to surfactant adsorption. This competitive adsorption of the surfactant onto the surface creates a more favorable environment for foam generation and propagation through the porous media.
Figure 5-5 Optical microscope images of initial stage of foam displacement of (a) paraffin oil and (b) crude oil. The zoomed in highlighted region at the displacement from illustrate oil lamellae connecting pore throats, indicative of an oil-wet condition. Optical microscope images at a later time of foam displacement in the (c) paraffin oil and (d) crude oil shows aqueous lamella bridges between pore throats, indicative of a transition to a water-wet system. Scale bar: 500μm

The wettability alteration by surfactant is further validated by the water contact angle measurement in presence and absence of 1:1 AOS/LB surfactant solution as shown in Table 5-4. Admittedly measuring water advancing contact angle would be more appropriate to rationalize foam displacing oil scenario. We conducted static water receding contact angle measurements. Both the crude oil and the paraffin oil in the AOS/LB solution have lower water receding contact angle than that in the pure water.
Table 5-4 Water receding contact angle measurement with water and surfactant solution

<table>
<thead>
<tr>
<th>Aqueous Phase</th>
<th>Water</th>
<th>1:1 AOS/LB surfactant solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Type</td>
<td>Crude Oil</td>
<td>Paraffinic Oil</td>
</tr>
<tr>
<td>Water Receding CA on NOA 81 (°)</td>
<td>71±4</td>
<td>58±4</td>
</tr>
</tbody>
</table>

Concurrent with the wettability alteration, oil emulsification took place in both oil systems. Figure 5-6(a) and (b) demonstrate the typical oil solubilization and emulsification observed. The emulsification occurred because the surfactant decreases water-oil interfacial tension. At zero salinity, an O/W emulsion of low-oil content, formed by solubilizing trapped oil into the aqueous phase to then be swept out of the field of view with further foam flooding. Most of the emulsification took place in the matrix region where the relatively higher shear rate and greater agitation led to the creation of new oil-water interfaces. Most of these emulsified oil droplets were then transported to the fracture zone to minimize flow resistance in the system.
5.3.3. The Foam Bank: In-Situ Lamella Generation in Water-wet Conditions

The longevity and strength of foam depends on the stability of the liquid lamellae films, which form between individual gas bubbles in the foam. According to bulk foam observations, foam undergoes constant coalescence due to liquid drainage, diffusion coarsening, capillary suction, and thermal/mechanical fluctuations. Concurrent with coalescence processes, foam flowing through porous media can be regenerated in-situ due to complex dynamic foam-solid interactions within the porous media. There are three conventional mechanisms described in
literature for foam generation in porous media. The first mechanism, called snap-off\textsuperscript{11,96,97,121}, occurs when liquid is drawn upstream due to capillary forces and accumulates in a constricted region until a bubble breaks off from the gas phase. The second mechanism, called lamella-division\textsuperscript{14,15,30}, occurs when a single lamella divides into two new lamellae because the local pressure gradient is strong enough to push a single lamella through a branching point and is large enough for the bubble train to have multiple branch points. The third mechanism, called leave-behind\textsuperscript{13}, occurs when liquid drains from a local region of porous media and leaves behind thin lamellae parallel to the direction of flow. Finally, a fourth unconventional mechanism, called pinch-off\textsuperscript{16}, was first identified and introduced in a smooth capillary microfluidic device with a constriction point. This mechanism refers a bubble-bubble interaction that occurs when two or more bubbles squeeze through a constriction in the direction of flow. One or both of the bubbles can be pinched into multiple bubbles that add new lamella, which in turn leads to a stronger foam in the foam bank region.

Previous studies have focused on systems with large pore body to pore throat aspect ratios for which snap-off readily occurs; however, in this study we decreased this parameter to better resolve the subtle fluid interactions. Roof et al.\textsuperscript{122} investigated the formation of oil droplets in 3-D capillary tubes. Based on their finding, the time for snap-off to occur in our pattern design approaches infinity. Therefore, snap-off is inherently prohibited from taking place in our micromodel, and the reader should interpret the following discussion with this constraint in mind.

Lamella-division and pinch-off are the two mechanisms responsible for in-situ foam generation in NOA 81 micromodels given our experiment conditions. This observation marks the first time that the pinch-off mechanism has been visually identified as a mechanism of in-situ foam generation in patterned porous media.
As shown in Figure 5-7(a), lamella division took place in areas of relatively dry foam in which foam bubbles exhibited polyhedral geometry and each bubble was larger than a single pore. It is important to recognize that lamella division can only generate bubbles no smaller than the void space between obstructions. Unlike lamella division, neighbor-induced pinch-off can generate bubbles much smaller than the pore size. Pinch-off is observed in relatively wet regions where bubbles can deform easily. As can be seen in Figure 5-7(b), a pink bubble pinned a green bubble against a post and stretched it until two points on the interface of the green bubble met and the bubble broke into two separate bubbles. Neighbor-induced pinch-off differs from lamella division in its driving force and in the size of bubbles it produces. The driving force for neighbor-induced pinch-off is the tensile stress that originates from the morphology change of individual bubbles whereas the driving force for lamella division is the pressure difference across the liquid film, and no significant bubble deformation is observed.

The observation of pinch-off in patterned porous media is notable because this mechanism offers a route to foam generation even at conditions under which the conventional mechanisms do not take place. Moreover, the size of bubble generated by pinch-off can be smaller than the characteristic dimension of the pore as shown in Figure 5-7(b). This new finding is intriguing because bubbles smaller than the pore-throat radius cannot be generated from the three previously described foam generation mechanisms. Theoretical calculations\textsuperscript{123} have shown that diffusion coarsening does not contribute to foam behavior in porous media. This theory rests upon the hypothesis that foam bubbles in porous media always occupy the whole pore structure. However, diffusion coarsening occurs at significant rates among small bubbles. Our observation of bubbles smaller than the pore structure sheds light upon the governing mechanisms that weaken foams residing in porous media. The previous finding\textsuperscript{32} that foam strength is correlated with the diffusion
rate of gas molecules across thin liquid films is also in line with the generation of small bubbles by pinch-off.

![Diagram](image)

**Figure 5-7** Time series of microscopy images taken to illustrate mechanisms by which new liquid lamellae is formed in the water-wet foam bank region. (a) Lamella division was observed as a gas bubble invades a pore throat and divides to generate new liquid lamellae. (b) Neighbor-bubble- pinch-off was observed to generate new liquid lamellae. Scale bar: 200μm.

Aqueous foam lamellae formed by the leave-behind mechanism was rarely observed at the selected experimental conditions. Since the porous media is initially saturated with only oil, and both gas and liquid are injected simultaneously into our micromodel, the leave-behind mechanism does not readily take place. However, as mentioned previously, oil films formed by the leave-behind mechanism were indeed observed which suggest the model is more oil-wet after being equilibrated with oil.

A sharp transition metric was not quantified between the three characteristic regions. The evolution from the displacement front zone to the foam bank region was instead illustrated by
tracking the change in average bubble effective radius as a function of total pore volumes of injected fluids. As shown in Figure 5-8, at small injected pore volumes (PV) values, the average bubble size is large due to coalescence of foam in the highly oil-saturated environment. This is indicative of a displacement front zone. With increasing PV, the average bubble size decreases in a manner signifying a transition whereby the wettability alteration of the channels begin to stabilize the foam. When the bubble size reaches a local equilibrium value, and most of the oil is displaced, the system is considered to be a foam bank in which the foam generation rate balances the foam coalescence rate.

Figure 5-8 Characteristic bubble size and oil recovery efficiency with respect to total injected pore volumes (PV) as dimensionless time. The bubble size increased dramatically in the displacement front zone and started to decrease in the transition zone. The average bubble size leveled off in the foam bank zone where most oil was displaced
5.3.4. The Smart Rheology of Foam

A comparison among water flooding, gas flooding, and foam flooding is shown in Figure 5-9. The oil saturation is plotted as a function of pore volume (PV) in Figure 5-9. For the purposes of our analysis, we define one PV as the volume of fluid required to saturate the total void space in the visualized portion of the porous media. From the plot in Figure 5-9(d), it is clear that foam flooding outperforms either water flooding or gas flooding. We also note that foam flooding is the only system where the three characteristic zones arise. Due to the low density and viscosity of $N_2$, gas almost exclusively swept oil from the fracture region and left the oil in the two matrix regions largely untouched. Gas failed to enter the matrix because of the relatively high capillary entry pressure required to do so compared to the pressure drop across the device. As shown in Figure 5-9(a), using gas as the displacing fluid, over 70% oil was left in the device after 1 PV of gas injection. As shown in Figure 5-9(b), water flooding is better than gas flooding at displacing oil. This is because the IFT between water and oil is lower than that of gas and oil. Water can enter both the low-permeability and high-permeability regions but failed to sweep oil trapped in small pores as efficiently as foam. Thus, the sweep efficiency of water is still low compared to that of foam. As shown in Figure 5-9(c), after 1PV of foam injection, almost all the oil in the fracture and high-permeability regions was displaced, and a large fraction of the oil in low-permeability region was also displaced. For this comparison study, the injection foam quality was 87.5%.
Figure 5-9 Optical microscopy images comparing crude oil displacement after injecting (a) N₂ gas, (b) water, and (c) foam after breakthrough. (d) Graph depicting crude oil saturation (%) versus pore volume injected, a nondimensional measure of injected fluid volume. Scale bar: 500μm
Figure 5-10 (a) Evolution of the foam gas-fraction in the high-perm and low-perm regions. Gas enters the high-perm region first followed by the low-perm region. At steady-state, the gas content in the high-perm region is significantly greater than that in the low-perm region; (b) Capillary pressure schematic in the high- and low-perm regions. The differences in capillary entry pressure and equilibrium water saturations are responsible for the smart rheological properties of foam.

The reasons for the superior oil removal efficiency of foam are twofold. First, as described thoroughly in the literature\textsuperscript{11,73,124–126}, the overall apparent viscosity of foam is greater than that of a single-phase displacing fluid. Second, foam displays responsive rheology when flowing through porous media. Foam rheology is self-tuning in response to reservoir heterogeneity in that the bulk fluid will separate into relatively dry and wet foam phases in the higher and lower permeability regions respectively. As shown in Figure 5-10(b), at equilibrium the water saturation in the low-permeability region is considerably larger than the high-permeability region. In this way, a higher flow resistance occurs in regions of high permeability which diverts fluids to lower permeability regions.
The driving force behind foam responsive rheology is partially explained by the difference in capillary entry pressures between the different permeability regions as described in Conn. et al. The capillary entry pressure $p_{g,\text{entry}}$ is inversely proportional to the radius of pore constriction $r_{\text{pore-constriction}}$ as shown in Equation 5-4.

$$p_{g,\text{entry}} = \frac{2\sigma_{wg}}{r_{\text{pore-constriction}}} \quad \text{Equation 5-4}$$

The value of $p_{g,\text{entry}}$ is higher in regions of lower permeability where the neighboring posts were closer as shown in Figure 5-10(b). In other words, $r_{\text{pore-constriction}}$ is smaller in the lower permeability region; thus, gas does not enter into this region as readily as it does in the high permeability region.

Beyond the initial points of entry into either the high- or low- permeability regions, fluid redistribution is dictated by the capillary discontinuity between these two regions. Specifically, given equal gas saturation between the regions, bubbles in the low-permeability region have a higher pressure than those in the high-permeability region. This is because the capillary pressure between gas and water is inversely proportional to the square root of the permeability as shown in Equation 5-5, in which $J(S_w)$ is the Leverett J function, $\theta$ is the contact angle, $\phi$ is porosity and $k$ is permeability.

$$p_g = p_w + P_c = p_w + J(S_w) \cdot \sigma_{wg} \cdot \cos \theta \cdot \sqrt{\phi/k} \quad \text{Equation 5-5}$$
This discontinuity in capillary pressure will drive the gas phase from low permeability region to high permeability region. Therefore, at capillary equilibrium, the gas content in the low-permeability region is expected to be less than that in high-permeability region. As can be seen in Figure 5-9(c), foam in the high permeability region was readily observed to be drier than that in the low permeability region.

Fluid redistribution ultimately resulted in morphological disparity between bubbles in the two matrix regions. Foam bubbles exhibit a more spherical shape on average in the low permeability region due to a higher liquid saturation. Conversely, a more polyhedral bubble shape in the high permeability region was observed due to the relative dryness of the foam here. From a rheological perspective, the increase in foam apparent viscosity originated from the liquid lamellae that blocked the flowing path of the gas phase. Therefore, foam showed a higher apparent viscosity in high-permeability region because of a higher lamella density compared to that in the low-permeability region. Consequently, foam was able to mitigate the reservoir heterogeneity because of this smart rheology.

The smart rheology of foam (which is the trend observed in the direction perpendicular to the primary direction of flow) ties into the discourse of the three characteristic zones we present here for the foam flood. In a homogenous porous media with an isotropic permeability, one would observe the same characteristic zones; however, these zones imply various degrees of mobility control which would not be observed in such a system. In our experiments, we are able to observe the relative diversion into the porous media matrixes from the fracture region as a function foam destabilization. In the foam front zone, we see little diversion from the fracture to the matrix as the foam is destabilized and the mechanisms of smart rheology break down along with the mobility control. In the transition zone, we observe this diversion into the matrix beginning to occur as the
foam starts to stabilize along with the “smart” rheological mechanisms. In the foam bank zone, we observe complete diversion into the matrixes.

The rheological properties of foam differ notably from other yield-stress fluids, such as emulsion flows, particularly in terms of mitigating the reservoir heterogeneity. In quality scan experiments, foam strength maximizes at transition water saturation and decreases as the water saturation decreases. This is because the relatively high water/gas surface tension leads to foam coalescence at low water saturation. However, emulsions do not coalesce as readily as foam. Instead of observing a maximum in the apparent viscosity, the emulsion can transition from water-external phase to oil external phase as the water saturation decreases from our previous experience. The water-in-oil emulsion can be very viscous and ultimately block the flow instead of diverting fluids to improve the displacement conformance.

5.4. Conclusion

Characterization of foam flooding of oil-wet porous media has been successfully explored using an NOA 81 microfluidic platform. Three distinct flooding zones: the displacement front, the transition zone, and the foam bank were characterized and rationalized in detail. Coalescence of the foam was observed upon first contact with crude oil, yet the foam remained intact upon contacting the paraffin oil. Insights into these differences in foam stability can be gained from the entering/spreading coefficients. Crude oil more readily to enters and spreads on the gas-aqueous interface. Oil lamellae formation and emulsification also occurs. In the transition zone, surfactants alter the wettability of NOA 81 surface and stabilize foam bank. The wettability transition from hydrophobic to hydrophilic was verified by contact angle measurements on the NOA81 surface. In this last region, lamella-division and pinch-off were the two mechanisms for in-situ foam
generation in our experiments. For the first time, bubbles smaller than the characteristic pore size were observed forming in situ in a model porous media.

Despite the detrimental effect of the crude oil on the foam, the displacement efficiency was not diminished as guaranteed by the “smart rheology” of the foam. The foam quality of each region of permeability was quantified via image analysis, and foam was shown to respond to the porous media heterogeneity by separating into a relatively dry and wet regime in the high- and low-perm regions respectively. Due to the capillary discontinuity between the layers of different permeability, the phase separation induced morphology disparity between the layers which resulted in responsive flow resistance.
Chapter 6

Foam-Oil Interaction in Porous Media Part II: Core-level Investigation with NMR Imaging*

6.1. Background

Understanding foam-oil interactions is crucial to the successful applications of foam as an enhanced oil recovery agent (EOR). A general consensus is that oil has a detrimental effect on foam stability. Figure 6-1 shows a schematic of the oil saturation profile in a typical foam EOR project. At the gas front where the oil bank is formed, the oil saturation is higher than the critical upper limit of oil saturation $S_{oUL}$, therefore foam collapses completely and no foam exists in the red region; whereas in the green region, most of the oil has been displaced and the oil saturation drops below $S_{oLL}$, therefore foam exhibits full strength. Of interest is the yellow region

* (i) Reza Amirmoshiri conducted many of the core flooding experiments and contributed equally
   (ii) NMR measurements attributed to Zeliang Chen
in which the foam strength is a function of the local oil saturation. Formation of foam in the red region may not even be desirable because formation of foam films can hinder the transfer of gas to the oil and limit its extracting efficiency. Schramm et al.\textsuperscript{130} found out that foam was not detectable in their core-flooding experiments if the oil saturation was higher than a critical value of around 10-15\%. In contrast, Simjoo et al.\textsuperscript{60} reported successful in situ foam generations with an initial oil saturation of 40\%. The interpretation of the pressure data from Snorre field in Norway reveals a value of 40\% for upper limit of the oil saturation\textsuperscript{131}. Mannhrdt et al.\textsuperscript{132} studied various foam formulations in the presence of residual crude oil and discovered that the maximum foam mobility reduction decreased monotonically with the increase in oil saturation. However, their experiments were not single-variable controlled, as the observations were based on coreflood tests with different surfactant formulations.

![Diagram of oil saturation profile in foam EOR](image)

**Figure 6-1** Schematic of the oil saturation profile in foam EOR: foam completely collapses in the red region whereas it preserves its full strength in the green region. Our research interest is the yellow region in which foam strength is dependent on oil saturation.
Besides the effect of oil saturation, foam stability is also dependent on the oil composition\textsuperscript{133}. Several mechanisms for foam destabilization have been proposed from the bulk foam and single film studies under the static conditions\textsuperscript{18,134–136}. Simjoo et al.\textsuperscript{137} conducted bulk foam stability tests and observed that all the model oils used in their experiments destabilized the foam column. In addition, short chain hydrocarbons were more detrimental to the longevity of foam compared to the long chain hydrocarbons. However, Suffridge et al.\textsuperscript{138} noticed that the presence of oil with long chain hydrocarbons resulted in an enhancement in the foam stability compared to the foam flow in oil-free conditions. Most recently, Tang et al.\textsuperscript{139} attempted to quantify the oil effect on foam by co-injecting foam and model oil in the porous media. They found out that the limited capillary pressure decreases when oil is present in porous media and an increase in the light component fraction in the model oil results in lower pressure gradients, a similar observation to what was reported by Simjoo et al.\textsuperscript{62} and Osei-Bonsu et al.\textsuperscript{140}. However, they were not able to differentiate the oil saturation effect and the oil composition effect due to the lack of oil saturation measurements.

Considering the inconsistent observations among previous studies in literature and the lack of sufficient experimental evidence in understating the foam-oil interactions, it is, therefore, our objective to quantitatively investigate the effect of oil saturation and composition on foam transport in porous media. We firstly discuss the steady-state foam strength at water-flooded remaining oil saturation with different foam qualities. We then calculate the apparent viscosity $\mu_{\text{app}}$ of using the measured pressure data under different oil fractional flows $f_{\text{oil}}$. In this chapter, the apparent viscosity $\mu_{\text{app}}$ is defined as the normalized pressure gradient with respect to the absolute rock permeability $k_{\text{abs}}$ and total superficial velocity $u_{\text{total}}$ as shown in Equation 6-1. All
of our core-flooding experiments are followed by the NMR imaging technique to quantify the 3-phase saturation profiles.

\[ \mu_{app} = -\frac{k_{abs} \times \nabla p}{u_{total}} = -\frac{k_{abs} \times \nabla p}{u_{gas} + u_{surfactant} + u_{oil}} \quad \text{Equation 6-1} \]

6.2. Methods and Materials

6.2.1. Chemicals and Materials

Anionic surfactant \( C_{14-16} \) alpha olefin sulfonate (AOS\(_{1416}\) from Stepan) was selected as the foaming agent and utilized as received without further treatment. The surfactant was dissolved in brine at a concentration of 0.5 \( wt\% \). A complete list of salts (all supplied from Sigma Aldrich) for preparing the synthetic sea water (brine solution) are provided in Table 6-1. The DI water used to prepare all solutions has a resistivity of 18.2 \( M\Omega \cdot cm \). The salts of \( MnCl_2 \cdot 4H_2O \) and \( Na_4EDTA \cdot 2H_2O \) are the doping agents added to the brine solution to differentiate the \( T_2 \) relaxation time of the aqueous phase from that of model oils. \( N_2 \) with the industrial grade was injected with surfactant solution to generate foam. In addition, n-octane (C8) and n-hexadecane (C16) were chosen as the model oils. The n-octane was supplied from Sigma-Aldrich, and the n-hexadecane was purchased from Acros Organics, both with the purity of \( \geq 99\% \). Rock materials were consolidated Berea Sandstone cores with the dimensions of 1.5” in diameter and 6” in length. Porosity of the samples was 20\% and the average absolute permeability was around 80 mD.
Table 6-1 The list of salts with their concentrations in the synthetic sea water

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>0.67</td>
</tr>
<tr>
<td>MgCl$_2$.6H$_2$O</td>
<td>10.15</td>
</tr>
<tr>
<td>CaCl$_2$.2H$_2$O</td>
<td>1.47</td>
</tr>
<tr>
<td>NaSO$_4$</td>
<td>38.34</td>
</tr>
<tr>
<td>NaCl</td>
<td>25.21</td>
</tr>
<tr>
<td>MnCl$_2$.4H$_2$O</td>
<td>0.40</td>
</tr>
<tr>
<td>Na$_4$EDTA.2H$_2$O</td>
<td>3.33</td>
</tr>
</tbody>
</table>

6.2.2. Core Flooding Apparatus

The schematic of the experimental set-up is shown in Figure 6-2. The core was first slid into a tight-fit rubber-sleeve and then placed horizontally inside a core-holder equipped with two pressure transducers at the inlet and the outlet, respectively. Core was confined under a net pressure of 500 psi higher than the inlet pressure to prevent fluids from bypassing the core. A syringe pump-accumulator system, with the capability of working in a double flow mode and the injection accuracy of 0.01 cc/min, was utilized for injecting the surfactant solution. Nitrogen gas ($N_2$) was injected simultaneously from a gas cylinder equipped with a pressure regulator. The gas injection rates were controlled using a mass flow controller (model SLA-5850-S) with the accuracy of 0.1 SCCM. Additionally, outlet pressure was controlled via a back pressure regulator. All the equipment and the valves were controlled using the AppliLab software and the measurements were recorded every 10 seconds via a data acquisition system. The setup was later modified through adding an oil-injection system for the purpose of three-phase co-injection tests.
Figure 6-2 Schematic of the core-flood apparatus, (Vinci model CFS 700)

6.2.3. Experiment Procedure

6.2.3.1. Saturation Measurement with NMR

Nuclear magnetic resonance (NMR) is a reliable tool in determining rock-fluid properties, such as fluid content, crude oil composition, crude oil viscosity, and surface wettability. A typical NMR analysis consists of transverse $T_2$ relaxation time measurements for the fluids confined in the porous rock. Being dependent on the chemical composition of the fluids, $T_2$ values can be utilized to quantify the amount of different fluids inside the rock. However, the $T_2$ responses of the brine and the oil are not typically well-distinguished. One solution for this problem is adding a paramagnetic doping agent, such as $Mn^{2+}$, to the aqueous solution, and thereby shifting the $T_2$ response of the brine to the values lower than that of oil.
In this study, we add $Mn(EDTA)^{2-}$, a paramagnetic dopant, to the aqueous solution to differentiate the $T_2$ responses. The optimum dopant concentration for achieving sufficient $T_2$ contrast was 2 $mM$, under our experimental conditions. Additionally, 8 $mM$ of $EDTA$ was dissolved in the aqueous phase with the purpose of chelating manganese ions, and thereby minimizing manganese exchange with the clay minerals in the sandstone. As we can see from Figure 6-3, NMR scan of a bulk sample, with the known amounts of doped brine and n-hexadecane, verified a high accuracy for the saturation measurements (less than 1% error).

![Figure 6-3](image)

Figure 6-3 NMR measurement of the bulk brine-hexadecane system in a glass vial: the actual water content was 44.9%, whereas the NMR measured value was 45.3%. The error was less than 1%.

6.2.3.2. Core Preparation

For all the experiments, fresh Berea sandstone core samples were first vacuum-saturated with the doped brine using Darcy’s law with varying flowrates. The porosity was measured from
the displaced brine volume and the absolute permeability was measured with doped brine. The 100% brine saturated core samples were then scanned with NMR imaging technique to ensure uniform porosity profiles along the core and to verify the porosity value measured from the first step. Table 6-2 summarizes all the rock properties measured under ambient conditions. After the brine saturation, the core samples were ready for the foam tests. Meanwhile, the following additional steps were implemented on sample B prior to the foam injection: oil (C16) flood until the irreducible water saturation ($S_{wi}$) (Oil injected from the both ends to minimize the capillary end effect); and then water-flood until establishing the residual oil saturation ($S_{or}$). Each core-flooding test was followed by the NMR measurement. Sample D and E were both used for two continuous foam-oil co-injection tests without any cleaning procedure between the tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity ($\phi$) (%)</th>
<th>Permeability ($k_{abs}$) (mD)</th>
<th>Test Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>82</td>
<td>Foam quality scan (oil-free)</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>96</td>
<td>Foam quality scan (with water flooded remaining C16)</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>79</td>
<td>Foam-C8 co-injection ($f_{C8}$=5%)</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>85</td>
<td>Foam-C8 co-injection ($f_{C8}$=10%, and 15%)</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>92</td>
<td>Foam-C16 co-injection ($f_{C16}$=10%, and 25%)</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>115</td>
<td>Foam-C16 co-injection ($f_{C16}$=15%)</td>
</tr>
<tr>
<td>G</td>
<td>20</td>
<td>108</td>
<td>Surfactant-C16 co-injection ($f_{C16}$=15%)</td>
</tr>
</tbody>
</table>
6.2.3.3. Surfactant Injection

Prior to all the foam tests, at least 2 PV of surfactant solution (0.5wt%) was injected into the core to satisfy its adsorption on the rock mineral. At this step, back pressure was increased to the constant value of 500 psi.

6.2.3.4. Foam Quality Scan

This set of foam-floods were carried out on Samples A (oil absent, as a reference case) and B (oil present) to determine the effect of remaining oil on different foam flow regimes. In particular, nitrogen was co-injected with the surfactant solution at different gas fractional flows (quality, \( f_g \)) until the pressure drop across the core reached steady-state. Total foam injection rate was constant at 1 cc/min, corresponding to 20 ft/day of the total interstitial velocity and all the foam tests were carried out under 500 psi back pressure and 94°C.

6.2.3.5. Foam-Oil Co-injection Experiment

In this set of experiments, nitrogen and surfactant solution were first co-injected with the fixed quality of 60% to generate foam inside the rock. After reaching the first steady-state, model oil with a specified fractional flow \( (f_o) \) was also co-injected while the total surfactant and gas injection rates were kept constant at 1 cc/min. Co-injection experiments were conducted on samples C-F (with roughly the same absolute permeabilities) by varying the oil fractional flow and the oil composition.
6.2.3.6. Surfactant-Oil Co-injection Experiment

To quantify the emulsification effect in our co-injection tests, surfactant and C16 were co-injected at the fixed oil fractional flow of 15% and under different superficial velocities (range of 1-20 ft/day). This velocity scan was conducted on sample G.

6.3. Results and Discussions

6.3.1. Foam Quality Scan Experiments

A set of foam scan experiments in the absence of oil were first performed in core sample A as a reference case. The apparent viscosity of foam in the absence of oil was calculated from the measured pressure drop using Equation 6-1 as a function of foam quality shown as the blue curve in Figure 6-4. The numbers on the curves show the order of the experiments. The calculated apparent viscosity increased with the foam quality before it peaked at 60% and then started to decrease with further increase in the foam quality. The trend of foam quality scan is fully explained and discussed in Chapter 7. In short, the increasing trend in the low quality region is due the increasing bubble density; whereas the decreasing trend in the high quality regime is because of the “dry-out” effect related to the limiting capillary pressure. Specifically, as the foam quality increases, the capillary pressure between the gas and the aqueous phase reaches a point where the liquid lamellae rupture and foam starts to coalesce. The foam quality at the maximum apparent viscosity is called the transition foam quality meaning that foam shifts from the low quality to the high quality regime. The transition quality is found out to be dependent on a number of factors, including surfactant type/concentration, gas type, salinity, and rock permeability etc. However, the oil dependence of the transition foam quality is not well understood.
Figure 6-4 Foam quality scan experiment in the absence and presence of remaining hexadecane (C16) in Berea Sandstone at 94°C. The numbers represent the order in which the data points were measured in lab.

A similar quality scan experiment was performed on core sample B in the presence of water-flooded remaining hexadecane to evaluate the effect of oil on foam strength. The core sample B was initially saturated with oil and then reduced to an oil saturation of 35% after 4 pore volumes (PV) of water flooding to mimic the secondary recovery in the reservoir. The saturation profiles after the primary drainage (oil flooding) and the water flooding steps are shown in Figure 6-5. After the NMR measurement, surfactant solution and gas were co-injected into the core sample B. We recorded the pressure drop when it did not change with time for each foam quality and calculated the apparent viscosity as shown with the green curve in Figure 6-4.
Figure 6-5 NMR saturation measurement of Core Sample B (A): at initial 100% water saturation; (B) after oil drainage experiment; (C) after 4 PV of water flooding to mimic the secondary recovery in the reservoir

It is well known that oil has a detrimental effect on bulk foam and single water lamella. Yet, it is notable from Figure 6-4 that except for the 95% and 98% foam qualities, the apparent viscosity was higher in the presence of residual oil compared to the oil free case. Such counterintuitive observation is likely due to the reduction in relative permeability to the non-oil phase by the trapped oil. Specifically, the residual oil remaining in the core occupied certain space in the pore volume, and thereby narrowing down the flow path of the foam. Such reduction in permeability is confirmed by the effective permeability measurement with brine at the residual oil saturation. The Berea sandstone effective permeability to water was reduced from 96 mD to 4.1 mD after the water flooding step.
A competing mechanism that weakens the measured apparent viscosity is the deleterious effect of oil on foam stability. Such effect was dominating when the foam quality exceeded 90% under our experimental conditions. Even though the relative permeability to the non-oil phase has been significantly reduced, the apparent viscosity is lower than the oil free case for foam qualities below 90%, which indicated that the thin liquid lamellae collapsed more readily in the presence of oil.

Another interesting phenomenon is the emulsification of oil, which will be discussed in detail in section 6.3.3. Even though there were multiple competing mechanisms that determine the overall apparent viscosity of foam in porous media, the transition foam quality does not seem to change much in the presence of hexadecane.

6.3.2. Oil Displacement Mechanism by Foam

Even though the foam quality scan experiments were conducted at the water flooded remaining oil saturation, NMR measurement showed that the oil saturation had decreased from 35% to 11% after total 15 quality scan measurements as shown in Figure 6-6.

![Figure 6-6 NMR measurement after the foam quality scan experiment with the water flooded residual hexadecane (C16). The yellow circle corresponds to the inlet area with no detectable oil as a result of the micellar solubilization by the AOS_{1416} surfactant.](image)
Approximately first 2cm of the core from the inlet was completely cleaned with no detectable oil, whereas the remaining part of the core had a nearly uniform oil saturation of around 13%. The oil saturation profile provided us the opportunity to look into the different oil displacement mechanisms and quantify their relative contributions to the oil recovery. Particularly, we will focus on quantifying the relative significance of the increased capillary number and the surfactant solubilization.

Capillary number \( N_{Ca} \) is a dimensionless number that quantifies the relative effect of the viscous force and the capillary force in porous media. Viscous force must overcome the capillary force to recover the oil droplets trapped in the pore structures. There are various forms of capillary number definition in the literature. In this chapter, we use the original form of definition as shown in Equation 6-2. The oil-water interfacial tension \( \sigma_{wo} \) is chosen at the denominator instead of the gas-water surface tension \( \sigma_{wg} \) or the gas-oil surface tension \( \sigma_{og} \). This is because we are examining the displacement of oil by the surfactant solution and foam. In the case of CO\(_2\) miscible foam flooding, a more appropriate choice of the denominator would be the gas/oil surface tension. Lake et al.\(^{41}\) illustrated the CDC relationship between the residual oil saturation in the porous media and the \( N_{Ca} \). Even though the measured pressure drop was dependent on the injected foam quality, on average, due to the reduction in oil/water IFT and the increased pressure gradient, the characteristic value of \( N_{Ca} \) was raised from the order of \( 10^{-6} \) to \( 10^{-3} \). Our NMR measured oil saturation is in good agreement with the non-wetting residual saturation curve for a typical sandstone rock as shown in the reproduced curve from Lake et al.\(^3\) in Figure 6-7.

\[
N_{Ca} = - \frac{k_{abs} \nabla p}{\sigma_{wo}} \tag{Equation 6-2}
\]
Figure 6-7 Comparison between the residual oil saturations in our experiment and the CDC curve schematics proposed by Lake et al.\textsuperscript{38} Foam recovered most of the oil by increasing the capillary number by 3 orders of magnitude.

However, the increased $N_{Ca}$ did not explain the complete removal of the oil within the first 2 cm from the core inlet, which could be explained by the micellar solubilization. During the process, the micelles absorb the oil molecules into the interior of the micelles at a surfactant concentration above the CMC. Even though the salinity under our conditions was below the optimal point, the solubilization can still be considerable if the PV of the injected surfactant is large (50 PV in our case). Figure 6-8 shows the percentage of hexadecane recovered by the water flooding ($N_{Ca} \sim 10^6$), the foam flooding ($N_{Ca} \sim 10^3$), and the micellar solubilization by AOS\textsubscript{1416}. Under our experimental conditions, oil was mostly recovered by the increased capillary number (reduced IFT, $\sigma_{wo} = 0.7$ mN/m and the increased $Vp$) and also the presence of the gas phase; In contrast, oil displacement due to micellar solubilization was limited.
Figure 6-8 Oil recovery mechanism comparison between water flooding, foam flooding, and surfactant micellar solubilization under our experimental condition; the oil recovery percentage was calculated based on original oil in place (OOIP)

6.3.3. Foam-Oil Co-injection Experiment

To keep the oil saturation constant while we measure the foam strength, a foam-oil co-injection experiment was designed.

Figure 6-9(a) and (c) show two examples of the pressure history for foam-oil co-injection tests with different hexadecane fractional flows. At low hexadecane fractional flow ($f_{C16}=10\%$), the effect of foam destabilization is pronounced. The overall apparent viscosity at steady state was lower after introducing the hexadecane stream into the system. The NMR measurement showed that the oil saturation leveled at 21\% at steady state (Figure 6-9(b)). However, at higher hexadecane fractional flow ($f_{C16}=15\%$), the pressure drop decreased first and then increased continuously until
exceeding the pressure transducer limit of our system. After the experiment, the measured oil saturation reached 38% (Figure 6-9(d)).

Figure 6-9 Foam-hexadecane co-injection experiment (a) pressure drop history for 10% hexadecane fractional flow; (b) 3-phase saturation profile of core sample E from NMR imaging after co-inject foam with 10% hexadecane fractional flow (c) pressure drop history for 15% hexadecane fractional flow; (d) 3-phase saturation profile of core sample F from NMR imaging after co-inject foam with 15% hexadecane fractional flow

We noticed from the effluent sample that emulsion slugs were produced from the core. We believe it is the hexadecane-AOS<sub>1416</sub> emulsion that caused the very high pressure drop. To quantify the viscosity of the emulsion generated inside the Berea sandstone, we performed an additional 2-phase (AOS<sub>1416</sub> surfactant solution and hexadecane) co-injection experiment in the absence of gas. We calculated the apparent viscosity of this emulsion flow starting from 1 ft/day to 20 ft/day. As shown in the Figure 6-10, emulsion displayed Newtonian rheology, apparent viscosity of around
10 cP, when the total interstitial velocity was between 1 to 10 ft/day. However, increasing the interstitial velocity to 20 ft/day (the same flowrate at which the foam-oil co-injection experiment was conducted) resulted in the “plugging” of the Berea sandstone. Therefore, it is concluded that the “plugging” was caused by the emulsification of the hexadecane.

![Figure 6-10 Shear rate scan for hexadecane-AOS1416 emulsion. The co-injected emulsion exhibits Newtonian rheology below 10 ft/day interstitial velocity. The emulsion viscosity increased sharply and finally exceeded the pressure transducer limit when the total interstitial velocity reached 20 ft/day.](image)

The velocity dependence of the emulsion apparent viscosity appears to be analogous to the in situ foam generation. It is reported in the literature that there is an “onset” pressure gradient for foam generation in many homogeneous cores. Strong foam is only generated when the pressure gradient exceeds a critical value called the minimum pressure gradient $\nabla p_{foam}^{min}$ [14,30,146]. The creation of lamellae sandwiched by the gas phase results in foam generation, whereas the creation of lamellae sandwiched by the oil phase results in emulsification. Therefore, we apply the same
idea and assume that there is a similar concept of the minimum pressure gradient $\nabla p_{\text{emulsion}}^{\text{min}}$ for
the generation of emulsion. We believe that in the 3-phase co-injection experiment, the pressure
gradient established by foam exceeded the $\nabla p_{\text{emulsion}}^{\text{min}}$ and therefore facilitated the emulsification
of hexadecane. With continuous hexadecane supply, the oil droplets accumulated in the core
sample and finally induced “core plugging”. Unlike the foam which dries out at high quality,
emulsion droplets are much more stable at high qualities compared to the gas bubbles. This is
because the interfacial tension between the aqueous phase and the oil phase ($\sigma_{w\omega} = 0.7$ mN/m) is
one order of magnitude lower than the gas/surfactant solution surface tension ($\sigma_{wg} = 30.1$ mN/m).
As a result, we believe that the necessary conditions for severe emulsification include (1) high
pressure gradient and (2) continues oil supply to the system.

It is also found that the severity of oil emulsification and the foam stability depends on the
oil type. As can be seen from Figure 6-11, we repeated similar experiments with octane as a shorter
chain hydrocarbon. Similar to the case of hexadecane, at low octane fractional flow ($f_{C8}=5\%$), the
foam destabilization effect dominated and the overall apparent viscosity decreased after oil co-
injection (Figure 6-11(a)); whereas at high octane fractional flow ($f_{C8}=15\%$), the apparent viscosity
decreased first and then started to increase (Figure 6-11(c)). Unlike the hexadecane emulsion that
plugged the core, the octane emulsion had a comparable flow resistance to foam and the pressure
drop leveled off at around 400 psi, comparable to its steady-state value during foam injection.
Figure 6-11 Foam-hexadecane co-injection experiment (a) pressure drop history for 5% octane fractional flow; (b) 3-phase saturation profile of core sample C from NMR imaging after co-inject foam with 10% octane fractional flow (c) pressure drop history for 15% octane fractional flow; (d) 3-phase saturation profile of core sample D from NMR imaging after co-inject foam with 15% octane fractional flow.

Figure 6-12 summarizes the results of the foam-oil co-injection experiments with hexadecane and octane. The measured apparent viscosities versus oil fractional flow and oil saturation exhibit similar trend. At low oil fractional flows ($f_{oil}$), the overall apparent viscosity decreased due to the dominance of the foam destabilization effect. Nevertheless, at high $f_{oil}$, the emulsified oil droplets started to accumulate and increase the flow resistance. In the case of hexadecane, the emulsion was very viscous and plugged the core at $f_{C16}$ values equal or higher than 15%. Octane, in contrast, did not show severe emulsification.
Figure 6-12 Apparent viscosity as a function of oil fractional flow and oil saturation: the apparent viscosity trend is governed by foam destabilization and oil emulsification. At low oil fractional flow, the apparent viscosity decreased with increasing oil saturation; whereas at high oil fractional flow, the apparent viscosity increased with oil saturation. The octane is more detrimental to foam stability whereas the hexadecane emulsion is more viscous than that of octane.

Admittedly, experiments with crude oil are needed to mimic the foam-oil interactions in the real reservoir. We doubt the likelihood of serious emulsification to happen under reservoir conditions for several reasons: (1) the flowrate in reservoir is considerably lower compared to our lab experiments. Therefore the minimum pressure gradient for emulsification might not be reached; (2) In a 3-D system, the emulsified oil droplets are likely to be diverted to different directions instead of accumulating in one location; (3) the emulsification is compositionally dependent on the oil and the choice of surfactant formulation. In the case of octane-like crude oil, the viscosity of the emulsion might be no greater than the viscosity of foam; (4) without continuous oil injection, the reservoir is less likely to be plugged by surfactant solution.
6.4. Conclusion

We investigated the effect of oil on foam rheology in porous media. Specifically, we measured the foam strength at residual hexadecane saturation and compared with the apparent viscosity in the absence of oil. It is found that even though oil has a detrimental effect on foam, the apparent viscosity in porous media is higher with residual hexadecane. This is mainly because of the reduction in relative permeability to non-oil phase caused by the trapped hexadecane. We analyzed the 3-phase saturation profile after the foam quality scan experiment and quantified the relative amount of oil displaced by various mechanisms.

In addition, foam-oil co-injection experiments were performed to quantify the effect of oil on foam transport in porous media. We mapped out the measured apparent viscosity at different oil fractional flows and oil saturations with the assistance of NMR imaging technique. It is found that at low oil fractional flow, the foam destabilization dominated and the measured apparent viscosity decreased with the increase in oil saturation; whereas at high oil fractional flow, the emulsification dominated and increased the apparent viscosity as a function of oil saturation.
Chapter 7

An Improved Model Parameterization Algorithm for Foam Simulation

7.1. Background

Depending on whether the local bubble density (or namely foam texture), $n_f$, is explicitly expressed, current foam transport models can be categorized into two different groups\cite{11,27,31,63,64,148}: texture-explicit population balance models and texture-implicit local-equilibrium models. The first approach requires not only an additional partial differential equation (PDE) for bubble transport, but also exact expressions to describe bubble generation and destruction. The second approach uses only an empirical algebraic formula to correlate the gas mobility reduction as a function of a series of local conditions, such as surfactant concentration, water saturation, shear-rate, and oil saturation. We believe the empirical texture-implicit local-equilibrium approach is more promising for field-scale applications. The physical foam dynamic mechanisms inside porous media are complex in the mechanistic texture-explicit population balance model, and the model parameters are often difficult to extract from simple core-flood
experiments. Additionally, an extra PDE for bubble transport in the population balance model would significantly increase the computational cost compared to an algebraic expression as in the implicit-texture-local-equilibrium model. Therefore, we model foam transport using a commercially available texture-implicit-local-equilibrium foam model in STARS™, and discuss insightful implications based on the parameters estimated using our improved algorithm.

A proper method to extract values for all the parameters to fit lab-scale experiments is needed with a well-defined foam model. Different algorithms have been proposed in the literature to estimate the foam model parameters in STARS™. Ma et al.80 developed a method to estimate the parameters in a water-saturation-dependent function and successfully described the dry-out effect. Ma et al.80 required an extra transient experiment where gas is constantly injected into a core 100% saturated with surfactant solution in addition to steady-state foam data. They realized that two different pairs of solutions match the experimental data based on different initial parameters values. Additionally, the maximum apparent viscosity data must be determined precisely in the experiment to locate the transition point between high- and low-quality regimes. Boeije et al.83 proposed another method in which five parameters can be extracted simply and simultaneously from steady-state data using just a pencil and a calculator. The method can quickly provide initial estimates to least square fitted values later determined using a computer. However, strong assumptions are made with conservations. A large epdry (10^5) is assigned arbitrarily to ensure that the foam collapses sharply and abruptly at the limiting water saturation value S_w. However, whether foam experiences such abrupt coalescence in all cases remains an open question. Additionally, Newtonian rheology is assumed valid for foam in the high-quality regime, which may be inconsistent with the experimental results reported in literature91.
We propose an improved algorithm to estimate STARS™ foam model parameters. Both the water-saturation-dependent function and shear-rate-dependent function are considered. We illustrate how this improved algorithm can be used to estimate five parameters in the water-saturation-dependent function and shear-dependent function, respectively. The insights gained regarding foam transport from the parameters estimated using our new algorithm allows for better design of flow through porous media.

Although we introduced apparent viscosity $\mu_{app}$ to quantify foam strength, foam in porous media is modeled as a two-phase flow instead of single-phase because gas and liquid are transported at different velocities\textsuperscript{80,82}. Phase separation occurs in the presence of permeability contrast\textsuperscript{95,98}. Gas mobility can be reduced by several orders of magnitude in the state of foam, whereas the liquid mobility for a given water saturation changes negligibly\textsuperscript{27,80}. Bernard et al.\textsuperscript{149} rationalized that the gas flow path is blocked by lamellae, whereas most water remains in small pores and in proximity to the solid surfaces as the wetting phase. Specifically, gas mobility in the state of foam is reduced by two mechanisms\textsuperscript{11}: first, the stationary or trapped gas decreases the cross-sectional area that gas can flow through, decreasing the relative permeability; second, the lamella must be forced to allow the discontinuous gas to flow, and therefore the effective viscosity of gas increases. The two mechanisms can be independently considered\textsuperscript{11,31} or combined into a single variable for the foam flow simulation\textsuperscript{80,81}.

Foam experiences major coalescence at the limiting capillary pressure $P_c^*$ when the disjoining pressure can no longer prevent the lamella from rupturing\textsuperscript{90}. This dry-out effect occurs near a given limiting water saturation $S_w^*$ when the foam quality $f_g$ is high\textsuperscript{80,87}. Operation at higher foam quality can reduce the cost of the expensive surfactant. However, a high foam quality $f_g$ significantly reduces the foam apparent viscosity, and therefore gas mobility control is lost. As gas
fractional flow is increased, the foam dries out as the water saturation approaches a value $S_w^*$ at which the foam coalesces at increasing rate. The limiting water saturation $S_w^*$ can be systematically estimated using our new algorithm by conducting quality-scan experiments where total velocity is held constant and the flow resistance is in a steady-state. $S_w^*$ is believed to be dependent on a variety of factors, such as surfactant, electrolyte, gas type, oil saturation and rock properties. The corresponding $P_c^*$ is also a dynamic property determined both by the system and operating conditions.

Another important feature of foam flow in porous media is its shear-dependent rheology. Foam strength might be completely different in the near-wellbore region than in the far-field region due to its decelerating propagating velocity. A mathematical model computing foam bubbles flowing in smooth capillary bundles has been well developed in the literature. Calculations agree with experimental observations that foam is a shear thinning fluid in a capillary tube, and the effective gas viscosity is inversely proportional to the bubble velocity raised to the minus one-third power. However, the real subsurface micro-structure is more complicated than the smooth capillary bundles. Lab observations indicate that foam can be either shear-thinning or shear-thickening under different conditions. Thus we simply correlate the shear-rate-dependent function with total velocity or the capillary number raised to an adjustable power.

STARS$^\text{TM}$ is a commercially available reservoir simulator including a texture-implicit local-equilibrium foam model in which the gas relative permeability in the presence of foam $k_{rg}^f$ is modified by multiplying the gas relative permeability without foam $k_{rg}^{nf}$ at a given water saturation with a mobility reduction factor $FM$, as shown in Equation 7-1.
Equation 7-1

\[ k_{rg}' = k_{rg}^{nf} \times FM \]

*FM* is inversely related to the product of different functions as shown in Equation 7-2.

These functions account for the foam dependencies on different factors, such as surfactant concentration, water saturation, shear-rate, etc.

Equation 7-2

\[ FM = \frac{1}{1 + f_{mmob} \times \prod_{i=1}^{n} F_i} \]

The *f_{mmob}* parameter refers to the maximum gas mobility reduction that can be achieved. \( F_i \) are different functions ranging from 0 to 1. When all \( F_i \) are equal to 1, foam obtains its maximum strength. A full description of the STARS™ foam model can be found in the literature\(^{63,64,82}\). This work only considers foam dependence on water saturation (\( F_{water} \)) and shear rate (\( F_{shear} \)). Consequently, Equation 7-2 is reduced to

Equation 7-3

\[ FM = \frac{1}{1 + f_{mmob} \times F_{water} \times F_{shear}} \]

\( F_{water} \) is the water saturation-dependent function, which is the inverse tangent function of water saturation \( S_w \). \( F_{water} \) is a continuous and monotonically increasing function of water saturation \( S_w \), as shown in Equation 7-4, and decreases significantly as water saturation \( S_w \) decreases across the limiting water saturation \( S_w^* \).

Equation 7-4

\[ F_{water} = 0.5 + \frac{\arctan(\text{epdry}(S_w - f_{mdry}))}{\pi} \]
\( F_{\text{water}} \) contains two parameters: \( f_{\text{mdry}} \) and \( e_{\text{dry}} \). \( f_{\text{mdry}} \) corresponds to the limiting water saturation \( S_{w}^{*} \), at which foam begins experiencing significant coarsening and drying and should be in the range of connate water saturation \( S_{wc} \) and \( (1 - S_{gr}) \). \( e_{\text{dry}} \) controls the collapse rate of foam. A large \( e_{\text{dry}} \) value indicates that foam dries out sharply, whereas small \( e_{\text{dry}} \) indicates that foam dries out more gradually.

\( F_{\text{shear}} \) is the shear rate-dependent function, which is a function of the local capillary number \( N_{Ca} \), as shown in Equation 7-5.

\[
F_{\text{shear}} = \begin{cases} 
\left( \frac{f_{\text{mcap}}}{N_{Ca}} \right)^{e_{\text{cap}}} & \text{if } N_{Ca} > f_{\text{mcap}} \\
1 & \text{otherwise}
\end{cases}
\]  
\text{Equation 7-5}

The adjustable parameter \( e_{\text{cap}} \) determines the shear-rate dependence of foam rheology in porous media. A positive \( e_{\text{cap}} \) corresponds to shear-thinning rheology. \( f_{\text{mcap}} \) is a parameter with which to normalize \( F_{\text{shear}} \), given the constraints that all dependent functions should fall within the interval of \([0,1]\).

Capillary number \( N_{Ca} \) is a dimensionless number in fluid mechanics, which characterizes the relative effect between viscous and capillary forces. The local capillary number is an indicator of the viscous shear rate of the system. The higher capillary number corresponds to a greater viscous shear stress. However, the exact expression of local capillary number remains controversial in the literature\(^{82,83,91}\). At least three methods exist to define \( N_{Ca} \), as shown in Equation 7-6, Equation 7-7, and Equation 7-8, where \( k \) is the rock permeability, \( \nabla p \) is the local pressure gradient, and \( \sigma \) is the surface tension between the gaseous and aqueous phases.
\[ N_{ca} = \frac{-k \nabla p}{\sigma} = \frac{\mu_{app} \times u_t}{\sigma} \quad \text{Equation 7-6} \]

\[ N_{ca} = \frac{\mu_w \times u_g}{\sigma} \quad \text{Equation 7-7} \]

\[ N_{ca} = \frac{\mu_w \times u_t}{\sigma} \quad \text{Equation 7-8} \]

Boeije et al.\textsuperscript{83} suggested that Equation 7-6 defines the local capillary number because it is consistent with its original definition in two-phase flow, where the wetting fluid displaces the trapped non-wetting glob. Including \( F_{shear} \) in the STARS\textsuperscript{TM} model with this capillary number definition could improve the data fit in the quality-scan experiment as described in Boeije et al.\textsuperscript{83} However, this definition would increase the computational cost by implicitly defining the mobility reduction factor \( F_M \) and requiring iteration for convergence.

Abbaszadeh et al.\textsuperscript{82} used the second definition as shown in Equation 7-7, because the shear thinning rheology of foam in a capillary bundle scales with the gas bubble velocity. However, \( u_g \) may not scale well with the shear rate in porous media because a large fraction of gas is trapped in real rock\textsuperscript{149}; thus, the bubble velocity deviates significantly from \( u_g \). Additionally, such a definition would entangle \( F_{water} \) and \( F_{shear} \) complicate the foam simulation.

The effects of \( u_g \) and \( u_w \) on the shear-rate on the foam in rock are difficult to quantify. Hence, we simply find their sum and scale the shear rate in porous media with total superficial velocity \( u_t \) whereby Equation 7-8 defines the local capillary number. We will demonstrate in section 7.4 that our algorithm provides an acceptable fit to the experimental data in a series of
varied foam systems. In particular, sections 7.3.1 and 7.3.2 will illustrate that it is easy to reduce the five-parameter estimation into two simple tasks with such a definition. We first estimate three parameters \((f_{m_{mob}}, e_{p_{dry}}, \text{and } f_{mdry})\) from the quality-scan experiment. Second, we estimate the other two parameters \((e_{pcap} \text{ and } f_{m_{cap}})\) from the flow-rate-scan experiment.

### 7.2. Materials and Methods

We investigate different foam systems with various surfactant formulation, gas types, etc. Gas was co-injected with surfactant solution in all cases, as shown in Figure 7-1. The pressure drop \(\Delta p\) at steady state along the core sample was recorded as a function of the gas and liquid velocities. The studied systems are listed in Table 7-1. System A is a demonstration case with which we will use our improved algorithm to estimate STARS\textsuperscript{TM} model parameters in sections 7.3.1 and 7.3.2. We examine the effect of different gas types on foam strength in system B and correlate foam strength with lamella stability. We compare the foamability of the anionic surfactant, C14-16 alpha olefin sulfonate (AOS1416, from Stepan) in system C with two different zwitterionic surfactants lauryl betaine (LB, from Solvay Mackam Lab) and lauryl sultaine (LS, from Solvay Mackam Lab), which are typically used as foam boosters in presence of crude oil\textsuperscript{153}. The surfactants listed are used without further treatment. Synthetic seawater was made with salts (from Sigma Aldrich) of approximately 0.67 g/L KCl, 10.15 g/L MgCl\textsubscript{2}·6H\textsubscript{2}O, 1.47 g/L CaCl\textsubscript{2}·2H\textsubscript{2}O, 3.83 g/L Na\textsubscript{2}SO\textsubscript{4}, and 25.21 g/L NaCl.
Figure 7-1. Schematic of foam flood experimental setup

Table 7-1 Foam flooding systems examined in this study

<table>
<thead>
<tr>
<th>System</th>
<th>Porous Medium</th>
<th>Surfactant Formulation</th>
<th>Gas</th>
<th>Brine</th>
<th>Flow rate (ft/day)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Bentheimer (0.65 Darcy)</td>
<td>0.15 wt% AOS1416 and 0.35 wt% LB</td>
<td>N₂</td>
<td>Sea Water</td>
<td>4.2</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Bentheimer (2.30 Darcy)</td>
<td>1 wt% AOS1416</td>
<td>N₂, CH₄, CO₂</td>
<td>Sea Water</td>
<td>4</td>
<td>Ambient</td>
</tr>
<tr>
<td>B</td>
<td>Bentheimer (2.70 Darcy)</td>
<td>0.5 wt% LS</td>
<td>N₂</td>
<td>Sea Water</td>
<td>4</td>
<td>45</td>
</tr>
<tr>
<td>C</td>
<td>Bentheimer (2.50 Darcy)</td>
<td>0.5 wt% LB</td>
<td>N₂</td>
<td>Sea Water</td>
<td>4</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Bentheimer (2.52 Darcy)</td>
<td>0.5 wt% AOS1416</td>
<td>N₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Two major foam experiments are primarily conducted in the literature to assess foam properties: a quality-scan experiment and a flow-rate-scan experiment. The total flow rate is constant in the quality-scan experiment so that the pressure decrease across the porous medium is measured as a function of foam quality $f_g$. The foam quality is fixed, while the total flow rate (or superficial velocity $u_t$) is varied in the flow-rate scan experiment.

We utilize the Corey relative permeability model for our two-phase (gaseous and aqueous) flow in absence of a surfactant, as shown in Equation 7-9 and Equation 7-10, where $k_{rw}^o$ and $k_{rg}^o$ are the end-point relative permeability for water and gas, respectively, $S_{wc}$ is connate water saturation, $S_{gr}$ is residual gas saturation, and $n_w$ and $n_g$ are the Corey exponents for water and gas, respectively. The relative permeability data for Bentheimer sandstone is listed in Table 7-2.

$$k_{rw} = k_{rw}^o \times \left( \frac{S_w - S_{wc}}{1 - S_{wc} - S_{gr}} \right)^{n_w}$$  \hspace{1cm} \text{Equation 7-9}

$$k_{rg}^{nf} = k_{rg}^o \times \left( \frac{S_g - S_{gr}}{1 - S_{wc} - S_{gr}} \right)^{n_g}$$  \hspace{1cm} \text{Equation 7-10}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bentheimer sandstone</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{rw}^o$</td>
<td>0.22</td>
</tr>
<tr>
<td>$k_{rg}^o$</td>
<td>0.94</td>
</tr>
<tr>
<td>$S_{wc}$</td>
<td>0.10</td>
</tr>
<tr>
<td>$S_{gr}$</td>
<td>0.05</td>
</tr>
<tr>
<td>$n_w$</td>
<td>4.00</td>
</tr>
<tr>
<td>$n_g$</td>
<td>1.80</td>
</tr>
</tbody>
</table>
7.3. Results and Discussions

7.3.1. Estimation of Parameters in $F_{water}$ Function

$N_2$ and an AOS1416/LB surfactant blend were co-injected into a 6.7-inch Bentheimer sandstone core in System A. Both the quality-scan and flow-rate-scan experimental results are shown in Figure 7-2.

![Figure 7-2](image)

**Figure 7-2 System A:** $N_2$ and surfactant solutions were co-injected into a 6.7-inch Bentheimer sandstone (0.65 Darcy) core at ambient temperature. A quality-scan experiment at a fixed flow rate of 4.2 ft/day is on the left, and a flow-rate-scan experiment with a fixed foam quality of 0.78 is on the right.

The general behavior in the quality-scan experiment (Figure 7-2, left) indicates that the foam apparent viscosity first increased with increasing foam quality. The viscosity reached a maximum and then decreased as the quality was further increased. The decrease in apparent viscosity results from the foam dry-out effect discussed earlier. The foam apparent viscosity
decreased with increasing total flow rate in the flow-rate-scan experiment (Figure 7-2, right). Foam showed a shear-thinning behavior in System A.

Estimations of the parameters in $F_{water}$ are discussed next. $F_{shear}$ is ignored because the total flow rate was held constant in the quality-scan experiment.

For any given pair of steady-state foam data ($f_g^{exp}$, $\mu_{app}^{exp}$), we can solve for corresponding $S_w$ and $FM$ values, as shown in Equation 7-11 and Equation 7-12.

$$S_w = \left( \frac{\mu_w \times (1 - f_g)}{\mu_{app} \times k_{rw}^o} \right)^{n_w} \left( 1 - S_{wc} - S_{gr} \right) + S_{wc} \quad \text{Equation 7-11}$$

$$FM = \frac{f_g \times \mu_g}{\mu_{app} \times k_{rg}^o \times \left( \frac{1 - S_w - S_{gr}}{1 - S_{wc} - S_{gr}} \right)^{n_g}} \quad \text{Equation 7-12}$$

Any given value of $f_{mmob}$, $epdry$ and $fmdry$ can be uniquely determined by conducting a linear regression between $\tan \left( \left( \frac{1}{FM} - 1 \right) \frac{f_{mmob}}{f_{mmob}} - 0.5 \right) \pi$ and $S_w$ by combining and rearranging Equation 7-3 and Equation 7-4, as shown in Equation 7-13. Moreover, the three-parameter estimation ($f_{mmob}$, $epdry$ and $fmdry$) can be optimized into a single variable $f_{mmob}$ that fits experimental data.

$$\tan \left( \left( \frac{1}{FM} - 1 \right) \frac{f_{mmob}}{f_{mmob}} - 0.5 \right) \pi = epdry(S_w - fmdry) \quad \text{Equation 7-13}$$

The objective function of our parameter optimization as shown in Equation 7-14 is to identify which $f_{mmob}$ value provides the optimal fit to experimental data. The first term in yellow is the normalized residual sum of squares deviation. The second term in blue is a penalty function
that regulates the calculated transition quality to within the interval of the two neighboring points, where the strongest foam is observed in the experiment \( f^\text{exp}_{g, \text{imax}} \). Hence, the foam quality transition between the low-quality and high-quality regimes must exist within the interval \((f^\text{exp}_{g, \text{imax}-1}, f^\text{exp}_{g, \text{imax}+1})\), as shown in Figure 7-3.

\[
\min f(\text{fmmob}) = \left\{ \begin{array}{ll}
\frac{1}{n} \sum_{i=1}^{n} \left( \frac{\mu^{\text{exp}}_{\text{app},i} - \mu^{\text{STARS}}_{\text{app},i}}{\mu^{\text{exp}}_{\text{app},\text{imax}}} \right)^2 & + P \times \left( \frac{f^\text{exp}_{g, \text{imax}} - f^\text{STARS}_{g, \text{transition}}}{f^\text{exp}_{g, \text{imax}}} \right)^2 \\
0 & \text{if } f^\text{STARS}_{g, \text{transition}} < f^\text{exp}_{g, \text{imax}-1} \\
1 & \text{if } f^\text{STARS}_{g, \text{transition}} < f^\text{exp}_{g, \text{imax}-1} \text{ or } f^\text{exp}_{g, \text{imax}-1} > f^\text{exp}_{g, \text{imax}+1}
\end{array} \right\}
\]

\text{Equation 7-14}

The largest \( f_{\text{fmmob}} \) observed in experiments is the upper bound given that \( F_{\text{water}} \) should nearly equal

![Figure 7-3 Quality-scan experiment for System A: the transition quality must fall within the interval of \((f^\text{exp}_{g, \text{imax}-1}, f^\text{exp}_{g, \text{imax}+1})\)](image)

The flowchart of our proposed method to search for \( f_{\text{fmmob}} \) is shown in Figure 7-4. The largest \( f_{\text{fmmob}} \) observed in experiments is the upper bound given that \( F_{\text{water}} \) should nearly equal
1 in the low-quality regime, where the water saturation is high. There are a number of numerical methods that can solve this constrained extreme-value problem, such as Newton’s method, Bisection’s method, Golden section search and simplex algorithm, etc. We simply plot the objective function in Figure 7-5, from which we can easily identify the global optimal value of $f_{mmob}$. The optimal of $f(f_{mmob})$ for our demonstration System A is 9551.8. The linear regression between $\tan\left(\left(\frac{1}{FM}\frac{1}{f_{mmob}} - 0.5\right)\pi\right)$ and $S_w$ is shown in Figure 7-6. The values of $f_{mmob}$, $epdry$ and $fmdry$ are listed in Table 7-3, and the final data fit for the quality-scan experiment is shown in Figure 7-7.

![Flowchart](image)

**Figure 7-4 Flowchart outlining numerical scheme used for the estimation of $f_{mmob}$, $epdry$, and $fmdry$**
Figure 7-5 The objective function $f(f_{mmb})$ vs. $f_{mmb}$

Figure 7-6 The linear regression between $\tan\left(\left(\frac{1}{FM}\right)^{-1} - 0.5\right)\pi$ and $S_w$
Table 7-3 Quality-scan experimental data fit to the STARS™ model

<table>
<thead>
<tr>
<th>$f_{mmob}$</th>
<th>$ep_{dry}$</th>
<th>$f_{mdry}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9551</td>
<td>26</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure 7-7 Quality-scan experimental data fit to the STARS™ model

7.3.2. Estimation of Parameters in $F_{shear}$ Function

The two parameters $ep_{cap}$ and $f_{mcap}$ in $F_{shear}$ will be estimated from the flow rate-scan experiments. We combine Equation 7-3 to Equation 7-5 and rearrange such that a linear regression is applied to compute $ep_{cap}$ and $f_{mcap}$. Given viscosity $\mu$ and surface tension $\sigma$, we can conduct a linear regression between $\log_{10} \left( \frac{1}{f_{mmob} \times f_{water}} \right)$ and $\log_{10}(N_{Ca})$, as shown in Equation 7-15.

The data fit results are shown in Table 7-4 and Figure 7-8.
\[
\log_{10}\left(\frac{\left(1/F_M\right) - 1}{fm\text{mob} \times F_{\text{water}}}\right) = -epcap \times \left(\log_{10}(N_{Ca}) + \log_{10}(fm\text{cap})\right)
\]

Equation 7-15

Table 7-4Flow rate-scan experimental data fit to the STARS\textsuperscript{TM} model

<table>
<thead>
<tr>
<th>epcap</th>
<th>fm\text{cap}</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.22</td>
</tr>
</tbody>
</table>

We have demonstrated how to fit the five parameters from the quality-scan and the flow-rate-scan foam flood experiments for the STARS\textsuperscript{TM} model. Next, we will apply this method to a variety of systems to validate robustness and establish interpretations from the data.
7.3.3. Effect of Gas Type: \( \text{N}_2\), \( \text{CH}_4\) and \( \text{CO}_2\) Foams

We investigate the effect of gas type on steady-state foam strength in porous media in System B. Three types of gases were co-injected with a 1 wt% AOS1416 surfactant solution into the Bentheimer sandstone core. It should be noted that the aqueous solution was pre-saturated with CO\(_2\) because of the relatively high solubility of CO\(_2\) in water. The experimental data and the STARS\textsuperscript{TM} model fits are shown in Table 7-5 and Figure 7-9, respectively. Only quality-scan experiments were completed, and therefore data to fit \( e_{pcap} \) and \( f_{mcap} \) in \( F_{shear} \) were unavailable. Our algorithm works well with this system and provides a satisfactory fit to the experimental data. We find that the nitrogen (N\(_2\)) foam is always the strongest, whereas the carbon dioxide (CO\(_2\)) foam is the weakest. The methane (CH\(_4\)) foam produced the intermediate foam strength for a given foam quality.

<table>
<thead>
<tr>
<th>Gas Type</th>
<th>( f_{mmob} )</th>
<th>( e_{dry} )</th>
<th>( f_{mdry} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>5.1E+4</td>
<td>412.0</td>
<td>0.20</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>3.5E+4</td>
<td>74.2</td>
<td>0.22</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>2.8E+4</td>
<td>24.1</td>
<td>0.25</td>
</tr>
</tbody>
</table>

We calculate the corresponding limiting capillary pressure based on \( f_{mdry} \) values in Table 7-5 to estimate the flowing foam film stability for foams of different gas types. We use the Leverett J function for Bentheimer sandstone\textsuperscript{47}, to estimate the limiting capillary pressure \( P_c^* \) as shown in Equation 7-16.
Figure 7-9 Data fit to STARS™ model for different gas type experiments

\[ P_c^* = J(S_w^*) \cdot \sigma \cdot \sqrt{\frac{\phi}{k}} = J(fmdry) \cdot \sigma \cdot \sqrt{\frac{\phi}{k}} \]  

Equation 7-16

If we use the transition foam apparent viscosity as a measure of the maximum foamability for the N\(_2\), CH\(_4\) and CO\(_2\) foams, we show in Figure 7-10 that the transition foam strength for different gas types is correlated significantly with limiting capillary pressure. N\(_2\) has the largest \( P_c^* \) value and thus produces the strongest foam, whereas CO\(_2\) has the weakest \( P_c^* \) value and thus produces the weakest foam. Consequently, we assume that the limiting capillary pressure is a good indicator of foam strength in porous media.
Figure 7-10 Transition foam strength for different gas types as a function of limiting capillary pressure estimated from \( f_{mdry} \)

7.3.4. Anionic surfactant foam (AOS1416) vs. zwitterionic surfactant foams (LB and LS)

We compare the anionic surfactant AOS1416 with two different zwitterionic surfactants, LB and LS, in terms of steady-state foam strength in porous media in System C. 0.5 wt% of AOS1416, LB and LS were co-injected with \( N_2 \). Applying the same algorithm as described, we can fit the experimental data to the STARS\textsuperscript{TM} model, as shown in Table 7-6 and Figure 7-11. As demonstrated, our algorithm provides a good fit to all three foam systems, although their general trends are quite different.
Table 7-6 STARS™ model fitted for experiments with two different zwitterionic surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>fmnomb</th>
<th>epdry</th>
<th>fmdry</th>
<th>epcap</th>
<th>fmcap</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS</td>
<td>1.9E+6</td>
<td>233</td>
<td>0.34</td>
<td>1.27</td>
<td>6.4E-08</td>
</tr>
<tr>
<td>LB</td>
<td>1.4E+5</td>
<td>44</td>
<td>0.29</td>
<td>1.28</td>
<td>3.3E-07</td>
</tr>
<tr>
<td>AOS416</td>
<td>7.7E+4</td>
<td>826</td>
<td>0.22</td>
<td>0.42</td>
<td>1.5E-07</td>
</tr>
</tbody>
</table>

Figure 7-11 Experimental data and STARS™ model fit for 0.5 wt% AOS1416, LB and LS foams

Figure 7-11 illustrates that AOS1416 is a more effective foamer in terms of apparent viscosity for both the quality and flow-rate scans compared to zwitterionic surfactants, such as LB and LS. Surface tension $\sigma$ is needed for different surfactant solutions against air to estimate the flowing foam film stability for different surfactant types. The $\sigma$ was measured in our experiment.
using Kibron–EZ Pi plus (Kibron Inc., Helsinki, Finland) based on the Du-Nouy Padday principle. The results are shown in Figure 7-12.

![Graph showing surface tension measurement for different surfactant types (AOS1416, LB and LS)](image)

**Figure 7-12** Surface tension measurement for different surfactant types (AOS1416, LB and LS)

We apply the same method to calculate the limiting capillary pressure $P^*_c$ to evaluate the foam film stability for different surfactant types, as shown in Table 7-7.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (wt%)</th>
<th>Surface tension $\sigma$ (mN/m)</th>
<th>$f_{mdry}$</th>
<th>$P^*_c$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOS1416</td>
<td>0.5</td>
<td>29.7</td>
<td>0.22</td>
<td>8.2</td>
</tr>
<tr>
<td>LB</td>
<td>0.5</td>
<td>34.7</td>
<td>0.29</td>
<td>7.2</td>
</tr>
<tr>
<td>LS</td>
<td>0.5</td>
<td>33.4</td>
<td>0.34</td>
<td>5.8</td>
</tr>
</tbody>
</table>
The limiting capillary pressure values agree with the transition foam strengths for the foam of three different surfactants. The AOS1416 foam shows the highest limiting capillary pressure $P_c^*$ and the strongest foam strength, whereas the LS foam shows the lowest $P_c^*$ and the weakest foam strength. We calculate the Gibbs surface excess $\Gamma^s$ as shown in Equation 7-17\textsuperscript{59,155} to estimate the packing of surfactant molecules onto the gas-liquid interface to understand the underlying mechanism that explains the difference in foam strength for different surfactant types. The $a$ is the surfactant activity, $a_t$ is the total activity of both surfactant and inorganic salts, $R$ is the gas constant, and $T$ is temperature.

\[
\Gamma^s = \frac{1}{RT} d \sigma \ln(aa_t)
\]

Equation 7-17

The Pitzer model\textsuperscript{156} was used to calculate the activity coefficients to account for the interactions between all inorganic salts and surfactant molecules. Derivation details and the interaction parameters can be found in the literature\textsuperscript{59,155,156}. The Gibbs surface excess as a function of surfactant concentration is shown in Figure 7-13 Gibbs surface excess adsorption on air-water interface for different surfactant types. AOS1416 has a higher surface excess concentration compared to both zwitterionic surfactants LB and LS. The different chemical structures of AOS1416 and LB/LS may explain their different foaming capability in porous media. As for the hydrophobic tails, surfactants with a longer hydrocarbon tail are more likely to be better foaming agents. Svorstoel et al.\textsuperscript{157} did an experiment on AOS with a series of different tail groups and found out that AOS16 is better than AOS1416 and both are better than AOS14 in foaming in porous media. In our experiment, AOS1416 has a longer hydrocarbon tail (C14 and C16) compared to LB/LS (C12 and C14). Besides the difference in tails, the head group repulsions between AOS
molecules are very sensitive to salinity\textsuperscript{59} and the electrostatic repulsion can be screened by the counter-ions, such as Na\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+} in the diffuse layer, which aide AOS1416, to pack tightly on the interface and create more stable foam films. However, the head group of zwitterionic surfactants is a permanent dipole moment which has zero net charge and thusly less sensitive to salinity\textsuperscript{158,159}. Thus the concentration of counter-ions will have less effect on the interface with zwitterionic surfactants.

![Graph](image.png)

**Figure 7-13** Gibbs surface excess adsorption on air-water interface for different surfactant types

### 7.4. Conclusion

In summary, we propose an improved algorithm to estimate the STARS\textsuperscript{TM} foam model parameters. The algorithm reduces the five-parameter estimation to a few simpler steps, such as linear regression and single-variable optimization, and avoids sensitivities of initial estimates and
non-uniqueness solution issues. No additional transition foam flooding experiment (gas displacing 100% surfactant solution) is required anymore. We also compare our improved algorithm with others reported in literature. The robustness of the algorithm has been validated by varied foam systems. We find that the limiting capillary pressure is a good indicator of film stability for flowing foam in porous media. We also realize that the anionic surfactant AOS1416 is a more effective foamer compared to zwitterionic surfactants LB/LS. The Gibbs excess adsorption is calculated to explain the difference in foamability of different surfactant types. Other future work includes (1) assessing the accuracy of our algorithm from flow-rate scan data for other foam qualities and (2) extending the algorithm to estimate the parameters in other dependent functions.
8.1. Background

With novel technologies being developed to capture CO$_2$ from industrial sites, CO$_2$ injection method is attracting more market interests. The sweep efficiency of CO$_2$ IOR can be improved by the injection mode of water-alternating-gas (WAG)$^{160-163}$. Ideally the injected water can reduce the relative permeability of the CO$_2$ phase and therefore delay the gas breakthrough. However, the improvement can be limited because of phase segregation. A more potent way to reduce the mobility of CO$_2$ is to disperse the gas in aqueous phase with surfactants$^{56,164,165}$. Depending on the reservoir temperature and pressure, CO$_2$ can be either gaseous-like or in the supercritical state. Yet, we do not differentiate the CO$_2$ foam and CO$_2$-in-water (C/W) emulsion here and only use the term CO$_2$ foam indicating that CO$_2$ is the internal phase.

Foam can decrease the mobility of CO$_2$ and increase the apparent viscosity of injection fluids by blocking the continuous gas path. Dispersed CO$_2$ bubbles in the state of foam have a
mobility that is orders of magnitude lower than continuous CO₂ flow. Therefore foam assisted CO₂ injection can effectively address the issue of poor mobility ratio and improve the volumetric sweep efficiency.

Commonly used ionic surfactants can only be injected in water because they are not soluble in the gas. Therefore the injection mode for these surfactants is called surfactant-alternating-gas (SAG). Well-known ionic surfactants have been introduced in detail from literature. Novel CO₂ soluble surfactants include the nonionic exthoxylated alcohols and switchable exthoxylated amines. These surfactants can be injected with CO₂ phase. If surfactant is injected with CO₂, we call it water-alternating-gas-plus-surfactant-in-gas (WAG+S) mode. WAG+S process has the potential to outperform SAG in different ways. Firstly WAG+S can improve the well injectivity when surface facilities switch from CO₂ injection to water injection. Secondly if surfactant is injected and transported in the CO₂ phase, it can foam with the water from secondary recovery, elongate the gas-water mixing zone and delay phase segregation.

Because the surfactant can dissolve in both the CO₂ and the water, it is critical to understand how the partitioning of the surfactant between the two phases can affect the foam transport in porous media. Partition coefficient \( K_{sgw} \) is a measure of the ratio in solubility of the surfactant in gaseous and aqueous phases. It is defined as the ratio of the surfactant concentration in gaseous phase \( C_{sg} \) to that in aqueous phase \( C_{sw} \) at thermodynamic equilibrium as in Equation 8-1. In some literature, surfactant partition coefficient is defined as the ratio of mass fraction rather than the concentration. The two definitions of partition coefficient are different by a factor that equals to the density ratio of the two phases, yet represent the same in nature.
The value of surfactant partition coefficient $K_{sgw}$ is dependent on several factors and can be experimentally measured in lab. Ren et al. tested a series of exthoxylated alcohols and discovered that the partition coefficient of these CO$_2$ soluble surfactants increases proportionally with the reservoir pressure, but decreases more dramatically with the increase in reservoir temperature. Additionally, the $K_{sgw}$ is very sensitive to surfactant formula and increases with decreasing EO groups. This chapter systematically simulates the transport of surfactant and foam in a 2-D homogeneous reservoir with different $K_{sgw}$ values. In Chapter 2, we established a 1-D 2-phase (water and CO$_2$) home-made foam simulator and demonstrated that when surfactant is approximately equally partitioning between gaseous phase and aqueous phase, foam is most favorable for oil displacement in regard with apparent viscosity and foam propagation speed. In this chapter, we extend the modeling to a 2-D 3-phase (water, CO$_2$, and oil) system with gravity at play. The simulation is done using Shell’s in-house Modular Reservoir Simulator (MoReS). We will briefly summarize the implicit-texture (IT) local-equilibrium (LE) foam model in Section 8.2.1, and review the three-phase relative permeability model in Section 8.2.2. We will introduce the initial and boundary conditions of the 2-D homogeneous model reservoir in Section 8.2.3. In section 8.3.1, we will discuss the effect of partition coefficient on foam by comparing the studied scenarios in which continuous CO$_2$ is injected with surfactants of varied partition coefficient into an aqueous reservoir to displace water. In section 8.3.2, we will compare the oil recovery efficiency between WAG, SAG and WAG+S modes and will show that CO$_2$ soluble surfactants with proper partition coefficient can outperform conventional ionic surfactants in terms of mobility control and
oil recovery efficiency by synchronizing the surfactant transport with gas phase propagation in a 2-D homogeneous model system.

8.2. Numerical Methods

8.2.1. Implicit-texture Local-equilibrium Foam Model

Foam can lower the gas phase mobility by orders of magnitude. Yet the water mobility is proven to remain the same at a given water saturation\(^{24}\). Therefore, the STARSTM version of the implicit-texture local-equilibrium model\(^{25,63}\) implemented here only modifies the relative mobility of the gas phase as shown in Equation 8-2. The correction factor for the gas phase mobility reduction \(FM\) is inversely related to the product of a series of dependence functions as shown in Equation 8-3. The parameter \(f_{mmob}\) sets a reference to the maximum foam strength. The dependent functions \(F_{surfactant}, F_{water}\), and \(F_{oil}\) are all in the range of [0, 1]. The surfactant concentration dependence function \(F_{surfactant}\) and the water saturation dependence function \(F_{water}\) are discussed in Chapter 7. We will only list the values assigned to the parameters here in Table 8-1.

In section 8.3.2 where the oil phase is present, function \(F_{oil}\) is introduced to account for the effect of oil on foam. Oil can destabilize foam in porous media by varied mechanisms\(^{18,165}\). In this simulation, the parameter \(f_{oil}\) represent the oil saturation below which oil does not affect foam strength and \(F_{oil}\) equals to 1, whereas the parameter \(f_{moil}\) represent the oil saturation above which foam is completely killed and \(F_{oil}\) equals to 0. The parameter \(e_{poil}\) regulates how \(F_{oil}\) deceases as oil saturation \(S_o\) increases from \(f_{oil}\) to \(f_{moil}\).
\[ \lambda_{rg}^f = \lambda_{rg}^{nf} \times \text{FM} \quad \text{Equation 8-2} \]

\[
\text{FM} = \frac{1}{1 + \text{fmmob} \times F_{\text{surfactant}} \times F_{\text{water}} \times F_{\text{oil}}} \quad \text{Equation 8-3}
\]

\[
F_{\text{surfactant}} = \begin{cases} 
\left( \frac{C_{sw}}{fmsurf} \right)^{\text{epsurf}} & \text{for } C_{sw} < fmsurf \\
1 & \text{for } C_{sw} \geq fmsurf
\end{cases} \quad \text{Equation 8-4}
\]

\[
F_{\text{water}} = 0.5 + \frac{\arctan[\text{epdry}(S_w - fmdry)]}{\pi} \quad \text{Equation 8-5}
\]

\[
F_{\text{oil}} = \begin{cases} 
0 & \text{for } S_o > fmoil \\
\left( \frac{fmoil - S_o}{fmoil - floil} \right)^{\text{epoil}} & \text{for } floil < S_o < fmoil \\
1 & \text{for } S_o < floil
\end{cases} \quad \text{Equation 8-6}
\]

**Table 8-1 STARSTM foam model parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>fmmob</td>
<td>500</td>
</tr>
<tr>
<td>( F_{\text{surfactant}} )</td>
<td>( fmsurf ) 0.2 wt%</td>
</tr>
<tr>
<td></td>
<td>( \text{epsurf} ) 1</td>
</tr>
<tr>
<td>( F_{\text{water}} )</td>
<td>( fmdry ) 0.25</td>
</tr>
<tr>
<td></td>
<td>( \text{epdry} ) 500</td>
</tr>
<tr>
<td>( F_{\text{oil}} )</td>
<td>( floil ) 0.1</td>
</tr>
<tr>
<td></td>
<td>( fmoil ) 0.4</td>
</tr>
<tr>
<td></td>
<td>( \text{epoil} ) 1.5</td>
</tr>
</tbody>
</table>
8.2.2. Three-Phase Relative Permeability Model

Corey model is used to calculate the relative permeability to water $k_{rw}$ and gas $k_{rg}^{nf}$ (no foam). Assuming strict water-wet condition for simplicity, $k_{rw}$ is only a function of water saturation $S_w$ and $k_{rg}^{nf}$ is only a function of gas saturation $S_g$. In 3-phase simulation, linear iso-perm is assumed to calculate the relative permeability to oil $k_{ro}$ as shown in Figure 8-1. The three-phase relative permeability parameters are listed in Table 8-2. It is worthwhile to mention that the water-oil relative permeability is measured in absence of gas whereas the oil-gas relative permeability is measured at connate water saturation $S_{wc}$.

![Figure 8-1 Schematic of the linear iso-perm relative permeability to oil in 3-phase region.](image-url)
Table 8-2 Three-phase relative permeability parameters to water, oil, and gas (no foam)

<table>
<thead>
<tr>
<th>Water-Oil Relative Permeability Parameters</th>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Connate water saturation</td>
<td>$S_{wc}$</td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>Residual oil saturation to water</td>
<td>$S_{orw}$</td>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>End-point relative permeability to water</td>
<td>$k^o_{rw}$</td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td>End-point relative permeability to oil</td>
<td>$k^o_{row}$</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Corey exponent for water</td>
<td>$n_w$</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Corey exponent for oil with respect to water</td>
<td>$n_{ow}$</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oil-Gas Relative Permeability Parameters</th>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual gas saturation</td>
<td>$S_{gr}$</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Residual oil saturation to gas</td>
<td>$S_{org}$</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>End-point relative permeability to gas</td>
<td>$k^o_{rg}$</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>End-point relative permeability to oil</td>
<td>$k^o_{rog}$, $k^o_{row}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corey exponent for gas</td>
<td>$n_g$</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>Corey exponent for oil with respect to gas</td>
<td>$n_{og}$</td>
<td></td>
<td>1.3</td>
</tr>
</tbody>
</table>

8.2.3. Initial and Boundary Conditions (I.C. and B.C.) for Reservoir Simulation

A 2-D homogeneous model reservoir with a permeability of 1 Darcy is initiated for the simulations in section 8.3.1 and 8.3.2. The model reservoir is 2000 ft in length and 200 ft in thickness. The initial reservoir condition is set at 100 bar in pressure and 100 °C in temperature. In all cases studied, fluids are injected at 1 ft/day interstitial velocity. The Peclet numbers for the surfactant dispersion in both phases (CO$_2$ and water) are equal to 50 for field-level simulation.

In Section 8.3.1, the reservoir is initially 100% saturated with water. CO$_2$ is injected continuously with surfactant of different $K_{sgw}$ values to displace the water as shown in Table 8-3. The injection surfactant concentration is 2.5 g/L CO$_2$, 1.25 times of the $fmsurf$ value. In this
section, we will focus on the effect of surfactant partitioning between CO₂ and aqueous phases on
the surfactant transport and foam propagation, and investigate the optimal partition coefficient that
maximizes the sweep efficiency of CO₂.

Table 8-3 Characteristic values for surfactant partition coefficient $K_{sgw}$ for the case studies
in both Section 8.3.1 and Section 8.3.2

<table>
<thead>
<tr>
<th>Surfactant Partition Coefficient</th>
<th>Characteristic Value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small $K_{sgw}$</td>
<td>0.01</td>
<td>Strong affinity to water</td>
</tr>
<tr>
<td>Unity $K_{sgw}$</td>
<td>1.00</td>
<td>Equal affinity to water and CO₂</td>
</tr>
<tr>
<td>Large $K_{sgw}$</td>
<td>50.0</td>
<td>Strong affinity to CO₂</td>
</tr>
</tbody>
</table>

In Section 8.3.2, we add one more degree of complexity by introducing black oil into the
model system. The hypothetical black oil has an API gravity of 45° and a viscosity of 0.4 cP under
the reservoir condition (100°C and 100 bar). The reservoir is initially at an oil saturation $S_{oi}$ of
$(1 - S_{wc})$ and the reservoir is water flooded for 1 PV before enhanced oil recovery techniques are
applied. After the water flooding, the average oil saturation is reduced to 0.4. WAG, SAG, and
WAG+S are applied to the water flooded reservoir respectively in Case A, B, and C. In this section,
we will focus on the comparison between these EOR applications.

8.3. Results and Discussions

In this section, we will first show the results of continuous CO₂ injection with CO₂ soluble
surfactant to displace water and then compare the various EOR techniques, highlighting the benefit
of injecting surfactant with CO₂ and the critical role of $K_{sgw}$. 
8.3.1. CO₂ displacing water with different partition coefficients

In Case I, CO₂ with a CO₂ soluble surfactant of small partition coefficient \( K_{sgw} = 0.05 \) is injected to displace water. The injected surfactant concentration is 0.25wt%. Figure 8-2 displays the snapshots of the saturation and the surfactant concentration profile at different dimensionless times, the total pore volumes (PV) of CO₂ injected. It appears that the surfactant transport is severely retarded with respect to the gas propagation. After 1PV of injection, the surfactant only penetrates a fairly small portion of the reservoir. The segregation between the surfactant and the CO₂ is because of the extremely high surfactant affinity to water. Upon water contact, most of the surfactant quickly partitions into the aqueous phase. Therefore the surfactant accumulates in the near well-bore region and the surfactant concentration in the water \( C_{sw} \) is predominately higher than that in the gas phase \( C_{sg} \). Once the surfactant is stripped off to the water, the CO₂ mobility control is lost. Consequently, the gas overrides the upper layer of the reservoir and streaks through early and the sweep of CO₂ is poor.
Figure 8-2 Case I: Continuous CO\textsubscript{2} (with dissolved surfactant) injection to displace water with small partition coefficient $K_{sgw} = 0.01$. (A) Saturation profile indicating that the gas overrides the reservoir and prematurely breaks through; (B) Surfactant concentration profile indicating that the surfactant is highly concentrated near the well and the transport is retarded.

In Case II, the surfactant partition coefficient is set to 1, which means that the surfactant has equal affinity to both the CO\textsubscript{2} and the water. In contact with water, the surfactant concentration in the gas phase $C_{sg}$ will be equal to that in the water $C_{sw}$. Figure 8-3 shows the snapshots of the surfactant distribution along with the phase saturation profile. In this case, the surfactant transport is synchronized with the gas propagation. The surfactant creates foam with the water residing in the reservoir wherever the gas sweeps. The foamed gas can effectively mitigate the effect of gravity. Therefore, the sweep efficiency of CO\textsubscript{2} is greatly improved. After 1PV of CO\textsubscript{2} injection, most of the reservoir has been swept.
In case III, the surfactant partition coefficient is increased to 50, which means that the surfactant prefers to stay with the CO₂ even if it is equilibrated with water. At equilibrium, the surfactant concentration in the CO₂ phase $C_{sg}$ will be a lot higher than that in the water $C_{sw}$. From $F_{\text{surfactant}}$ function, it is clear that foam strength is directly related to the $C_{sw}$. Therefore, very weak foam is generated because the surfactant concentration in the aqueous phase is too low to produce strong foam. In other words, the highly diluted surfactant concentration in the aqueous phase results in insufficient gas mobility reduction and the foam is not strong enough to fight against the gravity. Consequently, only the upper layer of the reservoir is swept by CO₂. Unlike Case I in which the CO₂ loses its mobility control completely, in Case III, the poor sweep efficiency results from the lack of surfactant in the aqueous phase.
Figure 8-4 Case III: Continuous CO₂ (with dissolved surfactant) injection to displace water with unity partition coefficient of $K_{sgw} = 50.0$ (A) Saturation profile indicating that the foam strength is insufficient to keep CO₂ from overriding the reservoir; (B) Surfactant concentration profile indicating that the surfactant concentration in the aqueous phase is highly diluted.

From the case studies above, we conclude that the foam transport is highly dependent on the surfactant partition coefficient. Figure 8-5 compares the water recovery efficiency with respect to different partition coefficient. In summary, unity partition coefficient is superior to either too large or too small partition coefficient in terms of mobility control and maximizing sweep efficiency. When the surfactant partition coefficient is too small, the surfactant will be highly concentrated near the well-bore, and the gas breaks through early. Too large partition coefficient result in weak foam, and the foam strength might not suffice to fight against gravity effect.
Figure 8-5 Water recovery efficiency comparison between cases of varied surfactant partition coefficients. Unity partition coefficient is superior to either too small or too large partition coefficient in terms of water recovery efficiency

8.3.2. Case Study: WAG, SAG and WAG+S

In this section, we will compare three EOR techniques (Case A: WAG, Case B: SAG, and Case C: WAG+S) to demonstrate the advantage of using conventional foam and foam with CO₂ soluble surfactant for residual oil recovery. In all cases, the reservoir is water flooded to the remaining oil saturation of 0.4. In Case A, WAG, water slugs and gas slugs are alternatively injected into the reservoir. Each cycle consists of 0.2 PV of gas and 0.05 PV of water. In other words, the average gas fractional flow is 0.8. In Case B, SAG, 0.5wt% of traditional surfactant (only soluble in water) is added to the aqueous phase to generate foam in situ. All the other operation conditions are kept exactly the same as Case A. In Case C, WAG+S, the same amount of CO₂ soluble surfactant is injected with CO₂ instead of water. The only difference between Case
B and C is that in Case C, the surfactant is injected with the gas phase and partitions to the aqueous phase to foam. The foam model parameters in Case B and C are kept exactly the same, meaning that the surfactants have the same foaming capability.

Figure 8-6 displays the 3-phase saturation profile snapshots for the WAG process. The gas only floods the upper part of the reservoir and breaks through during the first gas slug injection. The saturation profile does not change much after the first cycle is injected. Due to the density and viscosity contrast, the CO₂ pushes the oil down. An oil band is formed below the gas path way, however, is hardly produced due to the poor gas mobility control.

![3-Phase Saturation Profile](image)

**Figure 8-6 Case A: Water-Alternating-Gas.** The 3-phase saturation profile indicating that WAG mode has very limited improvement in oil recovery compared to waterflooding

Foam can effectively mitigate the gravity effect. Figure 8-7 shows the results of Case B in which 0.5 wt% surfactant (only soluble in water) is added to the aqueous phase. Gas mobility is significantly reduced by the generation of foam inside the porous medium. Gas (depicted in red) partially penetrates the lower part of the reservoir and an oil bank in green is formed in front of the foam. The oil is slowly produced from the production well on the right.
However, comparing the 3-phase saturation profile and the surfactant concentration profile in Figure 8-7, it is noticed that significant amount of surfactant drains down before the gas slugs catches up and is wasted during the water injection period. The gas slug overrides the reservoir; however, the surfactant slug underrides the reservoir. A better alternative to inject the surfactant is needed to synchronize the gas propagation and the surfactant transport such that the surfactant is available to make foam where the gas sweeps.

Figure 8-7 Case B: Surfactant-Alternating-Gas. (A) 3-phase saturation profile indicating that the gas mobility is reduced by foam in presence of surfactant and the sweep efficiency is greatly improved from WAG injection. (B) Surfactant concentration profile indicating that significant surfactant drains by gravity before the CO$_2$ slug catches up.

Figure 8-8 displays the results when the same amount of surfactant is injected with the CO$_2$ phase instead of the water. The partition coefficient between the water and the CO$_2$ in this case is unity ($K_{sgw} = 1.0$). With the favorable partition coefficient, it is shown that the sweep is further improved from the SAG process. The gas phase carries the surfactant and dissolves the right
amount to water to generate foam. It is notable that the gas penetrates into an even larger area in lower part of the reservoir. In addition, the oil bank accumulated is larger compared to the SAG process. All these improvement is because of the synchronization of the gas propagation and the surfactant transport.

Figure 8-8 Case C: Water-Alternating-Gas-plus-Surfactant-in-Gas. (A) 3-phase saturation profile indicating that a larger oil bank is formed and the oil recovery is further improved from SAG mode. (B) Surfactant concentration profile indicating that the surfactant transport is synchronized with the gas phase propagation.

However, it is important to point out that the recovery efficiency of WAG+S is highly dependent on the partition coefficient. As discussed in section 3.1, too small partition coefficient results in surfactant transport retardation whereas too large partition coefficient results in insufficient foam robustness. As shown in Figure 8-9(a), partition coefficient of either 0.01 or 50.0 leads to poorer oil recovery efficiency compared to SAG process. The sensitivity of surfactant
partition coefficient on oil recovery is displayed in Figure 8-9(b). The optimized surfactant partition coefficient for WAG+S process is in the range of around 0.1 and 1.

![Figure 8-9](image)

Figure 8-9 (a) Oil recovery efficiency comparison between WAG, SAG, and WAG+S with varied partition coefficient. (b) Sensitivity of surfactant partition coefficient on WAG+S oil recovery efficiency

### 8.4. Conclusion

We simulated the transport of CO$_2$ soluble surfactant in porous media and probed the effect surfactant partition coefficient on foam EOR. We firstly injected CO$_2$ with surfactant of different $K_{sgw}$ values to a 100% water saturated reservoir. It is found out that the sweep of CO$_2$ is highly dependent on $K_{sgw}$ values. Similar to Chapter 3, when the surfactant has equal affinity to both the water and the gas, the sweep efficiency is optimized. A 2-D thick homogeneous reservoir with residual light oil was then set up for numerical simulation to probe the use of CO$_2$ soluble surfactant for foam EOR. In our case, WAG process has marginally better recovery efficiency
compared to water flooding because of the low density and viscosity of the injected CO$_2$ phase. SAG process improves recovery efficiency by foaming the gas with surfactant solution and therefore providing mobility control. Yet, in the case of SAG injection, significant surfactant is wasted when the surfactant drains with the water before the following gas slug catches up to foam. A better alternative to SAG is WAG+S in which the surfactant is dissolved in the CO$_2$ phase and injected with gas instead of water. WAG+S can synchronize the transport of surfactant with the gas phase propagation when the partition coefficient is in the order of 0.1 to 1.
The previous chapters have elaborately described a multiscale study on the phase/components transport and the rheology of foam flow in porous media. The findings shed light upon the successful implementation of foam technology to various subsurface applications including gas mobility control, water production control, aquifer remediation, energized-fluid hydraulic fracturing, CO₂ sequestration, and improved oil recovery (IOR). Admittedly, the understanding of foam flow in porous media is far from complete. This thesis brings about some mechanistic discoveries regarding (1) the dependence of foam on its constituent components (gas type and surfactant partitioning), (2) the smart rheological properties of foam flows that respond to reservoir heterogeneity, (3) the foam-oil interactions in porous media, (4) the improvements in foam modeling techniques, and (5) the development of the next generation foam flooding process with CO₂ soluble surfactant. The remaining discussion highlights the major conclusions in each chapter and provides a recommendation for future directions.
9.1. Summary of Main Findings

9.1.1. Dependence of Foam Transport on its Constituent Components

The effect of gas type and composition on foam transport in porous media was probed in Bentheimer sandstones with a commonly used anionic foaming surfactant alpha olefin sulfonate \( \text{C}_{14}\text{C}_{16} \). Steady-state foam strengths with respect to three cases of distinct gases and two cases containing binary mixtures of these gases were compared. The effects of gas solubility, the stability of lamellae, and the gas diffusion rate across the lamellae were examined. Our experimental results showed that steady-state foam strength is inversely correlated with gas permeability across a liquid lamella, a parameter that is proportional to the product of diffusivity and solubility and characterizes the rate of mass transport. These results are in good agreement with existing observations that the foam strength for a mixture of gases is correlated with that of the less soluble component.

The effect of surfactant partitioning on foam transport is then discussed. Commonly chosen surfactants as foaming agents are either anionic or cationic in class. These charged surfactants are insoluble in either \( \text{CO}_2 \) gas phase or supercritical phase and can only be injected with water. However, some novel nonionic or switchable surfactants are \( \text{CO}_2 \) soluble, thus making it possible to be injected with the \( \text{CO}_2 \) phase. Since surfactant could be present in both \( \text{CO}_2 \) and aqueous phases, it is important to understand how the surfactant partition coefficient influences foam transport in porous media. Thus, a 1-D foam simulator embedded with STARS\textsuperscript{TM} foam model is developed. All test results, from different cases studied, have demonstrated that when surfactant partitions approximately equally between gaseous phase and aqueous phase, foam favors oil
displacement in regard with apparent viscosity and foam propagation speed. The test results from the 1-D simulation are compared with the fractional flow theory analysis reported in literature.

9.1.2. Dependence of Foam Transport on Rock Permeability: Smart Foam Rheology

The dependence of foam transport on rock permeability in actual reservoir cores at elevated temperature is studied. Laboratory research work was conducted to capture the effect of heterogeneity on foam using actual reservoir rocks of varied permeabilities. In most literature studies, experiments were conducted under conditions that might be less representative of the actual reservoir that has higher temperatures, and with different gas compositions. Our experiments were conducted at elevated reservoir temperature (94 °C) using actual reservoir cores of varied permeabilities, representative brine, methane gas and an in-house developed foaming surfactant formulation capable of withstanding high temperature and high oil saturation. It is observed that foam is more stable in high permeability cores compared to low permeability cores. Therefore the mobility reduction of the gas phase by foam was found to be selectively higher in cores of higher permeabilities. It is concluded that foam can effectively improve the conformance of the oil displacement in presence of reservoir heterogeneity. The permeability-dependent foam rheology can divert the displacing fluids from the high-permeability region to the low-permeability region, therefore enhancing the overall oil recovery efficiency. Our finding in actual reservoir rocks is consistent with the literature observations conducted in outcrop core samples.

Moreover, we used a texture-implicit local-equilibrium model to parameterize our foam system. Mobility reduction of the gas phase by foam was found to be selectively higher in cores of higher permeabilities. Another finding from the model is that, in all cases, the parameter $epcap$, which regulates the significance of shear-dependent rheological behavior, is approximately equal
Foam exhibit Bingham-like fluid properties where pressure gradient is irrelevant to the shear rates.

9.1.3. Foam-Oil Interactions in Porous Media at Multiple Scales

A NOA81 based micromodel was developed to visualize the foam-oil interactions at the pore level. Three characteristic zones were identified in experiments involving the displacement of crude oil from model porous media via surfactant-stabilized foam, and we describe a series of pore-level dynamics in these zones which were not observed in experiments involving paraffin oil. In the displacement front zone, foam coalesces upon initial contact with crude oil which is known to destabilize the liquid lamellae of the foam. Directly upstream, a transition zone occurs where surface wettability is altered from oil-wet to water-wet. After this transition takes place, a strong foam bank zone exists where foam is generated within the porous media. We visualized each zone using a microfluidic platform, and we discuss the unique physicochemical phenomena that define each zone. In our analysis, we also provide an updated mechanistic understanding of the “smart rheology” of foam which builds upon simple “phase separation” observations in the literature.

The effect of oil saturation and composition on foam transport is also investigated in Berea sandstone at elevated reservoir temperature using NMR imaging technique. Apparent viscosity of foam flow was first measured in the presence of residual hexadecane at different foam qualities. Compared to the oil-free case, the measured apparent viscosity was higher with residual hexadecane, indicating successful foam generation in the presence of hexadecane. Furthermore, the NMR imaging technique enabled us to map out the 3-phase saturation profile along the core. Mn$^{2+}$ was used as a dopant in the aqueous phase to differentiate the $T_2$ relaxation time of water from that of oil. A closer analysis of the fluid distribution allowed us to quantify the relative effect of various oil displacement mechanisms. Additionally, we developed a foam-oil (hexadecane and
octane) co-injection experiment, coupled with NMR imaging technique, to correlate the foam strength with the oil saturations. It is discovered that with increasing oil fractional flow, the apparent viscosity first decreased with the increasing oil saturation due to the foam destabilization by oil; and then increased due to the oil emulsification with the surfactant solution. We observed similar trend with respect to hexadecane and octane. Yet, the relative effects between the foam destabilization and the emulsification were very dependent on the oil composition. In the end, further investigation is recommended to unveil the complex interactions between foam and crude oil before the application of foam enhanced oil recovery (EOR) technology to the field.

9.1.4. Improvement in Model Parameterization Algorithms

An improved algorithm for the estimation of foam model parameters was proposed in this thesis. A widely used texture-implicit local-equilibrium foam model, STARS™, is used to describe the reduction of gas mobility in the state of foam with respect to free gas. Both the dry-out effect and shear-dependent rheology are considered in foam simulations. We estimate the limiting capillary pressure $P_c^*$ from $fmdry$ values in the STARS™ model to characterize foam film stability in a dynamic flowing system. We find that $P_c^*$ is good indicator of foam strength in porous media and varies with different gas types. We also calculate $P_c^*$ for different foaming surfactants and find that foam stability is correlated with the Gibbs surface excess concentration. We compare our improved parameter estimation algorithm with others reported in literature. The robustness of the algorithm is validated for various foam systems.

9.1.5. Development of the Foam Flooding Process with CO$_2$ Soluble Surfactant

Lastly, the transport of CO$_2$-soluble surfactant for foaming in porous media is probed using a Shell in-house reservoir simulator called MoReS. We numerically investigate the effect of
surfactant partitioning between the aqueous phase and the gaseous phase on foam transport for subsurface applications when the surfactant is injected in the CO₂ phase. A 2-D reservoir simulation is developed to quantify the effect of surfactant partition coefficient on the displacement conformance and CO₂ sweep efficiency. A texture-implicit local-equilibrium foam model is embedded to describe how the partitioning of surfactant between water and CO₂ affects the CO₂ foam mobility control when surfactant is injected in the CO₂ phase. We conclude that when surfactant has approximately equal affinity to both the CO₂ and the water, the transport of surfactant is in line with the gas propagation and therefore the sweep efficiency is maximized. Too high affinity to water (small partition coefficient) results in surfactant retardation whereas too high affinity to CO₂ (large partition coefficient) leads to weak foam and insufficient mobility reduction. This work sheds light upon the design of water-alternating-gas-plus-surfactant-in-gas (WAG+S) process to improve the conventional foam process with surfactant-alternating-gas (SAG) injection mode during which significant amount of surfactant could possibly drain down by gravity before CO₂ slugs catch up to generate foam in situ the reservoir.

9.2. Future Recommendations

Future research should look into the effect of formation wettability on foam transport in porous media. Foam is a closed system with enormous surface area of which the longevity requires the asymmetric films that spread on the rock surface stay stable. The de-wetting of the water on the solid surface leads to a faster foam destruction rate as shown in Figure 9-1. Of significant interest is to understand the conditions of foam generation and destruction in non-water wet conditions (both oil-wet and mixed wet conditions). An interesting observation from our micromodel experiments is that the surfactant can preferentially adsorb onto the rock surface to
restore the porous media surface to a hydrophilic condition and therefore stabilize the foam lamellae. Yet, further exploration at the core-level is required to validate the success of foam generation in non-water-wet conditions. The foam apparent viscosity from core-flooding experiments should correlate with a quantity such as the water advancing contact angle measurement and the Amott-Harvey index that measures the wettability.

![Image of foam flow in water-wet and oil-wet conditions]

**Figure 9-1 Foam flow in water-wet and oil-wet conditions**

The model porous media design in our micromodel can be improved to better represent the pore structures of real rock pore formations. A consensus is that foam generation is a strong function of the geometry of the pore structure. Visualization of foam flow in a more realistic design of the porous media (possibly based on the CT scan of real rock samples) would offer more convincing evidence to the mechanistic understanding of the bubble generation and destruction. In addition, the understanding of the shear-rate dependent foam rheology in porous media can be better advanced using micromodel visualization technique. Most of the shear-rate scan experiments were conducted in core samples by changing the total superficial velocity at a single fixed foam quality, usually at the transition quality. Yet, the shear rate dependent rheology might
be different between the high-quality foam and the low-quality foam. This hypothesis is based on the morphology disparity between foams of different qualities as shown in Figure 9-2. The low-quality foams exhibit sphere-like bubbles in porous media whereas the high quality foams exhibit polyhedral geometry. Therefore, the difference in foam quality is likely to cause different reactions to the shear-rate in porous media.

![Figure 9-2 Schematics of wet foam and dry foam morphology](image)

The development of foam modeling techniques and simulators should take into account the formation of emulsion. It is observed in lab that that the oil emulsification plays a critical role in determining the overall apparent viscosity of foam-oil 3-phase flow in porous media. The severity of emulsification is dependent on factors including both the oil fractional flow and the oil composition among others (surfactant, and salinity etc.). Yet, current foam models do not include the dependence of foam transport on the formation of emulsions, thus cannot accurately describe the 3-phase flow during the oil displacement experiment by foam flooding. An emulsification dependent function $F_{emulsion}$ should be developed based on the experimental observations.

The development of the CO$_2$ soluble surfactant for foam flooding should examine the effect of surfactant partitioning between the aqueous and the oleic phase, in addition to the partitioning between the aqueous phase and the CO$_2$ phase. Because the surfactant is CO$_2$ soluble, it is likely that the surfactant is soluble in oil as well. Therefore significant amount of surfactant depletion to
the oil should be avoided. Otherwise, it not only retards the surfactant transport, but also risks generating viscous Winsor II w/o emulsions.

This thesis has advanced the understanding of foam flow and transport in porous media at different levels. Both experiment and simulation results have demonstrated that foam offers promise to control the mobility of the gas phase and improve the sweep efficiency in porous media. Yet the use of foam for field-scale subsurface applications requires further investigation.
References


77. Ren, G. PhD Thesis: Dynamics of Supercritical CO₂ Foam in Porous Media with CO₂ Soluble Surfactuants. (University of Texas, Austin, 2012).


Appendix

Matlab Code for Foam Model Parameterization

Main Function:

clear all
clc
clf
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Last update: Feb 19, 2016
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% The code below is developed by Yongchao Zeng from Rice University to
% estimate STARS foam model parameters for F_water and F_shear Function.
% Input data will include quality scan data (total flowrate is fixed) and
% velocity scan data (foam quality is fixed).
% Also relative permeability data for the core sample is pre-requisite.
% Tips: if the estimation is off the trend, try to delete one or two of the
% lowest quality data

% AOS1416, 1.5 wt% in Berea Sandstone (70 mDarcy) at 94C
% Quality Scan Data
fg=[0.397695993,0.496327212,0.59854674,0.719181501,0.785171624,0.854222388,0.926853165,0.972418643];
miu_app=[107.9852165,116.4206514,147.0347625,152.3331479,148.344797,142.4002655,123.4976015,74.53189828]*1e-3;
% Pa*S
ut=3.06*3.52777778*1e-6;
% m/s = 4 ft/day total superficial velocity
% Velocity Scan (Shear Thinning Behavior) Data
ut_shear=[0.761336916,2.989140006,3.719875248,5.917230187,7.408829175]*3.52777778*1e-6;
% m/s
miu_shear=[476.3764938,147.0347625,123.9146074,83.03198189,65.10964948]*1e-3;
fg_shear=[0.60595632,0.59854674,0.594404827,0.59507772];
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Rel/Abs Perm Data for Berea Sandstone (Cited from Litrature)
Swc = 0.3;
Sgr = 0.05;
kr0 = 0.95;
ng = 2.2;
krw0 = 0.7;
nw = 4.3;
sigma_wg = 0.03; % N/m
miuw = 1.0e-3; % Pa.s
miug = 2e-5; % Pa.s
k=0.070*9.869233e-13; %Darcy to m^2
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Calculation begins
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Locate the highest value of apparent viscosity and the transient quality
% should be in the interval of \([fg(i-t-1), fg(i-t+1)]\)

\[ \text{miu}_{\text{app}, t} = \max(\text{miu}_{\text{app}}); \]

% Calculate \((1/FM-1)\)

\[ \text{krw} = \text{miuw} \times (1-fg) / \text{miu}_{\text{app}}; \]
\[ \text{krgf} = \text{miug} \times fg / \text{miu}_{\text{app}}; \]
\[ \text{Sw} = (\text{krw} / \text{krw0}) \times (1/\text{nw}) \times (1-\text{Sgr} - \text{Swc}) + \text{Swc}; \]
\[ \text{krngf} = \text{kr0} \times (1-\text{Sw} - \text{Sgr}) / (1-\text{Sgr} - \text{Swc}) \times \text{ng}; \]
\[ \text{FM} = \text{krgf} / \text{krngf}; \]
\[ \text{MRF} = 1 / \text{FM}; \]

\( \delta = \varepsilon; \) % "1-\delta" is the value of \(F7\) at \(Sw=1\);

\( \text{F7M}_{\text{lower}} = 0.5; \)
\( \text{F7M}_{\text{upper}} = 1 - \delta; \)
\( \text{F7M} = \text{linspace} (\text{F7M}_{\text{lower}}, \text{F7M}_{\text{upper}}, 200); \) % \(F7M\) is the value of \(F7\) at \(Sw=1\)

\( \text{pp} = 0; \)
for \( k = 1 : \text{length} (\text{F7M}) \) % optimize \(fmmob\) at given value of \(F7M\)
% \( k \) is the \(k\)th number of \(F7M\)
    \text{clc}
    \text{progress} = \text{pp} / \text{length} (\text{F7M})
    \text{pp} = \text{pp} + 1;

    % The range of \(fmmob\) for optimization
    \text{v1} = 1;
    \text{v2} = \text{max} (\text{MRF}) \times 1;

    % Calculate the value of objective function for differernt \(fmmob\)
    \text{fmmob\_range} = \text{linspace} (v1, v2, 1000);
    \text{for} \ i = 1 : \text{length} (\text{fmmob\_range})
        \text{Err}(i) = \text{Fmmob} (\text{fmmob\_range}(i), fg, \text{miu}_{\text{app}}, Sw, \text{MRF}, \text{krw0}, \text{kr0}, \text{nw}, \text{ng}, \text{Sgr}, \text{Swc}, \text{miuw}, \text{miug}, \text{F7M}(k));
    \text{end}

    % Find the initial value of \(fmmob\) for second round optimization
    \text{[Err\_min, ix]} = \text{min} (\text{Err});
    \text{v3} = \text{fmmob\_range}(ix);
    \text{[fmmobl(k), Err1(k)] = fminsearch (@(fmmob) Fmmob(fmmob, fg, miu_app, Sw, MRF, krw0, kr0, nw, ng, Sgr, Swc, miuw, miug, F7M(k)), v3);}
\text{end}

% Find the optimal value of \(F7M\)
\text{[Err1\_min, i\_err]} = \text{min} (\text{Err1});
\text{fmmob = fmmobl(i\_err);}  
\text{F7M(i\_err);}  
% optimize \(fmmob, \text{epdry}\) and \(\text{fmmdry}\) at the optimal \(F7M\)
% Do linear regression to calculate \(\text{epdry}\) and \(\text{fmmdry}\) for a given \(fmmob\)
\text{F7 = MRF/fmmob;}

\text{for} \ i = 1 : \text{length} (\text{F7})
    \text{if} \ F7(i) > F7M(i\_err);
\[ F7(i) = F7M(i_{\text{err}}); \]
end
end

\[ y = \tan((F7 - 0.5) \cdot \pi); \]
\[ x = Sw; \]
\[ n = \text{length}(Sw); \]
\[ X = \text{[ones(n,1),} x'] ; \]

\[ [A, \text{bint,} r, \text{rint,} s] = \text{regress(y',X)} ; \]
\[ \text{epdry} = A(2); \]
if \( \text{epdry} = 0 \)
\[ \text{fmdry} = 1; \]
else
\[ \text{fmdry} = -A(1)/\text{epdry}; \]
end

\[ xx = 0.9 \cdot x(\text{end}) : 0.00001 : 1.1 \cdot x(1); \]
\[ yy = A(1) + A(2) \cdot xx; \]

% Calculate the quality scan value based on fmmob, epdry and fmdry
S = 0:0.001:1;
Sww = S * (1 - Sgr - Swc) + Swc;
F7 = 0.5 + atan(epdry * (Sww - fmdry)) / pi;
krww = krw0 * S.^nw;
krggf = krg0 * (1 - S).^ng;
Vis_App = 1 ./ (krww / muw + krggf ./ (muu * (1 + fmmob * F7))) ;
fgg = 1 ./ (1 + krww / muw * muu ./ (krggf ./ (1 + fmmob * F7))) ;

% Find the transition quality and transition saturation based on STARS model fit
[Vis_App_t, ii_t] = max(Vis_App);
fgg_t = fgg(ii_t);
Sww_t = Sww(ii_t);

Vis_App1 = Vis_App * 1000;
muu_app1 = muu_app * 1000;

figure (1)
set(gcf, 'Units', 'centimeters', 'position', [5 2 30 25]);
set(gca, 'FontSize', 20);
plot(fg, muu_app1, 'ro', fgg, Vis_App1, 'b-', 'MarkerSize', 20, 'LineWidth', 5);
xlabel('Foam Quality');
ylabel('Apparent Viscosity (cP)');
legend('Experiment', 'STARS Model', 'Location', 'NorthWest');

% Calculate (1/FM-1) for Shear thinning data
krw_shear = muw * (1 - fg_shear) / muu_shear;
krgf_shear = muu * fg_shear / muu_shear;
Sw_shear=(krw_shear/krw0).^(1/nw)*(1-Sgr-Swc)+Swc;
krgnf_shear=krg0*((1-Sw_shear-Sgr)/(1-Sgr-Swc)).^ng;
FM_shear=krgf_shear./krgnf_shear;
MRF_shear=1./FM_shear-1;
F7_shear=0.5+atan(epdry*(Sw_shear-fmdry))/pi;
F3_shear=MRF_shear./F7_shear/fmmob;
Nca_shear=miuw*ut_shear/sigma_wg;

% Linear Regression to calculate epcap and fmcap
yyy=log10(F3_shear);
xxx=log10(Nca_shear);
n=length(xxx);
XXX=[ones(n,1),xxx'];
[AA,bint,r,rint,s]=regress(yyy',XXX);
epcap=-AA(2);
fmcap=10^(AA(1)/epcap);

xxxx=1.1*min(xxx):0.00001:0.9*max(xxx);
yyyy=AA(1)+AA(2).*xxxx;

M=[ut_shear',miu_shear',fg_shear',Nca_shear'];
M=sortrows(M,1);
ut_shear=M(:,1)';
miu_shear=M(:,2)';
fg_shear=M(:,3)';
Nca_shear=M(:,4)';

ut_s=linspace(min(ut_shear),max(ut_shear),100);
fg_s=sum(fg_shear)/length(fg_shear);
Nca_s=ut_s*miuw/sigma_wg;
for i=1:length(ut_s)
    SS=0:0.001:1;
    Swww=SS*(1-Sgr-Swc)+Swc;
    F777=0.5+atan(epdry*(Swww-fmdry))/pi;
    F333=(fmcap/Nca_s(i)).^epcap;
    krwww=krw0*SS.^nw;
    krgggnf=krg0*(1-SS).^ng;
    MRFFF=fmmob*F777*F333;
    FMMM=1./(1+MRFFF);
    fggg=1./(1+krwww./miuw*miug./(krgggnf.*FMMM));
    miu_shear_Scan=1./(krwww/miuw+krgggnf.*FMMM/miug);
    miu_shear_STARS(i)=interp1(fggg,miu_shear_Scan,fg_s);
end

ut_shear1=ut_shear/(3.52777778*1e-6); % m/s to ft/day
ut_s1=ut_s/(3.52777778*1e-6); % m/s to ft/day
miu_shear1=miu_shear*1000; % Pa.s to cP
miu_shear_STARS1=miu_shear_STARS*1000; % Pa.s to cP

figure (2)
set(gcf,'Units','centimeters','position',[5 2 30 25]);
set(gca, 'FontSize',20);
semilogy(ut_shear1,miu_shear1,'ro',ut_s1,miu_shear_STARS1,'b-',...
'MarkerSize',20,'LineWidth',5);
legend('Experiment','STARS Model','Location','NorthWest');
xlabel('Superficial Velocity (ft/day)');
ylabel('Apparent Viscosity (cP)');

fmcap1=min([miuw*min([ut_shear,ut])/sigma_wg,fmcap]);
fmmob1=fmmob*(fmcap/fmcap1)^epcap;
fmmob=fmmob1;
fmcap=fmcap1;
fg_t=fgg_t;
Sw_t=Swwt;

fmmob
fmdry
epdry
fmcap
epcap
fg_t
Sw_t
Fmmob Function:

```matlab
function y=Fmmob(fmmob,fg,miu_app,Sw,MRF,krw0,krg0,nw,ng,Sgr,Swc,miuw,miug,F2M)

% Do linear regression to calculate epdry and fmdry for a given fmmob
F2=MRF/fmmob;

    for i=1:length(F2)
        if F2(i)>F2M
            F2(i)=F2M;
        end
    end

y=tan((F2-0.5)*pi);
X=Sw;
n=length(Sw);
X=[ones(n,1),x'];
[A,bint,r,rint,s]=regress(y',X);
epdry=A(2);

    if epdry==0
        fmdry=1;
    else
        fmdry=-A(1)/epdry;
    end

% Calculate the quality scan value based on fmmob, epdry and fmdry
S=eps:0.001:1-eps;
Sww=S.*(1-Sgr-Swc)+Swc;
F2=0.5+atan(epdry*(Sww-fmdry))/pi;
krw=krw0.*S.^nw;
krggnf=krg0.*(1-S).^ng;
Vis_App=1./(krw/miuw+krggnf./(miug.*(1+fmmob*F2)));
fgg=1./(1+krw/miuw*miug./(krggnf./(1+fmmob*F2)));

    miu_app=interp1(fgg,Vis_App,fg);
    [miu_app_t,i_t]=max(miu_app);
    [Vis_App_t,ii_t]=max(Vis_App);

% Penalty Function applies if the the transition quality does not falls into the right interval
P1=1;

    if ((fgg(ii_t)<=fg(i_t+1)) && (fgg(ii_t)>=fg(i_t-1)))
        P1=0;
    end
```

end

y=sum(((miu_app-miu_app_t).^2)/length(miu_app)+P1*abs((fgg(ii_t)-fg(i_t))/fg(i_t))^2; % calculate the least square error between experiment data and model prediction