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**The Application of Microfluidics in the Study of Multiphase Flow and
Transport in Porous Media of Improved Hydrocarbon Recovery
Methods**

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**by
Yujing Du**

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Dedication

To my parents

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Abstract

The Application of Microfluidics in the Study of Multiphase Flow and Transport in Porous Media of Improved Hydrocarbon Recovery Methods

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Fundamental investigation of the underlying physics in multiphase flow and transport phenomena in porous media is crucial for many engineering processes, including environmental remediation, geological sequestration, and improved hydrocarbon recovery. Microfluidics are widely used to provide direct, in-time visualization of multiphase flow behavior at the pore-scale and sometimes extend to the representative elementary volumes (REV) scale. Qualitative and quantitative analysis are obtained from microfluidic experiments and are used for mechanisms interpretations. In this work, microfluidics and micromodels are designed to explore fundamental mechanisms in several enhanced/improved oil recovery processes by performing systematic experiments.

First, a study of the low salinity effects in improved oil recovery by microfluidics experiments is presented which explains a type of low-salinity effect with delayed oil recovery and without the presence of clay. Experiments were performed from single-pore microfluidics to a REV scale reservoir-on-a-chip model. A time-dependent, oil-water interaction controlled by diffusion was proposed based on the pore-scale observations.

Second, the time-dependent behaviors and the role of surfactant during the low salinity waterflood is further investigated by systematic experiments in a 2.5D, inch-long micromodel using mineral oils with different surfactant concentrations and water with different salinities. It is found that the low salinity effects are significant when the surfactant concentration is sufficiently high. The surfactant also dominates the time-dependent behaviors, where higher surfactant concentration leads to shorter delay time.

Third, three inch-long “*reservoir-on-a-chip*” micromodels were utilized to probe the impacts of the microfracture connectivity on the displacement efficiency and sweep patterns when the mobility ratio is unfavorable and the displacement is unstable. It was observed the presence of microfractures do not necessarily improve the displacement efficiency, but the microfracture connectivity, capillary number and wettability altogether impact on the displacement patterns and the ultimate recovery.

Last, the role of viscoelasticity’s effects in reducing residual oil saturation is investigated by performing microfluidic experiments in foot-long (30 cm), heterogeneous glass micromodels (“*coreflood-on-a-chip*”). Significant redistribution and reconnection of residual ganglia occur due to viscoelasticity induced instabilities during high-viscoelasticity polymer floods, which results in residual ganglia remobilization that ultimately reduces residual saturation.

Table of Contents

List of Tables	xviii
List of Figures	xix
Chapter 1: Introduction	1
1.1 Motivation.....	1
1.2 Research objectives.....	3
1.3 Chapter outlines	4
Chapter 2: Background and Literature Review	6
2.1 Microfluidics in the study of multiphase flow in porous media	6
2.1.1 Background of microfluidics	6
2.1.1.1 General description	6
2.1.1.2 Materials and fabrication	7
2.1.2.3 Experimental methodology	10
2.1.2 Application of microfluidics to multiphase flow processes in enhanced (EOR) and improved oil recovery (IOR)	13
2.1.2.1 Topology and connectivity	14
2.1.2.2 Surface property and modification.....	17
2.1.2.2 Scale and upscaling issues	18
2.2 Low salinity effects.....	19
2.2.1 Proposed mechanisms.....	21
2.2.1.1 Fluid-rock interaction.....	22
2.2.1.2 Fluid-fluid interaction	24
2.2.1.3 Debate on the role of clay	26
2.2.1.4 Time delayed effect.....	26

2.2.1.5 Microfluidics observations.....	27
2.3 Fractures in unconventional reservoirs	28
2.3.1 Unstable displacement	28
2.3.2 Previous studies	29
2.3.3. Background of the subsurface application.....	31
2.4 Viscoelastic effect in enhancing oil recovery	33
2.4.1 Deborah number	34
2.4.2 Viscoelastic flow instabilities	36
2.4.3 Previous results	36
Chapter 3: Experimental Methods	39
3.1 Micromodel design and fabrication	39
3.1.1 Design	39
3.1.2 Fabrication procedures and equipment	40
3.1.3 Micromodel examples.....	46
3.2 Experiment platform and equipment	47
3.2.1 Platform setups	47
3.2.2 Experimental equipment	48
3.2.2.1 Flow units.....	48
3.2.2.2 Image acquisition equipment	49
3.2.2.3 Measurement equipment.....	51
3.2.2.4 Other equipment.....	53
3.3 Image processing	55
3.4 Fluid preparation and analysis	57

Chapter 4: Microfluidic Investigation of Low Salinity Effects during Oil Recovery	61
4.1 Introduction.....	61
4.2 Experimental method	61
4.2.1 Fluids preparation and analysis.....	61
4.2.2 Microfluidic platform	63
4.2.3 Experiments	65
4.3 Single-pore scale observation: oil de-wetting and swelling	67
4.3.1 Observation from Experiment 1: undiluted crude oil with high salinity water.....	68
4.3.2 Observation from Experiment 2: undiluted crude oil with low salinity water.....	69
4.3.3 Oil swelling dynamics	72
4.3.4 Hypothesis and evidence of mechanisms	74
4.4 Pore network visualization: pore-pore interactions and upscaling	79
4.4.1 Observations from Experiment 5: well-swept region during low salinity waterflood	79
4.4.2 Observations from Experiment 6: partially-swept region during low salinity waterflood	81
4.4.3 Mechanisms from pore-scale perspective.....	83
4.4.4 Upscaling: from pore-scale model to reservoir model.....	86
4.5 Reservoir-on-a-chip validation: delayed increased in oil recovery	87
4.5.1 Improved oil recovery from tertiary low salinity flooding	90
4.5.2 Time-dependent behavior in the reservoir-on-a-chip model	92
4.6 Applications and limitations: core-scale and field scale implications.....	93
4.7 Conclusions.....	95

Chapter 5: Time-Dependent Displacement Dynamics of Low Salinity Effects: The Role of Surfactant Compounds in Oil.....	97
5.1 Introduction.....	97
5.2 Experimental method.....	97
5.2.1 Fluids preparation and analysis.....	97
5.2.2 Micromodel.....	99
5.2.3 Experiments	101
5.2.4 Image analysis.....	102
5.3 Results.....	103
5.3.1 Water displacing dynamics	103
5.3.1.1 High salinity water displacement patterns	104
5.3.1.2 Deionized water displacement patterns	105
5.3.2 Displacement efficiency	106
5.3.2.1 High salinity waterflood	108
5.3.2.2 Deionized waterflood.....	109
5.3.3 Interfacial tension	110
5.3.4 Emulsion and oil de-wetting.....	111
5.4 Analysis and discussion	113
5.4.1 Time-dependency.....	113
5.4.1.1 Delayed reaction	113
5.4.1.2 Long-tailed recovery	114
5.4.2 Role of surfactant.....	115
5.4.2.1 Emulsion and wettability	115
5.4.2.2 Interfacial tension.....	117

5.4.2.3 Oil recovery	117
5.4.3 Displacement mode.....	118
5.4.3.1 Slow imbibition.....	118
5.4.3.2 Sudden collapse	119
5.5 Conclusions.....	120
Chapter 6: Microfluidic Diagnostics of the Impact of Local Microfracture Connectivity on Hydrocarbon Recovery Following Water Injection	121
6.1 Introduction.....	121
6.2 Experimental method.....	121
6.2.1 Micromodels	121
6.2.2 Fluids preparation and analysis.....	124
6.2.3 Experiments	125
6.2.4 Image analysis.....	129
6.3 Sweep patterns	132
6.3.1 Qualitative observations	132
6.3.1.1 Base case (M1).....	134
6.3.1.2 Dead-end microfracture (M2)	134
6.3.1.3 Microfracture connecting macrofractures (M3).....	135
6.3.2 Quantitative analysis.....	136
6.4 Oil recovery	140
6.4.1 Base case (M1).....	142
6.4.2 Dead-end microfracture (M2)	142
6.4.3 Microfracture connecting macrofractures (M3)	143
6.4.4 Comments on qualitative small-scale microfluidic results	144

6.5 Oil ganglia analysis.....	145
6.5.1 Ganglia distribution post water-flooding.....	145
6.5.1.1 Base case (M1).....	146
6.5.1.2 Dead-end microfracture (M2).....	147
6.5.1.3 Microfracture connecting macrofractures (M3).....	147
6.5.2 Ganglia generation during displacement processes	148
6.6 Implications and limitations.....	151
6.7 Conclusions.....	154
Chapter 7: Coreflood-on-a-Chip Study of Viscoelasticity's Effect on Reducing Residual Saturation in Porous Media.....	156
7.1 Introduction.....	156
7.2 Experimental method.....	157
7.2.1 Micromodel.....	157
7.2.2 Fluids preparation and analysis.....	159
7.2.3 Experiments	162
7.2.4 Image analysis.....	165
7.3 Results.....	165
7.3.1 Qualitative results	165
7.3.2 Quantitative results	168
7.3.2.1 Residual saturation after secondary aqueous flood:.....	169
7.3.2.2 Saturation increase in tertiary polymer flood.....	169
7.3.2.3 Saturation reduction in post-tertiary aqueous flood.....	170
7.3.3 Schematic summary	170
7.4 Analysis and discussion	171

7.4.1 Microscopic observation.....	171
7.4.1.1 Residual ganglia swelling in tertiary polymer flood.....	172
7.4.1.2 Residual ganglia mobilization in post-tertiary aqueous phase flood.....	174
7.4.2 Ganglia analysis in single cross-sections.....	174
7.4.2.1 Residual ganglia swelling, redistribution and mobilization in tertiary polymer flood.....	174
7.4.2.2 Residual ganglia mobilization in post-tertiary viscous aqueous phase flood.....	180
7.4.3 Mechanistic discussion.....	182
7.4.3.1 Elasticity induced redistribution/mobilization & salinity related ganglia swelling.....	182
7.4.3.2 Comparison and discussion with existing studies.....	185
7.5 Limitation discussion.....	186
7.5.1 Micromodel.....	186
7.5.2 Fluids.....	187
7.5.3 Rheology and viscoelasticity estimation.....	187
7.5.4 Image analysis.....	188
7.6 Conclusions.....	188
Chapter 8: Conclusions and Recommendations for Future Directions.....	190
8.1 Conclusions.....	190
8.2 Recommendation for future directions.....	193
8.2.1 Microfluidic platform improvement.....	193
8.2.2 Future work on low salinity effects.....	194
8.2.3 Future work on viscoelasticity effects.....	195

Appendices.....	198
A Supplemental discussion for the study of low salinity effects	198
A1 Crude oil viscosity	198
A2 Ageing time.....	198
A3 Micromodel cleaning	199
A4 In-situ contact angle measurement.....	200
A5 Microscopic details of crude oil de-wetting and W/O emulsion generation during DI water injection in pore-network scale experiments	200
A6 De-wetting and water in oil emulsification behaviors of model oil (dodecane) mixed with surfactant (0.1% Span 80).....	201
A7 Limitations of microfluidics in this study	203
B Supplemental results for the study of microfracture's impacts.....	204
B1 Pore-Scale Visualizations of wettability	204
B2 Fractal Dimension Analysis	204
B3 Reproducibility Study	205
C Supplemental results and analysis for the study of viscoelasticity's effects.....	207
C1 Micromodel permeability.....	207
C2 Ganglia swelling during static experiment with high elasticity, low salinity polymer	208
C3 Non-monotonic ganglia swelling during tertiary high elasticity, low salinity polymer flood in experiment 1.....	210
C4 Ganglia swelling and redistribution during tertiary high elasticity, low salinity polymer flood in experiments 2 and 3	212
C5 Oil cluster mobilization process during tertiary high elasticity polymer flood in experiment 4.....	214
D Sensitivity analysis of the image analysis methods	216

D1 Histogram and threshold in image segmentation.....	216
D2 Saturation measurement through image analysis.....	219
D3 Codes (ImageJ) of the image analysis procedure in Appendix D.....	221
References.....	222

List of Tables

Table 4.1: Crude oil properties	62
Table 4.2: Brine properties	63
Table 4.3: Micromodel properties.....	65
Table 4.4: Experiments design.....	66
Table 4.5: Water injection in Experiments 7-10	90
Table 4.6: Literature on the delay behaviors	94
Table 5.1: Fluids	99
Table 5.2: Micromodel properties.....	101
Table 5.3: Experiments	102
Table 5.4: Oil displacement efficiency	107
Table 6.1: Summary of micromodel properties	123
Table 6.2: Summary of fluid properties	125
Table 6.3: Summary of the microfluidics experiments.....	127
Table 6.4: Summary of measured oil recovery for different geometries	141
Table 6.5: Pore volume injected at 95% recovery in different geometries.....	141
Table 7.1: Micromodel properties.....	158
Table 7.2: Compositions and properties of the displacing fluids.....	160
Table 7.3: Fluids and volumes used in each flood in experiments 1-10. Experiments 1-8 were visualized at the macroscale, and experiments 9 and 10 were visualized at the microscale	163
Table 7.4: Oil saturation and changes in each flood in Experiments 1-8	169
Table D.1: Threshold values for segmentation in different methods.....	219
Table D.2: Average oil saturation and saturation decrease using different thresholding methods	220

List of Figures

Figure 2.1: Microfluidics applications in (a) a single channel microfluidics (Xu et al., 2015), (b) a meso-scale pore-network (Ma et al., 2012), (c) inch-long porous media (Yun et al., 2020), and (d) foot-long porous media (Mejia et al., 2020).	7
Figure 2.2: Powder inkjet 3D printing process (Copyright 2008 Custom Part Net. http://www.custompartnet.com/wu/3d-printing).	10
Figure 2.3: Hydrofluoric acid etching procedures for fabrication of 2.5D micromodel proposed in Xu et al. (2017).	16
Figure 2.4: Micromodel pore network design examples. (a) Homogeneous pore network with round grains (Kang and Yun, 2017). (b) Homogeneous pore network with squared shaped grains (Auset and Keller, 2004). (c) Heterogenous pore network from CT-scan (Chang et al., 2019). (d) Heterogenous pore network generated by programming (de Castro et al., 2015).	17
Figure 2.5: Improved oil recovery by low salinity waterflooding in a coreflood experiment (Yousef et al., 2011).	21

Figure 2.6: (a) Schematic of a hydraulically fractured horizontal well with microfractures. Macrofractures and microfractures are identified with blue and red, respectively. (b) Close-up schematic of connected and dead-end microfractures. (c) Example of a fracture network in the vadose zone (fracture network conceptualization taken from Faybishenko et al., 2000). Lateral fractures can be considered microfractures for the purpose of the conceptualization of immiscible flow in this paper. Schematics presented here are not to scale and only serve as an illustration for the fracture connectivity classification implemented in this research.	32
Figure 2.7: Schematic chart of parameters that affect the behavior of unstable fluid displacement in porous media.....	33
Figure 2.8: Previous results from viscoelastic polymer flooding. (a) Residual oil saturation reduction in a coreflood experiment (Qi et al., 2017). (b) Oil droplet oscillation in a single channel – throat – channel microfluidics (Qi, 2018). (c) Oil mobilization in a 2D micromodel (Clarke et al., 2016).	38
Figure 3.1: AutoCAD user interface with a sample design of the 2.5D, inch-long micromodel with a connecting fracture in the middle of the porous matrix.	39
Figure 3.2: (a) A photomask generated from the AutoCAD design shown in Figure 3.1. (b) Pore-scale zoomed-in from the 2.5D photomask design in (a).	40

Figure 3.3: (a) Back of the original glass mirror used for fabrication. The grey color is the protection resin. (b) Cut and cleaned mirror with the protection paint layer removed and copper layer exposed. Glass in underneath the copper layer.....	41
Figure 3.4: Micromodel fabrication facilities in cleanroom. (a) Spincoater (Laurell) used for coating the glass surface with photoresists. (b) Mask aligner machine (Karl Suss MA6) used for photolithography. (c) Operation hood for hydrofluoric acid etching.	43
Figure 3.5: (a) Schematic sketch for hydrofluoric acid etching process for fabrication of 2.5D micromodel (taken from Xu et al., 2017). (b) Pore-scale image of the 2.5D micromodel with mineral oil and water. Cross-sectional sketches of view 1 and view 2 are shown in (c) as the pore throats are shallower and narrower than the pore bodies. (b) and (c) are revised from Du et al., 2020.	44
Figure 3.6: Drilling tool and glass cutter.	45
Figure 3.7: Two ovens used for glass micromodel bonding. (a) A smaller oven with manual temperature adjustment function. (b) A larger programmable oven with both manual and programmable temperature adjustment functions.....	46
Figure 3.8: Micromodel examples. (a) An inch-long 2.5D micromodel. The dimension of the chip is 2.5 inches by 1 inch. (b) A foot-long snake-shaped micromodel. The dimension of the chip is 4 inches by 4 inches	47
Figure 3.9: Experimental platforms for (a) Darcy-scale visualization and (b) microscopic visualization function, respectively.	48

Figure 3.10: Two syringe pumps used in different works. (a) Harvard PHD 2000 Infusion syringe pump. (b) Fusion 400 syringe pump.....	49
Figure 3.11: Flow experiments units including a syringe (Hamilton Gastight Syringe Model 1725 TLL), a piece of tube, connectors (IDEX Health & Science) and steel chip holders (house made).	49
Figure 3.12: Image capturing equipment used for Darcy-scale visualization including (a) Nikon D5600 DSLR camera, (b) light pad and (c) tripod.	50
Figure 3.13: Imaging capturing system used for microscopic visualization including (a) microscope (Accu-Scope EXI310) and microscopic camera (Lumenera Infiniti 2), (b) operating software (Lumenera) for the microscope camera.....	51
Figure 3.14: Profilometer (DEKTAK 6M) in cleanroom.	52
Figure 3.15: (a) Microfluidic pressure sensor (LabSmith) with a measurement range of 250 kPa. (b) Pressure manifold (LabSmith) which transfers the pressure signal to computer software. (c) User interface of the pressure measurement software (μ Process).	53
Figure 3.16: Sonicator (Branson 2800).....	54
Figure 3.17: Hot plate (Corning PC-6200).	54
Figure 3.18: (a) ImageJ user interface with sample functions shown in (b) basic image adjustment, (c) color editing, (d) contrast enhance, (e) image calculator, (f) image binary, (g) image measurements, (h) particle analyze and (i) image stack registration.	56

Figure 3.19: Image processing examples for a $2.5\text{cm} \times 1.5\text{cm}$ micromodel geometry. Oil phase is in pink in (a) and (b). (c) Grey scale image in black (water) and white. (d) Image with adjusted color in blue (water) and white. Images are from experiment 1.	57
Figure 3.20: Rotational rheometer (ARES-G2).	57
Figure 3.21: Spinning drop tensiometer (KRÜSS SDT).	58
Figure 3.22: Overhead stirrer (Caframo).	59
Figure 3.23: Digital balance with a precision of 0.001g (Adam Equipment HCB123).	60
Figure 4.1: Images of micromodels at the macroscale (left) and pore-scale (right). Micromodel A is a dead-end pore micromodel, Micromodel B is a narrow homogeneous micromodel, and Micromodel C (C1 and C2) is a homogeneous micromodel with a fracture. The scale on the left is in centimeters.	64
Figure 4.2: Schematic sketch of micromodel experimental set up.	67
Figure 4.3: Crude oil behavior in the dead-end pores during Experiment 1 and 2. Image (a): crude oil in contact with high salinity water at different times in Experiment 1. Image (b): crude oil in contact with DI water at different times in Experiment 2. The yellow phase in each image is the crude oil, and the channel in each image was filled with water. Circled areas with dark color in image (b) show oil swelling and the formation of water in oil emulsions.	69

Figure 4.4: (a) Higher magnification images of crude oil/water/solid contact angle in the dead-end pore captured at the beginning and after 2 days of DI water injection in Experiment 2. (b) Crude oil in contact with 650 ppm low salinity water at different times with the pore partially filled with oil. Here we clearly observe the mobilization of contact line, which indicates that the low-salinity water flooding does change the wettability, and contact line pinning is not the only reason for apparent contact angle decreasing.70

Figure 4.5: Contact angle in dead-end pores at different times in Experiment 2. The wettability changed from slightly oil-wet to strongly water-wet during 3 days of DI water injection.71

Figure 4.6: Image (a): Oil swelling ratio versus time in Experiments 2-4 with the original crude oil, the 3 times diluted crude oil and the 10 times diluted crude oil. Image (b): Scaled oil swelling ratio in Experiment 2-4 versus times after dividing the relative diffusivity factor due to the viscosity reduction.73

Figure 4.7: Illustration of different wettability behaviors in high and low salinity environment. The upper half represents the oil droplet immersed in high salinity water, in which case polar components stay at oil-water and oil-solid interfaces and thus keeps the oil wetting to the solid surface. The bottom half represents the oil droplet immersed in low salinity water, in which case the expanding of internal emulsion droplets' surface provides large area for polar components to adsorb on and thus the number of polar components on oil-water and oil-solid surfaces decrease, which results in less wetting condition. Yellow and blue represent the crude oil and water phase, respectively. The water emulsions in the oil phase come from the surrounding water by diffusion.....75

Figure 4.8: Crude oil-water interfacial tension at different brine salinities. The salinity of deionized water was plotted at 1 ppm. Error bars were calculated from multiple repeating measurements.77

Figure 4.9: A well-swept area of Micromodel B at different times in Experiment 5. Image (a) and (b): the beginning and the ending of the DI water injection at 1 microliter/hour. Circled areas in Image (a) and (b) show oil droplets swelling and deformation caused by the growth of water in oil emulsions. The flow direction in each image was from the left to the right. 130 pore volumes of water was injected during the low salinity injection.....80

Figure 4.10: A not-well-swept area of Micromodel B at different times in Experiment 6. Image (a): the beginning of the DI water injection. The flow direction in each image was from the left to the right. The black dashed line indicates the boundary of swept region after high salinity brine flooding, and the red dashed line indicates the boundary of the swept region after tertiary DI water flooding. The oil droplets circled by red dash lines in image (a) through (f) indicate the oil droplets de-wetting where contact lines also moved. 130 pore volumes of water was injected during the low salinity injection.	82
Figure 4.11: Oil saturation of the poorly-swept cross section of Micromodel B during low salinity waterflood performed in Experiment 6. The oil recovery has a long tail of 3 days, indicating a continuous change in a time period of tens of hours to several days. 130 pore volumes of water was injected during the low salinity injection.	83
Figure 4.12: (a) Illustration of the improvement of sweep efficiency during low salinity waterflood from pore-scale perspective. De-wetted and swelled residual oil droplets move to the pore body from the grain surfaces and throats, increasing the water flow resistance and re-directing the water into previous un-swept region. (b) Schematic sketch of relative permeability change during the residual oil de-wetting. The blue solid line is water relative permeability in the oil-wet state; blue dashed line is water relative permeability in the water-wet state; the black solid line is the oil relative permeability in the oil-wet state; the black dashed line is the oil relative permeability in the water-wet state.	85

Figure 4.13: Images of Micromodel C1 at different times in Experiment 7. High salinity water was injected from 0 hours to 23 hours, and DI water (low salinity) was injected from 23 hours to 85 hours. The yellow and the white represent crude oil and water, respectively. The scale bar in the left-top image is 500 μm and applies to all images. The injection direction is from the left to right for all images. The black dashed line indicates the boundary of the swept region after high salinity brine flooding and before DI water flooding; the red dashed line indicates the boundary of the swept region after tertiary DI water flooding. Both dotted lines are extrapolations for the purpose of better understanding, and not the actual experimental results.	89
Figure 4.14: Oil saturation versus time in Experiments 7 through 10. The horizontal lines mark the response time for the tertiary low salinity waterfloods.	90
Figure 5.1: The structure of the surfactant (Sorbitan monooleate) used in this chapter.	99
Figure 5.2: Micromodel used in Chapter 5. (a) Micromodel photomask design. (b) Photo of the fabricated glass micromodel saturated with mineral oil (pink). (c) Microscopic pore image after waterflood with mineral oil (reddish) and water (white).	100
Figure 5.3: Image processing samples for the results presented in Chapter 5. Oil phase is in pink in (a) and (b). (c) Grey scale image in black (water) and white. (d) Image with adjusted color in blue (water) and white. Images are from experiment 1.	103

Figure 5.4: (a)(b)(c) High salinity water displacement processes in experiments 1-6. (d)(e)(f)(g) DI water displacement processes following the high salinity water displacement processes in experiments 1-5. The water invasion patterns for high salinity brine flood and DI water flood are presented in red and blue colors, respectively. Images in each column are from the same experiment. Experiment numbers (#1-#6) are labeled beneath the corresponding columns.	104
Figure 5.5: Oil saturation versus injection time in experiments 1-6. High salinity brine flood is shown in red and DI water flood is shown in blue. Experiment numbers (#1-#6) are labeled at the top right corner in each plot.	107
Figure 5.6: (a) Interfacial tensions between oil/brine (red) and oil/deionized water (blue) versus surfactant concentration in the oils. (b) Zoomed-in from the initial region of plot in (a).	111
Figure 5.7: (a)-(e) Microscopic visualization after DI waterflood (2 nd flood) in experiment 1-5. (f) Microscopic visualization after high salinity brine flood in experiment 6. Note that the fracture is present in (b), (c) and (d) but is not present in (a), (e) and (f) because in the later three cases the area near the fracture was well-swept after the corresponding flood.	112
Figure 5.8: Delay time before water invasion in the DI waterflood against DI water injection time in real time (hours) and injected pore volumes.....	114
Figure 5.9: Breakthrough time versus surfactant concentration in oil during 1 st waterflood (high salinity brine).	116
Figure 5.10: Oil recovery versus the surfactant concentration in oil from (a) 1 st waterflood (high salinity brine) and (b) 2 nd waterflood (deionized water).	118

Figure 6.1: (a) Photomask design of the flow domains in micromodels 1, 2, and 3 denoted as M1, M2, and M3, respectively. (b) Photomask design of inlet, outlet, flow channels to/from the flow domain. (c) Microscopic image of the micromodel after flow experiment. (d) Cross-sectional schematic of micromodel pore body/grain at 45°. (e) Cross-sectional schematic of micromodel pore body/pore throat at 90°. Note that throats are etched shallower than pores as part of the 2.5D fabrication scheme. ...123

Figure 6.2: Pore-scale images of (a) mineral oil (red) remaining after water injection in M2, and (b) crude oil (beige) remaining after water injection in M3. Mineral oil and crude oil are the non-wetting and wetting phase, respectively. Contact angles are obtained by measuring along the contact lines at multiple liquids/solid interfaces from corresponding cases.125

Figure 6.3: Flow pattern classification based on capillary number (Ca) and viscosity ratio (M). Boundary lines are determined by Lenormand et al., 1988 (shown in blue) and Zhang et al., 2011 (shown in red). Drainage (crude oil recovery) is identified with black squares while imbibition (mineral oil recovery) is identified with brown X's.127

Figure 6.4: Experimental system, including a DSLR camera (Nikon D5500), a syringe pump (PHD 2000, Harvard Apparatus), a LED light pad, and a tripod.129

Figure 6.5: (a) Image processing steps for binarizing each frame and subsequently determining isolated oil ganglia. Note that the steps for image analysis effectively capture wetting-phase pendular rings. (b) Grey scale distribution of the raw and binarized image from imbibition (left) and drainage (right) at low capillary number in M1.131

Figure 6.6: Patterns of invading phase for three capillary numbers at breakthrough and steady state during (a) imbibition, and (b) drainage. The matrix micromodels (M1) demonstrate characteristic that resembles *viscous fingering* behavior by moving towards the outlet and not forming loops. (c) Conceptual picture for fingering fluid dendrite propagation in the presence of a microfracture. Flow direction is from one macrofracture (inlet, not shown) to another (outlet, not shown). Main microfracture dendrites are confined inside the microfracture. Macrofracture dendrites originate from the macrofracture (inlet) and traverse within the matrix. Secondary microfracture dendrites originate from the microfracture and traverse within the matrix.133

Figure 6.7: (a) Reference fractal dimension values for capillary and viscous fingering. The higher the fractal dimension, the more coalescent the immiscible front becomes (Chen et al., 2017). (b) Steady-state fractal dimension values calculated for the micromodels at all capillary numbers for the two wettability conditions. (c) Fractal dimension for micromodels throughout their water-flood experiments (top) imbibition and (bottom) drainage. We note that fractal dimension is a function of capillary trapped oil saturation. Error bars are the maximum range of values obtained when values of capillary trapped oil saturation were altered by $\pm 5\%$139

Figure 6.8: Capillary trapped saturation curves for each micromodel at three capillary numbers during imbibition (top) and drainage (bottom).140

Figure 6.9: (a) Oil recovery, and (b) pore volume injected at 95% recovery for each micromodel at three capillary numbers for imbibition and drainage processes.	141
Figure 6.10: Distribution of oil ganglia at steady state for each micromodel at three capillary numbers during imbibition (top) and drainage (bottom). Oil ganglion size is defined as the actual ganglion size divided by a single pore size. Oil ganglion percentage is defined as the area of a single oil ganglion as percentage of the total remaining oil in each size group.	146
Figure 6.11: (a) Number of oil ganglia as a function of capillary trapped oil saturation (S_{oil}) for (top) imbibition and (bottom) drainage. Aggregate plots of oil ganglia versus capillary trapped saturation are shown for (b) imbibition and (c) drainage.....	150
Figure 7.1: (a) Photomask design of the micromodel. (b) Image of the micromodel M2 saturated with crude oil (brown) captured by a DSLR camera. (c) Microscopic image of pores with crude oil (brown) and glycerol (white) from another case than (b). Two cross-sections at view 1 and view 2 are demonstrated in planar view. (d) Cross-sectional schematics of the micromodel pore body/grains at view 1 and pore bodies/pore throat at view 2. (e) Schematic sketch of the experimental setup.	158
Figure 7.2: (a) Rheological behaviors of HPAM polymers solutions denoted as elastic polymer, inelastic polymer 1 and inelastic polymer 2. G'/G'' plots of (b) elastic polymer 1, (c) elastic polymer 2, (d) inelastic polymer 1, and (e) inelastic polymer 2.....	161

Figure 7.3: Image processing procedures for the results presented in Chapter 7. Oil phase is in brown in (a) and (b). (c) Grey scale image in black (oil) and white. (d) Image with adjusted color in red (oil) and white.....	165
Figure 7.4: Oil (black) distribution in the micromodel at (a) initial oil saturation, (b) residual oil saturation at the end of secondary flood, (c) end of tertiary polymer flood, and (d) end of post-tertiary flood. Experiment number (#) is labeled at the top right corner in each image.	166
Figure 7.5: Displacement fronts during secondary glycerol flood in experiments 1-8 with oil phase (black) and aqueous glycerol solution phase (white). Swept regions are marked within red dashed rectangles.	167
Figure 7.6: Oil saturation curves in each experiment for experiments 1-8 with (a) high elasticity in tertiary flood and (b) low elasticity in tertiary flood. Experiment number (#) is labeled at the top left corner in each image.	168
Figure 7.7: Schematic summary of the results presented in Chapter 7.3.2. (a) Summary of behaviors using different polymer solutions. (b) Conceptual diagram based on polymer elasticity and salinity conditions.	171
Figure 7.8: Pore-scale visualization of residual oil ganglia in experiments 9 (top row) and 10 (bottom row) during (a) tertiary polymer flood (high elasticity and low salinity), and (b) post-tertiary glycerol flood with oil (brownish) and glycerol (white). Red circles in (a) highlight the emulsifications (dark) inside the oil phase; red arrows in (a) point to locations where oil interfaces change and oil ganglia reconnect.	173

Figure 7.9: Oil swelling and redistribution during tertiary polymer flood in experiment 1 (high elasticity and low salinity). Entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.176

Figure 7.10: Oil mobilization during tertiary polymer flood in experiment 4 (high elasticity and high salinity). Entire domain is shown at (a) 0.39 pore volumes of polymer flood (before oil mobilization) and (b) 1.1 pore volumes of polymer flood (after oil mobilization). (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.177

Figure 7.11: Oil distribution during tertiary polymer flood in experiment 6 (low-elasticity and high salinity). Entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.179

Figure 7.12: Oil swelling during tertiary polymer flood in experiment 7 (low elasticity and low salinity). Entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.	180
Figure 7.13: Oil saturation and distribution changes in a cross-section during post-tertiary glycerol flood in (a) experiments 1 (high elasticity and low salinity) in the left column, (b) experiment 4 (high elasticity and high salinity) in the middle column, and (c) experiment 7 (low elasticity and low salinity) in the right column. The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.	182
Figure 7.14: Contact angle between oil and glycerol solutions (a) before secondary flood and after tertiary flood when (b) elastic polymer 1, (c) inelastic polymer 1, and (d) elastic polymer 2 was used, respectively.	184
Figure A.1: Higher magnification images of crude oil droplets in pore networks in Experiment 3 (a) before DI water injection (oil was the wetting phase) and (b) after 3 days of DI water injection (oil was the non-wetting phase).	201
Figure A.2: Dodecane with 0.1% surfactant (Span 80) in dead-end pores during DI water injection at different times. Dodecane was in the pores and DI water was in the main channel. Circled dark areas contain water in oil emulsions.	202

Figure A.3: Contact angle between dodecane with 0.1% surfactant (Span 80) and DI water in dead-end pores vs. time.....	203
Figure B.1: Pore-scale images of (a) mineral oil (red) remaining after water injection in M1, M2 and M3, and (b) crude oil (beige) remaining after water injection in M1, M2 and M3. Mineral oil and crude oil are the non-wetting and wetting phase, respectively.	204
Figure B.2: Example of (a) an image divided into boxes with size ($\ell = 64$ pixels) and (b) log-log plot of the box numbers that contain an invading phase pixel. The slope of the plot is the fractal dimension (D_f) – in this case 1.73. The smallest box sizes are limited to the voxel resolution (approximately 12 μm).	205
Figure B.3: Repeated experiments (run #2) in 6 cases are shown in (a) - (f). Note that case (f) run #2 was conducted in a different micromodel which tended to be “mixed-wet” instead of water-wet compared with #1 in (f), therefore the oil saturation curve falls in-between the mineral oil case (water-wet) and crude oil case (oi-wet).	207
Figure C.1: Pressure drop at different water injection rates	208
Figure C.2: (a) Oil ganglia at 0 min, 40 min, 30 hours and 40 hours during static experiment with elastic polymer 1 (low salinity and high elasticity). (b) Ganglion swelling percentage versus time.	210

Figure C.3: Oil swelling and redistribution during tertiary polymer flood in experiment 1 (high elasticity and low salinity). Entire domain is shown at (a) the beginning of polymer flood, (b) 1.4 pore volumes of polymer flood at peak oil saturation, and (c) the end of polymer flood. (d), (e), and (f) are the same cross-section zoomed-in from (a), (b) and (c), respectively. (g) Changes from (d) to (e). (h) Changes from (d) to (f). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.212

Figure C.4: Oil swelling and redistribution during tertiary polymer flood (high elasticity and low salinity) in experiment 2 (A) and experiment 3 (B). In both (A) and (B), entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.214

Figure C.5: (a) Oil mobilization process at different times during tertiary polymer flood in experiment 4 (high elasticity and high salinity). (b) Mobilized cluster's length versus injected pore volumes.215

Figure D.1: Histogram changes during image enhancement procedure. (a) Initial raw images. (b) Histogram of the raw images. (c) Enhanced images. (d) Histogram of the enhanced images. The pink phase is mineral oil and the light phase is DI water.217

Figure D.2: Histogram changes during image segmentation using five different thresholding algorithms with (a) Otsu, (b) Default, (c) Moment, (d) IsoData and (e) Li methods. Oil is in black (histogram value = 255) and water and grains are in white (histogram value = 0).....218

Figure D.3: (a) Oil saturation measured from the image sequence (1-5) after binarizing using different thresholding methods. (b) Average oil saturation (black dash line) and the standard deviation of saturation (red bars) using different methods. (c) Saturation decrease of an image compared to the next one (black dash line) and the standard deviation of the saturation change (red bars) using different methods. E.g., image interval 1 is the saturation difference between image 1 and image 2.220

Chapter 1: Introduction

1.1 MOTIVATION

Multiphase flow and transport in porous media are encountered in many subsurface engineering applications, such as environmental remediation (Chu et al., 2003), groundwater processing (Chu et al., 2001; Cueto-Felgueroso and Juanes, 2008), geologic sequestration and storage (Benson and Surles, 2006; Juanes et al., 2006), and enhanced/improved hydrocarbon recovery (Willhite, 1986; Lake et al., 2014). Although theories are relatively well established to describe the basic flow and transport dynamics in porous media, many scientific and engineering questions remain because of the complexities of the subsurface geologic conditions and the involved processes. The geometrical, topographical and petrophysical properties of subsurface porous media are complicated, which can be described as low conductivity, high capillarity, elevated pressure and temperature, variations in heterogeneity, permeability, connectivity, spatial scales and surface characteristics, etc. To address these questions, novel methods and technologies for subsurface processes are continuously proposed and applied in the field. Therefore, experimental evidence that provides new, fundamental insights into fluid flow behavior in porous media during evolving subsurface processes are continuously required to link the existing theories and advancing methods/technologies across scales from pores to the field.

Enhanced oil recovery (EOR)/improved oil recovery (IOR), sometimes referred to tertiary recovery because EOR/IOR are often (with exceptions of several secondary recovery) operated after primary and secondary recoveries, contribute to a significant amount of incremental oil production (Lake et al., 2014). Significant reserves of hydrocarbon remain in reservoirs after primary production and secondary recovery (usually

by extensive waterflooding), because of macroscopic bypassing and/or microscopic capillary trapping (Sorbie, 1991). EOR/IOR is therefore applied to recover part of the remaining hydrocarbons. To develop the most efficient recovery strategies, experiments are usually performed prior to field operations. Corefloods are experiments performed on real 3D rock samples (drilled cores) extracted from outcrops or the subsurface. A complementary approach, microfluidics/micromodels have some unique advantages and have been more utilized in recent years because of their ability to provide fundamental, pore-scale details of EOR/IOR processes (Lifton, 2016; Anbari et al., 2018).

For decades, microfluidics has been widely applied in many science and engineering disciplines including biomedical screening (Mairhofer et al., 2009; Wang and Li, 2011), chemical synthesis (Dittrich et al., 2006; Song et al., 2008), and subsurface engineering applications to probe various natural and engineering processes (Mehmani et al., 2019a; Yun et al., 2020; Browne et al., 2020). In enhanced/improved oil recovery processes, microfluidics and micromodels are used as artificial pores or porous media that allow direct, in time visualization of the fluid flow and transport dynamics at the pore-scale and up to the representative elementary volume (REV) scale. Pore-scale and REV scale visualization are subsequently analyzed for qualitative and quantitative interpretations to provide fundamental, mechanistic descriptions of the investigated processes. In addition to their visualization capability, microfluidic experiments are usually less time-consuming and therefore have potential for screening purposes of new enhanced/improved oil recovery method. The motivation of this work is to utilize different microfluidics/micromodel devices for fundamental investigation of EOR/IOR related processes, and provide benchmark evidence for future model developments and mechanistic studies in this area.

1.2 RESEARCH OBJECTIVES

The overall objectives of this work are to reveal the underlying mechanisms of several EOR/IOR related topics using microfluidic and micromodel devices. First, the effects of low salinity brine on improved oil recovery are investigated by performing experiments in single dead-end pores, meso-scale pore-network (10^2 pores), and REV scale, inch-long “*reservoir-on-a-chip*” micromodels (10^4 pores) using crude oil and brines with different salinities. “*Reservoir-on-a-chip*” (ROC) refers to a technique to perform flooding experiments in micromodels (Gunda et al., 2011) which are traditionally performed in reservoirs (e.g., water/polymer/surfactant floods). The impacts of the pore-scale oil-water interactions on macroscale improved oil recovery are investigated using an experimental workflow over multiple spatial scales. A new physical mechanism of the low salinity effect is proposed based on the observations in different microfluidic systems.

Second, the role of the in-oil-surfactant in low salinity effects is investigated by analyzing the water-oil interaction dynamics during the low salinity waterflood. Systematic experiments were performed using mineral oils with different surfactant concentrations and water with different salinities in a 2.5D, inch-long, homogenous micromodel with a fracture in the middle of the porous matrix. The study provides further fundamental evidences and analysis for the mechanism proposed in the first part.

Third, three 2.5D “*reservoir-on-a-chip*” micromodels with different fracture connectivity (no fracture, dead-end fracture and connecting fracture) in the middle of the porous matrix are utilized to identify the impacts of the connectivity of microfracture on viscous hydrocarbon displacement at unfavorable mobility ratios. The findings demonstrate the impacts of capillary number, wettability, and microfracture connectivity on the hydrocarbon displacement efficiency.

Last, a “*coreflood-on-a-chip*” micromodel is utilized to explore the role of viscoelasticity on reducing residual oil saturation and improving oil recovery in enhanced oil recovery operations. “*Coreflood-on-a-chip*” refers a technique that performs flooding experiments in core-length (~1 ft.) micromodels that have realistic pore-network design compared to rocks used in a traditional coreflood (Mejia et al., 2020), it can be seen as an extension of the “*reservoir-on-a-chip*” model. This work demonstrates that viscoelasticity does help in reducing the residual NAPL/oil saturation without posing an extraordinarily large viscous force, as flow instabilities resulted from viscoelastic flow induce reconnection and redistribution of residual ganglia.

1.3 CHAPTER OUTLINES

This chapter, chapter 1, presents a brief introduction of the motivation, objectives, and outlines of this dissertation. Chapter 2 provides background and literature review of the studies conducted for the dissertation. In chapter 3, the experimental methodology, including experimental platforms, equipment, fluids and materials used in the studies are described. Chapter 4 presents the study of the low salinity effects between a viscous crude oil and brines using three microfluidics systems ranging from the single dead-end pore microchannels to inch-long “*reservoir-on-a-chip*” micromodel. One type of low-salinity effect with delayed oil recovery and without the presence of clay is explained using the experimental observations from the pore-scale to macroscale. Chapter 5 presents a follow-up study of the low salinity effect using surfactant contained mineral oil and brine. An inch-scale micromodel with a fracture in the middle of the porous matrix is utilized to investigate the effects of oil surfactant concentration on the time-dependency and the improved oil recovery efficiency. In chapter 6, a study of the impacts of microfracture connectivity, wettability, viscosity ratio on the displacement patterns and efficiencies is

presented using three inch-long micromodels with different fracture designs. Chapter 7 contains the work that explores the roles of viscoelasticity on reducing residual oil saturation and improving the oil recovery. The experiments are conducted in a foot-long “*coreflood-on-a-chip*” micromodel, and visualizations are obtained at both the REV scale of the entire model and at the pore-scale. Chapter 8 summarizes the findings in chapters 4 through 7, concludes the dissertation, and provides suggestions of future work directions.

Chapter 2: Background and Literature Review

2.1 MICROFLUIDICS IN THE STUDY OF MULTIPHASE FLOW IN POROUS MEDIA

2.1.1 Background of microfluidics

2.1.1.1 General description

Microfluidics is an experimental method that investigates fluid flow and transport in micrometer scale structures such as pores, pore-networks and micro-channels. The small chips, with built-in microscale structures, are referred to as microfluidic models or simply as microfluidics. Microfluidic models that contain pore-networks (both solid grains and interconnected void space) are called microfluidic pore models, or micromodels. Microfluidics enables direct, in-time visualization, flexible design and fast experiments, and has excellent reproducibility and vast screening capability.

Microfluidics/micromodels are widely used in many science and engineering disciplines such as biomedical screening (Mairhofer et al., 2009; Wang and Li, 2011), chemical synthesis (Dittrich et al., 2006; Song et al., 2008), environmental remediation (Zhong and Mayer, 2001; Ghosh et al., 2019), carbon dioxide geologic sequestration (Wang et al., 2016; Hu et al., 2017), and enhanced hydrocarbon recovery (Mehmani et al., 2019a; Li et al., 2020). In the applications shown in Figure 2.1, microfluidics has been developed as a platform to investigate multiphase flow and transport phenomena across scales from microscale pores and channels (Xu et al., 2015; Sun et al., 2018), to meso-scale pore-networks (Ma et al., 2012; Song et al., 2018), inch-scale (Yun et al., 2020) and foot-scale macroscopic porous media (Mejia et al., 2020).

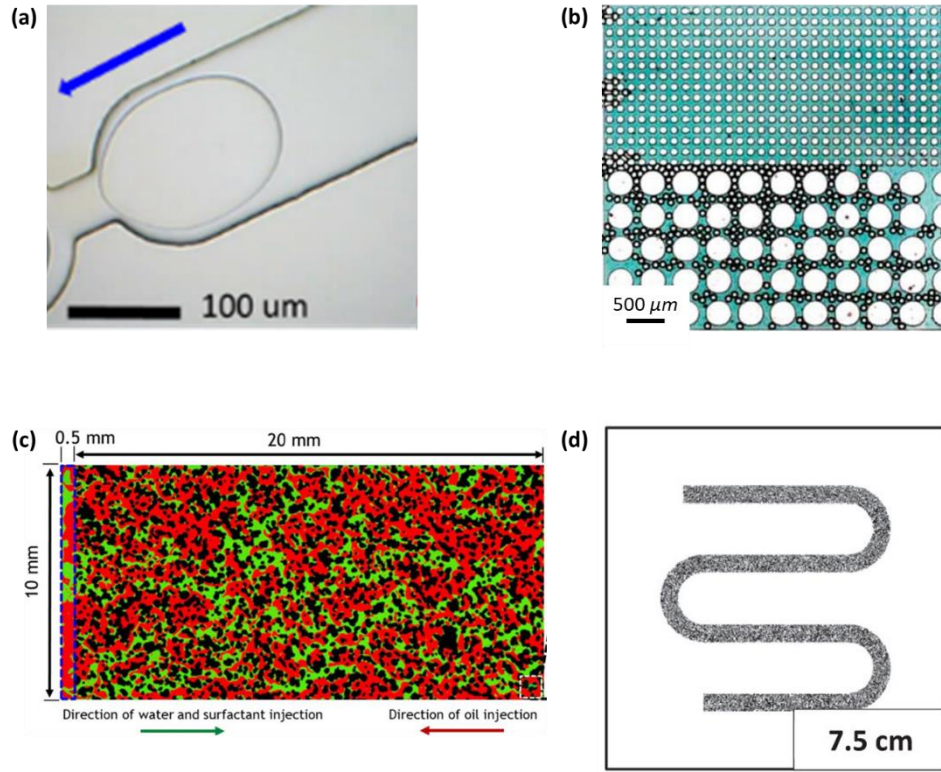


Figure 2.1: Microfluidics applications in (a) a single channel microfluidics (Xu et al., 2015), (b) a meso-scale pore-network (Ma et al., 2012), (c) inch-long porous media (Yun et al., 2020), and (d) foot-long porous media (Mejia et al., 2020).

2.1.1.2 Materials and fabrication

Materials used for microfluidics and micromodels fabrication include polymethyl methacrylate (PMMA), polydimethylsiloxane (PDMS), glass, silicon, thin rock slices, glass beads, Norland optical adhesive (NOA), as well as combinations of these materials, e.g., glass – PDMS, glass – silicon and glass – rock – glass (Karadimitriou and Hassanizadeh, 2012; Lifton, 2016; Anbari et al., 2018; Cao et al., 2019).

Polymeric materials such as PMMA and PDMS are relatively inexpensive and easy for mass manufacturing, and are therefore widely used for microfluidic experiments (Ma et al., 2011; Karadimitriou et al., 2013; Gitlin et al., 2015; Chen et al., 2016). The

fabrication using the two materials does not require wet etching such as hydrofluoric acid etching, or dry etching (e.g., plasma etching). Hot embossing is used to fabricate PMMA microfluidics and replica molding is used to fabricate PDMS microfluidics. However, PDMS and PMMA have relatively low chemical resistance; PDMS swells in contact with nonpolar solvents (such as hydrocarbons and toluene), and PMMA reacts with common organic solvents (such as ethanol and acetone). PDMS and PMMA have much lower stiffness compared to glass and silicon by having low to moderate Young's modulus of 0.0013 – 0.003 GPa and 1.3 – 1.8 GPa, respectively. The two polymeric materials are operational at low to moderate temperature – up to 50°C for PDMS and 100°C for PMMA. In addition, PDMS and PMMA are naturally hydrophobic, and their surface properties are qualitatively different from rocks in the subsurface geologic formation which are naturally hydrophilic. Surface modification by coating or plasma treatment is needed to alter the surface wettability of the polymeric materials (Soper et al., 2002; Gitlin et al., 2015; Zhou et al., 2009).

In comparison, silicon is resistant to most organic solvents and inorganic chemicals, stable at high pressure (with Young's modulus of 130 – 180 GPa) and temperature (up to 1400°C), and can achieve high etching precision using plasma or laser etching (Ren et al., 2013; Grate et al., 2013; Anbari et al., 2018; Cao et al., 2019). However, the lack of transparency of silicon requires a glass cover to be bonded with the silicon substrate. One concern with the silicon – glass microfluidics is the surface property differences between glass and silicon surfaces. Glass and silicon have different surface roughness and surface charges. The effects of the surface property differences of the top and bottom materials on fluid flow are usually ignored since the silicon is also hydrophilic, and the flow is highly capillary dominated and the distribution in the vertical direction is not considered (Xu,

2018; Grate et al., 2013). However, effects of the surface property differences may be effective in scenarios where corner flows and film flows along the surfaces are significant.

Glass is another commonly used microfluidics and micromodel material. Compared to other materials, glass has unique advantages. First, the transparency of glass allows direct visualization by relatively simple photographic technology, such as optical microscopy and digital camera. Second, glass has good chemical resistance and does not react with most organic solvents and inorganic chemicals (but reacts with hydrofluoric acid). Third, glass tolerates relatively high temperature up to 550 °C, and high pressure with Young's modulus of 50 – 90 GPa (Anbari et al., 2018; Cao et al., 2019). Fourth, glass has similar surface charges and wettability as quartz in sandstone rocks, which are the main components of a large number of hydrocarbon reservoirs (Xu, 2018; Song and Kovscek, 2015). Fourth, the chemical and mechanical processes (drilling, cutting, thermal bonding and wet/dry etching) in the fabrication procedures are relatively cost efficient for glass micromodels. Fifth, the surface property (wettability, roughness) of glass surface can be easily modified (Grate et al., 2013; Murison et al., 2014) which is discussed in section 2.1.2.2. The fabrication procedure is well-documented, normally includes pattern design in CAD software, photolithography, photoresist development, hydrofluoric etching or plasma etching and thermal bonding. The pore structures are either artificially designed or taken from a CT-scan of a real rock thin slice, depending on the specific purpose of the study.

In addition to the most widely used materials discussed above, other materials are used or will be used in future microfluidics design due to technology advancements and the evolution of research. Multilayered micromodels consisting of microscale glass beads is considered a type of micromodel with 3D pore-connectivity. The advancement of 3D printing technology is allowing more transparent, printable materials to be used in the fabrication of 3D printed micromodels (Au et al., 2015; Waheed et al., 2016; Watson et al.,

2019; Li et al., 2020). An example of the 3D printing platform is shown in Figure 2.2. 3D printing directly converts the microfluidics/micromodel design in computer-aided design (CAD) software into the actual devices, which allows fast fabrication of the real 3D structures.

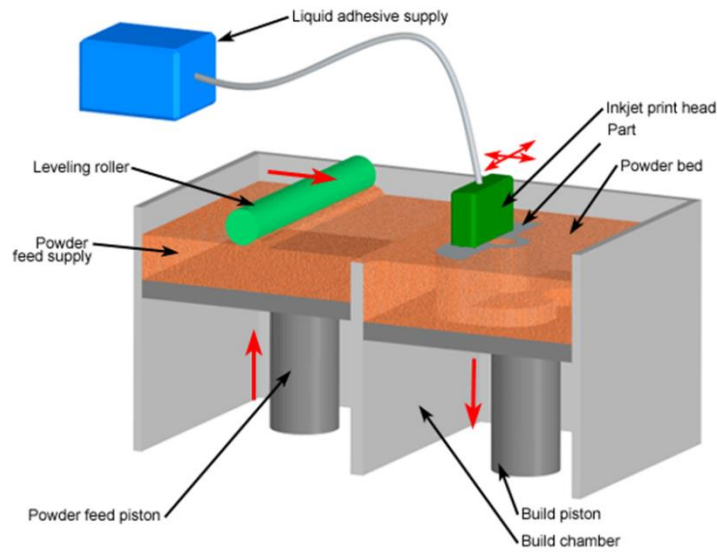


Figure 2.2: Powder inkjet 3D printing process (Copyright 2008 Custom Part Net. <http://www.custompartnet.com/wu/3d-printing>).

2.1.2.3 Experimental methodology

The apparatus for microfluidic experiments include the injecting module (syringe pump), flowing domain (microfluidic/micromodel chip), visualization or data acquisition equipment, measurement module, and environment control equipment. Visualization or data acquisition equipment is usually optical microscopes with microscope digital camera and digital single-lens reflex (DSLR) camera, especially for 2D and 2.5D micromodels that only contain one layer of features. Confocal microscopy is used to obtain layer by layer details in 3D micromodels and can also be used in 2D and 2.5D micromodels for specific

interests in the vertical direction. Scanning electron microscopy (SEM) and charge-coupled device (CCD) are sometimes used for probing the local details. Particle Image Velocimetry (PIV) is applied to track the instantaneous flow field in micromodels. An optical microscope mounted with a digital camera is used to observe and capture phenomena occurring in micromodels at the sub-pore scale, in a single pore or up to a millimeter-scale area containing tens to hundreds of pores. For macroscopic, inch-scale visualization of the entire “*reservoir-on-a-chip*” and “*coreflood-on-a-chip*” models containing $\sim 10^4$ pores, DSLR cameras are used to capture the domain of up to $\sim 10\text{cm} \times 10\text{cm}$. “*Reservoir-on-a-chip*” (ROC) refers to a technique to perform floodings in micromodels (Gunda et al., 2011) which are traditionally performed at the field scale (e.g., water/polymer/surfactant floods). “*Coreflood-on-a-chip*” refers a technique that performs flooding experiments in core-length (~ 1 ft.) micromodels that have realistic pore-network design compared to rocks used in a traditional coreflood (Mejia, et al., 2020). During the macroscale image acquisition process, to ensure the imaging quality, a LED light pad is mounted underneath the micromodel which provides a relatively invariant background light intensity. A pressure sensor and temperature transducer are the two most used measurement components used to measure and/or monitor the pressure and temperature in the systems during experiments. A pressure resistance box with observation and visualization windows (Kazemifar et al., 2015) and heating elements are used in experiments that require elevated temperature (Chang et al., 2019).

After data acquisition, image analysis is conducted to extract qualitative and quantitative information from images. The information extracted by image analysis includes phase saturations, droplet/bubble/ganglia sizes, number and distribution, interface curvature, contact angle, and more. Phase separation is required for microfluidic/micromodel systems with multiple phases. Some fluids used in experiments

have natural color and therefore are easy to be distinguished from other phases using optical visualization methods. For example, crude oil usually has yellow to dark brown color, therefore automatically distinguishes itself from other phases such as air or water. Air and water are both transparent, but they form a dark boundary at the fluid-fluid interface due to the difference in refractive index. When using multiple immiscible transparent fluids such as in a system with both mineral oil and water, dyeing is applied to one or more phases to enable phase identification. Dyeing can sometimes slightly change the interface properties such as interfacial tension and contact angle, which should be addressed in some specific scenarios (Xu, 2018). When a micromodel system contains more than one fluid that are miscible, phase boundaries between them is blurred, but the color intensity is still an indicator of the percentage of each of the components at a specific location. Another method to track the behaviors of a particular component that dissolves/mixes with one or more phases is by adding fluorescence to the target phase and using the fluorescence mode of the microscope.

ImageJ, an open source image processing software, is commonly used for image analysis of microfluidic experiment results. ImageJ is easy to use, robust and has many built-in functions. The most frequently used built-in functions include: “registration” for aligning a stack of image to the same location; “sequestration” that separates different phases; “binary” that transfers the image into binary format; “color adjustment” that assign artificial color to indicated phases; “particle analysis” that measures the number and sizes of droplets/ganglia, and “measurement” that measure the multiple geometric properties such as size and angle. In addition to ImageJ, Matlab and Python are used for image processing by self-developed codes. The self-developed codes are more flexible but less robust and sometimes need to be tested before applying them.

2.1.2 Application of microfluidics to multiphase flow processes in enhanced (EOR) and improved oil recovery (IOR)

In recent decades, microfluidics has become an important screening tool for EOR/IOR applications (Lifton, 2016; Anbari et al., 2018; Gogoi and Gogoi, 2019). Depending on the pore geometry and connectivity, wettability and surface properties, remaining oil in porous media after a conventional waterflood can exist in the form of capillary trapped droplets and ganglia and in the un-swept regions. Capillary trapped oil droplets/ganglia exist in the swept regions and are left behind after displacement due to high capillarity. Remaining oil left in the unswept regions are caused by geologic heterogeneity and/or unfavorable mobility ratio between the displaced and displacing fluids (Willhite, 1986; Lake et al., 2014; Sorbie, 1991). Both macroscopic and microscopic displacement patterns and the distribution of the residual fluids in porous media and in single pores, are important information for the study of recovery efficiency improvement.

Many microfluidics studies have been performed to analyze the performances of enhanced oil recovery processes, such as polymer flooding (Buchgraber et al., 2011; Clarke et al., 2016) surfactant flooding (Xu et al., 2017a; Tagavifar et al., 2017; Yang et al., 2020), nanoparticle fluids flooding (Xu et al., 2015), foam flooding (Ma et al., 2012; Conn et al., 2014), and low salinity water flooding (Emadi et al., 2013; Bartels et al., 2017; Song and Kovscek, 2015; Fredriksen et al., 2017). In these studies, the microfluidics/micromodels provide benchmark experimental evidence that enhance fundamental, mechanistic study and model developments. In many of the above studies, physical models are developed for interpretation of the underlying mechanisms of different EOR/IOR processes. Phenomena observed at the pore-scale are then upscaled to explain the behavior in larger scales (core-scale and reservoir-scale). Using microfluidics and upscaling is then a ‘bottom-up’ approach to study multiphase flow phenomena in porous media

In studying flow and displacement phenomena encountered in EOR/IOR processes, micromodels are used as artificial porous media that mimic real rocks in the subsurface environment. As a result, the geometrical, the topological and surface properties of the micromodels need to be considered for comparison with natural rocks (such as sandstones and carbonates).

2.1.2.1 Topology and connectivity

Natural geologic porous media have three-dimensional (3D) connectivity in the void space, have continuity of the grain phase, and are heterogeneous. In comparison, most microfluidics/micromodels are only connected in 2D, are not continuous in the grain phase, and have only one layer of pore-network. The most important advantage of using 2D micromodels is that they are relatively easy to fabricate and make observations using regular optical microscopy. In contrast, in a real three-dimensional pore-network micromodel (e.g. 3D glass beads or 3D printed micromodels), the visualization process is less direct. Confocal microscopy must be used to provide layer by layer scanning for reconstruction of the 3D structures and dynamic fluid distribution within them (Datta et al., 2013). A significantly larger amount of work and additional costs are imposed to use 3D micromodels for studying the same phenomena. Technology advances in 3D printing have enabled additional opportunities to fabricate 3D microfluidics and micromodels (Waheed et al., 2016; Watson et al., 2019; Li et al., 2020). However, 3D printing platform is expensive, and micromodel fabrication using 3D printing is still challenging, as the highest resolution is on the scale of 10^2 micrometers which does not meet the requirements for many research (Waheed et al., 2016; Macdonald et al., 2017).

The two-dimensional limitation of microfluidics devices is a challenge for translating quantitative observations to three-dimensional systems. However, two-

dimensional micromodels are still capable of serving as diagnostic tools for identifying multiphase flow dynamics phenomena and providing conceptual pictures of them. In a previous work, three-dimensional micromodels were fabricated and the observations of two-phase flow (imbibition) experiments were compared with a two-dimensional micromodel with similar pore structure (Avraam et al., 1994). The authors concluded that restriction of two-dimensional micromodels does not prevent them from providing qualitative findings that are generalizable to three dimensions (such as continuous break-up and coalescence of ganglia at “steady-state”). Presently, 2D (and 2.5D – discussed later) are still the most popular micromodel platforms in studying the flow and transport phenomena in subsurface applications.

In 2D micromodels, all features (pore bodies, pore throats, fractures) have the same depth, and the grains are separated. As a result, important petrophysical phenomena that occur in real rocks, such as capillary snap-off of the non-wetting phase, cannot be captured (Xu et al., 2017b). The drawback of the 2D design compromises the results where capillary trapping becomes significant or even dominant as in many enhanced oil recovery applications. To remediate this drawback and to include the important pore-scale 3D features into the 2D micromodels, a few modification methods have been proposed in the literature by utilizing multiple stages etching or multiple layers processing (Wan et al., 1996; Park et al., 2012; Chang et al., 2020; Tsao et al., 2021). Multiple stage etching/multiple layers processing creates pseudo 3D (or 2.5D) geometry by imposing different depths at the pore bodies and the pore throats. The femtosecond laser material processing (FLMP) method has been recently proposed to fabricate another type of 3D micromodel having four different depths on the surface of borosilicate glass substrates (Owusu-Ansah and Dalton, 2020). Both methods can capture the important features of 3D porous media but require more work in the design and fabrication. Another 2.5D design

was recently proposed to create different pore throat and pore body depths by single-time etching, taking advantage of the isotropic etching property of hydrofluoric acid as shown in Figure 2.3 (Xu et al., 2017b). In the photomask design in AutoCAD, the pores are separated by a certain distance. During the hydrofluoric acid etching, the acid etches in the horizontal direction and ultimately creates pore throats and connect separate pores. The resulting pore throats are narrower and shallower than pore bodies. Capillary snap-off of the non-wetting phase and the continuity of the wetting phase are both realized in these 2.5D micromodels.

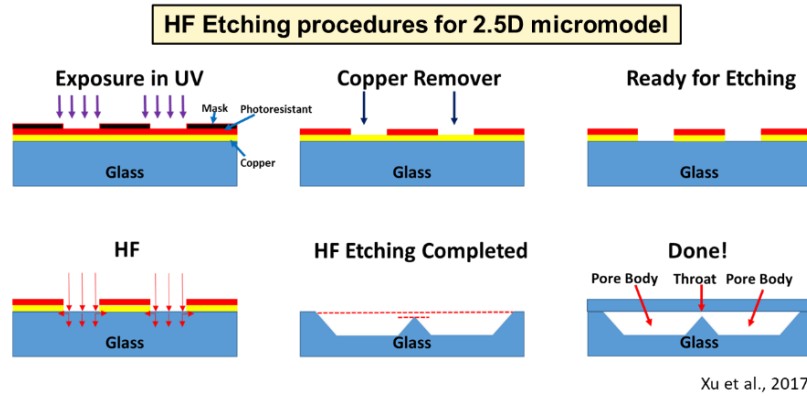


Figure 2.3: Hydrofluoric acid etching procedures for fabrication of 2.5D micromodel proposed in Xu et al. (2017).

Heterogeneity affects flow and displacement in porous media. Many fundamental studies that utilize microfluidics do not include heterogeneous structures. Micromodels with artificially designed homogeneous pore-networks usually have regular-shaped pores and grains such as round (Figure 2.4a) and square (Figure 2.4b). Heterogeneity in pore-network design can be achieved by either using the design from the CT-scan of real rock slice which is naturally heterogeneous (Figure 2.4c), or artificially generating by programming (Figure 2.4d).

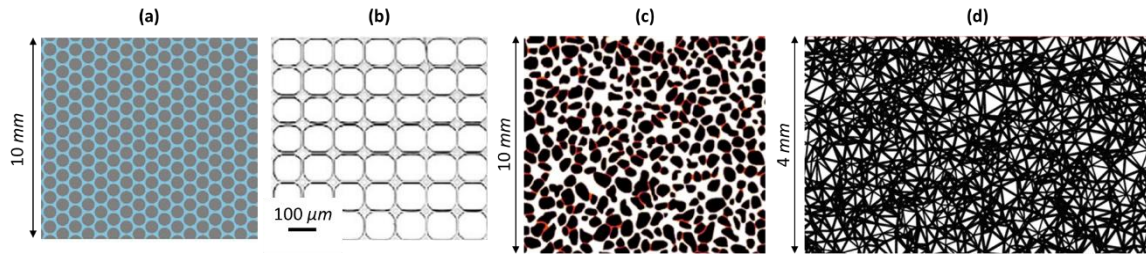


Figure 2.4: Micromodel pore network design examples. (a) Homogeneous pore network with round grains (Kang and Yun, 2017). (b) Homogeneous pore network with squared shaped grains (Auset and Keller, 2004). (c) Heterogenous pore network from CT-scan (Chang et al., 2019). (d) Heterogenous pore network generated by programming (de Castro et al., 2015).

2.1.2.2 Surface property and modification

As previously discussed, several materials, including silicon and glass, can be used for fabrication of microfluidics/micromodels. They both have similar surface charges with quartz (primary component of sandstone rocks that comprise many of the hydrocarbon reservoirs). However, real sandstone rocks are more than pure quartz and contain different types and percentages of clay. The effects of clay are sometimes negligible in scenarios where clay contents are very low or clay does not significantly affect the flow dynamics. Glass and silicon micromodels are used directly in these cases. However, when the reactions and behaviors of clay become important, the micromodel surface needs to be modified by clay coating. Previous studies have proved the applicability and efficiency of this technique (Song and Kovscek, 2015).

Glass, silicon, quartz, as well as sandstones are water-wet at natural conditions without surface modification. However, it is found that aging glass micromodels for days with chemicals such as crude oil may result in a different degree of wettability alteration to a more oil-wet state (Bartels et al., 2017). Some reservoir rocks, especially carbonates,

are oil-wet after aging with crude oil due to their surface properties. Silanization is commonly used to change the surface property of glass and make a glass micromodel oil-wet (Mejia et al., 2019). During silanization, a functional silane solution is injected to the micromodel to react with the surfaces for sufficient time (determined experimentally) at elevated temperature. To better mimic carbonate rocks, calcite coating is also utilized in some studies to make glass/silicon micromodels “carbonate like” by having the similar surface compositions as carbonates (Song et al., 2018).

Surface roughness is a microscopic characteristic that may impact the contact angle displacement process and microscopic fluid distribution (Ghanbarian et al., 2016; Botto et al., 2017). The grains in natural rocks are rarely smooth due to various mechanical and chemical processes that occur in the natural environment (Mehmani et al., 2019a). Roughness on glass micromodel surfaces is typically achieved using glass etching cream, and the degree of roughness can be controlled by adjusting the concentration of the etching cream in water (Mehmani et al., 2019c). Studies have shown that surface roughness has significant impacts on the displacement process by affecting sub-pore physical processes such as pore filling, capillary trapping, contact-line pinning, fluid invasion and sweep patterns, and displacement efficiency (Mehmani et al., 2019c; Sun et al., 2021).

2.1.2.2 Scale and upscaling issues

Microfluidics and micromodels usually have flow domains with a length of several millimeters to several centimeters. A major concern with such microfluidics is whether the flow observations in the relatively small geometry are applicable to larger scales. For example, capillary end effects may impact the distribution of fluids and the displacement efficiency (Huang and Honarpour, 1998; Kang and Yun, 2018; Tanino and Christensen, 2019), and can have significant impacts in some studies especially at strong water-wet

conditions (with most unmodified glass micromodels). Therefore, the experimental results, especially the quantitative analysis, are sometimes not able to upscale to large scale applications.

The idea of using long micromodels to eliminate possible capillary end effects and upscaling concerns was recently proposed. A novel, foot-long ($\sim 30\text{cm}$) micromodel that minimizes the capillary end effects, referred to as a “*coreflood-on-a-chip*” model, was used (Mejia et al, 2020). The “*coreflood-on-a-chip*” model better mimics real rocks than many other micromodels while maintaining the advantageous features of traditional microfluidics. The long length (30 cm) minimizes the potential scale issues in many micromodels, thus providing a more realistic experimental environment (Mejia et al, 2020). Pore-scale 3D (or 2.5D) features are achieved by etching the pore throats shallower than the pore bodies so that the grains are also connected, allowing the occurrence of Roof capillary snap-off (Xu et al., 2017b). Heterogeneity is an important feature that impacts the drainage dynamics and therefore the microscopic displacement. Heterogeneity is also incorporated in the “*coreflood-on-a-chip*” micromodel using a stochastic pore network generator which generates a heterogenous pore network with desired topological properties (pore size, porosity, connectivity and angularity).

2.2 LOW SALINITY EFFECTS

Low salinity effects refer to the improved oil recovery from low salinity water flooding (LSWF) after conventional, high salinity waterflooding. Low salinity water flooding has become a promising EOR method and has attracted much research interest. Compared to many other EOR methods that use chemicals or require large energy input, low salinity waterflooding is cost-efficient and environmentally friendly. The first systematic study of the low salinity’s effects on improved oil recovery dates back to 1997

(Tang and Morrow) when the authors reported that the oil recovery of a sandstone core increases by waterflooding with decreased salinity. Meanwhile, they found the decrease in salinity resulted in a wettability alteration towards a more water-wet state from the initial oil-wet state.

Since the pioneering work of Tang and Morrow (1997), many experimental studies conducted in the laboratory have demonstrated improved recovery from low salinity waterflooding (Webb et al., 2005; Zhang and Morrow, 2006; Zhang et al., 2007; Rivet et al., 2010; Nasralla et al., 2010; Yousef et al., 2011; Aghaeifar et al., 2018). Field and pilot tests have also shown promising results of low salinity effects in reducing the remaining oil in reservoir (Webb et al., 2003; McGuire et al., 2005; Robertson, 2007; Lager et al., 2011). Depending on the types of oil, brines, cores and flooding strategies, the incremental oil recovery from low salinity waterflooding varies from 0 to more than 20%. Figure 2.5 demonstrates an example of the improved oil recovery by low salinity waterflooding from a coreflood experiment from Yousef et al. (2011).

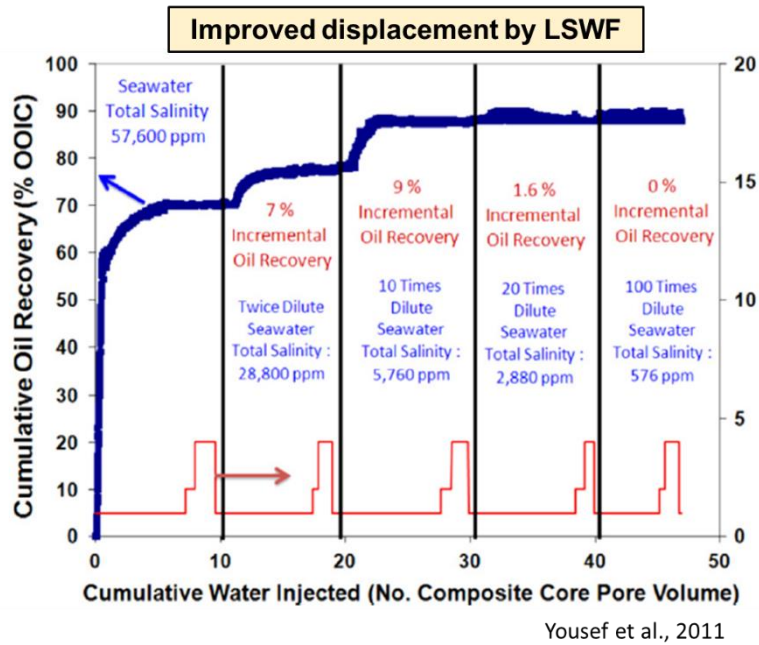


Figure 2.5: Improved oil recovery by low salinity waterflooding in a coreflood experiment (Yousef et al., 2011).

Despite all the positive results reported in a large number of literatures, there are still debates on the controlling mechanisms and inconsistencies in observations that may be intrigued by low salinity waterflooding. Popular discussed mechanisms can be roughly categorized into rock-fluid interactions and fluid-fluid interactions (Siadatifar et al., 2021). In both rock-fluid interactions and fluid-fluid interactions, multiple mechanisms can be effective.

2.2.1 Proposed mechanisms

In almost all mechanisms proposed in the literature, a general accepted consensus is that wettability alteration towards a more water-wet state occurs in the oil/water/rock system during low salinity water injection (Tetteh et al., 2020; Siadatifar et al., 2021). The wettability alteration is believed to be a result of the interaction between low salinity water and the oil/rock based on many experimental observations and measurements. Wettability

alteration changes the relative permeability of water and oil in the two-phase flow system (Lake et al., 2014). Specifically, it increases the relative permeability of oil and may reduce the residual oil saturation which help improve oil recovery. Therefore, the wettability alteration is the contributor, or at least one of the important contributors, to the observed improved oil recovery.

Based on the wettability alteration in the system, some numerical modeling works have simulated the performances of the low salinity waterflooding by interpolating the relative permeabilities between the water-wet and oil-wet state to account for the wettability alteration (Jerauld et al., 2006; Gupta et al., 2011; Masalmeh et al., 2014; Suijkerbuijk et al., 2014; Khorsandi et al., 2017(a)(b)). The relative permeabilities of water and oil at a location are interpolated between the initial oil-wet state and the final water-wet state according to the local salinity or the cation concentration.

Despite the importance of wettability alteration, the underlying mechanisms and the dynamics of the low salinity induced wettability alteration are still not well interpreted. Many mechanisms involving different fluid-rock interactions and fluid-fluid interactions have been proposed to explain the reason and the contribution of the wettability alteration. Different hypotheses explain the wettability alteration and the improved oil recovery from different perspectives. It is believed that more than one mechanism may simultaneously contribute to the improved recovery (Suijkerbuijk et al., 2012; Sandengen and Arntzen, 2013; Sheng, 2014), and none of the many proposed mechanisms have received a general acceptance (Jackson et al., 2016).

2.2.1.1 Fluid-rock interaction

Most widely accepted mechanisms involving fluid-rock interactions include clay swelling and fines migration (Tang and Morrow, 1999; Lager et al., 2008(a); RezaeiDoust

et al., 2011; Song and Kovscek, 2015), multi-component ion exchange between water and the rock surface (Lager et al., 2008(b), 2011), expansion of electrical double layer (Ligthelm et al., 2009; Myint and Firoozabadi, 2015), and rock dissolution (Den Ouden et al., 2015; Nasralla et al., 2015).

Sandstones usually contain clay. The water contained in clay at initial reservoir conditions has the same salinity as the formation water which is usually high. When exposed to water with lower salinity compared with the formation water, the clay absorbs the water molecules from the surrounding bulk water phase. As a result, the clay swells and some of the clay detaches from the sandstone surface when the equilibrium is broken. The swelling and detaching of the clay can result in the detachment of the oil that is originally attached to the clay surfaces because of surface charges and the properties of the polar groups in the crude oil phase. The detachment of oil from the solid surface is the reason for the improved oil recovery. The detached clay may migrate in the pore-networks and may change the local flow dynamics by changing the local permeability and porosity, which may lead to improved oil recovery.

Multi-component ion exchange occurs on the rock/brine and rock/oil interfaces. Multi-component ion exchange usually involves divalent cations such as Ca^{2+} although monovalent cations such as Na^+ may also be important (Lager et al., 2008; Al-Shalabi and Sepehrnoori, 2016). At an initial high salinity condition, oil is attached to the positively charged rock surfaces (such as Ca^{2+}) and the surface is considered oil-wet. With a decrease in the salinity and the concentration of the cations, the cations originally on the rock surfaces are replaced with cations with weaker attractive forces and the oil detaches from the surfaces as the attraction decreases. The wettability subsequently changes to a more water-wet state.

Electric double layer (EDL) swelling is another concept that is used to explain the wettability alteration (Ligthelm et al., 2009; Myint and Firoozabadi, 2015; Alshakhs and Kovscek, 2016). A thin water film exists between the oil and the rock surface in both sandstones and carbonates. The ionic strength decrease due to a salinity decrease causes the water film to expand, leading to the detachment of oil from the rock surfaces. According to DLVO theory, both the water/rock and the oil/water interfaces are electrically charged, positively or negatively. When the charges of the two interfaces have the same sign, the force between oil and the rock surface is repulsive, and when the charges have the opposite sign, the force is attractive. Zeta potential is a representative measurement of charges of the EDL on the interfaces. A decrease in salinity may increase the repulsive force or decrease the attractive force, and either changes will lead to oil detachment and the wettability alteration to water-wet.

Rock dissolution hypothesis is proposed for low salinity effects in carbonate rocks (Den Ouden et al., 2015; Nasralla et al., 2015). Carbonate rocks, under most reservoir conditions, are oil-wet due to the positively charged surfaces that attract the negatively charged groups such as -COOH in crude oil. Calcite mineral in carbonate rocks dissolves in brine at a rate affected by the brine composition and concentration. When the brine salinity decreases, calcite dissolution rate increases. The dissolution increases the pH, changes the surfaces ions and charges, and changes the overall electrical properties of the interfaces. As a result, oil detaches the rock surfaces it originally attached to and the wettability changes towards more water-wet.

2.2.1.2 Fluid-fluid interaction

In studies considering the fluid-fluid interactions between the low salinity water and oil, water micro-dispersion in oil (Emadi and Sohrabi, 2013), water osmosis

(Sandengen and Arntzen, 2013; Sandengen et al., 2016; Fredriksen et al., 2017), pH elevation (McGuire et al., 2005; Austad et al., 2010) and interfacial tension reduction (Fogden, 2011) are hypothesized to contribute to the low salinity effects.

When in contact with low salinity water, water-in-oil micro-dispersion/micro-emulsion form in the crude oil phase (Emadi and Sohrabi, 2013; Tetteh et al., 2018). The water micro-dispersion/micro-emulsion are formed due to the presence of the surface-active compounds in the crude oil. At low salinity, water molecules transport into the crude oil phase and form the micro-dispersion/micro-emulsion around the surface-active compounds. Formation of water micro-dispersion/micro-emulsion leads to the swelling of connate water, oil swelling and therefore contributes to oil detachment and improved oil recovery. From this hypothesis, it is essential that the crude oil has sufficiently high content of polar compounds/surface-active compounds for the micro-dispersion/ micro-emulsion, which means the oil should be active and have relatively high total acid number (TAN) (Siadatifar et al., 2021).

Water osmosis is observed by some researchers and is assumed to contribute to the low salinity effects (Sandengen and Arntzen, 2013; Sandengen et al., 2016; Fredriksen et al., 2017). Oil, either crude oil or model oil, serves as the semi-permeable membrane. Water molecules transport through the oil membrane by diffusion driven by the chemical potential difference between the high and low salinity water. The chemical potential in low salinity water is higher than that in high salinity water, therefore water molecules transport from the low salinity injected water to high salinity connate water. As a result, residual oil droplets are pushed out by the increasing connate water which leads to the observed improved oil recovery.

The pH is sometimes higher in low salinity water than high salinity formation brine, which is assumed to contribute to the low salinity effects (McGuire et al., 2005; Austad et

al., 2010; Fogden, 2011). In the cases when the pH is sufficiently high, the low salinity waterflood can be deemed as a weak “alkali” flood. High pH values lead to IFT reduction and wettability alteration to water-wet due to the generation of natural surfactants as a result of the reaction between alkali and the acidic groups in crude oil. Both IFT reduction and wettability alteration favor higher oil recovery efficiency.

2.2.1.3 Debate on the role of clay

Among the mechanisms discussed earlier, the impacts of clay on low salinity effects is under debate. Some studies suggest that the existence of clay in sandstones is essential for the low salinity effect to occur (Tang and Morrow, 1999; Lager et al., 2008(a); RezaeiDoust et al., 2011; Song and Kovscek, 2015), while other studies have shown that the low salinity effect can occur without the existence of clay (Emadi and Sohrabi, 2013; Sohrabi et al., 2017; Bartels et al., 2017). Furthermore, the clay swelling and the resulting fines migration may block the pore throats and reduce the permeability, which may have negative impact on oil recovery.

2.2.1.4 Time delayed effect

Although rarely discussed explicitly, some studies reported a delay before the low salinity waterflood starts to be effective (Emadi and Sohrabi, 2013; RezaeiDoust et al., 2011; Masalmeh et al., 2014; Suijkerbuijk et al., 2014). The delay usually lasts tens of hours to several days, after which the oil recovery starts to increase. It was explained that such a delay is caused by the mixing of the injected low salinity brine and the high salinity formation brine (Masalmeh et al., 2014; Suijkerbuijk et al., 2014), but it has not been well supported by direct experimental evidence.

2.2.1.5 Microfluidics observations

An important method to prove or disprove existing hypotheses and improve understanding of the low salinity effects is to directly visualize oil-water-rock interactions at the pore scale using microfluidics/micromodels (Song and Kovscek, 2015). In recent years, microfluidics has become a powerful tool in the investigation of flow in porous media, because of the ability to directly visualize fluid behavior at the pore-scale (Ma et al., 2012; Karadimitriou and Hassanizadeh, 2012; Yun and Kovscek, 2015; Lifton, 2016; Yun et al., 2017; Li et al., 2017; Xu et al., 2017(a)(b); Anbari et al., 2018). Pore-scale studies of the low salinity effect in microfluidics have been performed by many researchers. Emadi and Sohrabi (2013) performed micromodel experiments in 2D rock-like-pattern glass micromodels with different brines at a pressure and temperature of 2300 psig and 38 °C, respectively. They attributed the increased oil recovery to the coalescence and swelling of connate water. They also observed the formation of water micro-dispersion in crude oil and wettability alteration while low salinity brine is present; they hypothesized that the water in oil dispersion and the wettability alteration are both attributed to the release of surface-active components from the oil/water interface to the bulk oil. Song and Kovscek (2015) coated 2D silicon micromodels with clay and performed high and low salinity waterfloods in sequence. They showed that clay migration during low salinity waterflood can contribute to more oil recovery (up to 8%). Fredriksen et al. (2016, 2017) observed water in oil emulsions in 2D micromodels and attributed the low salinity effect to water osmosis and water in oil swelling. Bartels et al. (2017) performed a series of high and low salinity waterfloods in single channel 2D dead-end micromodels and observed contact angle change in single pores during low salinity waterflood regardless of the presence of clay or the initial wettability state. These previous fundamental studies provide

important pore-scale details, which can be valuable for developing core-scale or reservoir-scale models.

2.3 FRACTURES IN UNCONVENTIONAL RESERVOIRS

Microfractures, which we define as openings with aperture sizes similar to matrix pores, occur in the subsurface due to various chemical and mechanical processes related to weathering, tectonic activity, diagenesis, or reactivation of dormant natural fractures during hydraulic fracturing (Gale et al., 2014; Landry et al., 2014; Maréchal et al., 2004). Their presence between macrofractures (those with apertures orders of magnitude larger than matrix pores) can contribute to overall fracture connectivity which has been identified as having significant impact on subsurface flow (Wilke et al., 1985). However, much uncertainty regarding their *in situ* presence and aperture size exists such that seismic and borehole measurements need to be supplemented with transmitted light and scanning electron microscopy to achieve accurate fracture maps (Andres et al., 2014; Landry et al., 2014). In addition, the extent to which this uncertainty is relevant for oil production and NAPL recovery is not clear because predicting transport phenomena, in particular multiphase flow, in fractured rocks is not well established (Berkowitz, 2002). Predictive and conceptual pictures of fracture connectivity and fluid flow are critical for optimizing production (Odling et al., 1999; Matthäi and Belayneh, 2004; Faulkner et al., 2010).

2.3.1 Unstable displacement

Unstable immiscible multiphase flow (viscous and capillary fingering) (Saffman and Taylor, 1958; Lenormand et al., 1988) may occur in fractured formations during invasion of a less viscous fluid such as fracture fluid or when performing waterflooding to recover a more viscous non-aqueous phase liquid (DNAPL) such as oil. Unstable

displacements in reservoir applications involving enhanced/improved oil recovery are common, and the investigation of the unstable displacement is essential for improving recovery strategy and for predicting the displacement efficiency.

Previous work on unstable two-phase flow, however, has generally focused on either the competition between viscous and capillary forces, described by capillary number ($Ca = \mu_i v / \gamma$), or the viscosity ratio between the displacing and displaced fluid, quantified by the viscosity ratio ($M = \mu_i / \mu_d$). Berg and Ott (2012) and Armstrong et al. (2014) have explored the fingering phenomena at different macroscopic capillary numbers which is determined by the competition between the length scale of the capillary dispersion zone and the length scale of the observed domain at constant, unfavorable the viscosity ratio. The onset of front instability and capillary desaturation has been previously computed for homogenous rocks (Oughanem et al., 2015; Hilfer et al., 2015). Pore-scale geometrical effects, such as fracture connectivity, are typically not included when predicting viscous/capillary fingering behavior. In addition to capillary number and viscosity ratio, wettability effects on fingering patterns were recently investigated as a third dimension for a phase diagram in 2D flow cells (Zhao et al., 2016). The investigated pore-scale geometries have generally been 2D (Lenormand et al., 1988), 2.5D (Christensen et al., 2019), or 3D homogeneous porous matrices (Islam et al., 2014) or a single planar rough fracture (Chen et al., 2017). Whether and to what extent the existence of microfractures, connected or dead-end, can affect unstable flow is not yet well known.

2.3.2 Previous studies

Investigating unstable immiscible flow in fractured rocks through numerical modeling is challenging. Direct numerical simulation methods, such as the lattice Boltzmann method (Tsuji et al., 2016), are promising but can be computationally costly in

two-scale systems such as those of fractured rocks. Reduced-order methods, such as the dielectric breakdown model (Doorwar and Mohanty, 2014), rely on *a priori* rules for fluid movement that are derived from experimental observations. Although core-flooding has been used to provide measurements within fractured rocks (Rangel-German et al., 2002; Lu et al., 2014; Mirzaei et al., 2016), visualization of pore-level fluid flow behavior in cores (e.g., computerized topography) is difficult, especially in tight rock samples where pore sizes can be smaller than voxel resolution (Wildenschild and Sheppard, 2013; Akbarabadi et al., 2017; Mehmani et al., 2019b). Given that pore sizes in unconventional formations can fall into the nanometer range, nanofluidics and nanomodels are appealing to mimic tight rocks and probe their flow behavior at the subpore (single pores/channels) and pore scales (ensemble of pores) (He et al., 2014; Kelly et al., 2016; Zhong et al. 2018). However, despite their capacity to provide valuable information about nanoconfinement effects on fluid transport, challenges in nanofluidics fabrication and fluid flow visualization are considerable obstacles (Kelly et al., 2015). Given the complexity of nanoporous systems (which is a result of coupled nanoconfinement and geometrical effects) such as mudrocks, decoupling their pore-space geometrical impacts on fluid transport properties.

Microfluidic systems have been used to investigate multiphase flow and transport phenomena from sub-pore-scale features to more complex porous media (Lifton, 2016; Anbari et al., 2018). However, microfluidics studies generally have focused on geometries containing an intact porous matrix without fractures or a porous matrix with a single connected fracture (Wan et al., 1996; Er et al., 2010; Mejia et al., 2019), where the impact of fracture connectivity on flow was not systematically investigated. The two-dimensionality of micromodels may limit their quantitative discoveries to rocks with uniform geometries in the vertical direction or thin geological layers. However, 2D micromodels can capture qualitative two-phase flow trends associated with 3D porous

media (Avraam et al., 1994), providing useful observations on pertinent functional relationships. With regard to unstable flow, microfluidics work has generally been performed for probing fingering dendrites in matrix pores (Setu et al., 2013; Wang et al., 2013; Xu et al., 2014; Zhao et al., 2016) wherein the concept of coupled impacts of microfractures and an adjacent porous matrix were not investigated.

2.3.3. Background of the subsurface application

In this study, diagnostic microfluidics is utilized to investigate the effects of microfracture/macrophracture connectivity on oil recovery and viscous/capillary fingering patterns. Direct experimental observations of two-phase flow in analogue media can assist in reducing the complexity of microfracture transport into several key independent geometrical and flow property variables. Waterflood experiments were performed in three micromodel geometries: one with only a porous matrix, one with a connected microfracture (connecting two adjacent and macrofractures) and one with a semi-connected (dead-end) microfracture (only connected to one macrofracture). Figure 2.6a shows a schematic of a hydraulic fracturing operation where microfractures intersect with macrofractures. Figure 2.6b shows the two cases studied in this dissertation (i.e., the presence of connected microfractures and dead-end microfractures). Figure 2.6c describes an analogues framework for formulating immiscible flow in a fractured vadose system for NAPL remediation (Faybishenko et al., 2000). Both water- and oil-wet conditions were designed and implemented to determine the impact of wettability on recovery and fingering patterns. Capillary numbers ranging from 10^{-7} (capillary forces are comparatively dominant) to 10^{-5} (viscous forces are comparatively dominant) were selected by changing the flow rate of the injection water. Figure 2.7 shows a schematic of fluid and geometrical contributors to the flow patterns within the scope of our work. In addition to other extensively investigated

parameters (to the left of the chart), we propose that microfracture connectivity (to the right of the chart) can be regarded as an independent variable for both oil recovery and flow patterns.

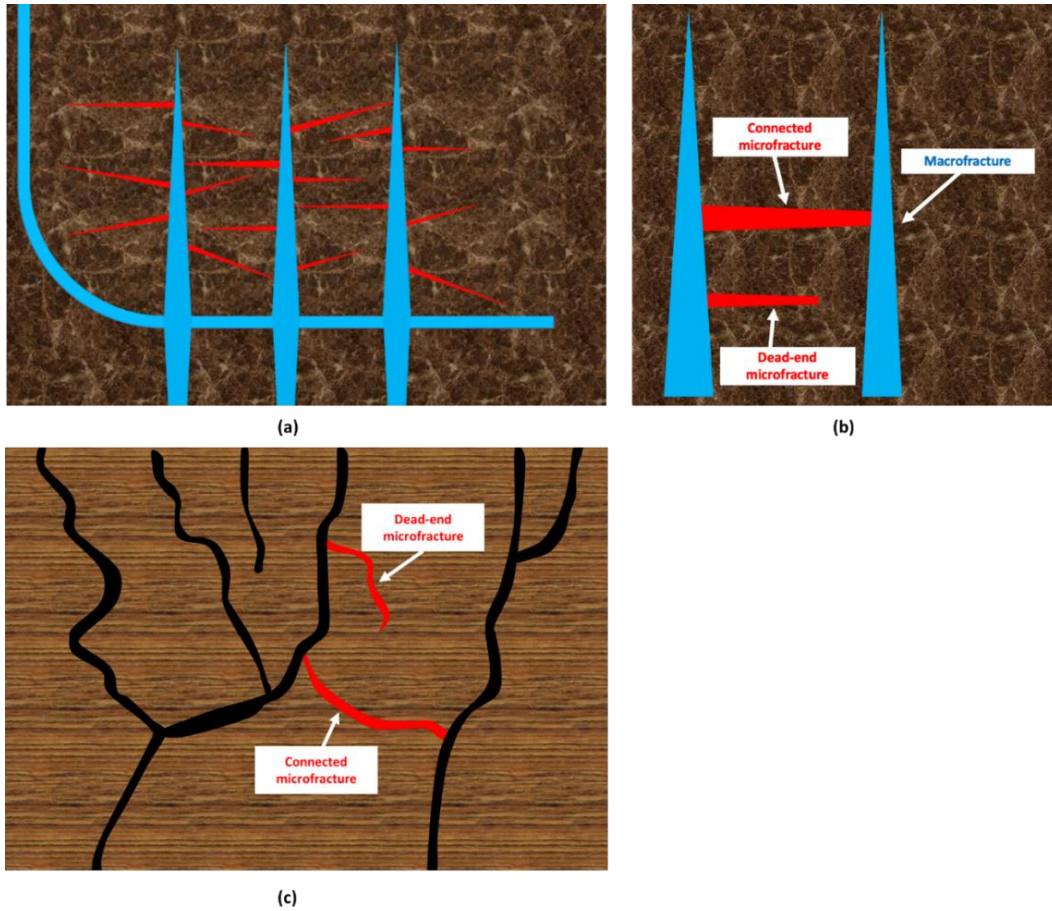


Figure 2.6: (a) Schematic of a hydraulically fractured horizontal well with microfractures. Macrofractures and microfractures are identified with blue and red, respectively. (b) Close-up schematic of connected and dead-end microfractures. (c) Example of a fracture network in the vadose zone (fracture network conceptualization taken from Faybishenko et al., 2000). Lateral fractures can be considered microfractures for the purpose of the conceptualization of immiscible flow in this paper. Schematics presented here are not to scale and only serve as an illustration for the fracture connectivity classification implemented in this research.

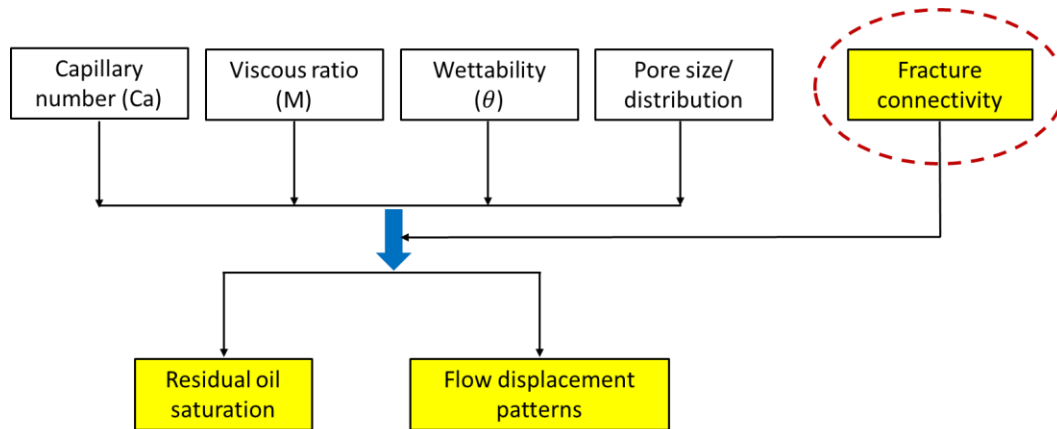


Figure 2.7: Schematic chart of parameters that affect the behavior of unstable fluid displacement in porous media.

2.4 VISCOELASTIC EFFECT IN ENHANCING OIL RECOVERY

Polymer flooding is a cost efficient, well-developed enhanced oil recovery method that has long been utilized in the field (Sorbie, 1991). Hydrolyzed polyacrylamide (HPAM) are a type of polymers that are widely used in polymer enhanced oil recovery operations (Sorbie, 1991; Lake et al., 2014). The addition of a small amount of polymers can significantly increase the viscosity of the injection water. As the viscosity of the injected water increases, the mobility ratio between the injected water and the displaced oil is reduced and sweep efficiency is improved (Sorbie, 1991; Lake et al., 2014; Lee, 2015). Therefore, the unswept, remaining oil left behind from previous low viscosity waterflood can be recovered by polymer flood. Recovering the remaining oil beyond the capillary trapped residual oil is the mechanism and the goal of a typical polymer flood in the reservoir applications.

Normally, mobilizing and recovering capillary trapped residual fluids is extremely hard in geologic formations such as hydrocarbon reservoirs due to high capillarity ($Ca < 10^{-4}$) and low inertia ($Re \ll 1$). It is believed that capillary trapped residual fluids

cannot be recovered without posing large viscous forces (at high Ca) which is supported by the capillary desaturation theory (Lake et al., 2014). However, this theory has been challenged when viscoelasticity comes into play ($De > 1$). Viscoelastic fluids, such as many high molecular weight HPAM polymer solutions, are non-Newtonian fluids that exhibit both elastic (solid-like) and viscous (liquid-like) characteristics in response to mechanical deformation (Chen et al., 2010). Traditional theories assume that the improved displacement efficiency by polymer injection is due to the high viscosity and sweep efficiency improvement, but capillary-trapped residual oil saturation did not decrease (Hirasaki and Pope, 1974; Sorbie, 1991; Delshad et al., 2008; Lake et al., 2014). However, many recent experimental studies have reported reduction of capillary-trapped, residual oil saturation after a high-viscoelasticity polymer flood, though the saturation reduction varies without consensus of its mechanisms (Wang et al, 2000; Wang et al., 2001; Xia et al., 2004; Xia et al., 2007; Vermolen et al., 2014; Erincik et al., 2018; Jin et al., 2020).

2.4.1 Deborah number

The Deborah number (De) is a dimensionless number that describes the ratio of elastic to viscous forces. It is a measure of the viscoelasticity of a fluid, where larger De indicates higher viscoelasticity. The viscoelastic effect that leads to residual oil reduction is assumed to occur only when De is sufficiently high. By theory, De is larger than 1 when viscoelastic flow instabilities initiate (Larson 1992), but higher values (>10) may be required in porous media to see significant residual oil saturation reduction as shown in several coreflood experiments (Erincik et al., 2018). In a previous work, Deborah number was quantitatively correlated to the amount of residual oil reduction (Qi et al., 2017). It is shown that the reduction of residual oil saturation is positively correlated to Deborah number, meaning the reduction of residual oil saturation increases as the Deborah number

increases. The exact correlation between De and the residual saturation reduction, however, is not yet well described.

When imploring the viscoelastic effect, it is important to determine the Deborah number of the flow. The rheological behaviors of polymers in porous media are complex, and many rheological related parameters in the porous media, including De , are determined using empirical methods based on many coreflood results (Marshall and Metzner, 1967; Delshad et al., 2008; Qi et al., 2017). De is defined by:

$$De = \frac{\tau_r}{\tau_E} \quad (2.1)$$

where τ_r is relaxation time, and τ_E is the characteristic residence time.

The characteristic residence time in porous media is difficult to calculate or measure directly due the complexity of the geometric properties, even in a very homogenous core rock or homogenous artificially porous media such as micromodels with homogenous pore arrays. Shear rate is often used to represent the characteristic residence time (Masuda et al., 1992; Koh, 2015). The equivalent shear rate in porous media at the experimental conditions is estimated using an empirical equation (Koh et al., 2017):

$$\dot{\gamma} = C \left(\frac{3n+1}{4n} \right)^{\frac{n-1}{n}} \frac{4}{\sqrt{8}} \frac{u_w}{\sqrt{KK_{rw}\phi S_w}} \quad (2.2)$$

where C is the shear correction factor for the porous medium and is taken to be 4.0 (Koh et al., 2017), n is the shear-thinning index, u is Darcy velocity, K is permeability, K_{rw} is relative permeability of aqueous phase, ϕ is porosity, and S_w is the aqueous phase saturation (glycerol and polymer solutions). It should be noted that for different porous media the shear correction factor can be different, but approximately in the similar range.

2.4.2 Viscoelastic flow instabilities

Viscoelastic flows exhibit nonlinear instabilities that lead to flow turbulence even at low inertia scenarios (low Re) (Ho and Denn, 1997; Groisman and Steinberg, 2000; Morozov and van Saarloos, 2007), which has been hypothesized as the cause of the observed residual oil saturation reduction in porous media. In theory, viscoelastic flows induce instabilities and velocity fluctuation when the Deborah number (De) is larger than 1 (Larson 1992), and this is also assumed to be the rule-of-thumb criteria for viscoelasticity's effect to occur in porous media. However, a recent study (Walkama et al., 2020) reveals that the geometric disorder (e.g., heterogeneity in porous media) suppresses viscoelastic instabilities and stabilizes the flow chaos, therefore, elevates the critical De for the onset of flow instabilities ($De_{critical} > 1$). This finding agrees with the observation in previous coreflood results (Erincik et al., 2018), where a Deborah number slightly larger than 1 but less than 10 does not always lead to significant viscoelasticity's effect and residual saturation reduction. Instead, the viscoelasticity's effect is more obvious when the De is larger than 10. Although the pore-scale viscoelastic flow instabilities are well predicted by theory and pore-scale experiments, the flow instabilities become more difficult to predict by theory when coupled with geometric complexities (Varshney and Steinberg, 2017; Walkama et al., 2020). So far, there is not a clear census on the onset criteria for the viscoelasticity's effect to occur in porous media.

2.4.3 Previous results

Macroscopic investigation by corefloods in rocks have demonstrated that the residual oil saturation after well-performed secondary waterfloods (or other inelastic aqueous phase floods) can be further reduced by the injection of high-viscoelasticity polymer solutions (Vermolen et al., 2014; Qi et al., 2017; Erincik et al., 2018; Jin et al.,

2020), as shown in Figure 2.8a. More surprisingly, residual oil reduction was observed not only during the high-viscoelasticity polymer flood, but also in a follow-up flood with low-viscoelasticity fluids (Erincik et al., 2018; Jin et al., 2020). Despite these and other positive results mentioned in the literature, other studies reported no, or very little, residual oil recovery from tertiary high-viscoelasticity polymer floods (Huh and Pope, 2008; Sandengen et al., 2017). The inconsistencies in the literature are not well explained by established theories or experimental evidences retrieved from core-scale.

Microfluidic studies have captured the occurrence of viscoelastic instabilities at the pore scale during viscoelastic polymer floods. Periodic oil droplet oscillation was observed when oil was displaced by viscoelastic polymer solutions in a contraction–expansion single channel geometry (Figure 2.8b), which was hypothesized to contribute to residual oil saturation reduction (Qi, 2018). Pore-scale, lattice Boltzmann simulations also showed that residual droplets can be oscillating as the flow streamlines become chaotic and form vortices that may finally recover the droplet (Xie et al., 2020). Residual ganglia fluctuation and mobilization caused by viscoelastic displacing fluids were observed in micromodels with a 2D pore-network as shown in Figure 2.8c (Clarke et al., 2016; Mitchell et al., 2016). However, despite these pore-scale viscoelastic instabilities, direct recovery of individual residual droplets by oscillation and fluctuation are observed only at large viscous forces that are rarely encountered in subsurface porous media.

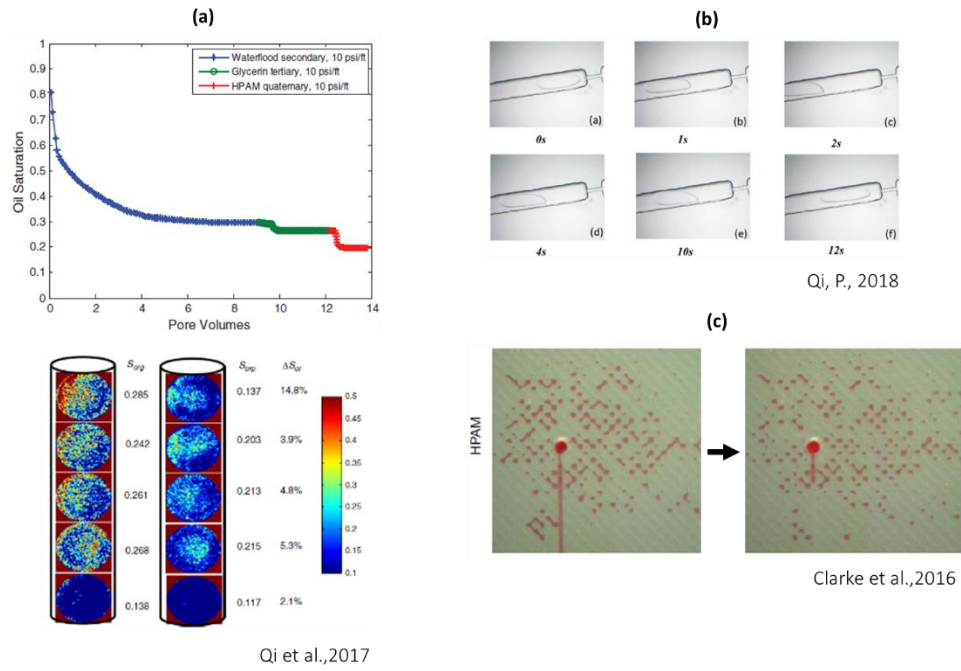


Figure 2.8: Previous results from viscoelastic polymer flooding. (a) Residual oil saturation reduction in a coreflood experiment (Qi et al., 2017). (b) Oil droplet oscillation in a single channel – throat – channel microfluidics (Qi, 2018). (c) Oil mobilization in a 2D micromodel (Clarke et al., 2016).

Chapter 3: Experimental Methods

3.1 MICROMODEL DESIGN AND FABRICATION

3.1.1 Design

The micromodel patterns are designed in AutoCAD software and the user interface is shown in Figure 3.1. The AutoCAD data file is subsequently sent to an external photomask vendor (CAD/Art Services, Inc.) to generate photomasks (shown in Figure 3.2a) according to the design.

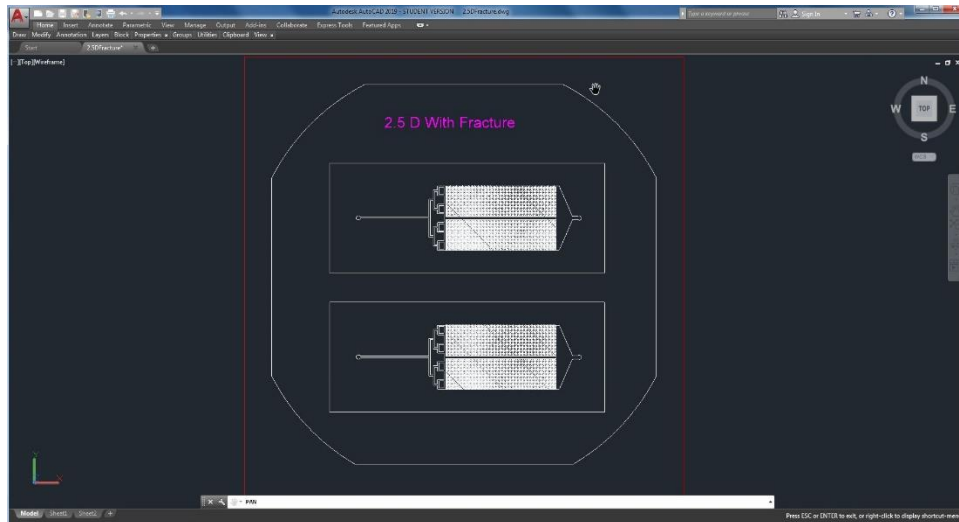


Figure 3.1: AutoCAD user interface with a sample design of the 2.5D, inch-long micromodel with a connecting fracture in the middle of the porous matrix.

The design of 2D structures is straightforward by drawing the patterns and their 2D dimensions in AutoCAD. In a 2.5D design, the pore throats are designed to be separated by a distance ($40\text{ }\mu\text{m}$ in Figure 3.2b), which allows for the generation of shallower depth at the pore throats during subsequent hydrofluoric acid (HF) etching as discussed in Chapter 3.2. The distance is designed according to the etching depth of the pore bodies and the preferred pore throat depth, and is determined experimentally. The distance of $40\text{ }\mu\text{m}$

shown in Figure 3.2b corresponds to an etching depth of $\sim 20\ \mu\text{m}$ of the pore bodies and a pore throat depth of $4 - 5\ \mu\text{m}$. During HF etching, the white area directly contacts and reacts with HF acid, and the black area between the pores does not contact with HF acid and is only etched by the HF acid in the horizontal direction, which results in different etching depths.

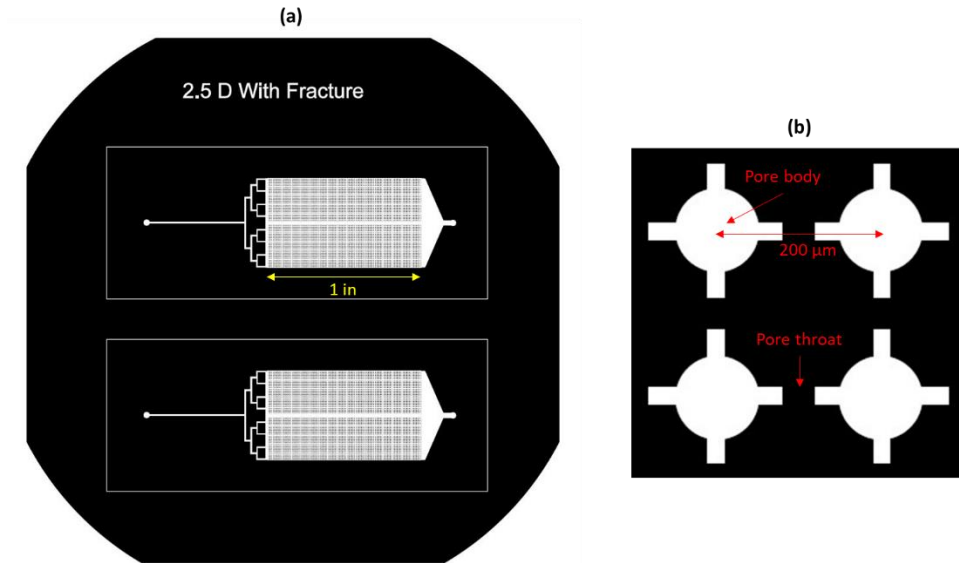


Figure 3.2: (a) A photomask generated from the AutoCAD design shown in Figure 3.1.
(b) Pore-scale zoomed-in from the 2.5D photomask design in (a).

3.1.2 Fabrication procedures and equipment

All glass micromodels presented in this dissertation are made from soda-lime glass mirror as shown in Figure 3.3a. A layer of copper is deposited at the back of the glass mirrors (brown color in Figure 3.3b). On top of the copper, there is a protection resin layer (grey color in Figure 3.3a) for to protect the back of the mirror. The copper layer provides additional protection for the glass in the unetched area (black area in Figure 3.2) in addition to the photoresist on top of it, which works better than when copper layer is not present.

Prior to fabrication, the mirror is cut into smaller pieces according to micromodel sizes. The protection resin layer is removed by submerging in high concentration NaOH solution (5 – 10wt%) for several hours (depending on the NaOH solution concentration) until the copper layer is fully exposed (Figure 3.3b).

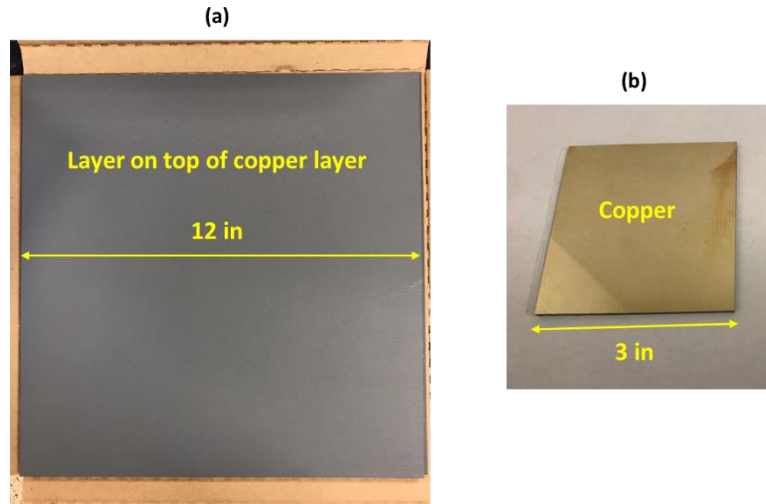


Figure 3.3: (a) Back of the original glass mirror used for fabrication. The grey color is the protection resin. (b) Cut and cleaned mirror with the protection paint layer removed and copper layer exposed. Glass in underneath the copper layer.

The obtained clean, copper layered glass is used as the substrate for photolithography and then hydrofluoric acid etching in the cleanroom at the Nanomaterials research center at UT Austin (<https://tmi.utexas.edu/research/nano>).

During the photolithography, first, a positive photoresist (Photoresist S1818) is deposited uniformly on top of the copper layer on the substrate using the spincoater (Laurell) shown in Figure 3.4a. A small amount of photoresist is applied and the substrate is spun in the spincoater for 30 s at 3000 rpm to get a uniform layer of photoresist. The spinning time and speed are determined by the type of the photoresist and can be found in the user manual. After the spinning, the substrate is baked on top of a hot plate at 115 °C

for 2 mins or slightly longer until the photoresist is completely dry which is required for the following ultraviolet exposure procedure.

After photoresist deposition, in the second step, the substrate is taken to the mask aligner (Karl Suss MA6) shown in Figure 3.4b for ultraviolet exposure which reacts with the photoresist. The photomask is used in this procedure which allows UV light to expose only the blank area (white region in Figure 3.2) but blocks the UV light from all other areas (black region in Figure 3.2).

In the last step, development is performed where the photoresist is removed in the exposed area but is kept intact in the unexposed area by submerging the substrate in a developer solution (MF319) for about 2 mins and can vary slightly.

After photolithography, the copper layer in the area without photoresist (removed in the previous step) is removed using a copper etchant (Copper etchant, Sigma-Aldrich) and glass is exposed in those areas. Two layers, a copper layer and a photoresist layer, protect the glass in the unexposed area during the following HF etching process. The processed substrate is then used for hydrofluoric (HF) etching performed in the HF hood in the clean room (Figure 3.4c).

During the HF etching, the glass is submerged in a container with a buffered HF solution (Buffered oxide etchant (BOE) 6:1, Sigma-Aldrich) on top of a stirring plate (Fisher Scientific) with a magnetic stirring bar stirring at 300 rpm. The buffered HF solution contains 7% HF, 34% NH_4F and 59% of H_2O and is commonly used in in glass etching. Continuous stirring of the solution during HF etching helps to have a homogeneous solution and to etch uniformly on the surface. Etching time is determined by dividing the designed depth by the etching rate. The etching rate is determined experimentally.

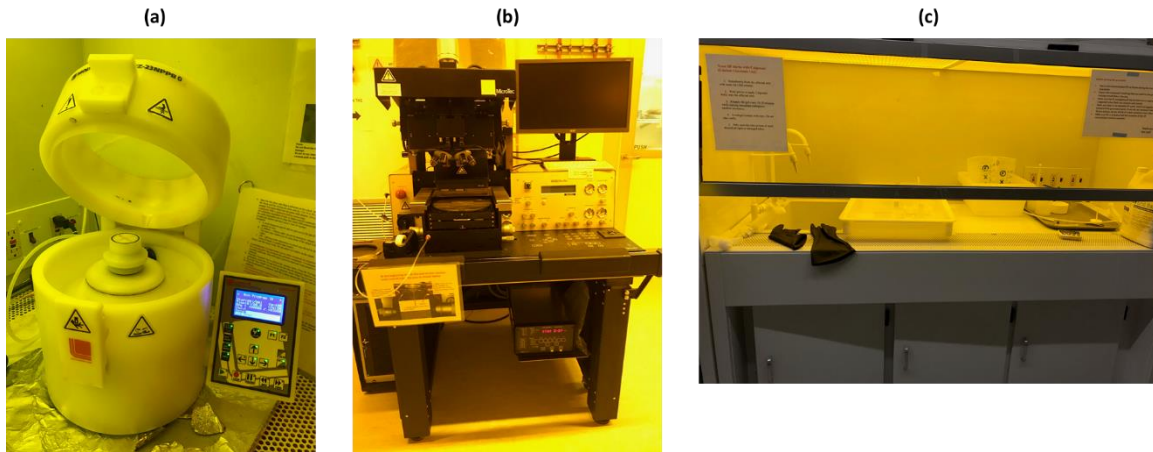


Figure 3.4: Micromodel fabrication facilities in cleanroom. (a) Spincoater (Laurell) used for coating the glass surface with photoresists. (b) Mask aligner machine (Karl Suss MA6) used for photolithography. (c) Operation hood for hydrofluoric acid etching.

With the HF etching, the 2.5D features are created as the hydrofluoric acid isotopically reacts with glass in both vertical and horizontal direction (Figure 3.5a). As a result of the horizontal etching, pore throats (which are designed to be separated) are connected, but the depth is shallower than that of the pore bodies. Figure 3.5b shows a pore scale image of the fabricated 2.5D micromodel and Figure 3.5b schematically illustrates the pore structures in the two cross-sectional views presented in Figure 3.5b.

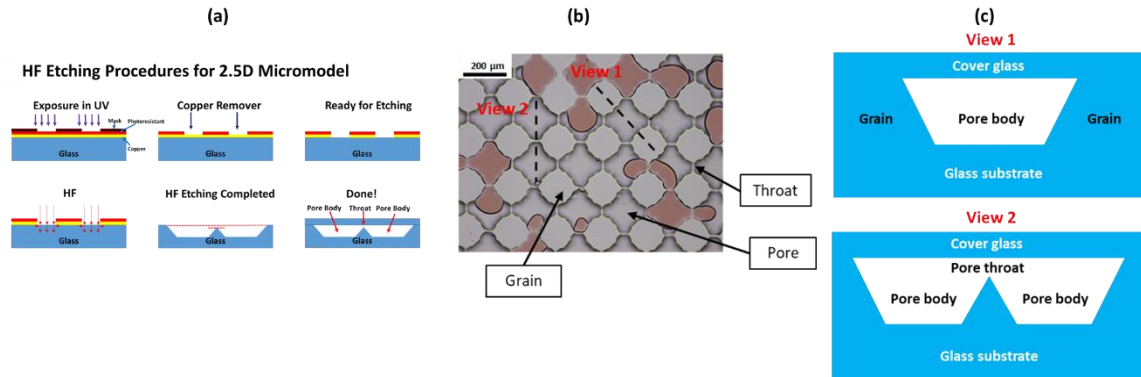


Figure 3.5: (a) Schematic sketch for hydrofluoric acid etching process for fabrication of 2.5D micromodel (taken from Xu et al., 2017). (b) Pore-scale image of the 2.5D micromodel with mineral oil and water. Cross-sectional sketches of view 1 and view 2 are shown in (c) as the pore throats are shallower and narrower than the pore bodies. (b) and (c) are revised from Du et al., 2020.

After HF etching, the substrate is cleaned and both the residual photoresist layer and the copper layer are removed using acetone and copper etchant, respectively. The substrate is then cut into the final dimensions and holes are drilled as inlets/outlets. This step can be performed in the lab using the drilling equipment and glass cutter (Figure 3.6) or sent to be processed at the glass shop.

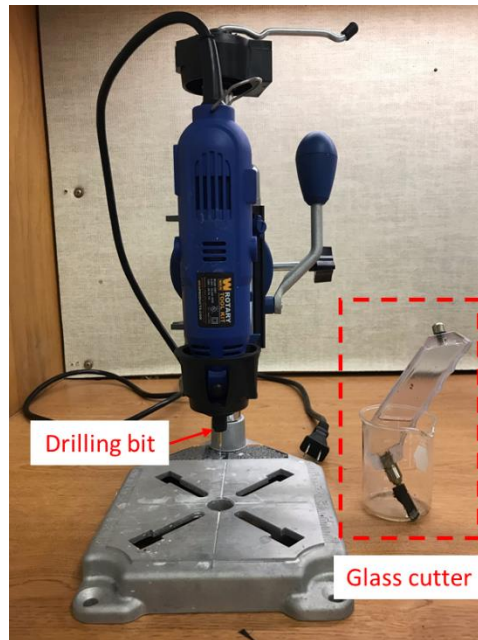


Figure 3.6: Drilling tool and glass cutter.

The cut and drilled substrate is bonded with a cover glass in an oven at elevated temperature at 690°C . The temperature of the oven is increased gradually from 200°C to 690°C in 3 – 4 hours, kept at 690°C for an hour, and gradually decreased to 400°C in 2 – 3 hours. The change of temperature (both increase and decrease) is operated in a step by step manner, where the oven temperature is adjusted by $100 - 150^{\circ}\text{C}$ higher (increase period) or lower (decrease period) at an interval of 1 – 1.5 hours. Two ovens are used for bonding as shown in Figure 3.7. The oven in Figure 3.7a needs manual temperature adjustment, and the oven in Figure 3.7b is programmable and the temperature can be adjusted both manually or by programming.

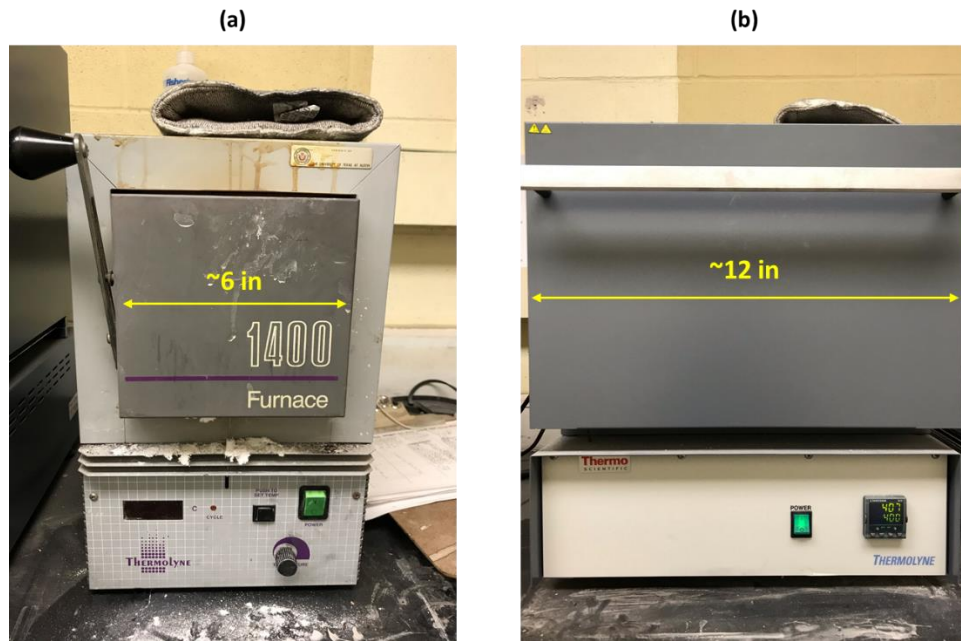


Figure 3.7: Two ovens used for glass micromodel bonding. (a) A smaller oven with manual temperature adjustment function. (b) A larger programmable oven with both manual and programmable temperature adjustment functions.

3.1.3 Micromodel examples

Two micromodels fabricated using the described procedures are shown in Figure 3.8. Figure 3.8a shows a glass micromodel chip with a dimension of 2.5 in by 1 inch and an inch-long flow geometry. Figure 3.5b shows a glass micromodel chip with a dimension of 4 in by 4 in and a foot-long flow geometry.

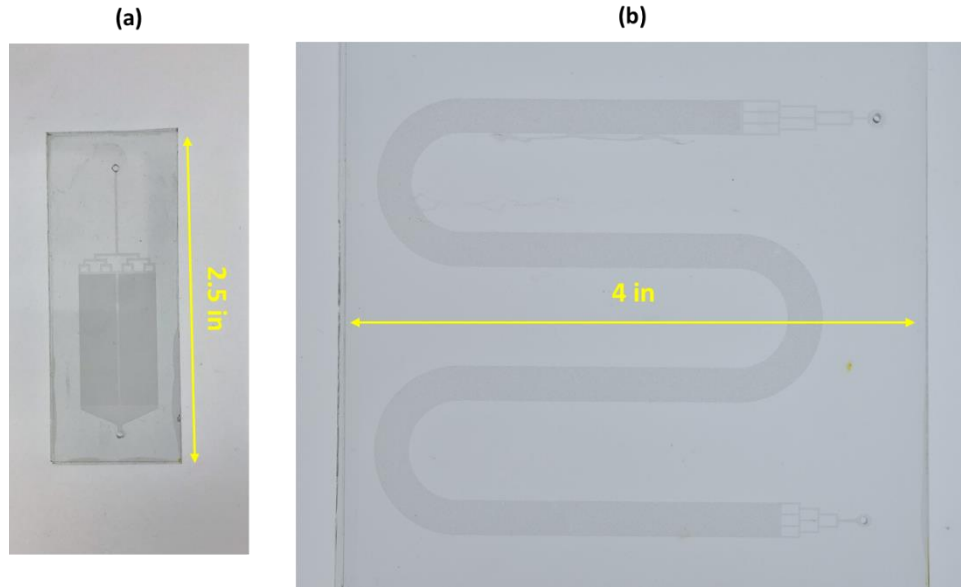


Figure 3.8: Micromodel examples. (a) An inch-long 2.5D micromodel. The dimension of the chip is 2.5 inches by 1 inch. (b) A foot-long snake-shaped micromodel. The dimension of the chip is 4 inches by 4 inches

3.2 EXPERIMENT PLATFORM AND EQUIPMENT

3.2.1 Platform setups

Two types of microfluidic experimental platforms are used in this work. The digital single-lens reflex (DSLR) camera (Nikon D5600) shown in Figure 3.9a is used for the Darcy-scale image visualization/acquisition in a domain size of $10^0 - 10^1$ cm. A microscope and microscope camera shown in Figure 3.9b are used for microscopic image visualization/acquisition in a domain size of $10^1 - 10^3$ μm . Other basic components and equipment, including syringe pump, syringe, tripod, and light pad are depicted in Figure 9.

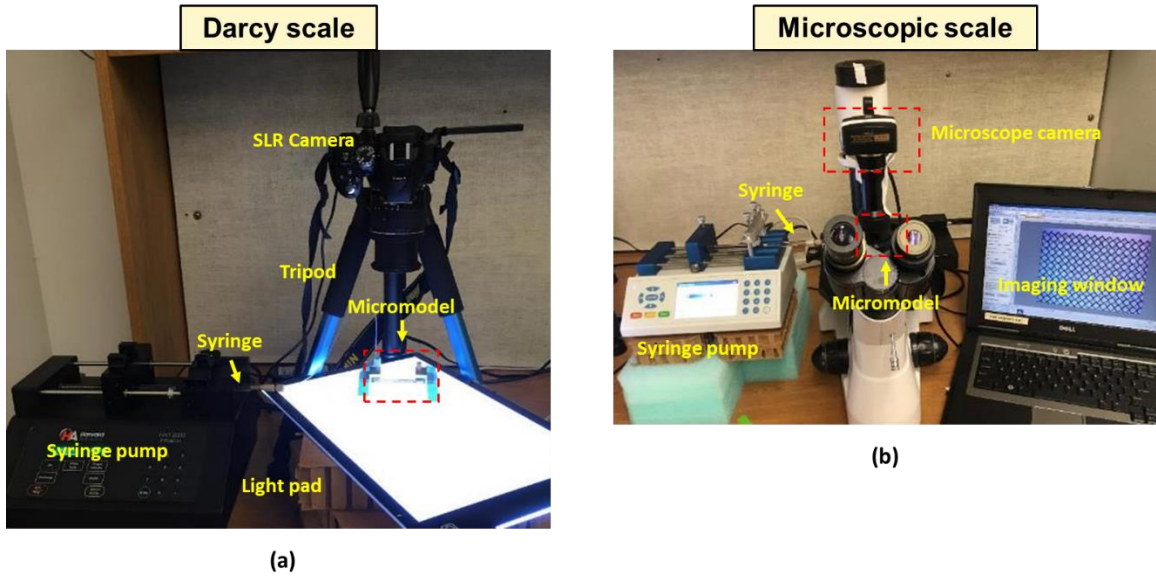


Figure 3.9: Experimental platforms for (a) Darcy-scale visualization and (b) microscopic visualization function, respectively.

3.2.2 Experimental equipment

3.2.2.1 Flow units

The flow equipment and units used in the platforms are shown in Figure 3.10 and Figure 3.11. Two syringe pumps are used interchangeably in the experiments, including a Harvard injection syringe pump and a Fusion syringe pump. Both pumps are able to operate at a given injection rate with syringes of different types, brands and volumes (10 μl – 10 ml).



Figure 3.10: Two syringe pumps used in different works. (a) Harvard PHD 2000 Infusion syringe pump. (b) Fusion 400 syringe pump.

To inject fluids/gas into the micromodel, a series of flow units are used (Figure 3.11). The syringe is operated by the syringe pump, and is connected to one end of the tube with connectors. The other end of the tube is connected to the inlet of the micromodel by a connector through the steel chip holders made in house. A couple of holders hold the micromodel on a horizontal surface/plate.

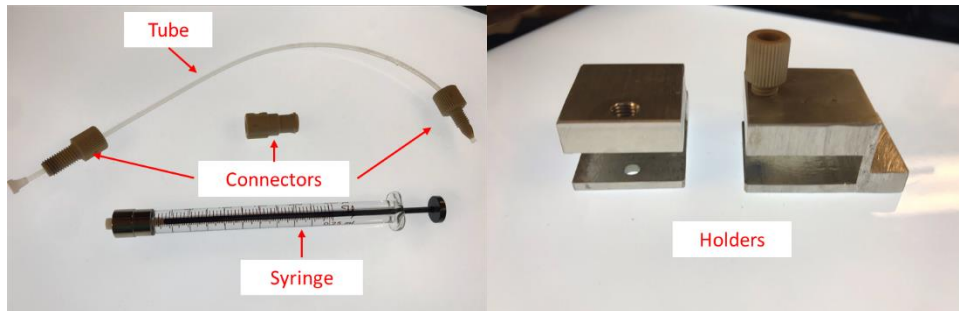


Figure 3.11: Flow experiments units including a syringe (Hamilton Gastight Syringe Model 1725 TLL), a piece of tube, connectors (IDEX Health & Science) and steel chip holders (house made).

3.2.2.2 Image acquisition equipment

Key equipment and units used in the image acquisition system shown in Figure 3.9a (Darcy-scale visualization) include a DSLR camera, a light pad, and a tripod which are

shown in Figure 3.12. During flow experiments, the micromodel is fixed horizontally on the light pad. The tripod is used to fix the camera to a certain height above the micromodel during the experiment. The camera is used to capture one-time images, time-lapse images and videos during the experiments.

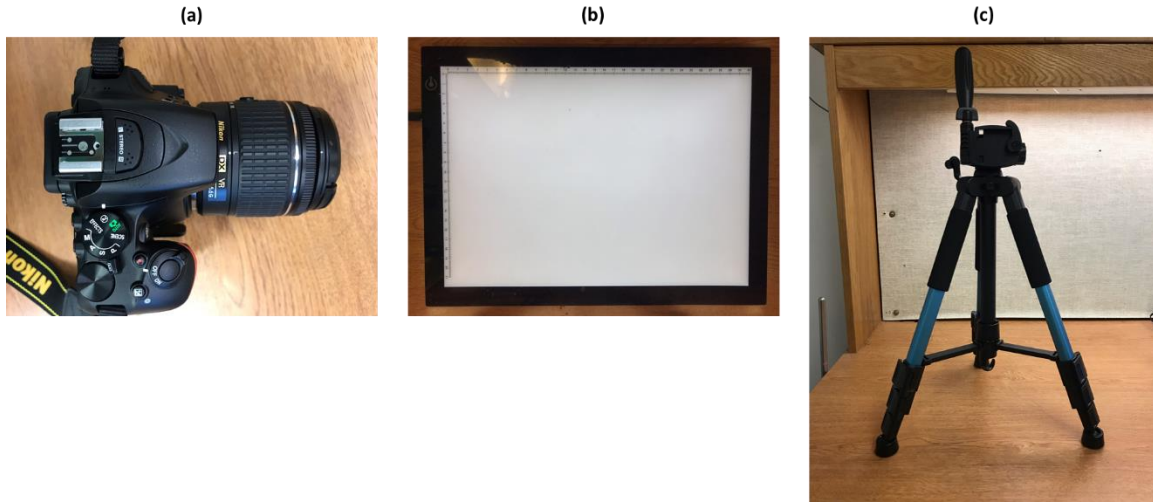


Figure 3.12: Image capturing equipment used for Darcy-scale visualization including (a) Nikon D5600 DSLR camera, (b) light pad and (c) tripod.

Key equipment and units used in the image acquisition system shown in Figure 3.9b (microscopic visualization) include a microscope, a digital microscope camera (Figure 3.13a) and the compatible operating software (Figure 3.13b). Microscopic images can be previewed, one-time captured and captured in time-lapse mode in the software.

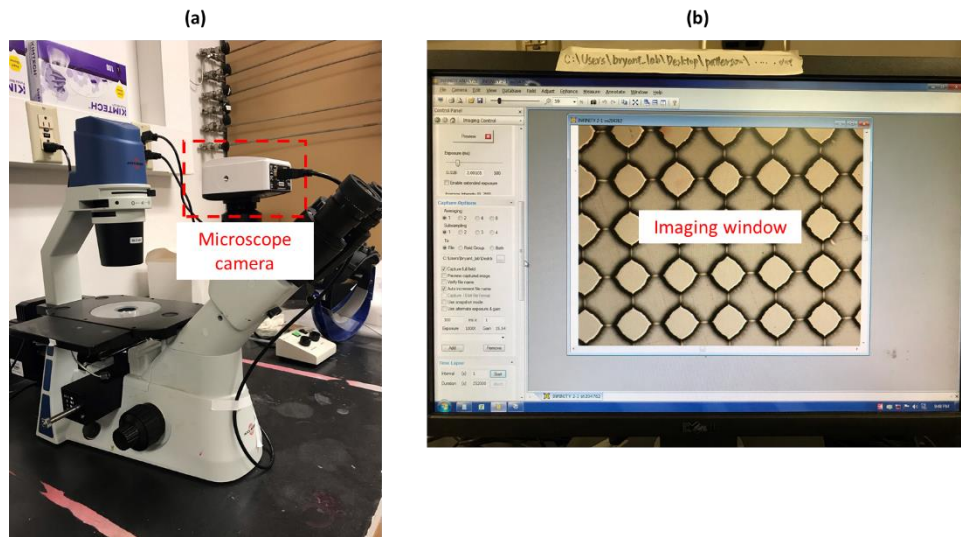


Figure 3.13: Imaging capturing system used for microscopic visualization including (a) microscope (Accu-Scope EXI310) and microscopic camera (Lumenera Infiniti 2), (b) operating software (Lumenera) for the microscope camera.

3.2.2.3 Measurement equipment

A profilometer (Figure 3.14) is used to measure the etching depth on the substrate before bonding with the cover glass. The profilometer stylus runs through the surface of the substrate and records the depth along its pathway.



Figure 3.14: Profilometer (DEKTAK 6M) in cleanroom.

The pressure at a location in the micromodel (e.g., inlets/outlets) is measured using the microfluidic pressure measurement system shown in Figure 3.15. A microfluidic pressure sensor (Figure 3.15a) is connected to the micromodel using the flow units (tube, connectors) at the cone-shaped end (left end in Figure 3.15a), and is connected to a pressure manifold (Figure 3.15b) by a compatible cable (white cable in Figure 3.15b) at the other end. The pressure manifold is connected to the computer's USB port by another cable (red cable in Figure 3.15b). The compatible pressure measurement software is shown in Figure 3.15c.

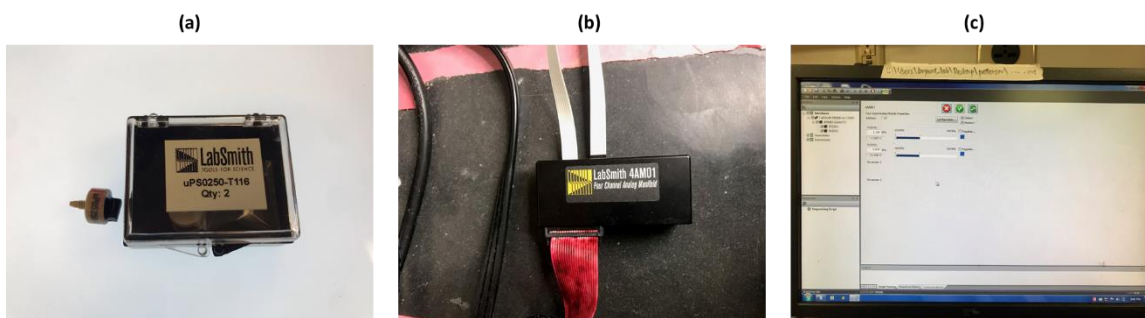


Figure 3.15: (a) Microfluidic pressure sensor (LabSmith) with a measurement range of 250 kPa. (b) Pressure manifold (LabSmith) which transfers the pressure signal to computer software. (c) User interface of the pressure measurement software (μ Process).

3.2.2.4 Other equipment

Other frequently used equipment includes a Sonicator (Branson 2800) and a stirring hot plate (Corning PC-6200) which are shown in Figure 3.16 and Figure 3.17, respectively. The sonicator is mainly used to clean the surface and mix fluids (e.g., mixing the dye in fluids) under the “Sonicate” function, and to remove gas bubbles under the “Degas” function. The stirring hot plat is used to dry micromodels and flow units, and to mix fluids such as when diluting polymer solutions.



Figure 3.16: Sonicator (Branson 2800).



Figure 3.17: Hot plate (Corning PC-6200).

3.3 IMAGE PROCESSING

An open sourced software, ImageJ, is used to process the images captured during the experiments with the DSLR camera as shown in Figure 3.18. The processing procedures are demonstrated in Figure 3.19. A series of raw images (Figure 3.19a) were imported into ImageJ as an image stack, then registration was applied to the stack of images using the “Linear Stack Alignment” function (Figure 3.18i) to align all images to the same position. Images were cropped into the geometry of interest subsequently and then enhanced using “Enhanced Local Contrast (CLAHE)” function (Figure 3.18d) or other contrast enhancement functions to improve the contrast and to make phase boundaries clearer (Figure 3.19b). The enhanced images were then binarized using the “Binary” function (Figure 3.18f) into black (water) and white colors (oil and grains) using the thresholding method “Otsu” (Figure 3.19c). The area fraction of the black phase (water phase in Figure 3.19c) was measured using the “Measurement” function (Figure 3.18g). Water saturation was subsequently calculated from the binarized images by dividing the fraction of the black area in each image to the fraction of the black area in the fully saturated image. Colors were added to binarized grey scale images in black and white by editing the LUT (Look-Up Table for color mapping) (Figure 3.18c) value to the index value of the corresponding color (Figure 3.19d). For example, the LUT value for blue is (0, 0, 255).

In addition, some other basic image operation functions are shown in Figure 3.18b. Image calculation (e.g., to add and subtract one image from one another) can be performed using the “Image Calculator” function (Figure 3.18e). Ganglia and bubbles can be analyzed by the “Analyze Particles” function (Figure 3.18h).

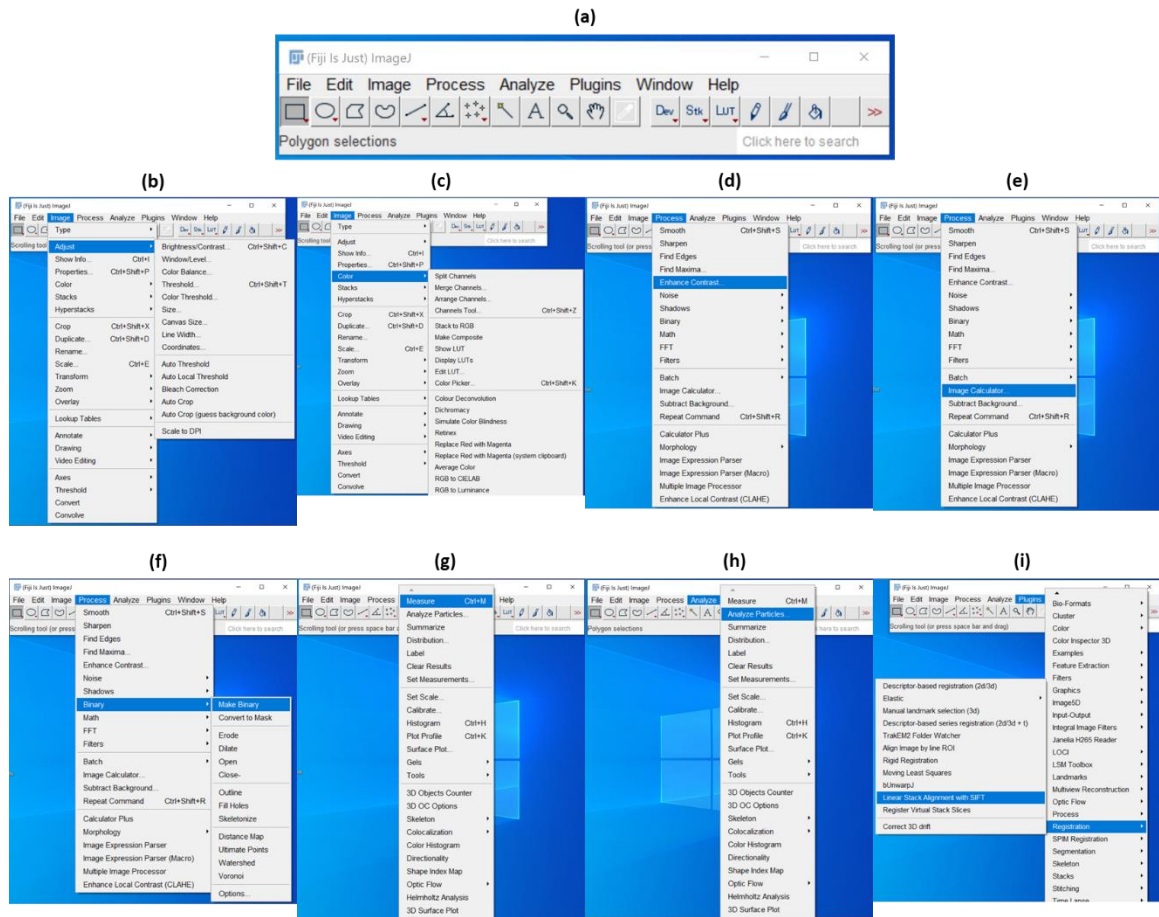


Figure 3.18: (a) ImageJ user interface with sample functions shown in (b) basic image adjustment, (c) color editing, (d) contrast enhance, (e) image calculator, (f) image binary, (g) image measurements, (h) particle analyze and (i) image stack registration.

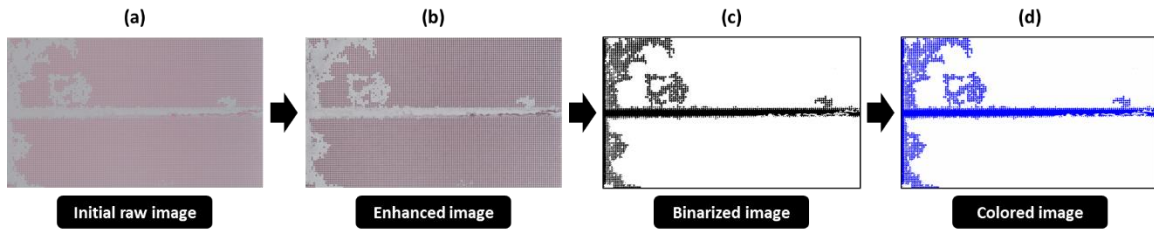


Figure 3.19: Image processing examples for a $2.5\text{cm} \times 1.5\text{cm}$ micromodel geometry. Oil phase is in pink in (a) and (b). (c) Grey scale image in black (water) and white. (d) Image with adjusted color in blue (water) and white. Images are from experiment 1.

3.4 FLUID PREPARATION AND ANALYSIS

In fluid preparation, an ARES-G2 rotational rheometer (Figure 3.20) is used to measure the viscosities or the rheological behaviors of fluids at a given range of shear rate. The double wall method is used for measurements and the measured fluids are injected into the double wall geometry. The operating program automatically rotates the geometry and measures the strain and torque at the designated shear rates which are used to calculate the viscosity, the storage modulus (G') and loss modulus (G'').

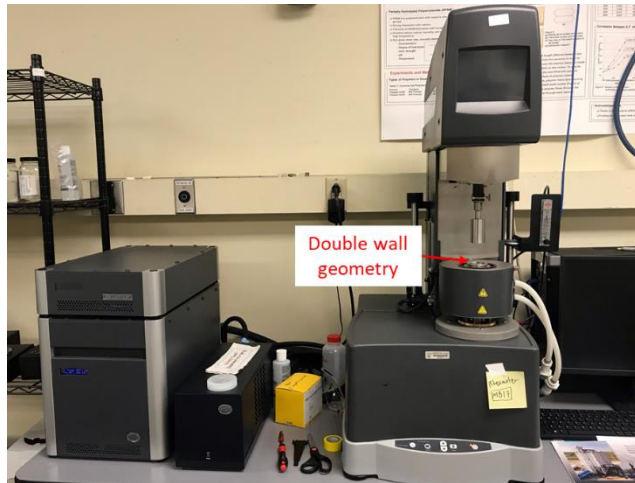


Figure 3.20: Rotational rheometer (ARES-G2).

A spinning drop tensiometer (Figure 3.21) is used to measure the interfacial tension (IFT) between two fluids is measured. The glass tube is filled with the denser fluid (e.g., water), and a droplet of the lighter phase is injected into the denser fluid. The glass tube is then installed behind the observing window, and the shape of the lighter fluid droplet at a given rotational speed is recorded by the camera on the tensiometer and used to calculate the IFT values.

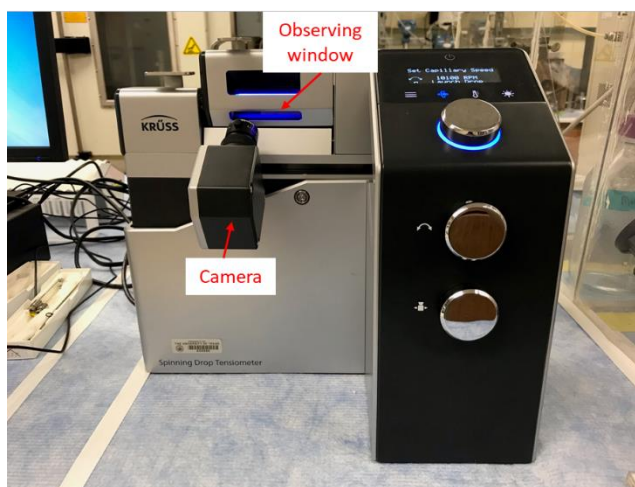


Figure 3.21: Spinning drop tensiometer (KRÜSS SDT).

An overhead stirrer (Figure 3.22) is used for polymer mixing in polymer solution preparation. When making a polymer solution, a mother solution of high concentration (e.g., 5000 ppm or 10000 ppm) is first made using DI water and polymer powder. A container with the mixture of the polymer powder and water is placed underneath the overhead stirrer. A magnetic stirring bar is mounted vertically to the stirrer at the top end, with the bottom end dipping into the fluid in the container and stirring at a given rotational speed (350 rpm) for at least 3 hours until the fluid is fully mixed. Diluted polymer solutions for experiments were made from the mother solution by adding water and mixing using a magnetic stirring bar on the stirring hot plate at 150 – 200 rpm.



Figure 3.22: Overhead stirrer (Caframo).

A high precision digital balance is used to measure the weight of chemicals and fluids. It can also be used for density calculation. In weight measurement, the digital balance is first set to zero by pressing the O/T button with any container/measure paper on top of the balance. In density measurement, different volumes of fluid are added and the corresponding weights are recorded. The density is subsequently calculated by interpolating the slope of the weight – volume plots.



Figure 3.23: Digital balance with a precision of 0.001g (Adam Equipment HCB123).

Chapter 4: Microfluidic Investigation of Low Salinity Effects during Oil Recovery¹

4.1 INTRODUCTION

Low salinity water flooding has been recognized as an enhanced oil recovery method that is economically viable and environmentally friendly. However, many mechanisms have been proposed and the inconsistencies are not well explained with current theory. This chapter presents a study of the low salinity effect during crude oil recovery by a series microfluidics experiments at three different scales. A microfluidic toolbox is utilized, including single-pore scale microchannels, a pore-network scale ($\sim 10^2$ pores) micromodel, and a “reservoir-on-a-chip” model ($\sim 10^4$ pores with heterogeneity), all with 2D connectivity. This study aims to narrow the gap between pore-scale observations and porous media flow mechanisms, and to explain one type of low-salinity effect with delayed oil recovery and without the presence of clay.

4.2 EXPERIMENTAL METHOD

4.2.1 Fluids preparation and analysis

A heavy crude oil with a viscosity of 220 cp was used in the study presented in this chapter. The oil properties are listed in Table 4.1. This oil is active, characterized by an acid number of 3.01 mg/g. The interfacial tension between the crude oil and deionized water is 9.5 mN/m. The relatively low IFT resulted from the high content of active compounds within the crude oil. Additional discussion of the oil properties is included in Appendix A1. Two crude oil dilutions were also used in this study. We diluted the crude

¹ Du, Y., Xu, K., Mejia, L., Zhu, P. and Balhoff, M. 2019. Microfluidic Investigation of Low-Salinity Effects during Oil Recovery: A No-Clay and Time-Dependent Mechanism. *SPE Journal* **24** (6): 2841-2858.

Yujing Du designed and performed the experiments, conducted data analysis, and wrote the manuscript.

oil 3 times and 10 times, by adding 2 volumes and 9 volumes of dodecane for every volume of crude oil, respectively. Dodecane and crude oil are completely miscible under the two mixing ratios. The viscosity of the two diluted oil samples are 4.4 cp and 2.2 cp, respectively. The viscosity of dodecane used in the dilution is 1.3 cp.

Table 4.1: Crude oil properties

Density	0.937 g/ml
Viscosity	220 cp
TAN (Total acid number)	3.01 mg/g
Interfacial tension with DI water	9.53 mN/m*
Interfacial tension with 500 ppm brine	8.97 mN/m*
Interfacial tension with 3000 ppm brine	8.06 mN/m*
Interfacial tension with 20000 ppm brine	7.24 mN/m*
Interfacial tension with 118000 ppm brine	5.32 mN/m*

*Crude oil-water interfacial tension vs. brine salinity is plotted in Figure 4.8.

A synthetic high salinity brine with a salinity of 1118000 ppm TDS (total dissolved solids) was used. Other brines with lower salinities (20000 ppm, 3000 ppm and 500 ppm) used in this study were diluted from this synthetic brine. The diluted brines with salinities of 20000 ppm and 500 ppm were used for characterization purposes, and the brine with a salinity of 3000 ppm was used for both flow experiments and characterization. Deionized water was also used as a model low salinity water (ideally should be close to 0 ppm). The formula and properties of the five brine/water samples are listed in Table 4.2. We measured the pH values of the 5 brine/water samples (pH is 5 – 7) and ensured that alkali-crude oil interactions do not exist in our experiments (Guo et al., 2006; Samanta et al., 2011). The pH values of the low salinity brine samples (DI water, 500 ppm brine and 3000 ppm brine)

are between 5 and 6 because of the dissolving and dissociation of CO₂ when the salt contents are low.

Table 4.2: Brine properties

Brine	Composition	Density	pH
High salinity brine (118000 ppm)	8.6% NaCl, 1.2% KCl, 2.0% CaCl ₂	1.070g/ml	6.80
High salinity brine (20000 ppm)	6 times diluted from 118000 ppm brine	1.013g/ml	6.32
Low salinity brine (3000 ppm)	40 times diluted from 118000 ppm brine	0.999g/ml	5.46
Low salinity brine (500 ppm)	240 times diluted from the 118000 ppm brine	0.997g/ml	5.78
DI Water (0 ppm)	N/A	0.997g/ml	5.25

4.2.2 Microfluidic platform

We fabricated 2.5D glass micromodels using the method developed in Xu et al. (2017a) as described in Chapter 3.1. Compared to the 2D micromodels, the 2.5D micromodels have pore-scale 3D features in addition to the 2D array of pores, which has continuity of both the pore-space and the grain phase. Therefore, capillary snap-off of the non-wetting phase and the continuity of the wetting phase are both allowed, making the system more realistic in studying multiphase flow behavior. In addition, glass is used as the material because it has similar surface properties to quartz which is the main component of sandstones, and has been widely applied by other researchers (Bowden et al., 2009; de Hass et al., 2013; Emadi and Sohrabi, 2013; Song and Kovscek, 2015; Bartels et al., 2017).

Three types of micromodels (A, B and C) were used in the experiments performed in this chapter. Actual images of these three micromodels and their microscopic details are shown in Figure 4.1. Micromodel A has a pair of dead-end pores connecting to a single

main channel by pore necks. The pores are $200\ \mu\text{m}$ in diameter and the channel is $200\ \mu\text{m}$ in width. The pore throats are narrower and shallower than the pore bodies and the channel. Micromodel B has a $0.2\text{cm} \times 2.4\text{cm}$ homogeneous pore network matrix; the matrix contains 1.4×10^3 identical inter-connected pores. Micromodel C has a $1.6\text{cm} \times 3.2\text{cm}$ fractured geometry, containing a pore network matrix of more than 10^4 identical pores and a fracture in the center of the geometry. Table 4.3 summarizes the pore and throat size and depth of each micromodel.

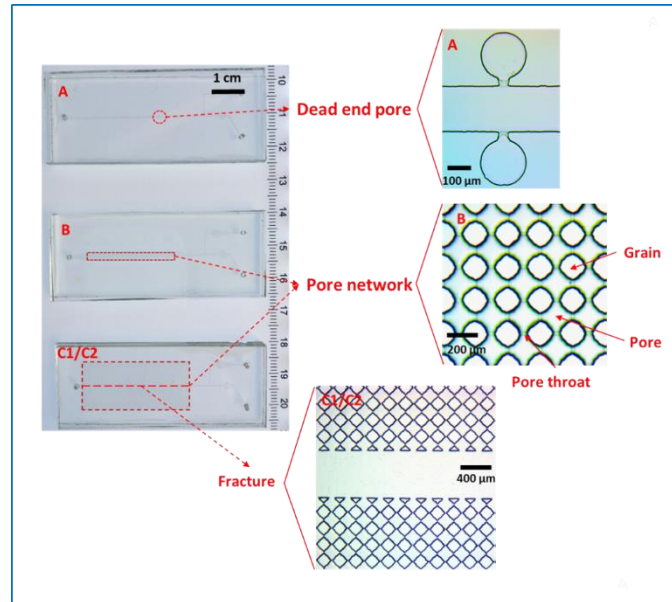


Figure 4.1: Images of micromodels at the macroscale (left) and pore-scale (right). Micromodel A is a dead-end pore micromodel, Micromodel B is a narrow homogeneous micromodel, and Micromodel C (C1 and C2) is a homogeneous micromodel with a fracture. The scale on the left is in centimeters.

Table 4.3: Micromodel properties

Micromodel		Pore body width (μm)	Pore throat width (μm)	Pore body depth (μm)	Pore throat depth (μm)	Aspect ratio (in width)
Micromodel A		200	37	$21 \pm 1 \mu\text{m}$	~ 5	5.4
Micromodel B		200	40	$21 \pm 1 \mu\text{m}$	~ 5	5
Micromodel C	C1	200	37	$22 \pm 1 \mu\text{m}$	~ 10	5.4
	C2	200	32	$21 \pm 1 \mu\text{m}$	~ 5	6.3

Two Micromodel C chips labelled as C1 and C2 were used. C1 and C2 have the similar pattern, except that C1 has slightly deeper etching depths ($\sim 1\mu\text{m}$ deeper for pore bodies and $\sim 5\mu\text{m}$ deeper for pore throats) compared to C2. Therefore, the pore throat/pore body ratio in C1 is larger than C2, which implies a higher pore-pore mass transfer efficiency. The pores and grains in Micromodels B and C have an average size of $200\mu\text{m}$ in diameter, resulting in a porosity of 0.55 and a permeability of ~ 1 Darcy in the porous medium. Table 4.4 shows the experiments performed in Micromodel A, B C1 and C2 and the observations scales in different micromodels. Micromodel C (“*reservoir-on-a-chip*” model) contains $\sim 10^4$ two-dimensional connected pores, and is considered above the REV (representative elementary volume) scale according to literature (Zhang et al., 2000; Hilpert and Miller, 2001; Joekar-Niasar and Hassanizadeh 2011). With 3D pore connectivity, a minimum of $\sim 10^4$ pores are required to be considered above the REV scale and with 2D pore connectivity, a minimum of 1×10^3 pores is required to be considered above REV scale.

4.2.3 Experiments

10 experiments were performed in this chapter. As shown in Table 4.4, Experiments 1-4 were performed in a dead-end micromodel, Micromodel A, Experiments 5 and 6 were

performed in a homogeneous porous matrix, Micromodel B, and Experiments 7-10 were performed in a “*reservoir-on-chip*” model, Micromodel C (C1 or C2). All experiments were performed at room temperature (20°C) and pressure (1atm). In all 10 experiments, we first saturated the clean and dry micromodels with crude oil, aged the micromodels for 10 hours, and then performed water injection. Discussions regarding the ageing time and the micromodel cleaning procedure are in Appendix A2 & A3. To ensure air was completely expelled, we saturated the micromodels by injecting the oil with a syringe pump at a high injection rate ($\sim 500 \mu\text{l}/\text{hour}$) for a long time (>0.5 hours), which equals to more than 50 pore volumes in Micromodel C. Under this condition the high pressure gradient and the dissolution of air in oil synergistically remove the air from the pore systems. We also viewed the micromodel under the high resolution microscope to ensure no air bubbles were present. Using the procedures, we effectively remove the air bubbles in all four micromodels (A, B, C1 and C2).

Table 4.4: Experiments design

Micromodel	Experiment	Dimension under observation	Number of pores under observation	Fracture/channel width - etching depth
Micromodel A	1 - 4	$400 \mu\text{m} \times 800 \mu\text{m}$	2	$200 - 21 \pm 1 \mu\text{m}$
Micromodel B	5, 6	$2 \text{ mm} \times 3 \text{ mm}$	1.65×10^2	No fracture/channel - $21 \pm 1 \mu\text{m}$
Micromodel C	C1	$1.6 \text{ cm} \times 3.2 \text{ cm}$	$\sim 10^4$	$600 \mu\text{m} - 22 \pm 1 \mu\text{m}$
	C2	$1.6 \text{ cm} \times 3.2 \text{ cm}$	$\sim 10^4$	$600 \mu\text{m} - 21 \pm 1 \mu\text{m}$

Fluids were injected via a syringe pump (PHD 2000, Harvard Apparatus). For visualization, in Experiments 1-6, a microscope digital camera (AmScope 10MP microscope digital camera) mounted on a microscope (AmScope IN300TC) was used to capture time-lapse images from under the micromodel. In Experiments 7-10, a DSLR

camera (Nikon D5500) was used to capture time-lapse images from above the micromodel. Figure 4.2 shows a schematic sketch of the microfluidics experiment set up. In this work, we quantified the oil saturation of the captured images using the open source image analysis software ImageJ as described in Chapter 3.3. We separated the oil phase by binarizing the color of the images and calculated the area percentage occupied by oil to obtain the oil saturation. A spinning drop tensiometer (KRÜSS SDT) was used for interfacial tension measurement between the crude oil and different brines.

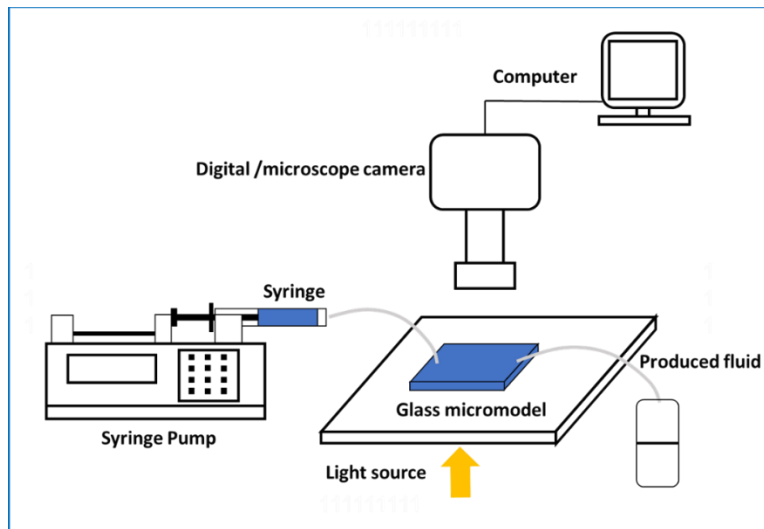


Figure 4.2: Schematic sketch of micromodel experimental set up.

4.3 SINGLE-PORE SCALE OBSERVATION: OIL DE-WETTING AND SWELLING

The oil used in Experiments 1 and 2 was the undiluted crude oil, and the oils used in Experiment 3 and 4 were the 3 times diluted crude oil and 10 times diluted crude oil, respectively. Experiment 1 provided visual observation of the crude oil's behavior with high salinity brine (118000 ppm TDS), while Experiment 2 provided visual observation of the crude oil's behavior with low salinity water (DI water). Experiments 3 and 4 provided

the dynamics of the two diluted crude oils during their interaction with DI water. It should be noted that Experiments 1-4 are typical secondary-flooding processes.

Dead-end pores and the channel in Micromodel A were first saturated with the oil. After 10 hours of aging, water was injected through the channel, removing the crude oil in the main channel and leaving the oil droplets trapped in the pores. In all 4 experiments, the water injection rate was kept constant at 1.0 microliter/hour and continued for at least 3 days. A microscope camera was used to capture images at different times of a fixed pair of dead-end pores in all 4 experiments.

4.3.1 Observation from Experiment 1: undiluted crude oil with high salinity water

In Experiment 1, when the crude oil came in contact with high salinity water, the system remained weakly oil-wet (the contact angle at the interface is greater than 90°) and did not change during the 3 days of high salinity water injection, as shown in Figure 4.3a. The oil droplets in the dead-end pores did not change in shape or in color. Small oil droplets were left on the channel surface and were hard to remove using brine due to the oil-wetting state of this oil-brine system. The wetting capability of crude oil were also addressed in previous wettability studies of crude oil on different surfaces (Buckley et al., 1998; Buckley and Liu, 1998).

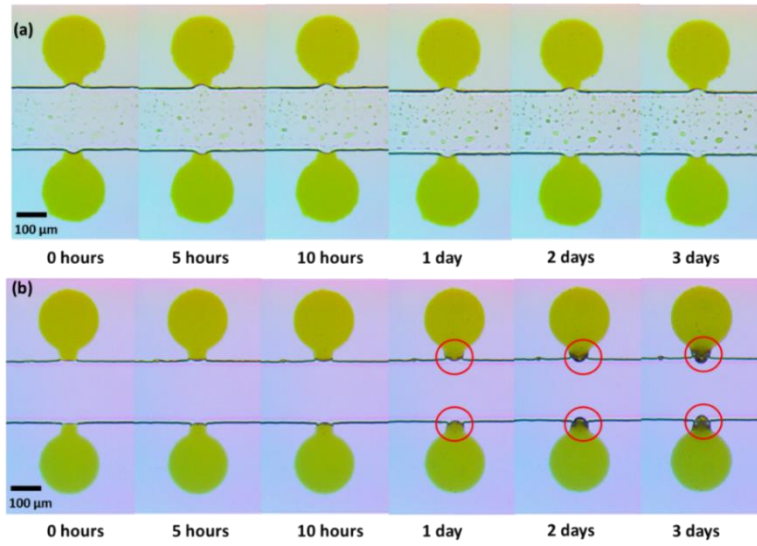


Figure 4.3: Crude oil behavior in the dead-end pores during Experiment 1 and 2. Image (a): crude oil in contact with high salinity water at different times in Experiment 1. Image (b): crude oil in contact with DI water at different times in Experiment 2. The yellow phase in each image is the crude oil, and the channel in each image was filled with water. Circled areas with dark color in image (b) show oil swelling and the formation of water in oil emulsions.

4.3.2 Observation from Experiment 2: undiluted crude oil with low salinity water

In Experiment 2, when the crude oil was placed in contact with DI water, the apparent contact angle gradually decreases as shown in the microscopic images in Figure 4.3b. Higher magnification images at the beginning and after 2 days of DI water injection are shown in Figure 4.4a. In the images, the phase boundaries (marked by the thick dark lines) moved inside of the pore, indicating the detachment of the oil from the surface. This confirmed that that this apparent contact angle decrease is due to wettability change. Wettability change indicated by a complete detachment of the oil droplet from the surface during low salinity water (650 ppm diluted synthetic seawater) injection was also observed as shown in Figure 4.4b. The dead-end pore was only partially filled with crude oil, unlike the pores in Figure. 4.3.

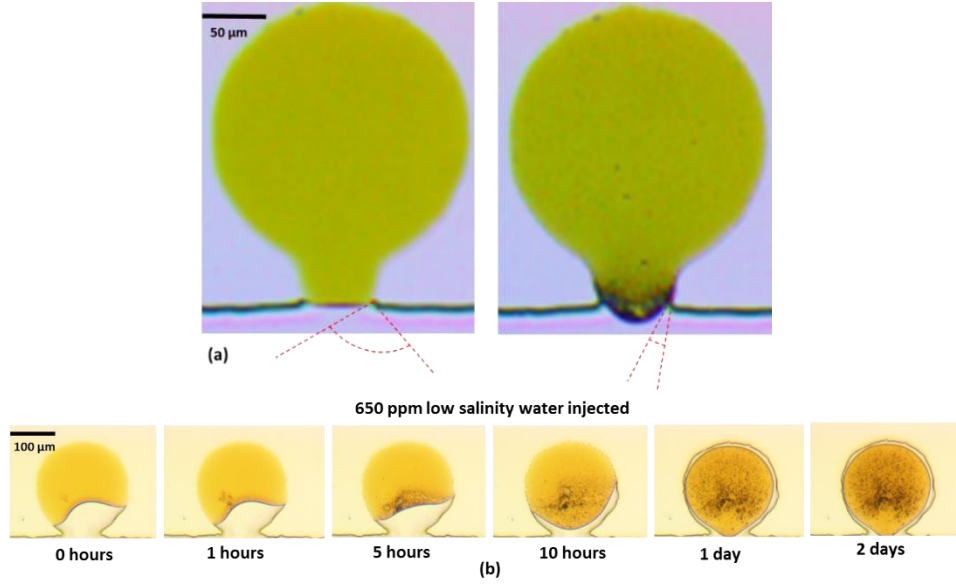


Figure 4.4: (a) Higher magnification images of crude oil/water/solid contact angle in the dead-end pore captured at the beginning and after 2 days of DI water injection in Experiment 2. (b) Crude oil in contact with 650 ppm low salinity water at different times with the pore partially filled with oil. Here we clearly observe the mobilization of contact line, which indicates that the low-salinity water flooding does change the wettability, and contact line pinning is not the only reason for apparent contact angle decreasing.

The in-situ contact angle measurements within the pores in Figure 4.3b are shown in Figure 4.5. Shortly after the DI water contacted the oil droplets (at 0 hours), oil was the wetting phase as the contact angle at the oil/water/solid interface was $110^{\circ} \pm 10^{\circ}$. After 3 days, the system became strongly water-wet as the contact angle became $20^{\circ} \pm 10^{\circ}$. Quantitative analysis was not performed with partially filled dead-end pores in Figure 4.4b. Detailed pore-scale observations and the contact angle measurements are discussed in Appendix A4 & A5. Contact line pinning results from the presence of surface heterogeneities can affect the macroscopic contact angle measurement (Joanny and De Gennes, 1984; Nadkarni and Garoff, 1992; Paxson and Varanasi, 2013; Liu and Zhang,

2013). Although we observed the decrease of the contact angle with the movement of the contact lines as shown in Figure 4.4ab, we do not exclude the possibility that the pinning of three phase contact line during oil swelling can also contribute to the apparent contact angle decrease, especially when contact location is at the convex tip of the grain surfaces (pore throat).

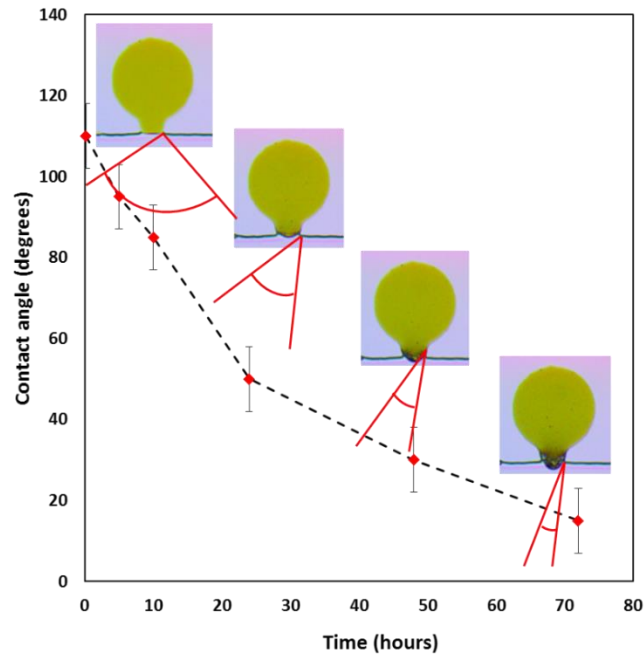


Figure 4.5: Contact angle in dead-end pores at different times in Experiment 2. The wettability changed from slightly oil-wet to strongly water-wet during 3 days of DI water injection.

Oil swelling was observed in Experiment 2 when the oil was placed in contact with low salinity water. The oil swelling behavior was also observed in Experiments 3-6 as discussed later in this chapter. This swelling is confirmed to be caused by the formation of a fine water-in-oil emulsion. During the water in oil emulsification process, small water droplets were generated within the crude oil droplets, especially near to the crude oil-bulk water interface. These water droplets/emulsions appear to be dark dots under transmitting

light, as shown in circled regions of Figure 4.3b. The water emulsions within the oil droplets come from the surrounding water by means of diffusion.

4.3.3 Oil swelling dynamics

Water diffusion and emulsification in the crude oil were observed in Experiment 2, resulting in the oil swelling. To further quantify the water diffusion process, we performed Experiments 3 and 4 with 3 and 10 times diluted crude oil samples, respectively. Experiments 3 and 4 also show water in oil spontaneous emulsion via water diffusion. We plotted the oil swelling ratio in Experiments 2-4 versus time in Figure 4.6a. The oil swelling ratio is defined as the ratio of the swelling volume to the initial oil droplets volume before swelling. For each experiment, two pores were analyzed and two sets of plots were obtained. In Figure 4.6a, the oil swelling ratio of the three oils after 70 hours was between 1.5% and 2.5%. It appeared that the oil swelling rate remained at the same order of magnitude in Experiments 2-4.

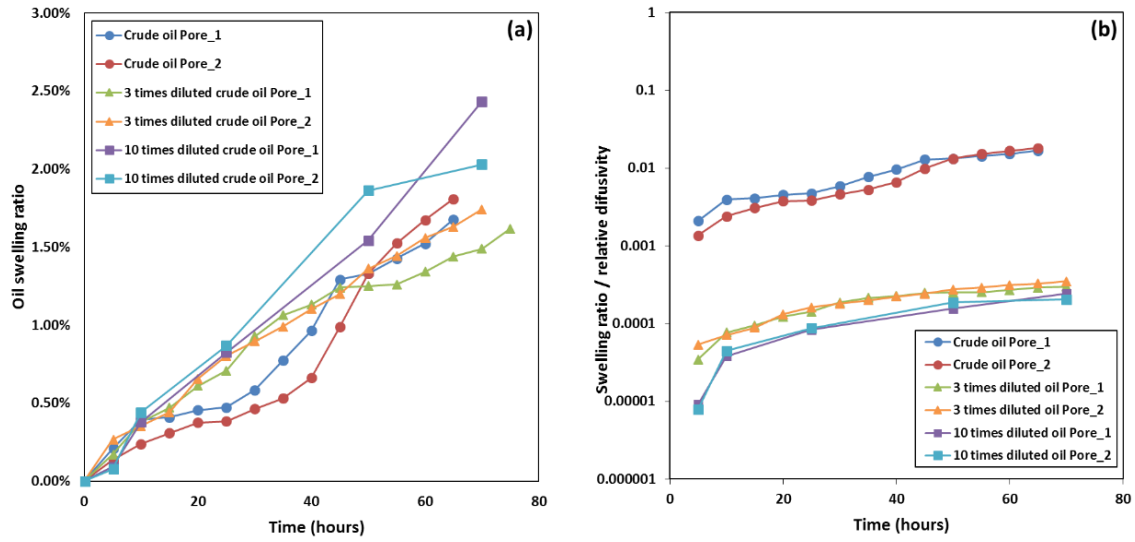


Figure 4.6: Image (a): Oil swelling ratio versus time in Experiments 2-4 with the original crude oil, the 3 times diluted crude oil and the 10 times diluted crude oil. Image (b): Scaled oil swelling ratio in Experiment 2-4 versus times after dividing the relative diffusivity factor due to the viscosity reduction.

In Experiments 3 and 4, the dilution of the crude oil resulted in two consequences: (1) a concentration reduction of the crude oil components, and (2) a reduction of the oil viscosity. From the Stokes-Einstein equation, the diffusion dynamics in a fluid is affected by atomic diffusion and viscosity (Brillo et al., 2011). Although the crude oil concentration decreased during the dilution, the viscosity reduction promoted the water diffusion process and counterbalanced the overall effect. To eliminate the effect of viscosity reduction, we performed a simple scaling. The swelling ratio of the two diluted oil samples is divided by the relative diffusion factor resulted from the viscosity reduction. The relative diffusion factor is calculated by Equation 4.1:

$$D_{r1} = \frac{D_1}{D_0} = \frac{\eta_0}{\eta_1} \quad (4.1)$$

where D_{r1} is the relative diffusion factor of water in the diluted oil 1 to the crude oil, D_0 and D_1 are the diffusion coefficient of the crude oil and the diluted oil 1, η_0 and η_1 are the viscosity of the crude oil and the diluted oil 1.

Scaled data was plotted in Figure 4.6b. In the scaled plots, it can be seen that the swelling ratio decreases by two orders of magnitude when the oil was diluted 3 times, and further reduced by half when the oil was diluted 10 times. The analysis here shows a decreased oil swelling rate, as well as a decreased water emulsification rate, when the crude oil concentration decreased. An essential inference is that both the components in the crude oil and the diffusion of water in crude oil determine the oil swelling and the wettability alteration dynamics observed in Experiments 2-4.

4.3.4 Hypothesis and evidence of mechanisms

The oil de-wetting and swelling observed in Experiments 2-4 agrees with the qualitative observations made in literature (Emadi and Sohrabi, 2013). It can be explained by an interplay between water chemical potential and polar compounds (e.g. acids, quaternized nitrogen, heterocyclic ring, etc.), as shown in Figure 4.7. Before a detailed description, we emphasize several points about the system that has been examined in the literature. The four points are:

(1) Reservoir crude oil was in equilibrium with formation high salinity water before the recovery. Thus, the water chemical potential in high salinity water is similar to that in the original crude oil.

(2) Water chemical potential in low salinity water is higher than that in high salinity water (Sandler, 2017).

(3) Water chemical potential in an oil phase with less polar compounds in bulk is higher than that with more polar compounds in bulk (De Gennes and Taupln, 1982; Lemaire et al., 1983; Karaborni et al., 1993).

(4) The concentration of polar compounds in bulk crude oil, on solid-oil interface and on water-oil interface are in equilibrium and competing; an increase in one of those will lead to a decrease in others (Emadi and Sohrabi, 2013; RezaeiDoust et al., 2011).

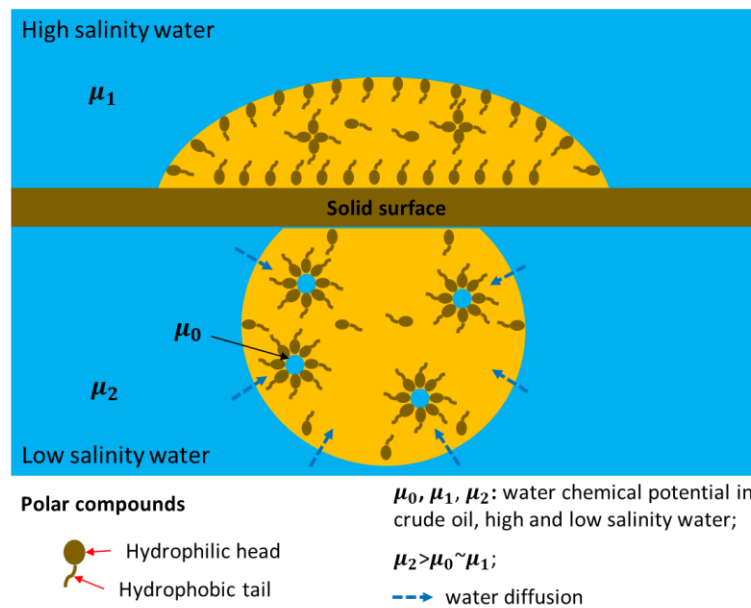


Figure 4.7: Illustration of different wettability behaviors in high and low salinity environment. The upper half represents the oil droplet immersed in high salinity water, in which case polar components stay at oil-water and oil-solid interfaces and thus keeps the oil wetting to the solid surface. The bottom half represents the oil droplet immersed in low salinity water, in which case the expanding of internal emulsion droplets' surface provides large area for polar components to adsorb on and thus the number of polar components on oil-water and oil-solid surfaces decrease, which results in less wetting condition. Yellow and blue represent the crude oil and water phase, respectively. The water emulsions in the oil phase come from the surrounding water by diffusion.

From (1) and (2), it can be inferred that the water chemical potential in low salinity water is higher than that in original crude oil, so there is a tendency to reduce this chemical potential difference when they are in contact. However, water concentration and salinity cannot significantly change in both phases. Thus, to reduce the water chemical potential difference by increasing the water chemical potential in the bulk oil phase, polar compound micelles in the oil phase capture the dissolved water and form small water droplets via water diffusion through the oil phase, providing more interfaces on which polar compounds can adsorb. As a consequence, polar compounds leave the bulk interface of the oil droplets and oil bulk to adsorb on newly generated droplets' interfaces. Therefore, the reduction of polar compounds concentration both in oil bulk and on oil-solid interface results in an increase of the water chemical potential in the oil phase, and thus reducing the chemical potential difference across aqueous-bulk oil interface. During this process, less polar compounds on the oil-glass interface makes the oil phase less wetting to the solid surface. To summarize, the wettability changes when the water-in-oil spontaneous emulsification occurs with the presence of surfactant like polar compounds. The spontaneous emulsification in a tertiary system (water, oil and surfactant) produced by diffusion at non-equilibrium state has been discussed in the literature (Miller, 1988), and our hypothesis provides an explanation for this phenomenon.

It is difficult to measure the dynamic distribution of polar compounds within the crude oil phase. However, there is an easy-to-examine inference of this hypothesis: the oil-water interfacial tension should increase when the concentration of the polar compounds on the interface decreases. The oil-solid interfacial tension γ_{os} and the water-oil interfacial tension γ_{wo} should both increase when there are less polar compounds on the surface. We measured the interfacial tension between the crude oil droplets and the water phase at different water salinities as shown in Figure 4.8. The results show that the oil-

water interfacial tension increases monotonically as the salinity decreases. The interfacial tension between the crude oil and the 118000 ppm high salinity brine is 5.32 mN/m, 44% lower than the crude oil-DI water interfacial tension which is 9.53 mN/m. The IFT data support the hypothesis that the decrease of water salinity reduces the polar compounds adsorbed on the surface. In addition, if the initial status is oil-wet, the contact angle θ ($>90^\circ$) decreases when γ_{os} and γ_{wo} increase, according to Young-Laplace equation ($\gamma_{os} = \gamma_{ws} + \gamma_{wo} \cos\theta$). This contact angle decrease results in the oil less wetting the surface. At later states when the contact angle is less than 90° , more complex analysis is required. However, assuming a constant γ_{os}/γ_{wo} ratio will result in further decreasing of contact angle θ . This inference of wettability change also agrees with the experimental observation.

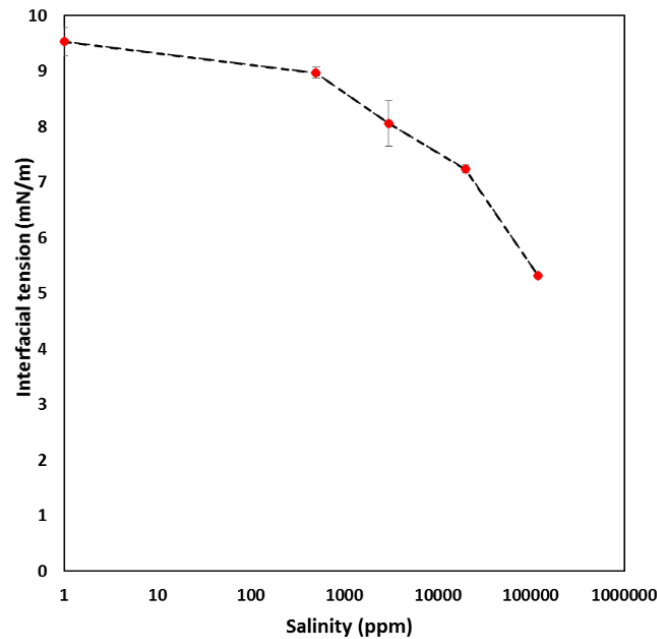


Figure 4.8: Crude oil-water interfacial tension at different brine salinities. The salinity of deionized water was plotted at 1 ppm. Error bars were calculated from multiple repeating measurements.

Given that the solubility of water in crude oil is low at the equilibrium state (Pedersen et al, 2014), the wettability alteration and the water in oil emulsification are both constrained. Given that the diffusion process is time-dependent, wettability change and the spontaneous emulsification also show time-dependency as shown in Experiments 2 through 4. This time dependent process agrees with previous observations in the literature (González-Ochoa and Arauz-Lara, 2007; Santana-Solano et al., 2012).

The observed response time of tens of hours in the dead-end experiments also agrees with the characteristic time of water diffusion into oil in the pore through a narrow throat. We denote the characteristic diffusion time as t_c , the characteristic throat length as L_t , and the characteristic pore length as L_p . We made a zero-order approximation of the characteristic time by linearizing Fick's Law of diffusion:

$$VC = \int_0^t D_w A_p \frac{dC}{dL} dt \quad (4.2)$$

From Equation 4.2 we have the estimation:

$$H_p L_p^2 C = D_w (L_t H_t) \frac{C}{L_p} t_c \quad (4.3)$$

In the above equations, V is the total volume of one pore, C is the water concentration in oil, D_w is the water diffusivity coefficient in oil, A_p is the pore throat cross area, H_t and H_p are pore throat and pore body depth, respectively. Therefore, we have:

$$t_c = \frac{L_p^3 H_p}{L_t H_t D_w} = \frac{(100\mu m)^3 \times 20\mu m}{40\mu m \times 5\mu m \times 0.23 \times 10^{-11} m^2 s} \sim 12 \text{ hours}$$

The diffusivity D_w is estimated by scaling the water-in-octane diffusivity ($\sim 10^{-9} m^2 s$) by a factor of viscosity ratio of 440 (the viscosity of octane is 0.5 cp and the viscosity of crude oil is 220 cp).

To provide additional evidence of this hypothesis, we repeated this experiment with model oil (dodecane) with the addition of surfactants (to mimic natural polar components). The wettability alteration and oil swelling were observed when model oil contains oleic surfactants, as shown in Appendix A6.

4.4 PORE NETWORK VISUALIZATION: PORE-PORE INTERACTIONS AND UPSCALING

An understanding of the pore-scale oil-water-grain behavior is necessary, but not sufficient, to explain the reservoir scale oil recovery performance, as the interactions between neighboring pores can be complex and nonlinear (Blunt, 2001; Xu et al., 2017b). To capture how pore-scale behavior of wettability alteration and oil swelling contribute to the oil-displacement in porous media, we performed intermediate-scale (pore-network scale) observations in Micromodel B (Experiment 5 and 6), where 1.65×10^2 interconnected pores are presented in every microscopic image. The pores under observation are a portion of the total 1.4×10^3 pores in Micromodel B. The major difference between Experiment 5 and Experiment 6 is whether the pore network was fully swept or only partially swept before DI water flooding.

Only a portion ($2\text{mm} \times 3\text{mm}$) of Micromodel B was visualized and presented in this work. The microscope platform could only provide observation of one fixed area with time. Once the experiment began, the observation location was fixed. The images we provided were taken from the middle section of Micromodel B, to minimize entry/end effects.

4.4.1 Observations from Experiment 5: well-swept region during low salinity waterflood

In Experiment 5, Micromodel B was well swept, with only discrete residual oil left in pores and no continuous un-swept oil remained. This sweep was achieved by flooding the oil-saturated micromodel with high salinity water at a high flow rate of 100

microliters/hour (with a capillary number of 1.3×10^{-4}) for 5 mins. About 16 pore volume high salinity water was injected during this procedure. The well-swept pore network is shown in Figure 4.9a (the oil saturation is 67% in Figure 4.9a). The injection rate was then slowed down to 1.0 microliter/hour. Three days of high salinity water injection of 130 pore volumes was first performed and then followed by low salinity water injection of 130 pore volumes for another three days. The capillary number for the high and low salinity injection was 1.3×10^{-6} and 7×10^{-7} , respectively. Capillary number denoted as Ca in this paper is calculated using Equation 4.4:

$$Ca = \frac{V_w \mu_w}{W D_p \phi \gamma} \quad (4.4)$$

where V_w is the injection rate, μ_w is the water viscosity, W and D are the width and the etching depth of the micromodel, ϕ is the porosity, and γ is the water-oil interfacial tension.

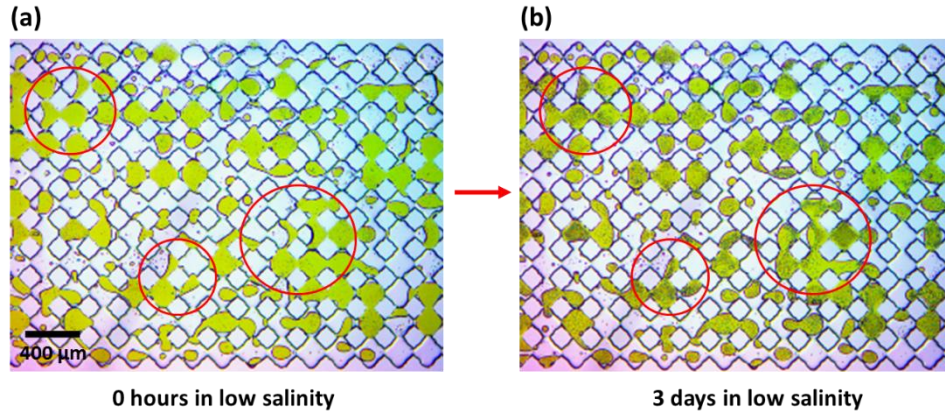


Figure 4.9: A well-swept area of Micromodel B at different times in Experiment 5. Image (a) and (b): the beginning and the ending of the DI water injection at 1 microliter/hour. Circled areas in Image (a) and (b) show oil droplets swelling and deformation caused by the growth of water in oil emulsions. The flow direction in each image was from the left to the right. 130 pore volumes of water was injected during the low salinity injection.

For accurate control of the syringe pump injection process, we used an injection rate of no less than 1 μ l/hour. Micromodel B has a relatively small pore volume of slightly over 0.5 μ l, therefore the total pore volume injected were high after several days of injection. The phenomena we observe were time dependent, so that the time duration rather than the injected pore volume is plotted in all figures.

Results show that residual oil saturation in this well-swept region did not significantly change after 3 days of DI water injection, although wettability alteration did occur and oil swelling (with spontaneous water emulsification) was also observed, as shown in Figure 4.9. The oil swelling was determined to be about 2% (the oil saturation increased by $\sim$ 2%) by comparing the oil saturation of the two images before and after 3 days of contact with DI water. This result suggests that the low salinity effect does not help in recovering residual (capillary trapped) oil. This result is not surprising, because the capillary resistance on a non-wetting oil droplet ($10^{-2} - 10^0$ psi/droplet) is orders of magnitude larger than a typical pressure gradient ($\sim$ 1 psi/ft) (Stegemeier, 1974; Morrow, 1979; Blunt et al., 1994), in which case only a slight swelling (2% as measured from Figure 4.9) will not mobilize residual oil droplets.

4.4.2 Observations from Experiment 6: partially-swept region during low salinity waterflood

In Experiment 6, Micromodel B was saturated with crude oil and flooded by 40 pore volumes of high salinity at an injection rate of 1.0 microliter/hour until steady state, and then 130 pore volumes of DI water was injected at constant flow rate of 1.0 microliter/hour for three days. The capillary number for the high and low salinity injection was 1.3×10^{-6} and 7×10^{-7} , respectively. Due to the fingering effect (Shraiman, 1986; Zhao et al., 2016), only about 60% of the observed region was swept after high salinity

waterflood, and the rest about 40% of the observed region was un-swept, as shown in Figure 4.10a.

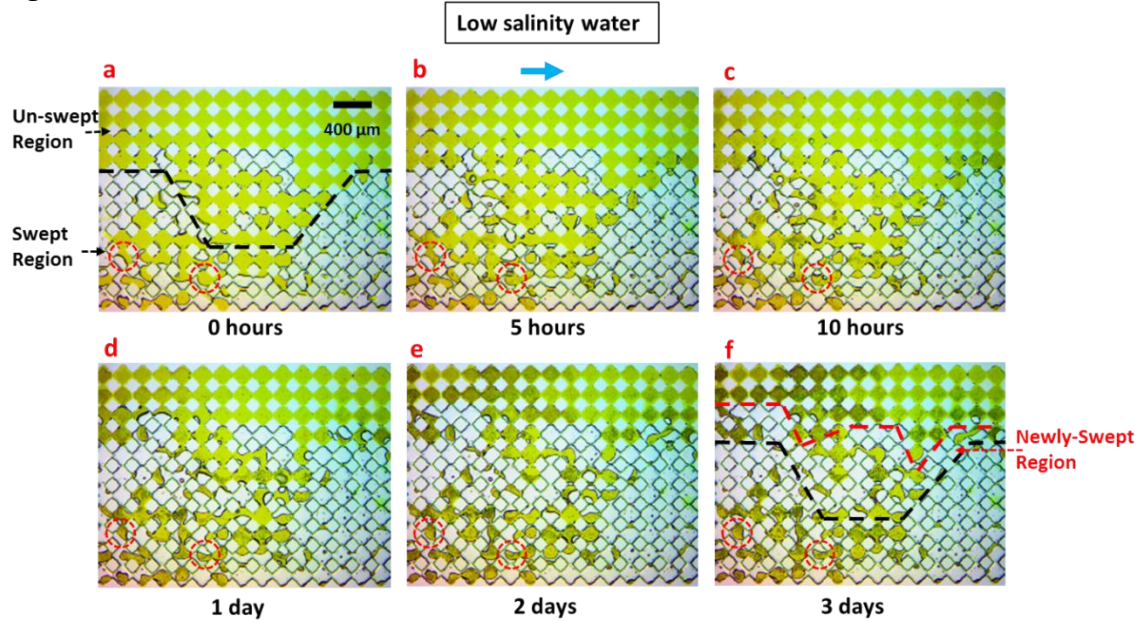


Figure 4.10: A not-well-swept area of Micromodel B at different times in Experiment 6. Image (a): the beginning of the DI water injection. The flow direction in each image was from the left to the right. The black dashed line indicates the boundary of swept region after high salinity brine flooding, and the red dashed line indicates the boundary of the swept region after tertiary DI water flooding. The oil droplets circled by red dash lines in image (a) through (f) indicate the oil droplets de-wetting where contact lines also moved. 130 pore volumes of water was injected during the low salinity injection.

Considerable further oil recovery was observed following DI water injection, as shown in Figure 4.10. The oil saturation was plotted against time in Figure 4.11. Similar to single pore scale experiments (Experiments 1 and 2) and Experiment 5, de-wetting and swelling of crude oil with spontaneous emulsification are observed. After tens of hours of DI water injection, although the residual oil droplets in the swept region were not mobilized, invasion of water into the previously un-swept oil-saturated region was

observed as shown in Figure 4.10d-f. This improvement in sweep finally brought 9% incremental oil production in the observation area as shown in Figure 4.10 in this homogeneous micromodel.

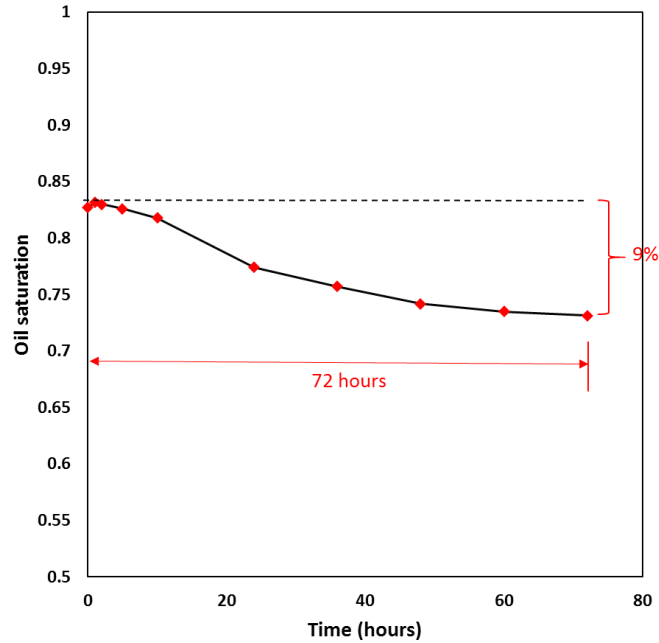


Figure 4.11: Oil saturation of the poorly-swept cross section of Micromodel B during low salinity waterflood performed in Experiment 6. The oil recovery has a long tail of 3 days, indicating a continuous change in a time period of tens of hours to several days. 130 pore volumes of water was injected during the low salinity injection.

4.4.3 Mechanisms from pore-scale perspective

From pore-network scale experiments, we demonstrated that although the oil de-wetting and swelling occurs during a low salinity waterflood, the outcomes can be very different depending on the initial sweep conditions. During the low salinity DI water flood in Experiments 5 and 6, we did not see a mobilization of the scattered residual oil droplets in the previous swept region. However, the mobilization of the remaining oil in the initially

un-swept region in Experiment 6 indicates that improvement of the sweep efficiency is potentially the major source of incremental oil recovery by low salinity waterflood.

Quantifications on 80 initially swept pores shows that oil and water specific area increased by ~18% and ~8%, respectively, during the tertiary DI water flood. The increase in the specific areas indicates the connectivity reduction and the flow resistance increase of the water in the swept region (Joekar-Niasar et al, 2007; Joekar-Niasar and Hassanizadeh 2011). Thus, we propose that the improvement of sweep efficiency is related to the de-wetting and swelling of residual oil droplets in the swept region. From a pore-scale perspective, non-wetting and swelled residual oil droplets can better block the pore-throats than wetting and smaller residual oil films (Gardescu, 1930). Therefore, the flooding water was re-directed towards the previously un-swept region. A cartoon illustration is shown in Figure 4.12a.

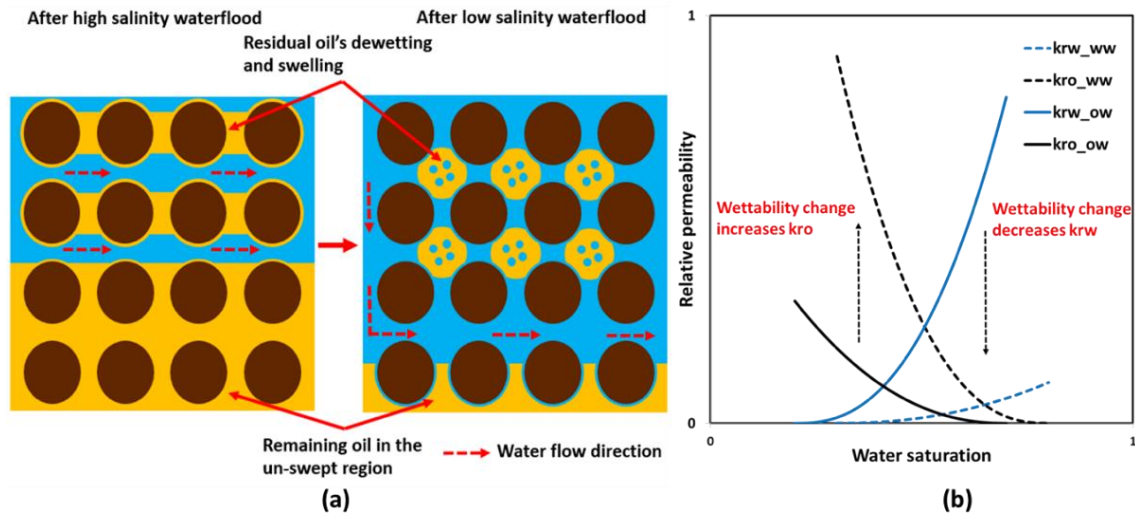


Figure 4.12: (a) Illustration of the improvement of sweep efficiency during low salinity waterflood from pore-scale perspective. De-wetted and swelled residual oil droplets move to the pore body from the grain surfaces and throats, increasing the water flow resistance and re-directing the water into previous un-swept region. (b) Schematic sketch of relative permeability change during the residual oil de-wetting. The blue solid line is water relative permeability in the oil-wet state; blue dashed line is water relative permeability in the water-wet state; the black solid line is the oil relative permeability in the oil-wet state; the black dashed line is the oil relative permeability in the water-wet state.

This observation differs from previously published statement that low salinity waterflood can increase the oil recovery by reducing the residual oil saturation (Sharma and Filoco, 2000; Masalmeh et al., 2014; Suijkerbuijk et al., 2014). Sweep efficiency improvement is also a popular hypothesis of the low salinity water flooding mechanism, but many researchers claim that it is related to the content of clay (Alhuraishawy et al., 2018; Aghaeifar et al., 2018; Abdelmoneim et al., 2018). Here we confirm the existence of sweep improvement without the existence of clay, but we do not exclude clay's importance as discussed by other authors.

4.4.4 Upscaling: from pore-scale model to reservoir model

The physical model shown in Chapter 4.4.3 clearly illustrates the oil recovery mechanism at the pore scale. However, similar to most other pore-scale studies, this micron-scale physical model cannot be directly used to describe reservoir performance, as they involve very different parameter systems (droplet size, droplet number, micron-scale contact angle, etc. versus saturations, relative permeability, etc.) (Garboczi, 1990; Shabro, 2011). To connect the pore-scale physics to a valid reservoir scale model, mechanisms shown in Chapter 4.4.3 and Figure 4.12a should be interpreted using traditional reservoir parameters.

The sketch in Figure 4.12b demonstrates a typical plotting of relative permeabilities of water and oil at different wetting conditions (water-wet and oil-wet) and different water saturations. When the reservoir changes from oil-wet to water-wet, the relative permeability of oil (k_{ro}) increases, and the relative permeability of water (k_{rw}) decreases. In addition, the oil swelling in the pore scale decreases local bulk water saturations, leading to the water relative permeability reduction. Both the wettability change and the oil swelling result in a relative permeability change in the same direction. Those changes will lead to a reduction of mobility ratio, M , of water to oil (Lake 1989; Sorbie, 1991). As the mobility ratio (M) gradually decreases, the sweep efficiency increases over a period of tens of hours to several days. The response time of 10^1 - 10^2 hours agrees with the characteristic diffusion time estimated using Equation 4.3. The observations and the explanation agree with studies where the wettability alteration is accounted by tuning the relative permeability parameters (Delshad et al., 2006; Jerauld et al., 2006; Khorsandi et al., 2017(a) (b); Jung et al., 2018), and studies that upscale the low salinity effect from the laboratory scale to the field scale by adjusting the relative permeability model according to experimental measurements (Gupta et al., 2011; Masalmeh et al., 2014; Suijkerbuijk et al.,

2014). The assumption in these works is that the relative permeability and the wettability state are static functions of the saturation and the brine composition (salinity, ion types, etc.) at a specific time step and grid block. This means an equilibrium is achieved instantaneously and the low salinity effect is triggered instantaneously when the salinity changes.

However, our work shows that the process is time-dependent and the relative permeability should also be a function of the oil-water contact time. Therefore, future work is required to determine the validity of the assumption of the equilibrium state. Since the wettability alteration and the oil swelling both are functions of time after contacting with low-salinity water, the improvement of sweep efficiency should also be a function of time over a period of $10^1 - 10^2$ hours. The time is not negligible compared to the time step used in reservoir simulations where the maximum time step is usually restricted to 1 day (Nolen and Berry, 1972; Jensen, 1980; Ganis et al, 2017).

4.5 RESERVOIR-ON-A-CHIP VALIDATION: DELAYED INCREASED IN OIL RECOVERY

To validate the observation of the sweep efficiency improvement, we performed Experiments 7-10 in a “*reservoir-on-a-chip*” micromodel, Micromodel C (C1 or C2). Model B and C are both at the scale of an inch-long pore network. However, the observation scale of Micromodel C was larger than Micromodel B. Micromodel C1 used in Experiment 7 has deeper throat depth of 10 μm compared to Micromodel C2 used in Experiment 8-10, where the throats depth was 5 μm . The pore throat/pore body ratio in C1 is larger than C2.

In Experiments 7-10, the micromodel was first saturated 100% with the crude oil and was aged for 10 hours. In Experiments 7 and 8, the 118000 ppm salinity brine was injected to the oil saturated micromodel, followed by the injection of DI water. The high

salinity brine injection continued for 23 hours and 21 hours before switching to DI water injection, respectively. In Experiment 9, the high salinity brine was injected for 20 hours, followed by the 3000 ppm low salinity brine injection. Experiment 10 was a control experiment, where the 118000 ppm high salinity brine was injected continuously into the micromodel for 8 days. In Experiments 7-10, water injection rate was kept at 1 microliter/hour (0.5 ft/day), corresponding to a capillary number of 1.8×10^{-7} for high salinity injection and 0.9×10^{-7} for low salinity injection. Figure 4.13 shows a series of visualizations captured during Experiment 7 (Experiments 8 and 9 were qualitatively similar). The oil saturation at different times in Experiments 7-10 were calculated using ImageJ and plotted in Figure 4.14. Table 4.5 summarizes the injection procedures during Experiments 7-10.

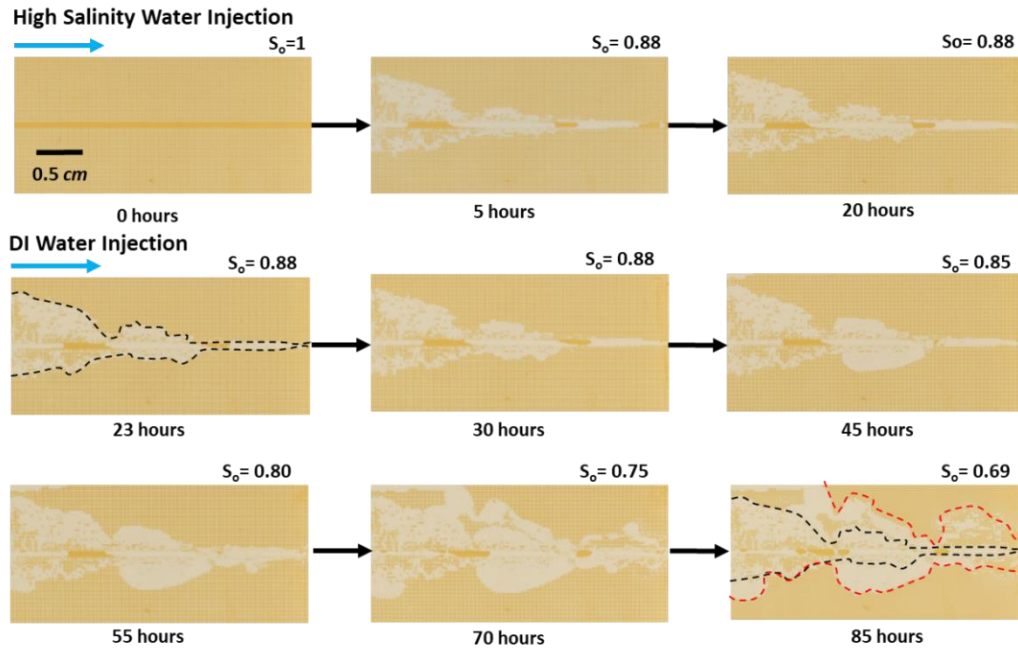


Figure 4.13: Images of Micromodel C1 at different times in Experiment 7. High salinity water was injected from 0 hours to 23 hours, and DI water (low salinity) was injected from 23 hours to 85 hours. The yellow and the white represent crude oil and water, respectively. The scale bar in the left-top image is 500 μm and applies to all images. The injection direction is from the left to right for all images. The black dashed line indicates the boundary of the swept region after high salinity brine flooding and before DI water flooding; the red dashed line indicates the boundary of the swept region after tertiary DI water flooding. Both dotted lines are extrapolations for the purpose of better understanding, and not the actual experimental results.

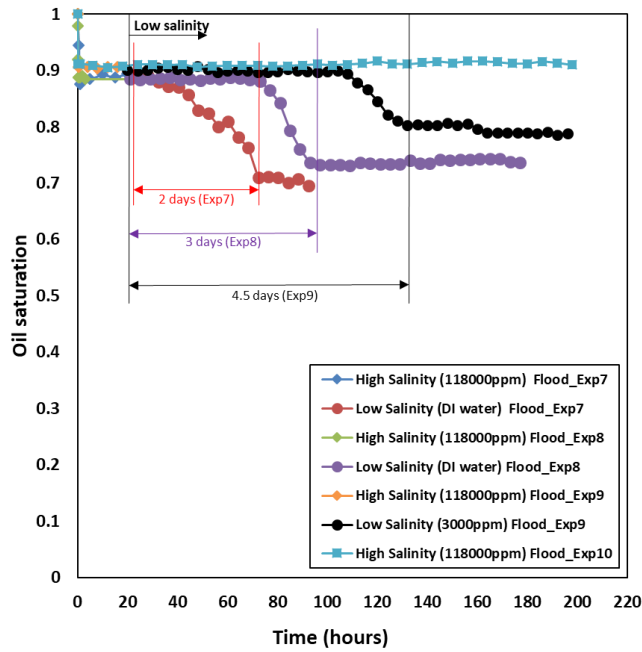


Figure 4.14: Oil saturation versus time in Experiments 7 through 10. The horizontal lines mark the response time for the tertiary low salinity waterfloods.

Table 4.5: Water injection in Experiments 7-10

Experiment	High salinity brine	HS injection duration	Low salinity brine	LS injection duration
7	118000 ppm	4.6 PV / 23 hours	DI water	14 PV / 70 hours
8	118000 ppm	4.2 PV / 21 hours	DI water	31 PV / 156 hours
9	118000 ppm	4 PV / 20 hours	3000 ppm brine	35 PV / 176 hours
10	118000 ppm	39.6 / 198 hours	N/A	N/A

4.5.1 Improved oil recovery from tertiary low salinity flooding

In Experiments 7-10, the oil recovery from the secondary high salinity waterflood was 9% – 12%. The oil saturation in all 4 experiments reached a steady state after a short time of high salinity water injection when the water broke through (less than 0.5 hours).

The relative low oil recovery (9% – 12%) from the high salinity flooding was caused by the existence of the fracture and the high viscosity of the crude oil. The oil recovery is primarily from the fracture and nearby region, leaving a large amount of un-swept oil in the porous matrix.

In the tertiary DI waterflood, 18% of incremental oil recovery was obtained after 2 days of DI water injection in Experiment 7, and 15% of incremental oil was obtained after 3 days of DI water injection in Experiment 8. In Experiment 9 where the salinity of the tertiary flooding water was 3000 ppm, the incremental oil recovery was 10% after 4.5 days of injection. In Experiment 10 where the salinity of the injection water was kept unchanged at 118000 ppm, no further oil recovery was obtained after water breakthrough. The incremental oil recovery from the tertiary low salinity waterflood in Experiments 7-9 was significant, considering the heterogeneity of the geometry and the high mobility ratio. During the tertiary low salinity waterfloods in Experiments 7-9, the low salinity water gradually swept to the un-swept region in the porous matrix and improved the sweep area, as demonstrated in the images in Figure 4.13. Meanwhile, the residual oil ganglion in the swept region during high salinity waterflood was not observed to mobilize. These observations on the “*reservoir-on-a-chip*” model support the hypothesized mechanism that the low salinity effect enhances the oil recovery by improving the sweep efficiency.

Experiments 7-10 show the positive correlation between the low-salinity effect and the incremental oil recovery. The tertiary flooding with lower salinity brings higher and sooner recovery: the tertiary oil recovery from the 3000 ppm waterflood in Experiment 9 (10%) was lower than that from the DI waterflood in Experiments 7 (18%) and 8 (15%), and happened much later.

Comparison of Experiment 6 with Experiments 7 and 8 shows that the incremental oil recovery from the tertiary DI water flood in our idealized heterogeneous geometry (15%

– 18%) was larger than that in our idealized homogeneous pore-network (9%). Heterogeneity tends to decrease the sweep efficiency compared to the homogeneous porous medium, and the sweep efficiency improvement was more significant in such a geometry. This observation also supports that the sweep efficiency is the primary cause of incremental oil recovery for our model systems.

4.5.2 Time-dependent behavior in the reservoir-on-a-chip model

Time-dependent behavior was clearly presented in Experiments 7-9. A delay of tens of hours to days occurred before the oil saturation started to decrease during the tertiary low salinity waterflood. Specifically, the delay in Experiments 7-9 was 10 hours, 48 hours and 84 hours, respectively. In addition, the oil saturation decrease resulting from the sweep improvement is a gradual and continuous process. The oil saturation decrease or the sweep improvement in Experiments 7-9 lasted for tens of hours (39 hours, 24 hours and 30 hours, respectively), showing a time-dependent effect.

Clearly, lower salinity results in faster recovery in the same geometry, as shown by the comparison between Experiments 8 and 9. The delay during the 3000 ppm brine flood was significantly longer than the delay during the DI water floods. In addition, the delay in Experiment 7 was shorter than Experiment 8. This is compatible to our theory as Experiment 7 has larger throat /pore body ratio, which corresponds to faster mass-transfer rate from water to oil.

The tens of hours to days of delay, as well as the continuous oil recovery curves, agrees well with our observations and hypotheses formed from the pore scale (Chapter 4.3) and pore-network scale experiments (Chapter 4.4). The delay time observed at all three scales are similar and all agree well with the estimated characteristic diffusion time using

Equation 4.3. Combining the three scales, the wettability change, the oil swelling and the improved oil sweep, are all time-dependent, dynamic processes.

4.6 APPLICATIONS AND LIMITATIONS: CORE-SCALE AND FIELD SCALE IMPLICATIONS

The findings from our micromodel toolbox help to narrow the gap between the pore-scale and the larger scale flow behavior. Our results can be used to explain certain phenomena, e.g., the time-delay behavior and oil recovery improvement without clay, mentioned in several published corefloods. Table 4.6 summarizes some published coreflood results and the reported and/or estimated delay time of the low salinity effect. The delay of tens of hours to days agrees well with our observations at all three scales and the characteristic diffusion time estimated using Equation 4.3. Our hypothesized mechanisms can be used to explain one type of low salinity effect which is caused by the oil/brine interactions and requires the existence of active compounds in the oil phase. Also, the oil swelling and the increase of flow resistance can explain the pressure gradient increase reported in some coreflood and field tests (Zhang et al., 2007; Boussour et al., 2009; Austad et al., 2010; Robertson, 2010; Masalmeh et al., 2014). In addition, a recent study (Collins et al., 2018) reported an increase of the aliphatic carboxylate acid in the produced oil during low salinity waterflood and hypothesized that the release of aliphatic carboxylate acid (fatty acid) from the rock surface contributes to the wettability alteration. This finding and proposed mechanism agree with our theory that the release of polar compounds from the surface to the bulk oil resulted in the wettability alteration.

Table 4.6: Literature on the delay behaviors

Literature	Experiment #	Delay (PV/hours)	Change duration time (PV/hours)	Improved oil recovery
RezaeiDoust et al., 2011	Low salinity flood in Fig. 8	2 PV / 12 hours*	0.8 PV / 4.8 hours*	2 - 3%
	Low salinity flood in Fig. 10	2 PV / 12 hours*	4 PV / 24 hours*	7 %
Masalmeh et al., 2014	Tertiary low salinity flood case 1	3 PV / 25 hours	4 PV* / 30 hours	3 - 4%
	Tertiary low salinity flood case 2	4 PV / 30 hours	6 PV* / 50 hours	7%
Suijkerbuijk et al., 2014	Tertiary low salinity flood	3 PV / 35 hours*	3 PV / 35 hours*	6%

* Calculated from the data in the literature

Although the mechanisms we proposed in this work are time-delayed rather than instantaneous, they are not prohibitively slow thus making the process uneconomic at the field scale. The timescale for the response is in days, which is not long compared to the timescale in reservoir operations (months to years) but is also not negligible compared to time steps used in numerical reservoir simulators. Many recent low salinity models assume an instantaneous wettability change therefore an instantaneous relative permeability change when the salinity decreases (Al-adasani et al., 2012; Jackson et al., 2016; Qiao et al., 2016; Al-Ibadi et al., 2019), where time steps as small as about 0.1 day are applied. Therefore, during the first tens of time steps after a location experiences a salinity change, the accuracy of the wettability and relative permeability calculation trigger concerns given our experimental results on time-dependency. Incorporating contact time as a parameter in relative permeability functions or using a much larger time step may address this problem. The effect of time-dependency of wettability alteration and oil swelling on field-scale behavior needs further investigation with numerical modeling and other large-scale tools.

Our model system is idealized, such as the pure glass surface, artificially designed pore-networks and the limited geometry scale up to inches (although still about or above

REV scale). Thus, based on our experiments, we do not exclude the possibility that other mechanisms can also contribute to the low salinity effect in field applications. To test the proposed hypotheses in coreflood, it is necessary to use a design where the interactions and performance are analyzed by analyzing the oil recovery, pressure drop and oil characteristics in real time. For other complex systems, additional assumptions and conditions (the oil type, brine salinities, etc.) need to be examined. Limitations of the microfluidics platform in this study are discussed in Appendix A7.

Nevertheless, the idealization reduced complications and focused on the first order effect resulting from the fluids' interactions. Following the model framework from the single pore scale up to the intermediate pore-network scale and then up to a “*reservoir-on-a-chip*” model, we showed how the pore-scale behaviors affect macro-scale parameters. The use of such a microfluidic toolbox demonstrated a possible method to narrow the gap between observations at micron/pore-scale and the understanding of porous media flow behaviors by qualitative and quantitative analysis.

4.7 CONCLUSIONS

This chapter presents the microfluidic experiments conducted on single-pore scale, pore-network scale and reservoir-on-a-chip scale. Micron-scale observations and theories are upscaled to a porous medium scale model, which explains one type of low salinity effect with delayed oil recovery and in the absence of clay.

In Chapter 4.3, observations on the single-pore scale reveal a considerable de-wetting and swelling of crude oil in contact with low salinity water. This can be explained from the interplay between the water chemical potential and the polar compounds in the oil phase. In Chapter 4.4, flow experiments on the pore-network scale (with $\sim 10^2$ pores) show that the oil de-wetting and swelling under low salinity water flooding leads to a re-

direction of flooding liquid from the swept region to un-swept region, thus help to recover originally un-swept oil. In Chapter 4.5, flooding experiments on the heterogeneous porous micromodel (“*reservoir-on-a-chip*” containing $\sim 10^4$ pores) with 2D connectivity support the hypothesis that sweep efficiency (not mobilization of capillary-trapped residual oil) is the primary cause of incremental oil recovery and this low salinity effect is time-dependent. The response time after low-salinity water injection remains at the same order of tens of hours, regardless of that the experiment is scaled-up from 1 to $\sim 10^4$ pores. This time-dependency agrees with the estimated characteristic time of the water in oil diffusion process. A 10% – 18% incremental oil recovery is obtained during tertiary low salinity waterfloods in this model system.

The time-dependent oil de-wetting/swelling-induced sweep efficiency improvement can explain some observations in published corefloods, such as the pressure gradient increase and the delay/long tail of coreflood recovery curves. In addition, this observation also shows that the presence of clay is not necessary for low salinity water flooding to be effective, although additional mechanisms may exist between low salinity water and clays.

Chapter 5: Time-Dependent Displacement Dynamics of Low Salinity Effects: The Role of Surfactant Compounds in Oil

5.1 INTRODUCTION

This chapter presents a further study of the low salinity effects, where the impacts of the polar compound's concentration on the low salinity effects and the time-dependent behavior observed in Chapter 4 are investigated. In Chapter 4, it is hypothesized that the polar compounds in the crude oil phase cause the initial oil-wet state by adsorption on the solid/oil surface, and the subsequent desorption from the interfaces leads to the wettability alteration and generates water-in-oil emulsions. A time-dependent dynamic was identified and a delayed, sudden oil saturation decrease was obtained during the low salinity and DI water injection period. The time-dependency behavior is explained to be controlled by the polar compounds/natural surfactant components in the crude oil. To test the hypotheses and provide more quantitatively analysis, in this chapter, systematic waterflood experiments are performed in the inch-scale “*reservoir-on-a-chip*” micromodels saturated with synthetic oil mixed with nonionic surfactant using high salinity brine and deionized water. The water displacement dynamics and ultimate recovery efficiency from both high and low salinity water are analyzed. This study shows that water emulsion in oil and improved oil recovery are observed only when the surfactant concentration is sufficiently high, and higher surfactant concentration leads to shorter delay time before the low salinity effects become effective.

5.2 EXPERIMENTAL METHOD

5.2.1 Fluids preparation and analysis

Seven synthetic oil samples (Oil 1 – Oil 7) and two water samples were prepared for the experiments performed in this work and the properties are shown in Table 5.1. Oil

1 – Oil 6 are mixtures of a mineral oil and different concentrations of a nonionic surfactant (Sorbitan monooleate, Figure 5.1) ranging from 0.01% to 3% in volume fraction, and Oil 7 is the same mineral oil without surfactant. The mineral oils with surfactant are used to mimic the active crude oil in Chapter 4 which contains active, surfactant-like polar components. Using the surfactant containing mineral oils simplifies the composition of the oils to be investigated (the crude oil has complex composition), and allows for systematic change of the surfactant concentration. The mineral oil has a viscosity of 31 cp and is a mixture of the original mineral oil (Sigma-Aldrich) with a viscosity of 700 cp at 20 °C and decane (VWR International, LLC) by a ratio of 2:1 to decrease the viscosity to the desired value. As shown in Figure 5.1, Sorbitan monooleate (Span 80, Sigma-Aldrich) is nonionic surfactant and consists of both hydrophilic groups (-OH) and hydrophobic groups (-CH₃). It is soluble in oil and fits the description of polar compounds described in Chapter 4. The oil samples are colorless and were dyed by Oil Red (VWR International, LLC). Deionized water (DI water) and a high salinity brine with a salinity of about 118000 ppm (8.6 wt% NaCl, 1.2 wt% KCl, 2.0 wt% CaCl₂) were used for the high salinity and low salinity waterflood in the experiments. Thus, two water samples with the same properties as used in Chapter 4 (Figure 4.2) were used, which allows for direct comparison. In particular, DI water was used because it excludes the impacts of salts in brine that can be related to other mechanisms in addition to the proposed mechanism attributing to diffusion and emulsification. The viscosities were measured using an ARES-G2 rotational rheometer in the shear rate range between 1 – 300 s⁻¹ at room temperature. The mineral oil samples show Newtonian behavior and have constant viscosity in the shear rate range. The interfacial tensions (IFT) between seven oil samples and the two water samples were measured using a spinning drop tensiometer (KRÜSS SDT) at room temperature and the results are discussed later in Chapter 5.

Table 5.1: Fluids

Fluids	Composition	Density (g/cm ³)	Viscosity (cp)	IFT with brine (mN/m)	IFT with DI water (mN/m)
Oil 1	Mineral oil, 3 vol% Sorbitan monooleate	0.84	31	1.80	2.8
Oil 2	Mineral oil, 1 vol% Sorbitan monooleate	0.83	31	1.68	3.0
Oil 3	Mineral oil, 0.3 vol% Sorbitan monooleate	0.82	31	1.86	5.2
Oil 4	Mineral oil, 0.1 vol% Sorbitan monooleate	0.82	31	1.80	6.0
Oil 5	Mineral oil, 0.03 vol% Sorbitan monooleate	0.82	31	14.0	13.8
Oil 6	Mineral oil, 0.01 vol% Sorbitan monooleate	0.82	31	22.2	16.1
Oil 7	Mineral oil	0.82	31	23.9	23.2
Brine	8.6 wt% NaCl, 1.2 wt% KCl, 2.0 wt% CaCl ₂	1.07	1	–	–
DI water	Deionized water	1.0	1	–	–

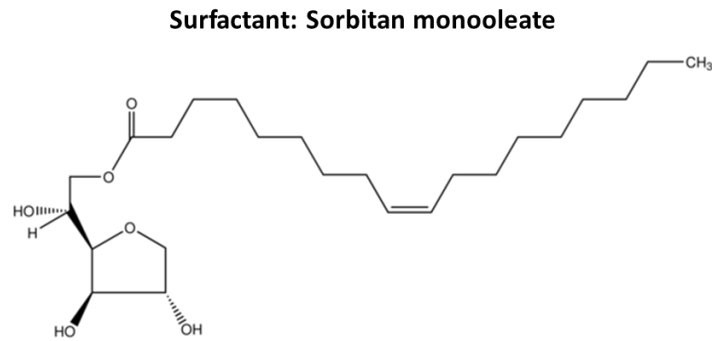


Figure 5.1: The structure of the surfactant (Sorbitan monooleate) used in this chapter.

5.2.2 Micromodel

An inch-long, 2.5D glass micromodel with a fracture in the middle of the porous matrix was utilized as shown in Figure 5.2. Six micromodels were fabricated for the experiments performed for the study and were labeled as M1 – M6. The glass micromodels are water-wet by nature with water and the mineral oil without surfactant as demonstrated in previous work (Du et al., 2020). The properties of the six micromodels are listed in Table

5.2. In summary, all six micromodels have the dimensions of $2.5\text{ cm} \times 1.5\text{ cm}$ with a porosity of about 0.55 in their flow geometry. The etching depth is $\sim 19\text{ }\mu\text{m}$ for the pore bodies and $\sim 4\text{ }\mu\text{m}$ for the pore throats. The diameter of the pore bodies is $\sim 200\text{ }\mu\text{m}$ and the width of the pore throats are $\sim 30\text{ }\mu\text{m}$. The fracture has a width of $600\text{ }\mu\text{m}$ and has a depth of $\sim 19\text{ }\mu\text{m}$ (actual depth is the same as the pore bodies in each micromodel). The depths were measured using a stylus profilometer (DEKTAK 6M). The fracture exists in the middle of the porous matrix and connects to both the inlet and the outlet. The combination of the fracture/porous matrix in the geometry enhances the contrast between the displacement of the imbibition and the drainage processes, and improves the quantitative repeatability in the recovery comparison. In Chapter 4, a similar design with fracture and porous matrix was used for the same purposes.

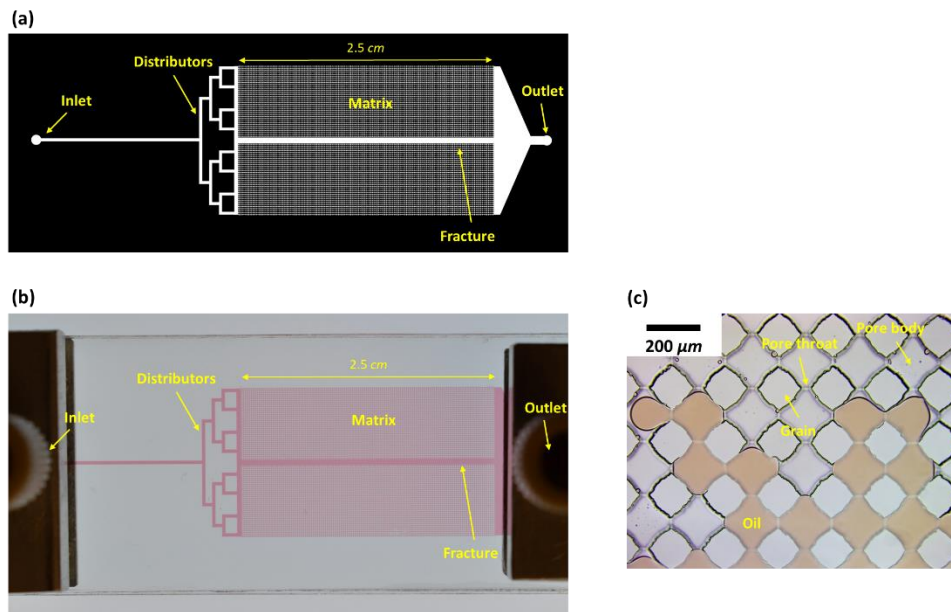


Figure 5.2: Micromodel used in Chapter 5. (a) Micromodel photomask design. (b) Photo of the fabricated glass micromodel saturated with mineral oil (pink). (c) Microscopic pore image after waterflood with mineral oil (reddish) and water (white).

Table 5.2: Micromodel properties

Micromodel #	Dimensions	Pore body depth/width	Pore throat depth/width	Fracture depth/width	Porosity	Pore volume
M1	2.5 × 1.5 cm	19 µm / 200 µm	4 µm / 30 µm	19 µm / 600 µm	0.55	3.9 µl
M2	2.5 × 1.5 cm	19 µm / 200 µm	4 µm / 30 µm	19 µm / 600 µm	0.55	3.9 µl
M3	2.5 × 1.5 cm	18 µm / 200 µm	4 µm / 30 µm	18 µm / 600 µm	0.55	3.7 µl
M4	2.5 × 1.5 cm	19 µm / 200 µm	4 µm / 30 µm	19 µm / 600 µm	0.55	3.9 µl
M5	2.5 × 1.5 cm	20 µm / 200 µm	4 µm / 30 µm	20 µm / 600 µm	0.55	4.1 µl
M6	2.5 × 1.5 cm	19 µm / 200 µm	4 µm / 30 µm	19 µm / 600 µm	0.55	3.9 µl

5.2.3 Experiments

Six flow experiments were performed in the micromodels M1 – M6 at ambient conditions as described in Table 5.3. Two waterfloods were performed in experiments 1-5 and one waterflood was performed in experiment 6. Before waterflooding, the micromodels were firstly saturated with the synthetic oils by injecting at 150 µl/hour from the inlet for 1 hour using a syringe pump (PHD 2000, Harvard Apparatus) until gas bubbles disappeared from the system. After the initial saturation, oils were continuously injected into the micromodels at 0.5 µl/hour for 48 hours, which allows sufficient time for oil-solid interaction as discussed in Chapter 4.

In the 1st flood in experiments 1-6, a high salinity waterflood was performed in the micromodel saturated with synthetic mineral oil for 28 – 30 hours (~14 – 15 pore volumes) at an injection rate of 2 µl/h (~0.5 ft/day) using the syringe pump. Following the 1st waterflood, a 2nd flood using DI water was performed in the same micromodel in experiments 1-5 at the same injection rate of 2 µl/h. The second injection continued until no significant changes were visually observed and the time varied in different experiments (usually longer for experiments with oils of lower surfactant concentration). A DSLR camera (Nikon D5600) was mounted above the micromodels to capture time-lapse images

of the entire flow domain during the experiments at an interval of 6 mins (~ 0.05 PV). After each experiment, pore-scale images were taken using the microscope (AmScope 10MP).

Table 5.3: Experiments

Experiment #	Initial fluid	1 st flood		2 nd flood		Micromodel #
		Fluid	Injection rate / duration	Fluid	Injection rate / duration	
1	Oil 1	Brine	2 μ l/h / 29 hours	DI water	2 μ l/h / 68 hours	M1
2	Oil 2	Brine	2 μ l/h / 30 hours	DI water	2 μ l/h / 69 hours	M2
3	Oil 3	Brine	2 μ l/h / 30 hours	DI water	2 μ l/h / 69 hours	M3
4	Oil 4	Brine	2 μ l/h / 29 hours	DI water	2 μ l/h / 119 hours	M4
5	Oil 5	Brine	2 μ l/h / 29 hours	DI water	2 μ l/h / 168 hours	M5
6	Oil 6	Brine	2 μ l/h / 28 hours	N/A	N/A	M6

5.2.4 Image analysis

The images captured in the experiments were processed using ImageJ as discussed in Chapter 3.3. Figure 5.3abcd show the raw image captured by the DSLR camera, enhanced image, segmented image (binarized) and the colored image, respectively. The image segmentation separated the water phase (black) from oil and grains using the thresholding method “Otsu” as shown in Figure 5.3c. The water saturation in each binarized image was calculated and oil saturation was calculated as one minus the water saturation. Blue color was assigned to water phase by adjusting the LUT (Look-Up Table for color mapping) value in the binarized grey scale image (Figure 5.3d).

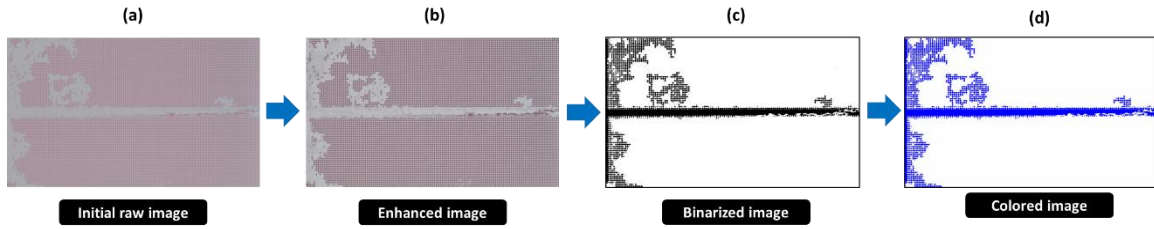


Figure 5.3: Image processing samples for the results presented in Chapter 5. Oil phase is in pink in (a) and (b). (c) Grey scale image in black (water) and white. (d) Image with adjusted color in blue (water) and white. Images are from experiment 1.

5.3 RESULTS

5.3.1 Water displacing dynamics

Figure 5.4 summarizes the water invasion processes obtained in experiments 1-6. The displacement process of each experiment is presented in a same column and is labeled with the experiment number (#1-#6) from the left to the right. Figure 5.4a, Figure 5.4b and Figure 5.4c present the high salinity water displacement patterns at the initial, breakthrough and final state of the 1st flood in experiments 1-6, respectively. Figure 5.4d and Figure 5.4g present the DI water displacement patterns at the initial and final state of the 2nd flood in experiments 1-5. Figure 5.4e and Figure 5.4f present two visualization in the middle of the 2nd waterflood before and after a significant change in water invasion patterns in experiments 1-4, and present two randomly selected visualizations in the middle of the 2nd waterflood in experiment 5. The significant water invasion changes in experiments 1-4 is discussed later in Chapter 5.4. In comparison, minimal change was observed in experiment 5 where the four visualizations are qualitatively similar as shown in Figure 5.4, column #5.

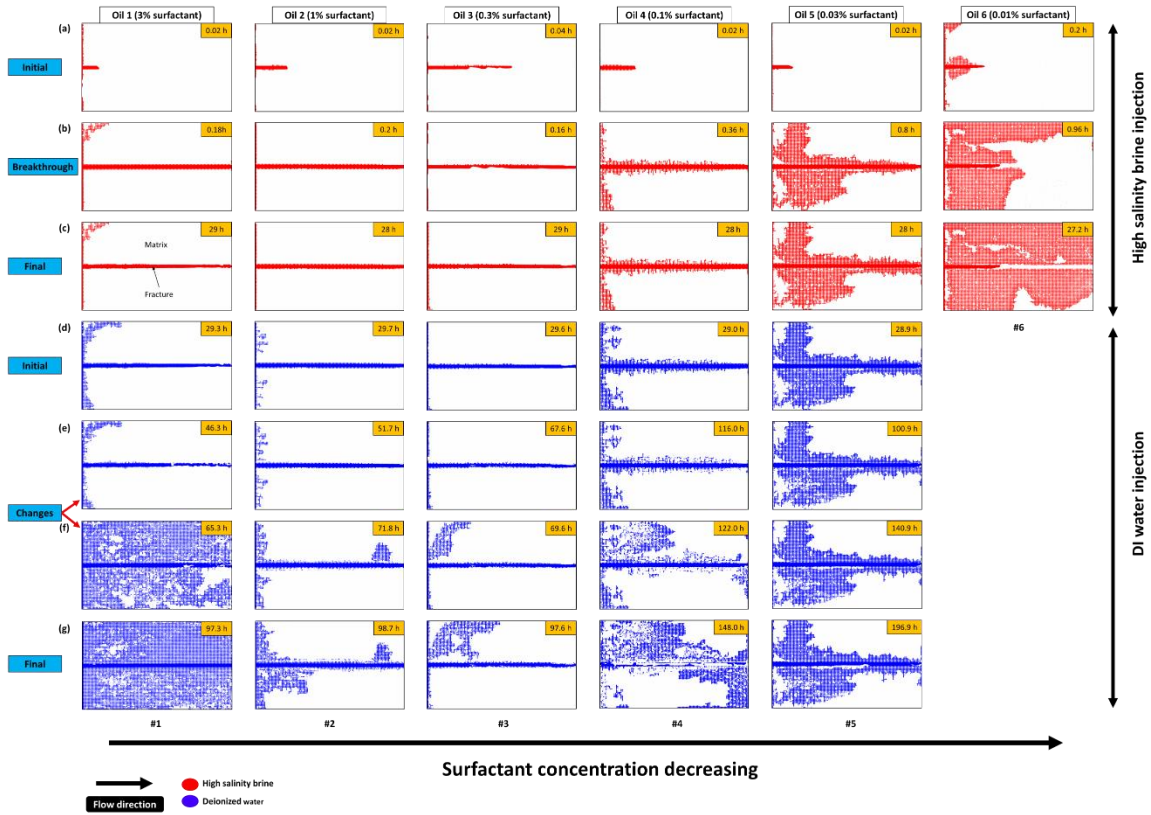


Figure 5.4: (a)(b)(c) High salinity water displacement processes in experiments 1-6. (d)(e)(f)(g) DI water displacement processes following the high salinity water displacement processes in experiments 1-5. The water invasion patterns for high salinity brine flood and DI water flood are presented in red and blue colors, respectively. Images in each column are from the same experiment. Experiment numbers (#1-#6) are labeled beneath the corresponding columns.

5.3.1.1 High salinity water displacement patterns

During the high salinity waterflood in experiment 1-3 where the surfactant concentration in oil is 3%, 1% and 0.3%, respectively, water preferentially flowed through the fracture in the middle of the geometry, and water breakthrough was early at ~ 0.1 pore volumes of injection (Figure 5.4abc). The resulting water invasion patterns in the three experiments are qualitatively similar along the fracture and water invasion in porous matrix area was minimal.

In experiment 4 where the surfactant concentration in oil is 0.1%, the primary flow pathway for water was also the fracture, but water also slightly invaded into the porous matrix from the inlet and the fracture before breakthrough at 0.18 pore volumes of injection (Figure 5.4b). After breakthrough, water did not invade further into the porous matrix and the water displacement pattern remained the same during further water injection (Figure 5.4c).

In experiment 5 where the surfactant concentration in oil is 0.03%, in addition to flowing through the fracture, a large amount of water invaded into the porous matrix from the inlet and the fracture before breakthrough at 0.4 pore volumes of injection (Figure 5.4b). The swept area in the porous matrix was much larger compared to that in experiment 4. After breakthrough, the water invasion did not continue and the water displacement pattern remained the same during further water injection (Figure 5.4c).

In experiment 6 where the surfactant concentration is the lowest (0.01%), water primarily invaded through the porous matrix, leaving the oil occupied in the fracture before breakthrough at 0.48 pore volumes of injection (Figure 5.4b). After breakthrough, water continued invading into the porous matrix and swept the largest area at the final state, leaving small amount of residual oil in the flow domain in the micromodel (Figure 5.4c).

In summary, larger area in the porous matrix is invaded by high salinity waterflood as the surfactant concentration decreases. The primary pathways for water change from the fracture to the porous matrix at the surfactant concentration of 0.03%.

5.3.1.2 Deionized water displacement patterns

During the DI waterflood in experiments 1-4 where the surfactant concentration in oil is 3%, 1%, 0.3% and 0.1%, respectively, water initially did not invade into the porous matrix occupied with remaining oil left behind from the 1st waterflood as shown from

Figure 5.4d to Figure 5.4e. As a result, the water displacement pattern remained the same for a long time period for more than 28 hours/~14PV in all experiments. During further injection, water invaded into the porous matrix from the inlet and from the fracture as shown in Figure 5.4f.

In experiment 5 where the surfactant concentration is 0.03%, water did not invade further into the porous matrix with remaining oil left from the 1st waterflood with high salinity brine and the displacement pattern remained the same (Figure 5.4defg).

In summary, DI water invades into the unswept porous matrix and considerable incremental oil recovery is obtained when the surfactant concentration is larger than 0.1%.

5.3.2 Displacement efficiency

Oil saturation versus injection time in experiments 1-6 is shown in plots #1-#6 in Figure 5.5. The red and blue curves in each plot represent the high salinity water flood and the DI waterflood, respectively. The recovery from the two floods are summarized in Table 5.4.

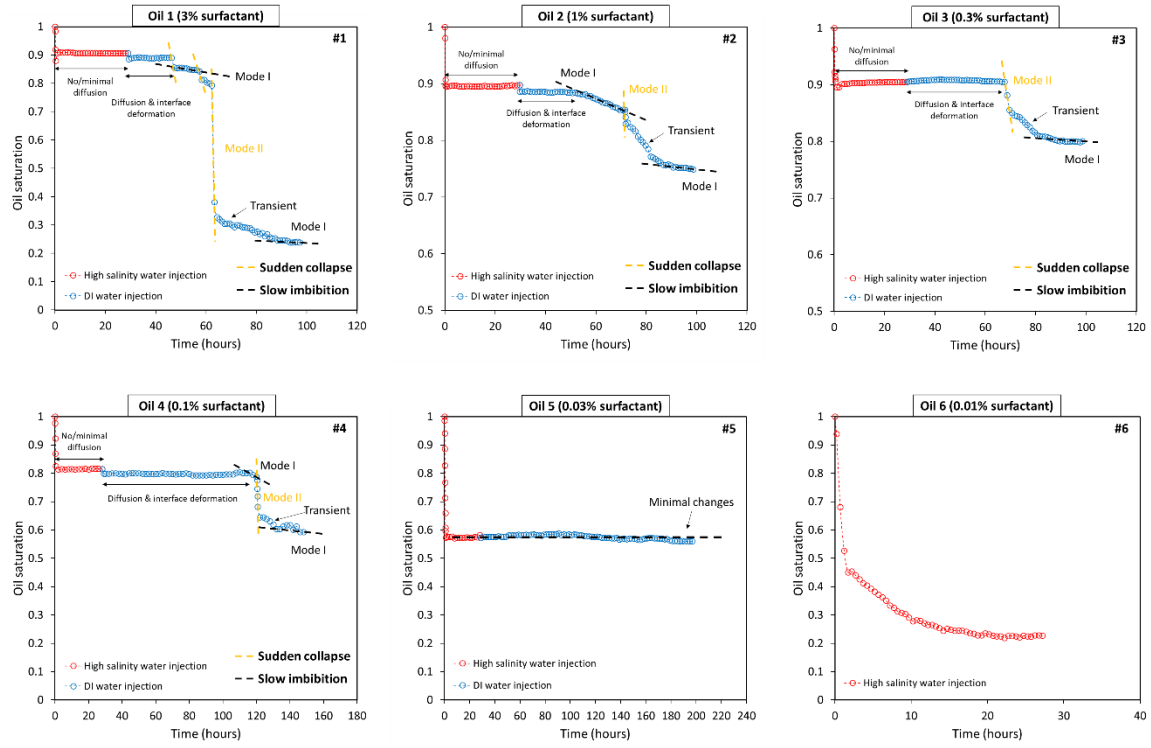


Figure 5.5: Oil saturation versus injection time in experiments 1-6. High salinity brine flood is shown in red and DI water flood is shown in blue. Experiment numbers (#1-#6) are labeled at the top right corner in each plot.

Table 5.4: Oil displacement efficiency

Experiment #	Breakthrough time	1 st flood recovery	2 nd flood recovery
1	0.18 hours / 0.09 PV	9.3%	65.1%
2	0.2 hours / 0.1 PV	10.4%	14.6%
3	0.16 hours / 0.08 PV	9.6%	10.4%
4	0.36 hours / 0.18 PV	18.4%	20.8%
5	0.8 hours / 0.4 PV	42.6%	0.8%
6	0.96 hours / 0.48 PV	77.4%	N/A

5.3.2.1 High salinity waterflood

During the high salinity waterflood in experiments 1-3 where the surfactant concentration in oil is 3%, 1% and 0.3%, respectively, oil saturation quickly decreases to ~90% at breakthrough (Figure 5.5, #1-#3) as oil is exclusively recovered from the fracture. Oil saturation does not decrease during further injection of ~30 hours/~15 pore volumes until the end of the high salinity waterflood as seen from the flat saturation curve in plots #1-#3. The ultimate oil recovery from the flood is ~10%, leaving a high remaining oil saturation of about 90% in the micromodel.

In experiment 4 where the surfactant concentration in oil is 0.1%, oil saturation decreases to ~82% at breakthrough (Figure 5.5, #4) as oil is recovered from both the fracture and the porous matrix adjacent to the fracture and the inlet. Oil saturation does not decrease during further injection of ~29 hours/~15 pore volumes until the end of the high salinity waterflood as observed in the flat saturation curve in plots #4. The ultimate oil recovery from the flood is 18.4%, leaving a high remaining oil saturation of more than 80% in the micromodel.

In experiment 5 where the surfactant concentration is 0.03%, oil saturation decreases to ~60% at breakthrough (Figure 5.5, #5) and most of oil is recovered from the porous matrix adjacent to the fracture and the inlet in addition to the recovery in the fracture. Oil saturation remains almost the same during further injection of ~29 hours/~15 pore volumes until the end of the high salinity waterflood as seen from the flat saturation curve in Figure 5.5. The ultimate oil recovery from the flood is 42.6%, leaving more than 50% of remaining oil in the micromodel.

In experiment 6 where the surfactant concentration is the lowest (0.01%), oil saturation decreases to about 50% at breakthrough and continued to decrease during further

injection of ~28 hours/14 pore volumes. The ultimate oil recovery from the flood is 77.4%, leaving a small amount of remaining oil of 22.6% in the micromodel.

In summary, during high salinity waterflood, the oil displacement efficiency is low at ~10% and is not impacted by surfactant concentration above 0.3%. When the concentration is lower than 0.1%, the displacement efficiency increases with the decrease in surfactant concentration.

5.3.2.2 Deionized waterflood

During the DI waterflood in experiments 1-4 where the surfactant concentration in oil is 3%, 1%, 0.3% and 0.1%, respectively, the oil saturation remains constant during an initial stage of $\sim 10^1$ hours of DI water injection (Figure 5.5, #1-#4). After the initial stable period, oil saturation starts to decrease in all four experiments, and a considerable oil recovery is obtained in experiments 1-4 of 65.1%, 14.6%, 10.4% and 20.8%, respectively.

In experiments 1-4, the saturation decrease appears to have two different modes through the quantitative analysis: Mode I is characterized with a slow, gradual decrease as marked by the black dashed line in the plots; Mode II is characterized by an abrupt decrease in saturation as marked by the yellow dashed line in the plots. In between the two modes, there is usually a transient period with a behavior in between Mode I and II. The two modes can appear more than once in each experiment.

In experiment 5 where the surfactant concentration is 0.03%, oil saturation does not show significant change as depicted by Figure 5.4, column #5. The slight changes in oil saturation, the increase in the early stage and the decrease in the later stage, are both within 1%, mostly caused by image analysis fluctuation due to the oil-water interaction and redistribution. The oil recovery is less than 1% in this case.

5.3.3 Interfacial tension

The interfacial tension between the seven oil samples with different surfactant concentrations and the high salinity brine (red curve) and DI water (blue curve) are plotted in Figure 5.6a. Figure 5.6b zoomed in the low concentration region in Figure 5.6a. Both IFTs decrease significantly with the increase of surfactant concentration above 0.1% from 24 mN/m to 1.8 mN/m and from 23 mN/m to 2.8 mN/m for brine and DI water, respectively.

The IFT between oil and high salinity brine decreases more than the IFT between oil and DI water as the surfactant concentration increases. When the surfactant concentration is lower than 0.03%, the IFT between oil and brine is higher than that between oil and DI water. When the concentration is higher than 0.03%, the IFT between oil and brine decreases faster and becomes lower than that between oil and DI water with the increase in surfactant concentration up to 3%.

The two IFTs are similar when the surfactant concentration is zero, and the IFT difference is the largest when the surfactant concentration is at 0.1% and then decreases with the increase of surfactant but is still significant up to the concentration of 3%.

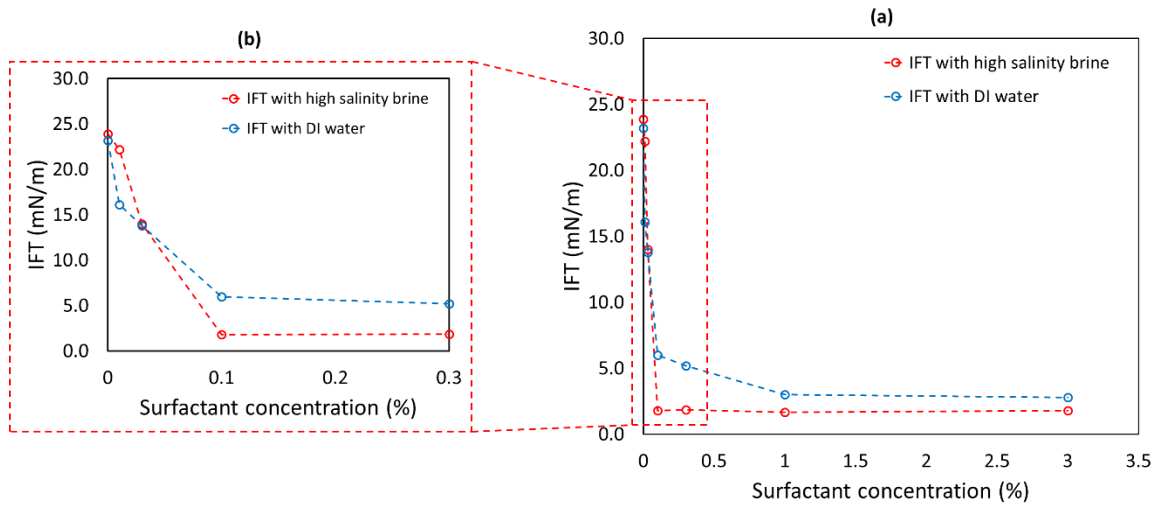


Figure 5.6: (a) Interfacial tensions between oil/brine (red) and oil/deionized water (blue) versus surfactant concentration in the oils. (b) Zoomed-in from the initial region of plot in (a).

5.3.4 Emulsion and oil de-wetting

Pore-scale images were taken using a microscope after each experiment as shown in Figure 5.7. The images in Figure 5.7abcde were taken after the 2nd DI water flood in experiments 1-5 to compare the fluids interactions that resulted from DI water flooding. The image in Figure 5.7f was taken after the 1st high salinity brine flood in experiment 6 and is provided as a comparison case when the interactions were not present.

In Figure 5.7abcd from experiments 1-4, significant amount of emulsions (dark) were generated in the oil phase (pink). The emulsions were generated both inside the porous matrix at a distance from the fracture (Figure 5.7a) and near the fracture, but were most significant in the region near the fracture where the most water-oil interactions were encountered. Furthermore, oil was seen to detach from the glass surface at multiple locations.

In Figure 5.7e from experiment 5, emulsions also appeared inside the mineral oil but the amount is much less than in experiments 1-4. Oil de-wetting/detaching at the grain surfaces was occasionally observed.

In Figure 5.7f from experiment 6, the mineral oil with 0.01% of surfactant is clear and emulsion was not observed. The system is clearly water-wet, consistent with observations in previous work where the mineral oil – water system is water-wet in glass micromodels (Chapter 2; Du et al., 2020).

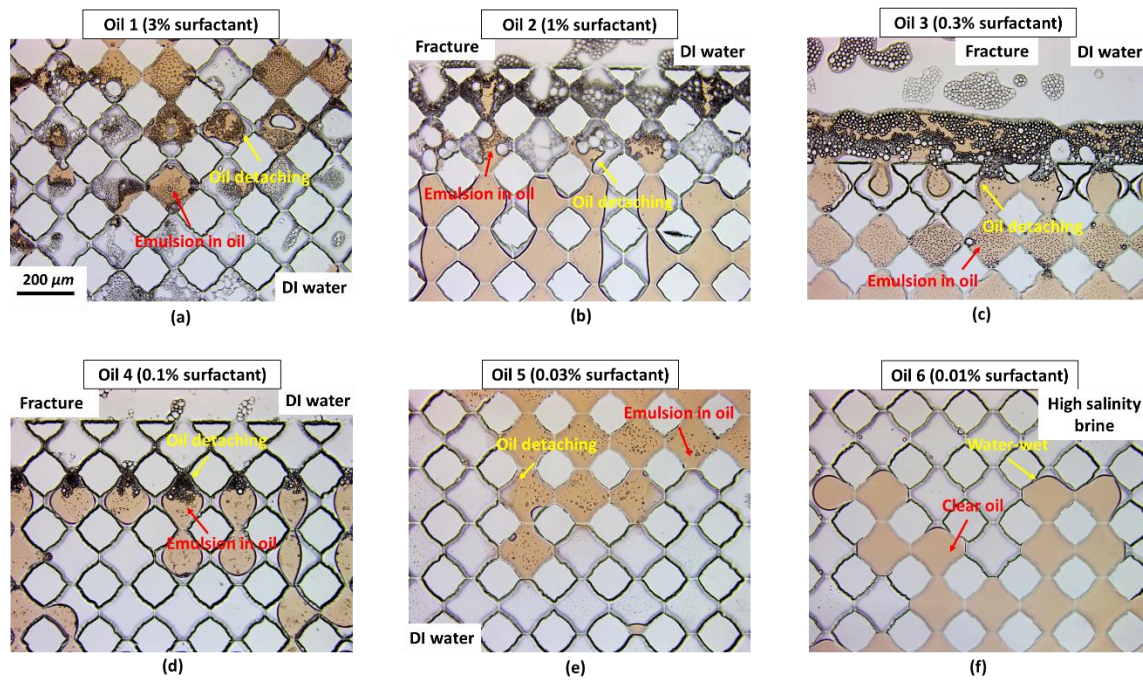


Figure 5.7: (a)-(e) Microscopic visualization after DI waterflood (2nd flood) in experiment 1-5. (f) Microscopic visualization after high salinity brine flood in experiment 6. Note that the fracture is present in (b), (c) and (d) but is not present in (a), (e) and (f) because in the later three cases the area near the fracture was well-swept after the corresponding flood.

5.4 ANALYSIS AND DISCUSSION

5.4.1 Time-dependency

5.4.1.1 *Delayed reaction*

A delay of $\sim 10^1$ hours in a second oil recovery was observed in experiments 1-4 during the DI water injection as shown in Figure 5.8, by analyzing the data in Figure 5.5. The delay time is calculated as the time between the start of DI water injection and when an identifiable change was observed either qualitatively (Figure 5.4) or quantitatively (Figure 5.5) in the water displacement process. The delay time decreases with the increase of the surfactant concentration. In this work, the highest delay time of 87 hours was obtained for surfactant concentration of 0.1% and the lowest delay time of 17 hours was obtained for surfactant concentration of 3%.

The delay time in experiments 1-4 with synthetic mineral oil agrees well with the experiments using active crude oil presented in Chapter 4.3 – 4.4 and many references as discussed in Chapter 4.5.2. In Chapter 4.3 – 4.4, the delay time is 10 – 84 hours with crude oil in similar glass, 2.5D micromodels. In the references shown in Table 4.6, a delay of ~ 12 – 35 hours is obtained from previous studies from different experiments.

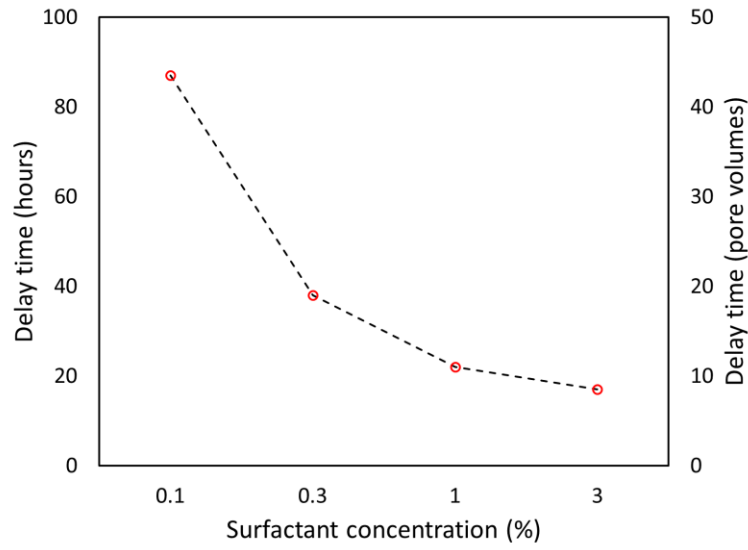


Figure 5.8: Delay time before water invasion in the DI waterflood against DI water injection time in real time (hours) and injected pore volumes.

5.4.1.2 Long-tailed recovery

As seen from Figure 5.5, in experiments 1-4, the recovery during the DI water injection continued for a relatively long-time, 20 – 50 hours. The same trend was reported in experiments in Chapter 4.3 – 4.4 and in the literature (Table 4.6) as discussed in chapter 4.5.2 where the long recovery tail continued up to 50 hours.

The overall time-dependency behavior, the delay and long recovery trend, presented in this chapter agrees with the results presented in Chapter 4. Therefore, the physical model of the low salinity effects of the crude oil proposed in Figure 4.7 is well supported with the synthetic model oil used in this work. Moreover, the findings demonstrate the critical role of the polar compounds/natural surfactant in affecting the time-dependent behavior of the low salinity effects. The delay time decreases as the surfactant concentration increases, which can be explained as higher surfactant

concentration leads to stronger oil-water interactions described in the model (water in oil emulsions, oil swelling, wettability alteration) and therefore causes a shorter reaction time.

5.4.2 Role of surfactant

5.4.2.1 Emulsion and wettability

Figure 5.4abc demonstrates that the initial wettability with oil and high salinity brine in the micromodel gradually changes from oil-wet to water-wet state with the decrease in surfactant concentration. At the highest concentration of 3%, water preferentially flowed through the fracture and did not invade into the porous matrix. As the surfactant concentration decreases, water invades more into the porous matrix (Figure 5.4abc) and recovers more oil during the high salinity waterflood (Table 5.4). The breakthrough time increases as the surfactant concentration decreases (Figure 5.9), which also supports the wettability changes to more water-wet state because breakthrough occurs earlier for a more oil-wet state (Lake et al., 2014). The trend in the initial wettability supports the hypothesis that the adsorption of the polar compounds/natural surfactant causes the oil-wetness, and higher surfactant concentration leads to stronger initial oil-wetness.

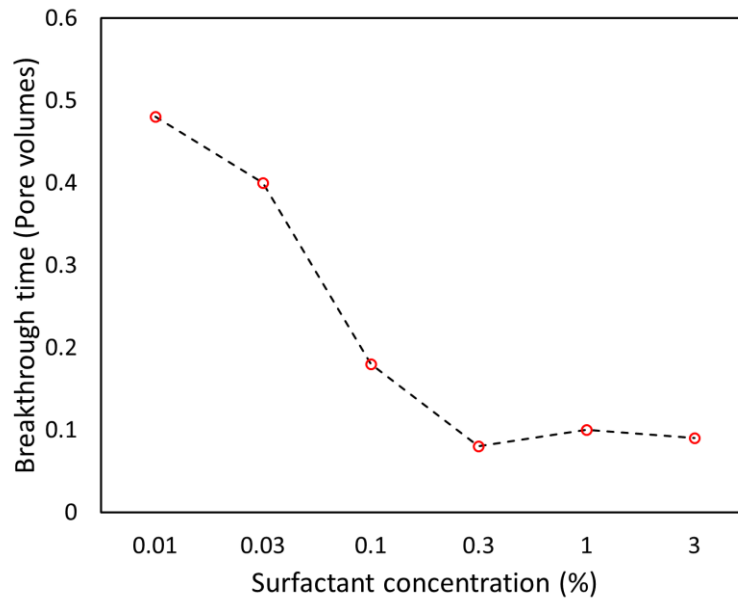


Figure 5.9: Breakthrough time versus surfactant concentration in oil during 1st waterflood (high salinity brine).

Water-in-oil emulsions, along with oil detaching, are observed with the synthetic mineral oil – surfactant mixture during DI water injection in experiments 1-4 (Figure 5.7). Stronger emulsions are generated in regions with more oil-water contact, such as near the fracture. The additional water invasion into the porous matrix (Figure 5.5defg) and the incremental oil recovery (Figure 5.6, #1-#4) during the DI waterflood are consistent with the oil de-wetting observed in the microscopic observations. As discussed in Chapter 4, the water-in-oil emulsion is generated when water molecules diffuse into oil and form micelles when surfactant is present. The desorption of the surfactant from the oil/solid surface causes the oil detaching and the wettability alteration to stronger water-wetness. The emulsification and wettability alteration take $\sim 10^1$ hours to occur and cause the delay as discussed in Chapter 5.4.1.

5.4.2.2 Interfacial tension

At zero to low surfactant concentration ($<0.01\%$), the IFT between oil and the high salinity brine and between oil and DI water are similar (Figure 5.6). When the surfactant concentration increases, the IFT between oil and DI water is considerably higher than that between oil and brine. The trend agrees with the IFT measurements in Figure 4.8 where higher salinity leads to lower IFT between water and crude oil containing natural surfactant components. This phenomenon can be explained by the theory proposed in Chapter 4.3.4 in that high salinity leaves more surfactant on the interfaces which reduces the IFT between oil and water.

5.4.2.3 Oil recovery

The oil recovery from the high salinity waterflood decreases with the increase of surfactant concentration up to a concentration of 0.3% as shown in Figure 5.10a. The increase in surfactant leads to strong oil-wetness in the micromodel as discussed in Chapter 5.4.2.1, and causes lower oil recovery from the waterflood. When the surfactant concentration is higher than 0.3%, the system is sufficiently oil-wet and the recovery remains at $\sim 10\%$ with oil only recovered from the fracture.

The trend of oil recovery from DI waterflood versus surfactant concentration is non-monotonic, and the incremental recovery varies from less than 1% to more than 60% (Figure 5.10b). On one hand, higher surfactant concentration causes strong initial oil-wetness that impedes further water invasion into the regions with less oil-water contact. On the other hand, higher surfactant concentration also results in stronger, faster oil-water interactions (emulsification, oil swelling) that enhance oil displacement. The variation in incremental oil recovery with oils of different surfactant concentration explains the inconsistencies in the incremental oil recovery caused by low salinity waterflood in the

literature as discussed in Chapter 2.2, since the content of polar compounds vary for different oils. However, with a moderate surfactant concentration of 0.1 – 1%, the incremental recovery (10 – 20%) is in good agreement with the results from Chapter 4 and in the literature.

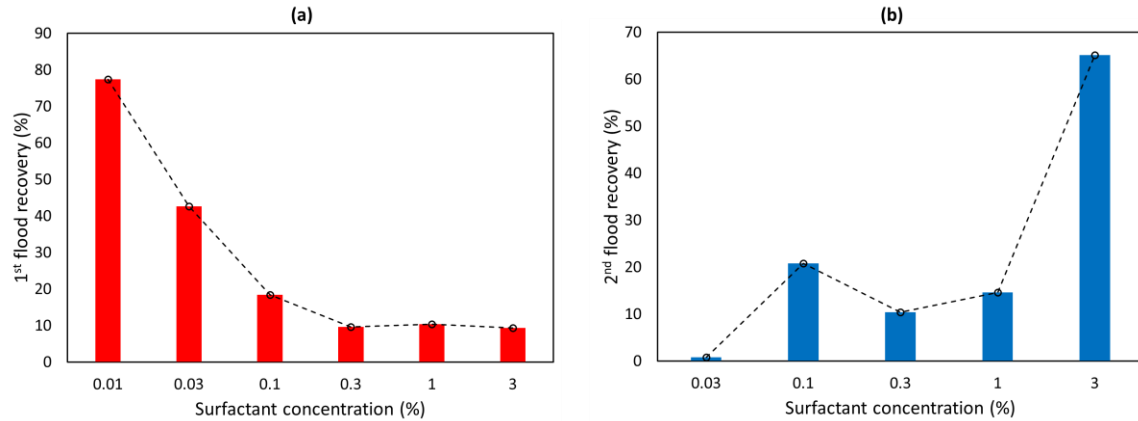


Figure 5.10: Oil recovery versus the surfactant concentration in oil from (a) 1st waterflood (high salinity brine) and (b) 2nd waterflood (deionized water).

5.4.3 Displacement mode

Two displacement modes are identified from experiments 1-4 as labeled in Figure 5.5. Mode I is “*slow imbibition*” characterized with gradual decrease/recovery of the oil in porous matrix, and Mode II is “*sudden collapse*” characterized with a sudden decrease/recovery oil in porous matrix.

5.4.3.1 Slow imbibition

Mode I, *slow imbibition*, is observed from all four experiments, 1-4. The mode is previously observed in Chapter 4.5 where the long, gradual recovery tail is obtained during the low salinity waterflood. In this work, it occurs during the entire flood period: at the beginning (Figure 5.5, #2, #4), in the middle (Figure 5.5, #1), and in the later stage of oil

saturation decrease (Figure 5.5, #1-#4). This mode is controlled by the local capillary force as the wettability alters from more oil-wet towards more water-wet. When the wettability alters to more water-wet, local capillary equilibrium is broken and water imbibes into the porous matrix mostly from the inlet and the fracture where the oil has the largest contact area with the invading water. The wettability alteration and oil swelling processes are continuous, time-dependent, and the water imbibition is also a gradual, continuous process. These reactions altogether contribute to the slow, gradual recovery trend observed in Mode I.

5.4.3.2 Sudden collapse

Mode II, *sudden collapse*, is also observed from all four experiments, 1-4. The mode is also captured in Chapter 4.5 when the incremental oil recovery starts with a sudden jump in oil saturation. In this work, it occurs at the beginning (Figure 5.5, #1, #3) or in the middle (Figure 5.5, #1, #2 and #4) of the oil saturation decrease. This mode results from the global imbalance of the capillary force over the large (or entire) region in the porous matrix. The large remaining oil ganglia extend in the porous matrix and contact with water at different locations and from different directions near the inlet and the fracture. The rate of change in capillary force due to wettability alteration (changes contact angle) and oil swelling (changes the interface curvature as indicated in Figure 5.5) is not homogeneous at different locations. Oil ganglia remain unmoved because of the large trapping force from the viscosity. When the net capillarity imbalance accumulates and overcomes the viscous force over certain pores, a sudden water invasion occurs and causes the sudden decrease in oil saturation.

5.5 CONCLUSIONS

In this chapter, systematic waterflood experiments are performed in the inch-scale “*reservoir-on-a-chip*” micromodels saturated with synthetic oils using high salinity brine and DI water. Different mineral oil and surfactant mixtures were utilized to experimentally model the behavior of the crude oil in the presence of the low salinity water. Overall this work demonstrates that:

- Low salinity effects are significant when there is a sufficient amount of surfactant in the oil. The relationship between the incremental oil recovery and the surfactant concentration is non-monotonic.
- Presence of surfactant contributes to the water-in-oil emulsion and the wettability alteration to a more water-wet state, which are critical for the occurrence of low salinity effects observed in Chapter 4.
- The low salinity effects by surfactant dominated oil-water interactions show time-dependency, as higher concentration corresponds to shorter reaction/delay time.
- Higher surfactant concentration leads to strong oil-wetness for an oil/brine system, but does not necessarily lead to higher recovery. However, the incremental recovery of oils with moderate surfactant concentration agrees with the findings in Chapter 4 and literature.

Chapter 6: Microfluidic Diagnostics of the Impact of Local Microfracture Connectivity on Hydrocarbon Recovery Following Water Injection²

6.1 INTRODUCTION

Microfractures originate in hydrocarbon reservoirs and groundwater aquifers either in the form of pore-scale authigenic apertures or secondary openings during well stimulation. Microfractures are often difficult to detect and can act as an invisible impediment when predicting hydrocarbon recovery. In this chapter, microfluidics was used to identify the flow conditions at which microfracture connectivity with macrofractures becomes impactful. Water-flood experiments in three micromodel geometries: one with only a porous matrix, one with a connected microfracture (connecting two adjacent and macrofractures) and one with a semi-connected (dead-end) microfracture (only connected to one macrofracture). The analysis focuses on fluid displacements at unfavorable mobility ratios, which are difficult to capture with high-order numerical methods. Two configurations of microfracture type with the porous matrix, either dead-end (only connected to one macrofracture) or connecting two macrofractures, were investigated as case examples for both water and oil-wet conditions.

6.2 EXPERIMENTAL METHOD

6.2.1 Micromodels

In this chapter, three 2.5-dimensional (2.5D) glass micromodels were fabricated and utilized using the method developed by Xu et al. (2017), where the pore throats are shallower than pore bodies, as described in Chapter 3.1. In such 2.5D micromodels,

² Du, Y., Mehmani, A., Xu, K., Kelly, S., Balhoff, M.T. and Torres-Verdín, C. 2020. Microfluidic Diagnostics of the Impact of Local Microfracture Connectivity on Hydrocarbon Recovery Following Water Injection. *Water Resources Research* **56** (7): e2019WR026944.

Yujing Du designed and performed the experiments, conducted data analysis, and wrote the manuscript.

important pore-scale flow phenomena such as the continuity of the wetting phase and capillary snap-off of the non-wetting phase can be captured by having pore-scale 3D features in the 2D pore arrays. This 2.5D feature is important for studying the unstable immiscible flow, where finger initiation has been shown to be sensitive to pore-scale geometries (Chen and Wilkinson, 1985). The three micromodels used in this work are denoted as M1, M2 and M3, with all having a domain size of 2.5 cm in length and 1.5 cm in width and the same porous matrix. M1 is only a homogenous matrix between the inlet and the outlet, M2 has a microfracture in the middle of the matrix connecting only to the inlet side, and M3 has a microfracture in the middle of the matrix connecting the inlet to the outlet (which connects the two macrofractures). In the microfractured micromodels, the microfractures are of comparable size to matrix pores (the depths are both $\sim 21\text{ }\mu\text{m}$). However, there are two key features that distinguish microfractures from matrix pores, therefore affecting the flow significantly. Firstly, microfractures are lacking in frequent diverging-converging structures, therefore posing little capillary barriers during drainage and serves as “highway” for imbibition along the flow path. Meanwhile, matrix pores have frequent diverging-converging structures, posing capillary barriers to fluid invasion. Secondly, matrix pores are approximately isotropic in average, while microfractures are directional. The photomask designs of the flow domain in M1, M2 and M3 are depicted in Figure 6.1a, where the boundary conditions are also specified. The inlet, outlet and flow channels to/from the flow domain Figure 6.1b. Micromodels are made of soda-lime glass. The grains are cylinders with a near-square cross-section as seen from Figure 6.1c, and the surfaces are macroscopically smooth. The pore-scale geometric features are illustrated in two schematic sketches of the vertical cross-section from two angle (45° and 90° from horizontal direction) as shown in Figure 6.1d and Figure 6.1e. Details regarding the

fabrication and micromodel properties can also be found in the paper by Xu et al (2017). Other relevant geometric properties of the three micromodels are summarized in Table 6.1.

Table 6.1: Summary of micromodel properties

Model	Pore body width	Pore body depth	Pore throat width	Pore throat depth	Fracture length	Fracture width
M1	200 μm	$\sim 21 \mu\text{m}$	25 μm	$\sim 5 \mu\text{m}$	N/A	N/A
M2	200 μm	$\sim 21 \mu\text{m}$	25 μm	$\sim 5 \mu\text{m}$	2.2 cm	600, 400, 200 μm
M3	200 μm	$\sim 21 \mu\text{m}$	25 μm	$\sim 5 \mu\text{m}$	2.5 cm	600 μm

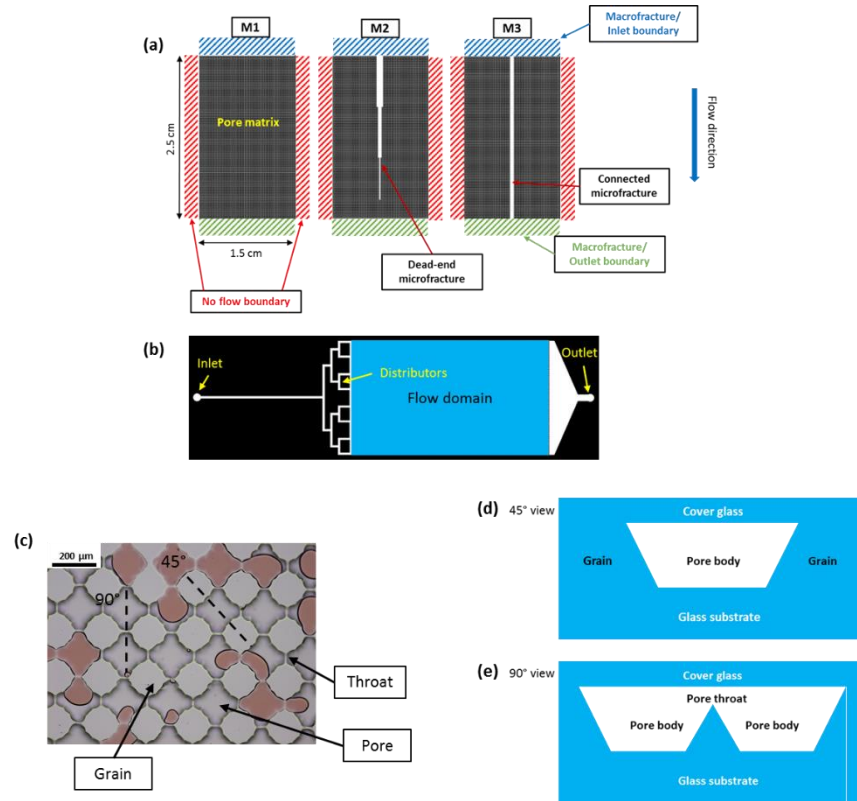


Figure 6.1: (a) Photomask design of the flow domains in micromodels 1, 2, and 3 denoted as M1, M2, and M3, respectively. (b) Photomask design of inlet, outlet, flow channels to/from the flow domain. (c) Microscopic image of the micromodel after flow experiment. (d) Cross-sectional schematic of micromodel pore body/grain at 45°. (e) Cross-sectional schematic of micromodel pore body/pore throat at 90°. Note that throats are etched shallower than pores as part of the 2.5D fabrication scheme.

6.2.2 Fluids preparation and analysis

Mineral oil and a crude oil (undisclosed composition) were used as the displaced fluids with viscosities of 170 cp and 230 cp, respectively. The viscosities of water and both oils were measured using Rheometer DHR3 from TA Instrument at 20°C, in the range of 0.1 – 100 s⁻¹ which covers the shear rate range in the experiment. The viscosities of both oils stayed constant within the measurement range, thus both oils can be approximated as Newtonian fluids in the range of interest. The displacing fluid is deionized (DI) water with a viscosity of 1 cp. Viscosity ratios of the displacing fluid (DI water) and the two displaced fluids (mineral oil and crude oil) are 5.8×10^{-3} and 4.3×10^{-3} , respectively. Table 6.2 lists the properties of fluids used in this work including their density, viscosity and interfacial tensions. The density of water was computed from the weight of water measured with a digital balance (Adam Equipment HCB123 Highland Digital Precision Balance, with a precision of 0.001g). We measured the weight of 1 ml – 5 ml (1 ml interval) of water and calculated the density from the weight – volume slope. The equipment used for interfacial tension measurement is a spinning drop tensiometer (KRÜSS SDT). The crude oil was pre-equilibrated with deionized water before IFT measurements. We added equal volume of crude oil and deionized water in the same tube and agitated the mixture in an ultrasonic equipment (Branson 2800) for 50 mins when the two fluids were completely mixed. After one week of resting at ambient conditions, oil and water separated into two layers with oil staying on the top layer. 70 and 27 measurements were conducted at 20°C for crude oil – water IFT and mineral oil – water IFT, respectively. The average interfacial tension values along with the standard deviations were reported in Table 6.2. While having similar viscosity ratios, the two oils give rise to different wetting states with the glass surface. From the microscopic images shown in Figure 6.2, it is clear that the mineral oil-water-glass system is water-wet, while the crude oil-water-glass system is oil wet. The crude oil-

wet state was achieved by aging the micromodel for 24 hours prior to flow experiments. Surface reactions that cause the glass surfaces oil-wetting, such as the adsorption of polar components on the surface, were previously reported in literature (Du et al., 2019).

Table 6.2: Summary of fluid properties

Fluid	Density (g/ml)	Viscosity (cp)	IFT with water (mN/m)
Crude oil	0.92	230	10 ± 0.82
Mineral oil	0.86	170	19 ± 0.97
Water	1.0	1	N/A

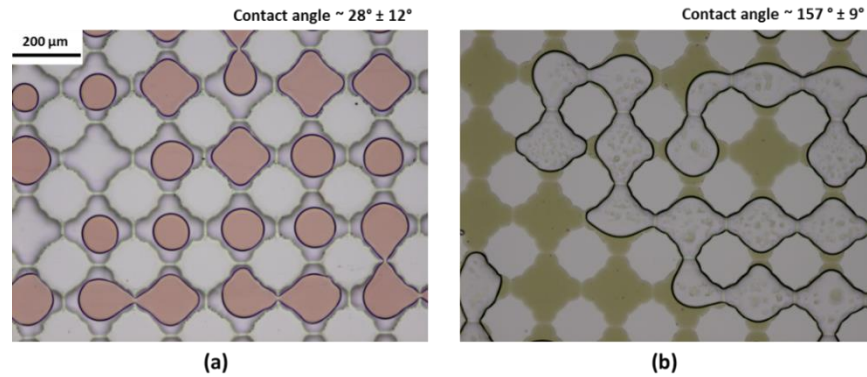


Figure 6.2: Pore-scale images of (a) mineral oil (red) remaining after water injection in M2, and (b) crude oil (beige) remaining after water injection in M3. Mineral oil and crude oil are the non-wetting and wetting phase, respectively. Contact angles are obtained by measuring along the contact lines at multiple liquids/solid interfaces from corresponding cases.

6.2.3 Experiments

A total of 18 experiments were performed in this chapter with the three micromodels (M1, M2 and M3) by systematically varying the capillary number from 10^{-7}

to 10^{-5} at two different wettability states (water-wet and oil-wet). To ensure the desired wettability for each experiment, we designed the experiment sequence so that we conducted mineral oil experiments in 3 new micromodels before crude oil experiments, therefore the wettability can be confirmed to be water-wet in 3 mineral oil experiments. The capillary number, Ca , was varied by changing the water flow rate from 4 $\mu\text{l}/\text{hour}$ to 400 $\mu\text{l}/\text{hour}$, and is given by

$$Ca = \frac{Q_w \mu_w}{WD\gamma} \quad (6.1)$$

where Q_w is the injection rate, μ_w is water viscosity, W and D are the width and the etching depth of the micromodel, respectively, and γ is the water-oil interfacial tension. Table 6.3 summarizes the capillary number and other properties for each of the 18 experiments. Figure 6.3 shows an overlay of experiments conducted in this work in the context of a capillary number-viscosity ratio phase diagram. The viscosity ratio of our experiments is on the order of 5×10^{-3} , and the capillary number is between 10^{-7} and 10^{-4} . We note that according to two phase boundaries determined in the literature (Lenormand et al., 1988; Zhang et al., 2011), our experiments fall approximately into the capillary fingering to viscous fingering cross-over and viscous fingering regions. As is discussed subsequently in Chapter 6.3.1, the dendrite propagations demonstrate characteristic viscous fingering behaviors by moving forward and not forming loops (Lenormand et al., 1988; Zhang et al., 2011). We classify each drainage and imbibition data point into low ($\sim 10^{-7}$), medium ($\sim 10^{-6}$) and high ($\sim 10^{-5}$) capillary number experiments.

Table 6.3: Summary of the microfluidics experiments

Model	Oil	Wettability	$Ca_{low} \sim 10^{-7}$	$Ca_{medium} \sim 10^{-6}$	$Ca_{high} \sim 10^{-5}$
M1	Crude oil	Oil wet	Exp. 1, $Ca = 3.5 \times 10^{-7}$	Exp. 2, $Ca = 3.5 \times 10^{-6}$	Exp. 3, $Ca = 3.5 \times 10^{-5}$
	Mineral oil	Water wet	Exp. 4, $Ca = 1.9 \times 10^{-7}$	Exp. 5, $Ca = 1.9 \times 10^{-6}$	Exp. 6, $Ca = 1.9 \times 10^{-5}$
M2	Crude oil	Oil wet	Exp. 7, $Ca = 3.5 \times 10^{-7}$	Exp. 8, $Ca = 3.5 \times 10^{-6}$	Exp. 9, $Ca = 3.5 \times 10^{-5}$
	Mineral oil	Water wet	Exp. 10, $Ca = 1.9 \times 10^{-7}$	Exp. 11, $Ca = 1.9 \times 10^{-6}$	Exp. 12, $Ca = 1.9 \times 10^{-5}$
M3	Crude oil	Oil wet	Exp. 13, $Ca = 3.5 \times 10^{-7}$	Exp. 14, $Ca = 3.5 \times 10^{-6}$	Exp. 15, $Ca = 3.5 \times 10^{-5}$
	Mineral oil	Water wet	Exp. 16, $Ca = 1.9 \times 10^{-7}$	Exp. 17, $Ca = 1.9 \times 10^{-6}$	Exp. 18, $Ca = 1.9 \times 10^{-5}$

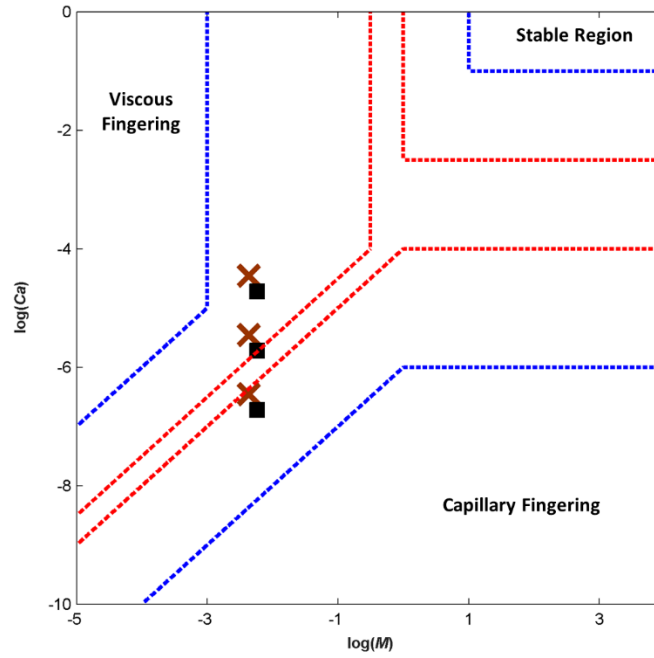


Figure 6.3: Flow pattern classification based on capillary number (Ca) and viscosity ratio (M). Boundary lines are determined by Lenormand et al., 1988 (shown in blue) and Zhang et al., 2011 (shown in red). Drainage (crude oil recovery) is identified with black squares while imbibition (mineral oil recovery) is identified with brown X's.

For each experiment, the micromodels were saturated with mineral oil or crude oil and aged for 24 hours for crude oil. The aging time needed to create an oil-wet condition

is dependent on the type of the system as reviewed by Bartels et al., 2017. In previous microfluidic experiments, many different aging times, from days to weeks, were used to create an oil-wet condition (Song and Kovscek, 2015; Bartels et al., 2017; Du et al., 2019). For our system, we did not have connate water in the glass micromodels before oil invasion, therefore the aging time was shorter as oil contacted the surface the moment it was injected in the micromodels. To expel air from the systems, we injected the oils at a high injection rate using a syringe pump (PHD 2000, Harvard Apparatus) for tens of pore volumes. After saturating micromodels with crude oil, we kept injecting crude oil at a flow rate of 1-2 $\mu\text{l/h}$ during the ageing process. Each of the micromodels was reused in 3 mineral oil and 3 crude oil experiments in order, to eliminate the effects due to even small fabrication difference when using different micromodels. Between experiments, we cleaned the micromodels by injecting hexane, acetone and DI water in sequence. Both organic and inorganic components can be efficiently removed from the system with this cleaning procedure. After cleaning, the micromodels were placed on a hot plate at 110°C for drying. Micromodels were checked under the microscope (Olympus IX73) before each experiment to confirm cleanliness. During the water injection, the micromodels were placed horizontally on top of a light pad. A DSLR camera (Nikon D5500) was mounted on top of the micromodel to capture time-lapse images. Auto-exposure mode of the camera was enabled to ensure optimal imaging quality according to the background light intensity. Exposure time varied slightly among experiments in the range of 1/160 – 1/250 s. The image resolution is 300×300 dpi, and the image dimension is 6000×4000 pixels. Time intervals for the injection with low, medium, and high capillary number are 6 mins, 1 min 12 seconds, and 9 seconds, respectively. Figure 6.4 shows the experimental system. Immediately after flow experiments, we checked the wettability under the microscope and documented the

wettability. Pore-scale images captured immediately after flow experiments are included in Appendix B1.

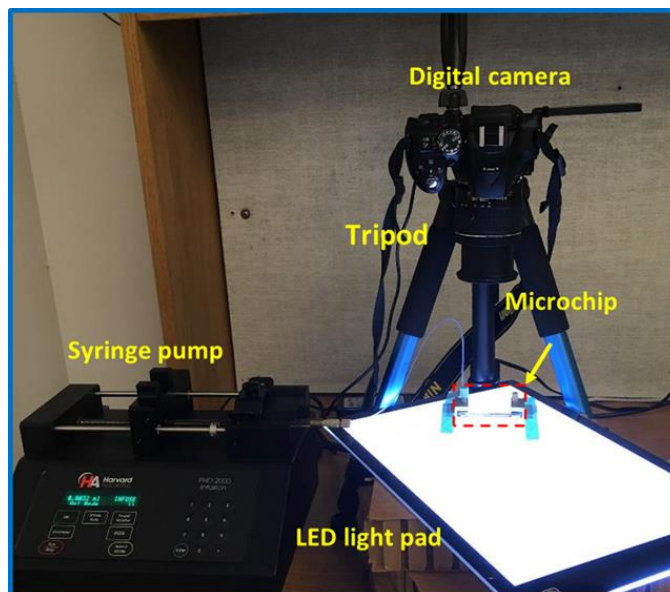


Figure 6.4: Experimental system, including a DSLR camera (Nikon D5500), a syringe pump (PHD 2000, Harvard Apparatus), a LED light pad, and a tripod.

6.2.4 Image analysis

The images captured in the experiments were processed using ImageJ as discussed in Chapter 3.3. The segmentation and ganglia identification process of an image from an experiment performed in this work is shown in Figure 6.5a. The grey scale distribution (measured using ImageJ’s “histogram” function) of the raw and binarized image from a mineral oil experiment and a crude oil experiment conducted in this chapter (both conducted in M1 at low capillary number) are shown in Figure 6.5b.

In addition to general image processing protocols, number of ganglia were determined via a Forest Fire Algorithm (Mehmani et al., 2019a) in which each oil pixel is designated as “unburned” initially. A “fire” is set at each pixel which “burns” all the

neighboring pixels until an oil/water interface is reached and isolated oil ganglia are identified. We find that images reveal whether pendular rings between grains can form and are sensitive enough to determine their contribution to fluid film connectivity. However, the non-binary phase distributions within a single pore (which in our results is only the case at high capillary numbers in an unfractured medium) are not captured. We therefore consider the images in meso/Darcy-scale (in contrast to the pore scale where a non-binary phase distribution within a single pore can be captured). For fractal dimension calculation, we focused on the morphology of the invading phase in the mesoscale as well. For this purpose, any influence of grains on fractal dimension values was removed by conducting erosion and dilation procedures on the binarized image (see similar examples by Islam et al (2014), Ferer et al. (2014), and Chen et al. (2017)).

Voxel resolution in the experiments is approximately 12 micrometers/pixel. Sub-resolution features, in particular film thickness and roughness size, are therefore not captured in our analysis. However, they can potentially impact fractal dimension and oil ganglia numbers/sizes if the image resolution were higher. Presence of film in the invaded zones can potentially reduce fractal dimension and increase the number of oil ganglia by fragmenting the invading phase at the subpore-scale (Mehmani et al. 2019a). In addition, when surface roughness is considerable, a two-dimensional quantification of the pore space for fractal analysis is potentially inadequate as the surface roughness generates subpore-scale dynamics, such as pinning and corner flow, which may not be captured at plan-view images such as our experiments. We selected smooth micromodels for our experiments that have surface roughness to pore depth ratios of less than 1%, which according to Mehmani et al. 2019c, subpore-scale dynamics are not enhanced in such surface conditions. Nevertheless, a thorough investigation of sub-resolution impacts is merited as future work.

The fractal and ganglia analysis in our work therefore is restricted to the image resolution of experiments.

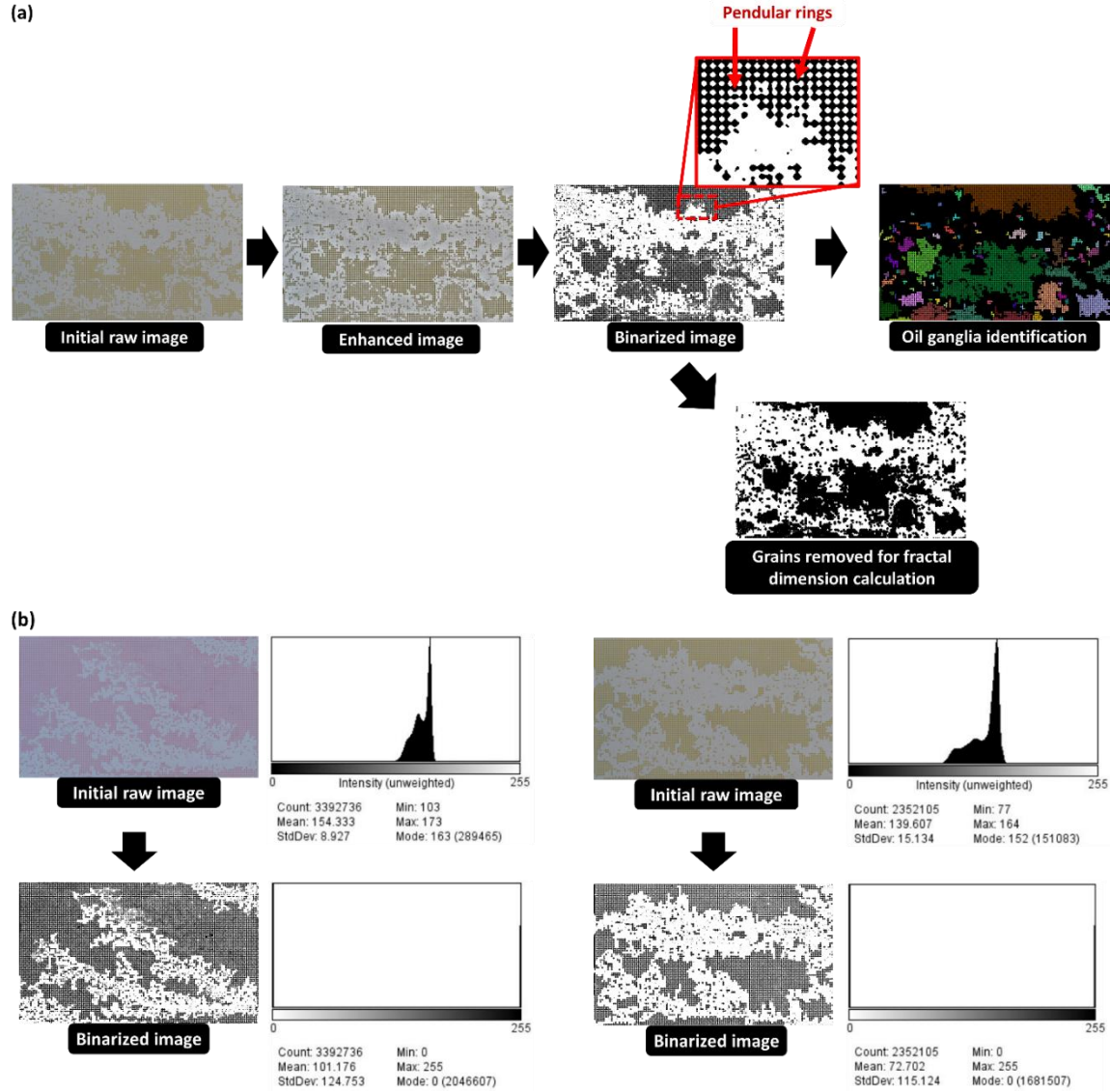


Figure 6.5: (a) Image processing steps for binarizing each frame and subsequently determining isolated oil ganglia. Note that the steps for image analysis effectively capture wetting-phase pendular rings. (b) Grey scale distribution of the raw and binarized image from imbibition (left) and drainage (right) at low capillary number in M1.

6.3 SWEEP PATTERNS

6.3.1 Qualitative observations

Experiments show that microfracture connectivity can significantly alter upscaled fingering morphology. Figure 6.6ab shows the sweep patterns for both imbibition and drainage at breakthrough and steady state. Figure 6.6c summarizes our observations in a conceptual picture for fluid-fluid displacement under unfavorable viscosity ratio in the presence of microfractures (discussed below).

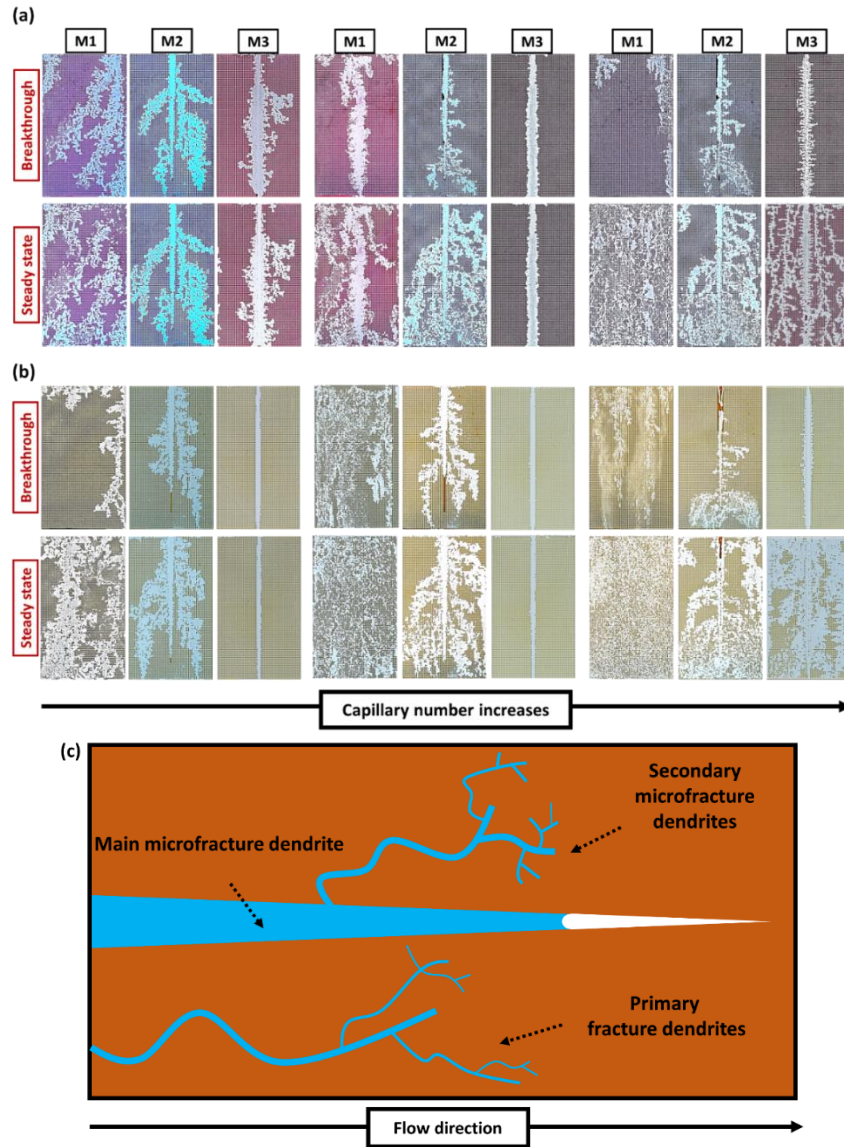


Figure 6.6: Patterns of invading phase for three capillary numbers at breakthrough and steady state during (a) imbibition, and (b) drainage. The matrix micromodels (M1) demonstrate characteristic that resembles *viscous fingering* behavior by moving towards the outlet and not forming loops. (c) Conceptual picture for fingering fluid dendrite propagation in the presence of a microfracture. Flow direction is from one macrofracture (inlet, not shown) to another (outlet, not shown). Main microfracture dendrites are confined inside the microfracture. Macrofracture dendrites originate from the macrofracture (inlet) and traverse within the matrix. Secondary microfracture dendrites originate from the microfracture and traverse within the matrix.

6.3.1.1 Base case (M1)

In the absence of microfractures, fingering is generated only from the macrofracture, as shown in Figure 6.6ab. We refer to this finger type as macrofracture dendrite (Figure 6.6c). At the time of breakthrough, the initial macrofracture dendrites have penetrated from one macrofracture (inlet side) to the other (outlet side). Macrofractures are not shown in Figure 6.6. Dendrites become narrower as capillary number increases. At steady state, as capillary number increases (regardless of wettability) macrofracture dendrites become narrower but dispersed, which is consistent with observations made by Doorwar and Mohanty (2017). However, the divergence of macrofracture dendrites increases considerably at high capillary numbers in water-wet systems, while in oil-wet systems macrofracture dendrites become considerably dispersed starting from medium capillary numbers. Macrofracture dendrites are chaotic and do not indicate preferential displacement pathways regardless of capillary number and wettability condition.

6.3.1.2 Dead-end microfracture (M2)

A porous system with a dead-end (semi-connected) microfracture, demonstrates a fingering morphology that is qualitatively distinct from that of an unfractured system (M1), as shown in Figure 6.6ab. Unlike an unfractured system, fingering dendrites do not exhibit a chaotic movement, but a preferential one determined by the dead-end microfracture. In a dead-end microfractured system, fingering dendrites originate from the dead-end microfracture and are referred to as main microfracture dendrites in Figure 6.6c. At breakthrough, the single main microfracture dendrite has penetrated along the dead-end microfracture while several secondary microfracture dendrites invade the porous matrices. The dendrite patterns are qualitatively similar at low to high capillary numbers for both imbibition and drainage, while secondary microfracture dendrites become narrower as the

capillary number increases. At steady state, macrofracture dendrites only emerge at high capillary numbers but are less dominant than secondary microfracture dendrites. Once the secondary microfracture dendrites develop from the microfracture, they do not traverse backward, causing poor sweep near the upstream end (near the inlet macrofracture). At the tip of the dead-end microfracture, dendrites coalesce more readily and result in a higher sweep compared to the matrix adjacent to the microfracture. Dendrite patterns are qualitatively similar for both imbibition and drainage, highlighting the dominant role played by the dead-end microfracture compared to wettability.

6.3.1.3 Microfracture connecting macrofractures (M3)

A connected microfractured system demonstrates a distinctly different unstable flow pattern than unfractured (M1) or dead-end microfractured (M2) systems. At low to medium capillary numbers, the displacing phase traverses mainly through the microfracture and is referred to as main microfracture dendrite in Figure 6.6c. At breakthrough, a main microfracture dendrite prevents the invading phase from entering the matrix which suppresses oil recovery at all capillary numbers. The suppression of fingering is stronger for drainage than imbibition, as a small amount of secondary microfracture dendrites develop during imbibition and in particular at low capillary numbers. After breakthrough, when the capillary number reaches a threshold value (between 10^{-5} and 10^{-4}), macrofracture and microfracture dendrites begin to form, which results in an increase in oil recovery, as observed in the steady state images in Figure 6.6ab. Although additional data points are required to determine the exact threshold capillary number, our results indicate that the threshold is between the viscous fingering and transient regions, as shown in Figure 6.3. The capillary number threshold is furthermore likely to depend on the flow capacity contrast (e.g., permeability contrast) between the microfracture and matrix for

which additional experiments are needed. Interestingly, a capillary number threshold for fingering dendrite development is not observed for a dead-end microfractured system (M2). Invasion of secondary microfracture dendrites is more prominent for imbibition at low to medium capillary number, while the generation of macrofracture dendrites widens for drainage at high capillary number.

6.3.2 Quantitative analysis

Fractal dimension (D_f) is used to describe and quantify two-phase flow sweep patterns into capillary fingering or viscous fingering regimes (Lenormand and Zarcone, 1984; Lenormand et al., 1988; Zhang et al., 2011; Islam et al., 2014; Chen et al., 2017). The fractal dimension varies from 1 to 2, with higher values indicating a coalescent dendrite evolution. Quantifying sweep patterns can have other applications as well, such as determining functional relationships for a chemical's dissipation rate at the evolving immiscible interface. We therefore utilize fractal dimension to investigate the impact of dead-end and connected microfractures on unstable flow morphology. Figure 6.7a, adapted from Chen et al. (2017), compares the visual morphology of fingering patterns and fractal dimension. The fractal dimension of an immiscible front has generally been investigated as a function of capillary number and viscosity ratio, while (as discussed in the Introduction) geological effects such as connectivity of microfractures, are typically not considered when studying their variability. For the computation details of the fractal dimensions, an example of the box-counting method is described in Appendix B2.

Figure 6.7b shows the fractal dimension of the micromodels at steady state. We observe that the lowest fractal dimension belongs to the connected microfractured system at oil-wet conditions and low capillary numbers. As is revealed in Figure 6.6, a connected microfractured system predominantly displays a main microfracture dendrite pattern prior

to reaching a capillary number threshold. We also observe that changing the wettability from oil wet to water wet slightly increases the fractal dimension. This behavior is partly due to the presence of secondary microfracture dendrites which give rise to a more coalescent fingering pattern. At low capillary number and regardless of wettability, a dead-end microfracture reduces the front fractal dimension as well, even though its impact is less than due to a connected microfracture. The effects of a dead-end microfracture on fractal dimension are consistent with our observation in Figure 6.6ab; the microfracture decreases the chaotic movements of the dendrites by providing a preferential pathway in the middle of the porous domain. Similar to a connected microfractured system, the main microfracture dendrite traverses through the microfracture itself and effectively develops a Saffman finger with low dendrite divergence. At medium capillary numbers, the impact of a connected microfracture is similar to low capillary numbers in reducing the front fractal dimension. However, the ability of a dead-end microfracture to confine dendrite divergence decreases at medium capillary numbers while secondary microfracture dendrites increase the fractal dimension compared to the unfractured system. At high capillary numbers, differences between fractal dimension for the three micromodel types and two wettability conditions decrease considerably. This reduction is due to the inefficacy of microfractures, dead-end or connected, from influencing the sweep patterns of the invading phase beyond a capillary number threshold.

Figure 6.7c, illustrates the fractal dimension of the dendrites throughout the evolution of the invading front. We notice that as capillary trapped oil saturation decreases, fractal dimension generally increases. This increase is due to the evolution of fingering dendrites as they become more likely to coalesce and decrease the capillary trapped oil saturation. However, at equal oil recovery values, only a connected microfracture (M3) at high capillary numbers (regardless of wettability) suppresses the divergence of fingering

dendrites. This contrast in microfracture connectivity effects with the steady-state values shown in Figure 6.7b highlights the importance of capillary trapped saturation in properly assessing dendrite morphology. In other words, if a recovery operation is conducted at low and medium capillary numbers, the recovered oil saturation is sufficient information for monitoring its performance, while connectivity effects of microfractures on sweep patterns become negligible. This assumption is valid for both water- and oil-wet systems but becomes invalid at high capillary numbers where microfracture connectivity is a relevant parameter in determining flow patterns when monitoring recovery.

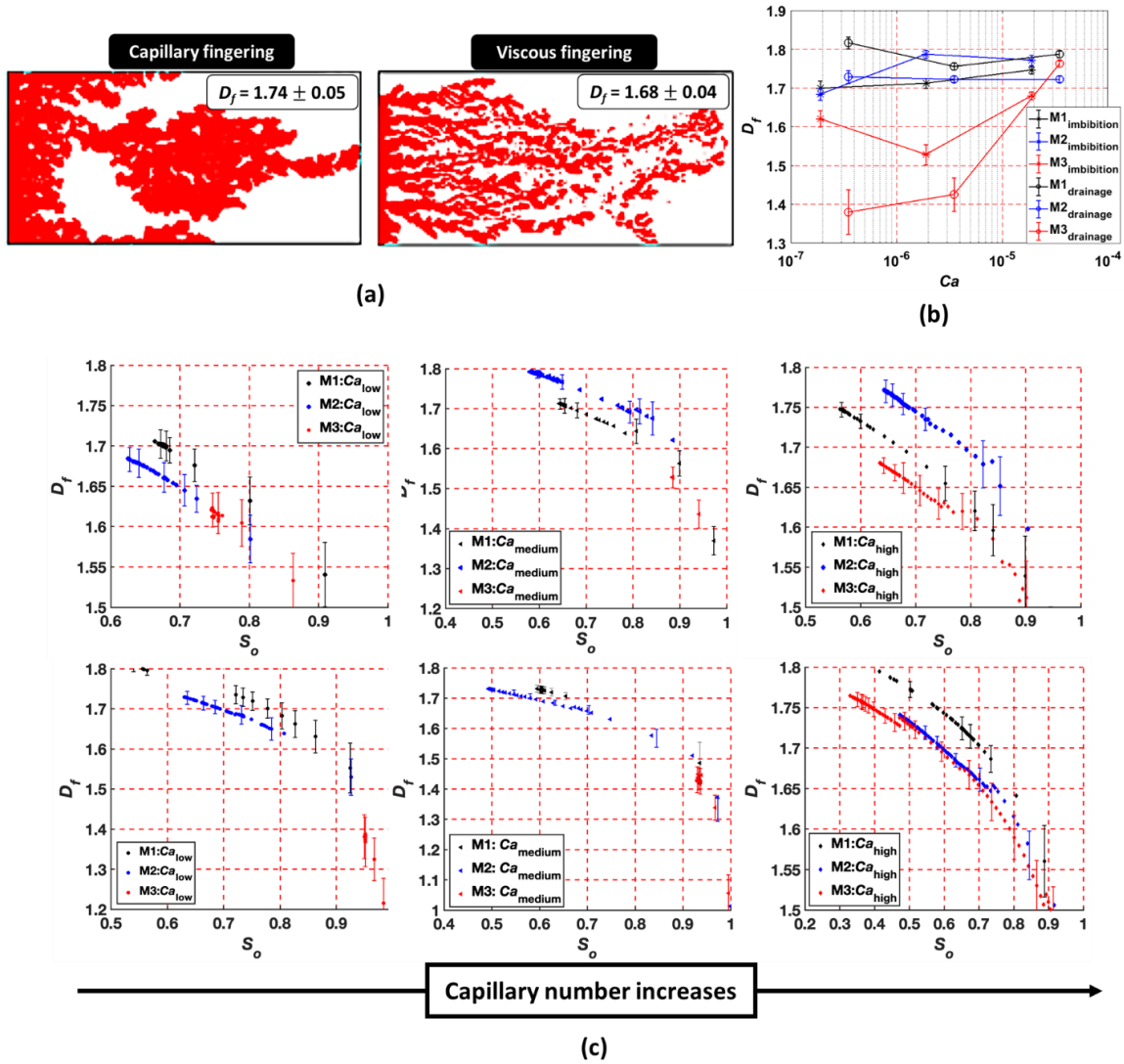


Figure 6.7: (a) Reference fractal dimension values for capillary and viscous fingering. The higher the fractal dimension, the more coalescent the immiscible front becomes (Chen et al., 2017). (b) Steady-state fractal dimension values calculated for the micromodels at all capillary numbers for the two wettability conditions. (c) Fractal dimension for micromodels throughout their water-flood experiments (top) imbibition and (bottom) drainage. We note that fractal dimension is a function of capillary trapped oil saturation. Error bars are the maximum range of values obtained when values of capillary trapped oil saturation were altered by $\pm 5\%$.

6.4 OIL RECOVERY

Figure 6.8 shows the oil saturation versus pore volumes injected for each microfractured system at three capillary numbers and both wettability conditions. Figure 6.9 shows functional relationships for ultimate oil recovery and pore volumes required to reach steady state as functions of capillary number. The recovery and pore volume values shown in Figures 6.8 and 6.9 are also summarized in Tables 6.4 and 6.5.

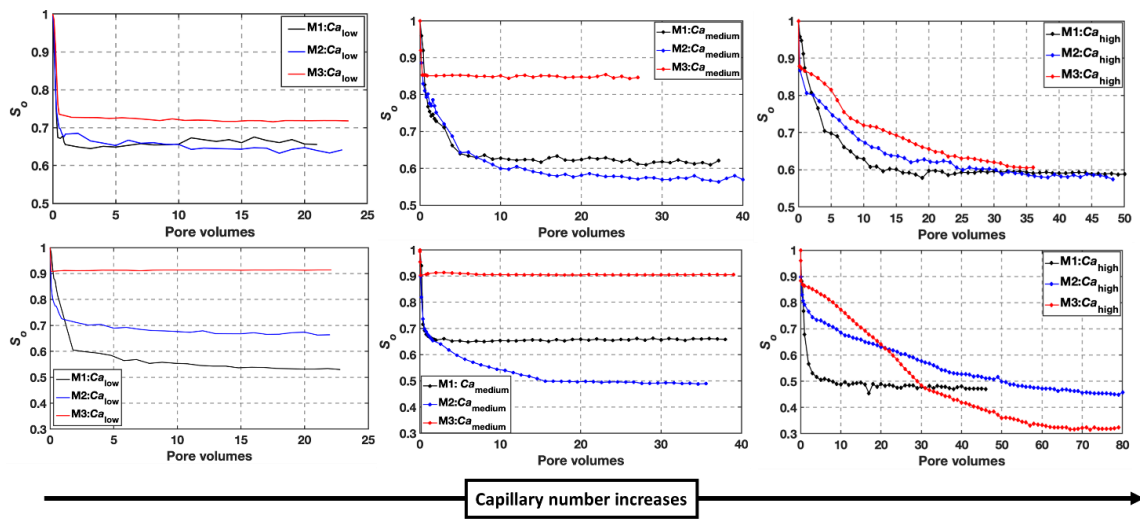


Figure 6.8: Capillary trapped saturation curves for each micromodel at three capillary numbers during imbibition (top) and drainage (bottom).

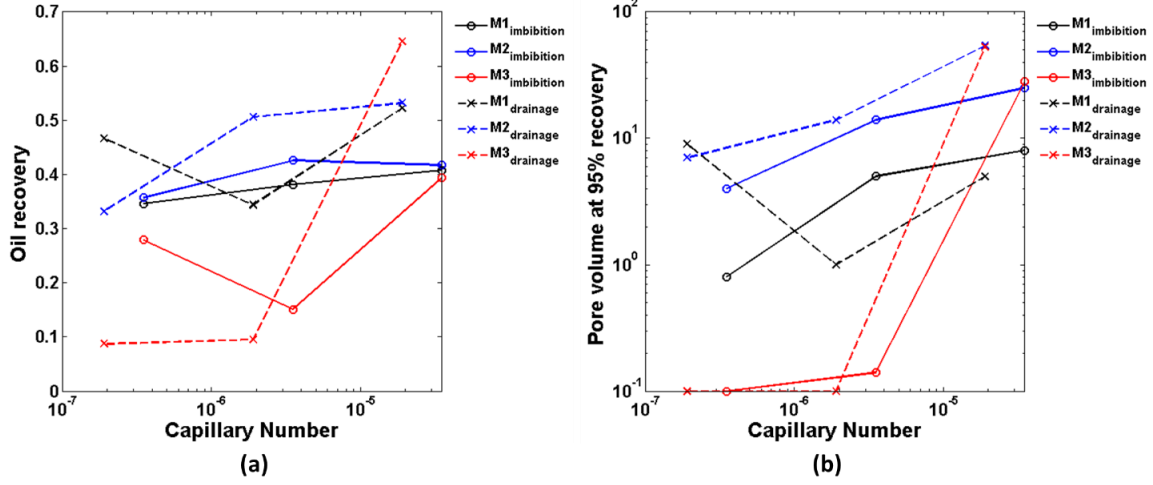


Figure 6.9: (a) Oil recovery, and (b) pore volume injected at 95% recovery for each micromodel at three capillary numbers for imbibition and drainage processes.

Table 6.4: Summary of measured oil recovery for different geometries

Ca^*	M1 _{imb}	M2 _{imb}	M3 _{imb}	M1 _{dra}	M2 _{dra}	M3 _{dra}
$\sim 10^{-7}$	0.35	0.36	0.28	0.47	0.33	0.09
$\sim 10^{-6}$	0.38	0.43	0.15	0.34	0.51	0.10
$\sim 10^{-5}$	0.40	0.42	0.39	0.52	0.53	0.65

* Capillary numbers are 3.5×10^{-7} , 3.5×10^{-6} , and 3.5×10^{-5} for imbibition, and 1.9×10^{-7} , 1.9×10^{-6} , and 1.9×10^{-5} for drainage.

Table 6.5: Pore volume injected at 95% recovery in different geometries

Ca^*	M1 _{imb}	M2 _{imb}	M3 _{imb}	M1 _{dra}	M2 _{dra}	M3 _{dra}
$\sim 10^{-7}$	0.8	4	0.1	9	7	0.1
$\sim 10^{-6}$	5	14	0.14	1	14	0.1
$\sim 10^{-5}$	8	25	28	5	54	53

* Capillary numbers are 3.5×10^{-7} , 3.5×10^{-6} , and 3.5×10^{-5} for imbibition, and 1.9×10^{-7} , 1.9×10^{-6} , and 1.9×10^{-5} for drainage.

6.4.1 Base case (M1)

The analysis in Figures 6.8 and 6.9a shows that recovery slightly increases with capillary number by up to 5% in water-wet systems, where fingers become more dispersed and sweep larger areas. During drainage, however, recovery at medium capillary number is the lowest while recovery at high capillary number is highest. The largest recovery difference is 18%. As shown qualitatively in Figure 6.6, fingers become more dispersed but narrower with the increase in capillary number. The two effects compete with each other, resulting in a non-monotonic trend in recovery versus capillary number.

6.4.2 Dead-end microfracture (M2)

Dead-end microfractures in water-wet systems, despite changes in dendrite generation mechanism, do not alter ultimate recovery significantly regardless of capillary number (see Figures 6.8 and 6.9a). In fact, recovery differences due to presence of a dead-end microfracture are less than 5%. In oil-wet dead-end microfractured systems, recovery discrepancies can increase up to 17% but unlike water-wet systems, oil recovery can both increase or decrease depending on the capillary number. This higher dependence on capillary number for drainage can be due to the dominance of pore-scale bulk velocities (in contrast to the presence of corner films for imbibition) on immiscible flow (Zhao et al., 2016). However, additional numerical simulations (Alpak et al., 2019) or particle image velocimetry experiments (Kazemifar et al., 2015) are needed to determine the precise impact of wettability on capillary number dependence for oil recovery. Figure 6.9b and Table 6.5 show that dead-end microfractures, at almost all capillary numbers, delay oil recovery by increasing the amount of injected pore volumes required to reach 95% recovery. This delay is most significant in oil-wet systems and high capillary numbers. In an unfractured system (M1), oil recovery reaches steady state rapidly once preferential

pathways are established at the early stages of injection and leave oil ganglia trapped in the remaining regions. By contrast, in a dead-end microfractured system after the early stage pathways are formed, water continues to sweep into the remaining regions, resulting in long tails of up to tens of pore volumes in the recovery curves shown in Figure 6.8.

6.4.3 Microfracture connecting macrofractures (M3)

As shown in Figures 6.8 and 6.9, prior to reaching a capillary number threshold, a connected microfracture decreases oil recovery significantly. The decrease in recovery is more prominent in oil-wet systems because water can enter the matrix from the microfracture during imbibition (secondary microfracture dendrites as shown in Figure 6.6c). However, at high capillary numbers, ultimate recovery in a connected microfractured system is similar to (1% lower in water-wet systems) or higher (12% in oil-wet systems) than for an unfractured system. The increase of oil recovery could indicate that the pressure difference from upstream to downstream in porous matrices in the connected microfracture system overcomes the largest capillary pressure pinning the oil between two macrofractures. As observed in Figure 6.9b, similar to a dead-end microfracture, a connected microfracture can delay oil recovery but only beyond a capillary number threshold (i.e. high capillary numbers). The long tail in capillary trapped saturation curves indicates that water continues to sweep into the matrix after breakthrough along the microfracture. The tail lengths for M3 are comparable to those of M2 because the pore volumes injected at 95% oil recovery are similar. From Figure 6.9a, we find that an increase of capillary number improves oil recovery for unfractured and dead-end microfractured systems regardless of wettability. In a connected microfractured system, however, oil recovery can significantly improve (up to 56% in drainage and up to 24% in imbibition) at high capillary numbers, especially during drainage. From observing the immiscible phase

distributions in Figure 6.6, we interpret that the connected microfracture establishes hydraulic connectivity for the invading phase between the two macrofractures at breakthrough. Given (1) the narrow cross-section of the microfracture compared to the domain cross-section, and (2) the constant flow rate condition, the pressure difference for the invading phase between the two macrofractures becomes highest compared to those of the dead-end and matrix systems. The heightened pressure difference gives rise to a higher imposed “global” capillary pressure which drives the oil-in place considerably to the outlet.

6.4.4 Comments on qualitative small-scale microfluidic results

As discussed by Tanino and Christensen (2019), capillary end effects can become considerable for water invasion in oil-wet media that are conducted in micromodels with domain sizes similar to this work. Our predictions of oil recovery with those cases are therefore smaller than what would be expected if capillary end effects did not exist. However, in fractured tight reservoirs, capillary end effect can be naturally present due to extreme small matrix pore sizes (2 – 3 orders of magnitude smaller than in micromodels) and frequent microfractures, where the increased capillary end effective length would become comparable to fracture spacing. Our designs can therefore serve as analogues for investigating recovery in the presence of naturally occurring capillary end effects in the subsurface, where the results are quantitatively significant. In addition, our aim is to capture the invasion patterns qualitatively and parameterize them quantitatively, even though the precise values presented in this work may not translate to subsurface conditions. In qualitative aspect, as presented in Figure 6.6ab the invasion patterns are mostly determined at an early stage prior to breakthrough conditions when end effects are not yet effective (that is the invading phase has not yet sensed the domain end). Finally, given that similar domain sizes were used in this work, conclusions based on comparing flow patterns

at various capillary numbers for each wettability condition, even though capillary end effects are potentially present, are still valuable for our understanding of microfracture effects during unstable flow.

So far by demonstrating an extensive amount of quantitative analysis of the flow visualization, we aimed to provide a straight-forward, semi-quantitative comprehension of the interplay between the microfractures and the porous matrix and their effects on unstable two-phase flow. A comprehensive reproducibility study is not within the scope of this work but will be a promising topic of future work. From several replicate experiments performed in the 3 micromodels, the trend of the water invasions in all three geometries are qualitatively reproducible and very robust. Quantitatively, we were also able to obtain good reproducibility as the remaining saturations are comparable with reasonable variations, which agrees with the literature on the reproducibility of micromodels' study on unstable two-phase flow (Ferrari et al., 2015). All replicated experiments are included in Appendix B3.

6.5 OIL GANGLIA ANALYSIS

6.5.1 Ganglia distribution post water-flooding

Figure 6.10 depicts the distribution of oil ganglion size at steady state for our experiments. We define oil ganglion size as the actual size of each ganglion divided by the size of one pore. Ganglion sizes are divided into 10 size groups with the calculated areal percentage of remaining oil for each group.

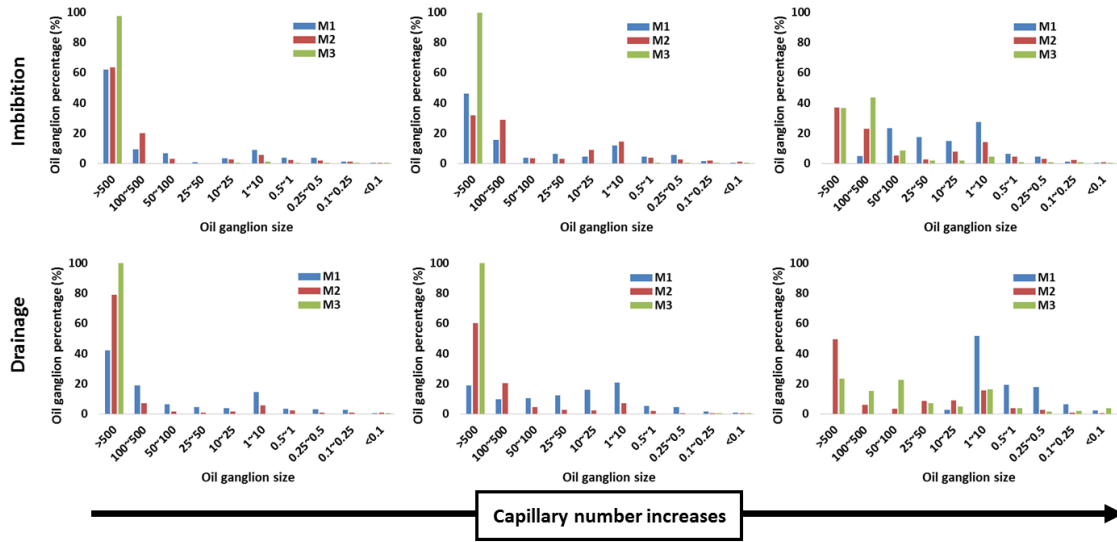


Figure 6.10: Distribution of oil ganglia at steady state for each micromodel at three capillary numbers during imbibition (top) and drainage (bottom). Oil ganglion size is defined as the actual ganglion size divided by a single pore size. Oil ganglion percentage is defined as the area of a single oil ganglion as percentage of the total remaining oil in each size group.

6.5.1.1 Base case (M1)

In both imbibition and drainage processes, oil ganglion size decreases with an increase in capillary number as the plot shifts to the right (smaller size groups). During imbibition, oil ganglia larger than 500 take 62% of the total remaining oil at low capillary numbers and decrease to 46% at medium capillary numbers and 0% at high capillary numbers. During drainage, the percentage of oil ganglia larger than 500 decreases from 42% to 19% and 0% as the capillary number increases. This discrepancy due to wettability alteration agrees with the qualitative observation made from Figure 6.6 that the fingers are narrower under oil-wet conditions, resulting in overall smaller ganglion sizes.

As was shown in Figure 6.9a, oil recovery increases with capillary number, therefore smaller oil ganglia correspond to higher recovery factors. However, the increase

in oil recovery is less significant than the decrease in oil ganglion size because the increase of oil recovery is only 5-15% under both wetting conditions. As shown in Figure 6.10, although the percentage of the biggest oil ganglia decreases, the distribution tail containing smaller oil ganglia widens. For a given capillary trapped saturation, smaller oil ganglia can result in a higher spread of the injected phase, which is advantageous in chemical treatments. However, we observe that smaller remaining oil ganglia at the earlier stages are more difficult to recover compared to larger ones during continuous water flooding.

6.5.1.2 Dead-end microfracture (M2)

In a dead-end microfractured system, oil ganglion sizes decrease with capillary number but not as considerably as in an unfractured system. The decrease in the percentage of the largest oil ganglion group (>500) is 27% and 29% for imbibition and drainage processes which is much lower than the 62% and 42% decrease observed in an unfractured system. In contrast to M1, oil ganglia in the porous matrix in M2 are more difficult to mobilize even at high capillary numbers, as shown in Figure 6.6. Number of fingers that are generated in the porous matrix from the inlet (macrofracture) and microfracture increases with capillary number. The finger generation phenomenon decreases the size of large oil ganglia (>500) and contributes to the increase in oil recovery. Compared to M1, we found that the fragmentation of the large ganglion may not be efficient for improving recovery because smaller oil ganglia are harder to mobilize than larger ones at later stages.

6.5.1.3 Microfracture connecting macrofractures (M3)

Recovery from the porous matrix is low at low to medium capillary numbers, leaving large oil ganglia (occupying >1000 pores) trapped in the porous matrix. Figure 6.10 shows that approximately 99% of the remaining oil is in the largest size group (>500 pores).

At high capillary numbers $\sim 10^{-5}$, the oil ganglion size decreases significantly compared to unfractured and dead-end microfractured systems. In a connected microfractured system, the largest oil ganglia is 100 to 500 times the pore volume when water wet and 10 to 25 times the pore volume when oil wet. This sharp decrease of oil ganglion size in the porous matrix is consistent with the significant increase of oil recovery observed at high capillary numbers. At low to medium capillary numbers, water flows primarily through the microfracture, leaving large oil ganglia trapped in the matrix. At high capillary numbers, however, water dendrites enter into the matrix from the macrofracture and shrink the oil ganglia into smaller and more scattered oil ganglia. The fragmentation of the large oil ganglia contributes to the significant increase of oil recovery as capillary number increases.

6.5.2 Ganglia generation during displacement processes

Figure 6.11a shows the number of generated oil ganglia as a function of capillary trapped oil saturation. We notice that the presence of a connected microfracture suppresses oil ganglia generation significantly. This reduction in oil ganglia number is for all capillary numbers and wettability conditions as long as fingering dendrites other than the main dendrite type shown in Figure 6.6c is generated. Flow patterns shown in Figure 6.6ab verify that a connected microfracture can act as a point of convergence for fingering dendrites such that they are precluded from entering the matrix. In addition, given its higher hydraulic conductivity, a connected microfracture decreases the local velocity of the invading phase inside the matrix. A reduction in local velocity can enhance the coalescence of fingering dendrites. In contrast to a connected microfracture, a dead-end microfracture does not suppress oil ganglia generation significantly. This difference in oil ganglia generation is due to the ability of the invading dendrites to enter the matrix from the microfracture. Such a behavior results in front divergence similar to that of an unfractured

system. As discussed in Chapter 6.3.2, capillary trapped oil saturation may not be sufficient information for monitoring an enhanced oil recovery operation because it does not capture the spatial distributions of two immiscible phases. In Figure 6.11a we observe that capillary trapped oil saturation alone cannot predict the total number of oil ganglia at a particular oil recovery step. Whether a microfracture is present and is connecting two macrofractures needs to be determined when predicting oil ganglia generation. Information about oil ganglia number can in fact become critical information during the development of a tertiary recovery operation. Figures 6.11bc show aggregate depictions of all the data into a single plot for both imbibition and drainage. The plots clarify that the highest number of ganglia form in the absence of microfractures and at high capillary numbers. Furthermore, we find that variations between each ganglia generation plots are more prominent during drainage than imbibition. The increase in variation indicates a higher sensitivity to capillary number for oil ganglia generation in oil-wet systems. This difference is likely due to the absence of corner film percolation during drainage, which results in the bulk flow within channels becoming the main displacing mechanism. The higher sensitivity to capillary numbers at oil-wet conditions is consistent with measurements made in micromodels for immiscible displacement with varying wettability (Zhao et al., 2016).

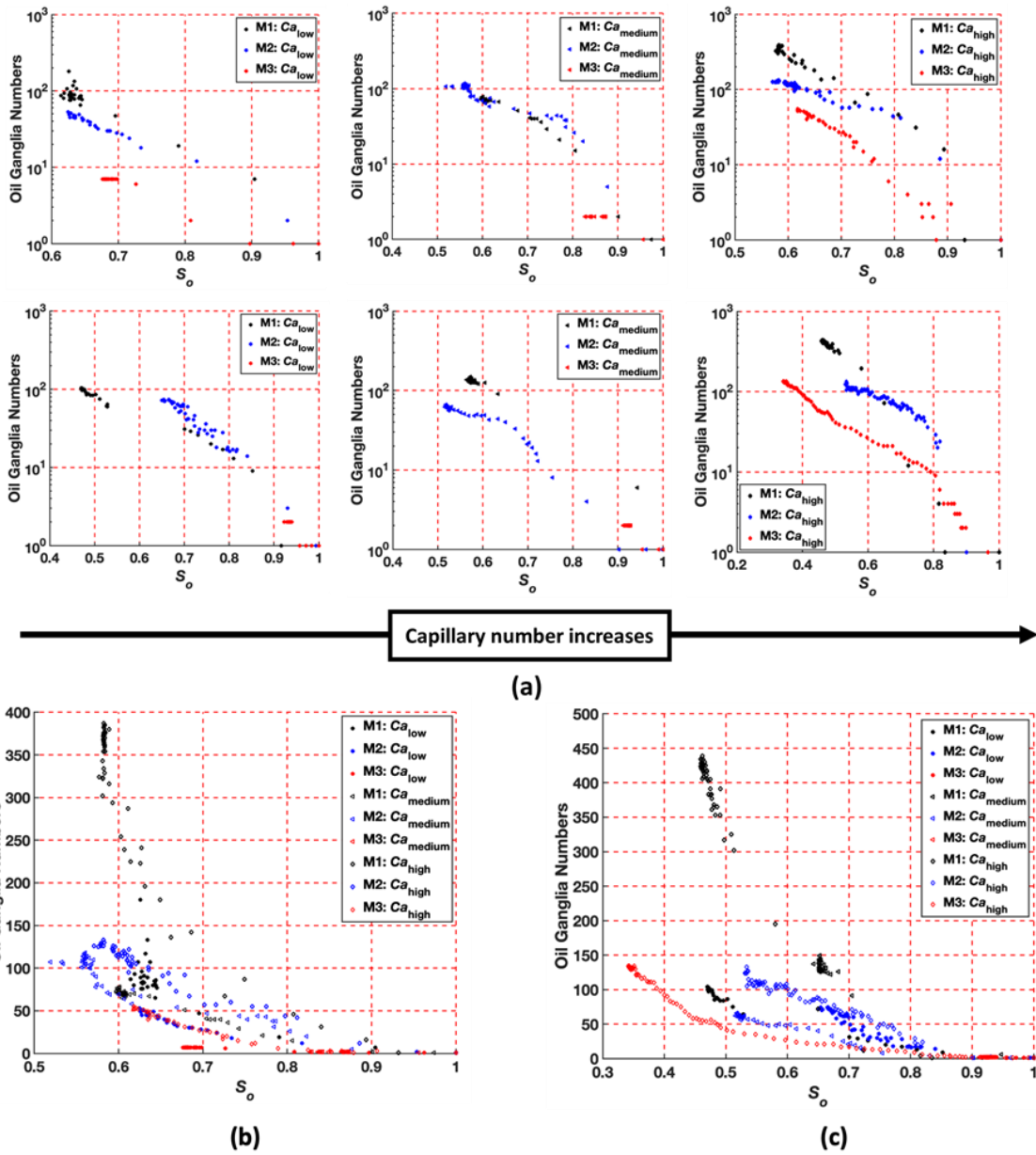


Figure 6.11: (a) Number of oil ganglia as a function of capillary trapped oil saturation (S_{oil}) for (top) imbibition and (bottom) drainage. Aggregate plots of oil ganglia versus capillary trapped saturation are shown for (b) imbibition and (c) drainage.

6.6 IMPLICATIONS AND LIMITATIONS

Fractures are ubiquitous in subsurface systems, potentially influencing the outcome of many hydrocarbon recovery and environmental remediation projects. Although fractures are recognized to affect transport phenomena, quantifying the various uncertainties about their impact on two-phase immiscible flow is still an important and open research topic. This is largely due to the technical challenge of quantifying fluid transport in fractured systems which takes place through multiple length scales. The need for experimental data that visualize fluid transport in fractured rocks is also necessary to verify multiscale numerical models. However, the majority of experimental research has currently focused on single fractures to understand the impact of fracture surface rugosity and aperture distribution. Our work provides direct observations of fluid transport in macrofracture/microfracture ensembles. These observations can guide the development and verification of numerical algorithms for immiscible fluid dynamics with near-wellbore reservoir simulators for hydraulically fractured formations (Wang and Leung, 2015) and remediation projects in the vadose zone (Faybishenko et al., 2000). For instance, our results indicate using geological markers to determine if natural fracture presence or healing is relevant only below a critical capillary number threshold. Furthermore, we find that formation wettability is an irrelevant parameter when determining the implications of natural fracture openness based on geological investigations. Although not pursued in this article, a hybrid numerical-experimental approach based on our framework can be a next step in investigating transport properties of fractured rocks during unstable flow. This approach would follow the approach by Li et al. (2020) and Berg et al. (2016) and can potentially determine several key functional relationships such as that between relative permeability (k_{rw}) and water saturation (S_w). A hybrid numerical-experimental approach

can furthermore be used to assess the viability of cost-effective computational fluid dynamics within a broad capillary number/wettability parameter space.

While capturing the essential features of fracture rock systems, our experimental models have certain simplifications, especially concerning geometrical design. More specifically:

- The porous matrices in the three micromodels are artificially designed as homogeneous pore arrays. Such homogeneity, when coupled with fractures, may affect the flow behavior. This limitation could be improved by replicating the patterns observed in thin sections of fractured rocks.
- Although the 2.5D pore models have pore-scale 3D features by having pore-to-pore connections in the third dimension, they are still insufficient to quantify the effects of connectivity in true 3D space. However, two-dimensional micromodels are still capable of serving as diagnostic tools for identifying multiphase flow dynamics phenomena and providing conceptual pictures of them (Avraam et al., 1994; Armstrong et al., 2014). The qualitative findings of our work, such as the viscous fingering generation mechanisms shown in Figure 6.6c are likely applicable for three-dimensional fractured formations. In contrast, our quantitative observations (and microfluidics research in general), are more useful for concluding trends and providing first order approximations for characterizing two-phase flow dynamics. A review of utility of microfluidics (and nanofluidics) in improving predictions of subsurface operations are provided in Mehmani et al. (2019d).
- Measurements are all acquired at the inch-long scale restricted by the size of the models. Upscaling by experimental or numerical methods is needed before applying our results to the spatial scales of actual subsurface operations.

- The microfracture-porous matrix system is simplified because the fractures are designed to be straight and symmetric through the porous matrices, constant in depth, and to exhibit rectangular cross-sections. Such basic designs could be modified for examining different rock conditions and consequences on multi-phase fluid flow.
- This work explores phenomena at different macroscopic capillary numbers which is determined by the competition between the length scale of the capillary dispersion zone and the length scale of the observed domain (Berg and Ott, 2012; Armstrong et al., 2014) while the viscosity ratio was kept constant. It is also of great interest to systematically change the viscosity ratio and study the corresponding effects on fluid flow for various fracture rock systems. Future work may consider a wider capillary number, viscosity ratio, and wettability parameter space to provide insight into the validity of both macroscopic and microscopic dimensionless parameters in fractured systems. The onset of front instability and capillary desaturation (which has been computed for homogenous rocks by Oughanem et al. (2015) and Hilfer et al. (2015)) can be determined thereafter when channeling due to microfractures is present. Whether the presence of microfractures is of great influence in the competition of the two length scales (capillary and viscous length scales), and whether microfractures introduce a critical third length scale, remain in question and require additional work.
- Micromodels were chosen instead of nanomodels due to their low cost, tractable fabrication steps, and strong visualization ability to complete the systematic experimental research effort described in this paper (18 flooding experiments in total). Results obtained from our investigation are therefore suitable for formations with micrometer-scale pores (such as aquifers and certain multiscale tight

formations). However, our results can be extended to nanoporous systems such as mudrocks, in order to decouple the impact of pore topology from nanoconfinement effects on fluid phase distributions and oil/NAPL recovery.

6.7 CONCLUSIONS

In this chapter, controlled microfluidic experiments yielded the following insights concerning the combined effect of microfracture connectivity, wettability, and capillary number on oil recovery:

- Three distinct viscous fingering generation mechanisms in the presence of microfractures were identified. The dominance of each mechanism depends on both microfracture connectivity and capillary number. Wettability does not affect the conceptual pictures for the generation of fingering dendrites.
- Each dendrite generation mechanism affects front morphology, oil ganglia number, and, ultimately, oil recovery depending on capillary number and wettability conditions.
- A connected microfracture has the most influence in (1) suppressing oil recovery, (2) dendrite coalescence, and (3) oil ganglia generation. However, this influence decreases beyond a threshold capillary number between 10^{-5} and 10^{-4} .
- Despite confirming a unique dendrite generation mechanism, dead-end microfractures have only minor impact on oil recovery under water-wet conditions.

Overall, the experimental observations (1) challenge the single-phase conceptual picture that microfracture connectivity necessarily improves recovery, and (2) highlight the complexity of multi-phase transport within microfractures. The systematic experimental data presented in this paper provide benchmark opportunities for mechanistic models and

shed valuable insight for the development of reliable conceptual pictures of two-phase flow in spatially complex fractured rocks.

Chapter 7: Coreflood-on-a-Chip Study of Viscoelasticity's Effect on Reducing Residual Saturation in Porous Media³

7.1 INTRODUCTION

Polymer aqueous solutions are widely used in enhanced oil recovery and due to their high viscosity. Extra reduction of residual saturation by polymer's viscoelasticity is recently discovered which elevates the ultimate displacement efficiency. However, there is no consensus on how, and under what conditions, viscoelasticity reduces residual saturation. This is in part because most studies utilize relatively low salinity and high viscosity, which also contribute to higher recoveries. In this chapter, systematic experiments utilizing a long (30 cm), heterogeneous 2.5D glass micromodel (“*coreflood-on-a-chip*”) were performed. Direct visualization at the REV scale and the pore-scale are obtained and analyzed. Through the observations and analysis, we are able to bridge the gap between the theoretical prediction of pore-scale, single-phase viscoelastic instabilities and the experimental observation of residual saturation reduction in complex porous media. In the experiments, a highly viscous Newtonian aqueous phase flood is first performed so that the system reaches residual saturation, followed by polymer flood with varying elasticity and salinity. This is followed by another highly viscous Newtonian aqueous phase flood.

³ Du, Y., Xu, K., Mejia, L. and Balhoff, M.T. 2021. A Coreflood-on-a-Chip Study of Viscoelasticity's Effect on Reducing Residual Saturation in Porous Media. *Water Resources Research*: e2021WR029688, in press.

Yujing Du designed and performed the experiments, conducted data analysis, and wrote the manuscript.

7.2 EXPERIMENTAL METHOD

7.2.1 Micromodel

Experiments were performed in a 30 cm long, 2.5D, water-wet glass micromodel with heterogeneous porous matrix (“*coreflood-on-a-chip*” micromodel) as shown in Figure 7.1abcd. The micromodel was designed and fabricated in house using the protocols described in previous works as introduced in Chapter 3.1 (Xu et al., 2017; Mejia et al., 2020). The patterns of the micromodel were designed in a CAD software and were then used to generate a photomask for photolithography. Photolithography and wet-etching using hydrofluoric acid were conducted to engrave the designed patterns onto the glass substrate. Holes were drilled through the substrate glass at both ends of the geometry as the inlet and the outlet. Soda-lime glass (2 mm thick) was used for both substrate and cover glass. The etched and drilled substrate glass and the smooth cover glass were subsequently bonded together using the thermal bonding method. The micromodel was designed to be serpentine-shaped (Figure 7.1ab) to reduce the overall size considering space limitations.

The novel “*coreflood-on-a-chip*” micromodel better mimics real rocks than many other micromodels while maintaining the advantageous features of traditional microfluidics. Pore-scale 3D (or 2.5D) features (Figure 7.1d) are achieved by etching the pore throats shallower than the pore bodies so that the grains are also connected, allowing the occurrence of Roof capillary snap-off (Xu et al., 2017). Heterogeneity is included in the pore-network (Figure 7.1c) which is an important feature that impacts the drainage dynamics and therefore the microscopic displacement. The long length (30 cm) minimizes the potential scale issues in many micromodels, e.g., capillary end effects, thus providing a more realistic experimental environment (Mejia et al, 2020). Two micromodels denoted as M1 and M2 with the same design and nearly identical geometric properties were used

in this work. The permeability for the micromodels was 0.87 Darcy determined by Darcy's law by measuring pressure drops under constant injection rates (see Appendix C1). The geometric properties of the micromodels are listed in Table 7.1.

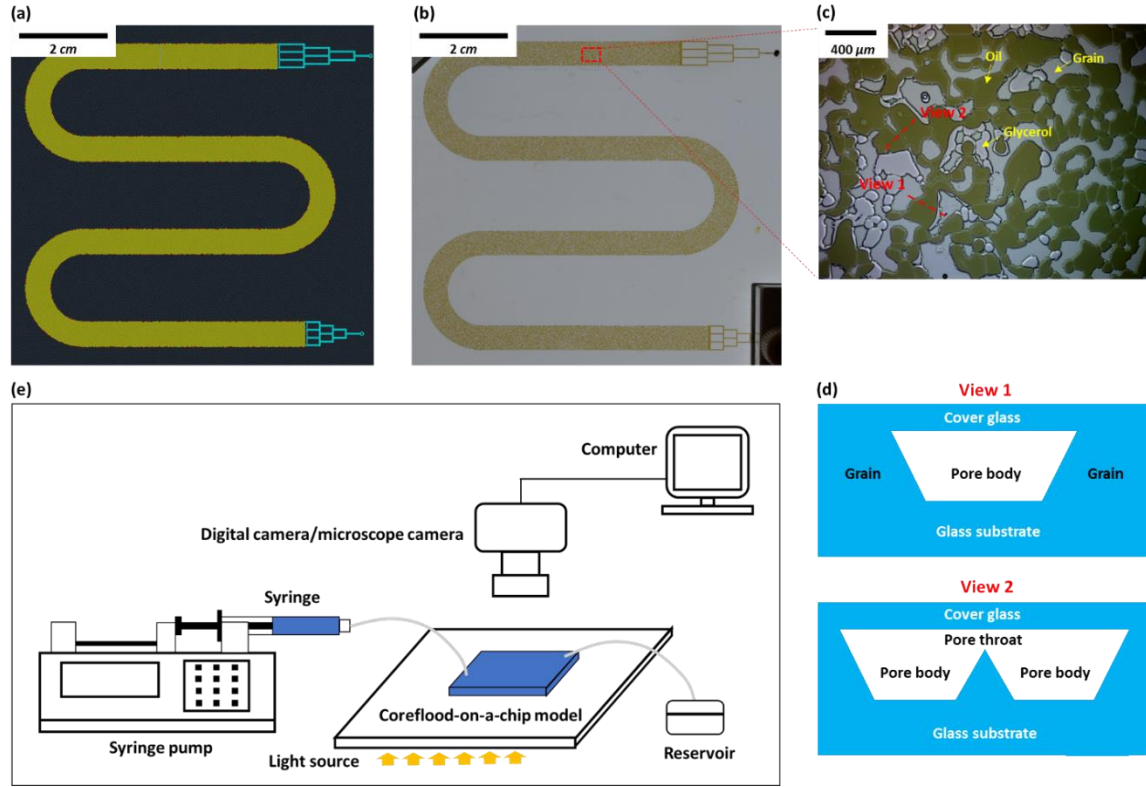


Figure 7.1: (a) Photomask design of the micromodel. (b) Image of the micromodel M2 saturated with crude oil (brown) captured by a DSLR camera. (c) Microscopic image of pores with crude oil (brown) and glycerol (white) from another case than (b). Two cross-sections at view 1 and view 2 are demonstrated in planar view. (d) Cross-sectional schematics of the micromodel pore body/grains at view 1 and pore bodies/pore throat at view 2. (e) Schematic sketch of the experimental setup.

Table 7.1: Micromodel properties

Micromodel	Length	Width	Pore body depth	Pore throat depth	Porosity	Pore Volume
M1	30 cm	5.6 mm	15.5 μm	6 ± 1 μm	0.60	15.9 μl
M2	30 cm	5.6 mm	15.0 μm	6 ± 1 μm	0.55	14.1 μl

7.2.2 Fluids preparation and analysis

A crude oil sample with a viscosity of 13 cp and a density of 0.8 g/cm³ at room temperature was used in all 10 flow experiments (denoted as experiments 1-10) as the displaced phase. Two glycerol solutions (glycerin mixed with deionized water), were used in the experiments as the Newtonian non-polymer aqueous phases instead of water. The glycerol solutions were more viscous than the crude oil which can prevent the generation of viscous fingering caused by an unfavorable mobility ratio. Two viscosities were used to exclude potential impact of initial viscosity variation on the results. Viscosity of the two glycerol fluids were measured using ARES-G2 rotational rheometer. The properties of the two glycerol solutions at ambient conditions are listed in Table 7.2.

Four polymer solutions prepared with three different molecular weight HPAM (partially hydrolyzed polyacrylamide) polymer powders (Table 7.2) were used in the experiments and denoted as “elastic polymer 1”, “elastic polymer 2”, “inelastic polymer 1” and “inelastic polymer 2”, respectively. The terms “elastic” and “inelastic” used in this study are relative, which refer to high elasticity polymers ($De > 100$) and low elasticity polymers ($De < 10$), respectively. Elastic polymer 1 and inelastic polymer 2 were at low salinity (1000 ppm NaCl), and elastic polymer 2 and inelastic polymer 1 were at relatively high salinity (20000 ppm NaCl). All polymer solutions were made significantly less viscous than the glycerol solutions at the experimental conditions (Figure 7.2a) so that any additional recovery was not due to sweep efficiency improvement by elevated viscosity. The rheology of the polymer solutions was measured using an ARES-G2 rotational rheometer, and the interfacial tensions between oil and the four displacing fluids were measured using a spinning drop tensiometer (KRÜSS SDT) at room temperature. The compositions and properties of the polymer solutions at experimental conditions are listed in Table 7.2.

Table 7.2: Compositions and properties of the displacing fluids

Displacing fluids	Glycerol solution1	Glycerol solution2	Elastic polymer1	Elastic polymer2	Inelastic polymer1	Inelastic polymer2
Content	Glycerol	Glycerol	HPAM3630 (molecular weight of 18-20 million Daltons)	HPAM6035 (molecular weight of 24-28 million Daltons)	HPAM3630 (molecular weight of 18-20 million Daltons)	HPAM3130 (molecular weight of 3-4 million Daltons)
Concentration	84 vol%	70 vol%	1000 ppm	1800 ppm	2200 ppm	1800 ppm
Salts	–	–	1000 ppm NaCl, 400 ppm NaHCO ₃	20000 ppm NaCl, 400 ppm NaHCO ₃	20000 ppm NaCl, 400 ppm NaHCO ₃	1000 ppm NaCl
Relaxation time (τ_r)	–	–	1.49 s	1.34	0.048 s	0.013
Shear rate* ($\dot{\gamma}$)	–	–	122 – 132 s ⁻¹	~122 s ⁻¹	133 – 145 s ⁻¹	159 – 163 s ⁻¹
Apparent viscosity (μ)	118 cp	33 cp	12 – 13 cp	~16 cp	14 – 15 cp	14 – 15 cp
Deborah number (De)	–	–	182 – 196	163	6.4 – 7	~2
Density (ρ)	1.25 g/ml	1.20 g/ml	1.02 g/ml	1.04 g/ml	1.04 g/ml	1.02 g/ml
IFT** with crude oil (γ)	20.0±0.3mN/m	18.7±0.5mN/m	5.4±0.6 mN/m	0.93±0.06mN/m	0.84±0.006mN/m	12.5±0.2mN/m

* Some parameters used to determine shear rate were estimated according to consensually accepted empirical data in literature; variations in the reasonable range would not qualitatively affect the results presented in this paper

** IFT is short for interfacial tension; multiple measurements were conducted and averages values were reported

The viscosity versus shear rate curves of the polymer solutions are shown in Figure 7.2. The polymer solutions have similar viscosity in a shear rate range of 10 – 300 s⁻¹ which covers the approximate flow regimes in the experiments. Relaxation times of the polymer solutions were estimated as the inverse of angular frequency at the crossover point of storage (G') modulus and loss modulus (G'') which were measured from dynamic rheology tests (Volpert et al., 1998; Castelletto et al., 2004; Vermolen et al., 2014; Qi et al., 2017) as shown in Figure 7.2bcde. The relaxation time of the elastic polymer solutions (1.49 s⁻¹ and 1.34 s⁻¹) is one to two orders of magnitude higher than the two inelastic polymers solutions (0.048 s⁻¹ and 0.013 s⁻¹), indicating much higher elasticity in the former two polymers.

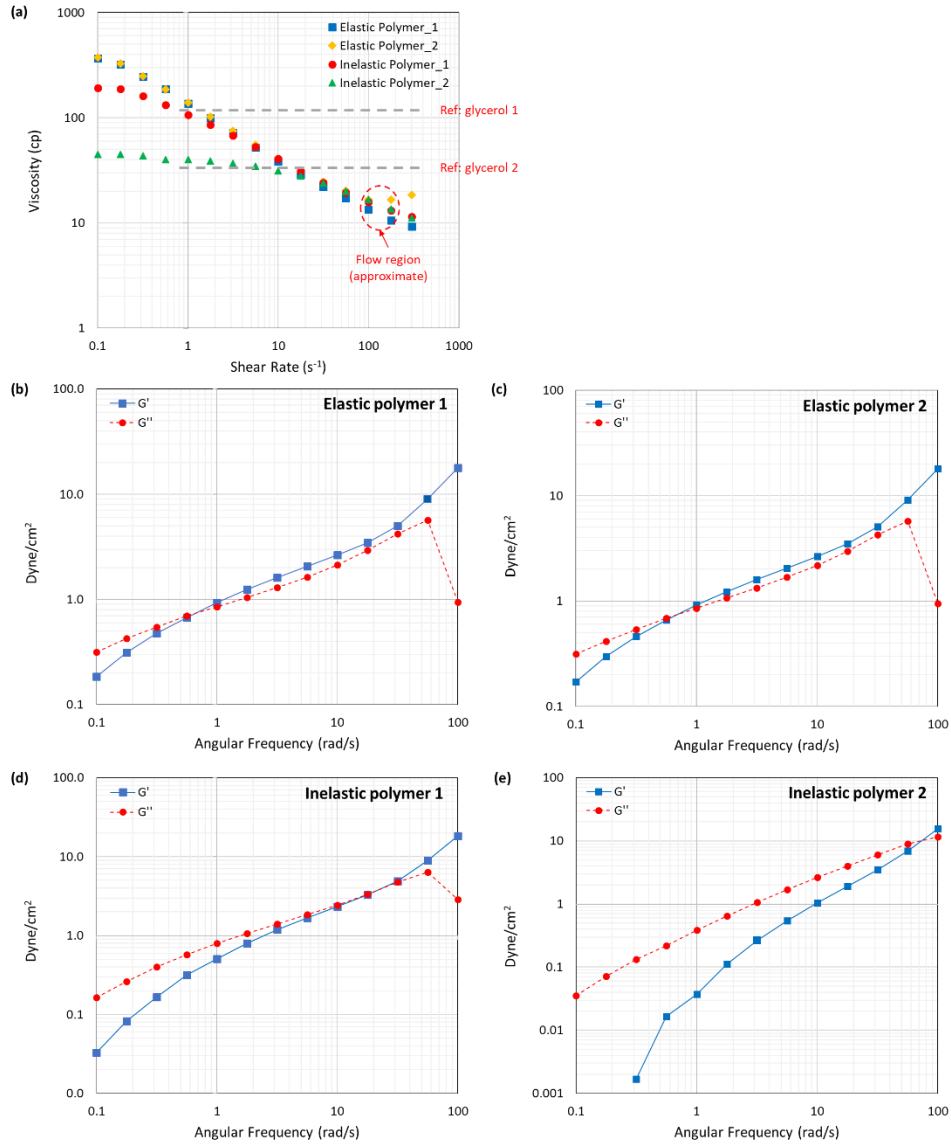


Figure 7.2: (a) Rheological behaviors of HPAM polymers solutions denoted as elastic polymer, inelastic polymer 1 and inelastic polymer 2. G'/G'' plots of (b) elastic polymer 1, (c) elastic polymer 2, (d) inelastic polymer 1, and (e) inelastic polymer 2.

To estimate the apparent viscosity of polymers in the experiments, shear rate in porous media at the experimental conditions is estimated using an empirical equation (Qi et al, 2017):

$$\dot{\gamma} = C \left(\frac{3n+1}{4n} \right)^{\frac{n-1}{n}} \frac{4}{\sqrt{8}} \frac{u_w}{\sqrt{K K_w \phi S_w}} \quad (7.1)$$

where C is the shear correction factor for the porous medium and is taken to be 4.0 (Koh et al., 2017), n is the shear-thinning index, u is Darcy velocity, K is permeability, K_{rw} is relative permeability of aqueous phase, ϕ is porosity, and S_w is the aqueous phase saturation (glycerol and polymer solutions). A value of 0.1 was used as aqueous phase relative permeability in the water-wet porous media as obtained from many published results (Qi et al., 2017; Erincik et al., 2018; Jin et al., 2020), and aqueous phase saturation at the end of secondary flood experiments 1-8 were used for S_w . Using Equation 7.1, the shear rates and the corresponding viscosities are determined for each of the polymer solutions at the experimental conditions (Table 7.2). The estimated shear rates of different polymers in different experiments vary in a reasonably range, and the corresponding apparent viscosities are similar but all of them are lower than the viscosities of the glycerol solutions (Figure 7.2a).

Deborah number (De), a dimensionless number that describes the ratio of elastic to viscous forces, is defined in this work by:

$$De = \tau_r \dot{\gamma} \quad (7.2)$$

where τ_r is relaxation time, and $\dot{\gamma}$ is shear rate.

7.2.3 Experiments

10 flow experiments were conducted in the “*coreflood-on-a-chip*” micromodel at ambient conditions on the experimental platform illustrated in Figure 7.1e. Experiments 1-8 were visualized at the macroscale, and experiments 9 and 10 were visualized at the microscale. In each experiment, an initial condition with oil and residual aqueous fluid was established by a primary oil flood into the micromodel saturated with viscous Newtonian

aqueous fluids to mimic the subsurface environment. After establishing the initial condition, three floods were performed in order. The 1st, 2nd and 3rd flood are termed as secondary, tertiary and post-tertiary flood, respectively, in this paper. The secondary flood used a highly viscous Newtonian aqueous fluid to achieve the residual saturation of oil, and to exclude the effect of viscosity on residual saturation reduction in following floods. The tertiary flood used polymers with different elasticity and salinity to explore the effects of these factors. The post-tertiary flood used the same fluid as in the secondary flood to determine the potential longer-term impacts of the tertiary flood. Table 7.3 summarizes the saturating fluids and displacing fluids used in each experiment.

Table 7.3: Fluids and volumes used in each flood in experiments 1-10. Experiments 1-8 were visualized at the macroscale, and experiments 9 and 10 were visualized at the microscale

Experiment	1	2	3	4	5	6	7	8	9	10
Elasticity* of 2 nd flood	High	High	High	High	Low	Low	Low	Low	High	High
Salinity** of 2 nd flood	Low	Low	Low	High	High	High	Low	Low	Low	Low
Initial saturating fluid	Glycerol1	Glycerol1	Glycerol2	Glycerol1	Glycerol1	Glycerol2	Glycerol2	Glycerol1	Glycerol1	Glycerol2
1 st flood fluid type	Glycerol1	Glycerol1	Glycerol2	Glycerol1	Glycerol1	Glycerol2	Glycerol2	Glycerol1	Glycerol1	Glycerol2
2 nd flood fluid type	Elastic polymer1	Elastic polymer1	Elastic polymer1	Elastic polymer2	Inelastic polymer1	Inelastic polymer1	Inelastic polymer2	Inelastic polymer2	Elastic polymer1	Elastic polymer1
3 rd flood fluid type	Glycerol1	Glycerol1	Glycerol2	Glycerol1	Glycerol1	Glycerol2	Glycerol2	Glycerol1	Glycerol1	Glycerol2
1 st flood pore volumes	6.7	3	4.5	4.3	3	3.5	2.6	3.2	2	2
2 nd flood pore volumes	5	6	6.2	7.9	8	8.7	8.7	8.7	7.4	7.5
3 rd flood pore volumes	2.3	3.6	3	3.5	3	3.5	3.5	3.5	2.3	2.5
Micromodel #	M1	M1	M1	M2	M1	M2	M2	M2	M1	M1

*The high and low elasticity refer to $De > 100$ and $De < 10$, respectively, using the definition in this work

** The high and low salinity refer to 20000 ppm and 1000 ppm NaCl, respectively

In experiments 1-8, the micromodel was placed on top of a white LED light pad, and a DSLR camera (Nikon D5600) was mounted above the micromodel using a tripod stand to capture time-lapse images of the entire flow geometry. The image dimensions are 6000×4000 pixels with voxel resolution of approximately 20 micrometers/pixel. The exposure time was constant for each experiment (1/250 s in experiments 1-3 and 5, and 1/200 s in experiments 4 and 6-8). Experiments 9 and 10 were conducted under a microscope (AmScope IN300TC), where pore-scale images of a fixed area of 2mm × 2.6mm were captured by the microscope camera (AmScope 10MP) mounted above the micromodel. The image dimensions are 3584×2748 pixels with voxel resolution of 0.8 micrometers/pixel. The exposure time was fixed once an optimal exposure was achieved before each experiment. The exposure time was 1/23 s and 1/30 s for experiments 9 and 10, respectively.

When performing the experiments, the micromodel was firstly saturated with the saturating fluids (glycerol solutions) by injecting at about 50 µl/hour from the inlet for sufficient time (>24 hours) using a syringe pump (PHD 2000, Harvard Apparatus). If necessary, another syringe was used to vacuum from the outlet until gas bubbles disappeared from the system. After the saturation, oil was injected at 20 µl/hour until no more existing aqueous phase was produced and a steady state was reached. The subsequent three floods were performed in order at an injection rate of 1.65 µl/hour (~1.5 ft/day). The capillary numbers ($Ca = \mu_i u / \gamma$) of the floods by the four displacing fluids were in the range of $6 \times 10^{-6} - 9 \times 10^{-5}$, therefore capillary desaturation was minimal and residual oil saturation was not affected by varying capillary number (Lake et al., 2015; Qi et al., 2017). After each experiment, the micromodel was cleaned by injecting solvents (hexanes and acetone) and DI water in order, and ultrasonic cleaner (Branson 2800) was also used to help clean solid debris on the surface. After cleaning, the micromodels were dried on a hot plate at 110°C.

7.2.4 Image analysis

The images captured in the experiments were processed using ImageJ as discussed in Chapter 3.3. Figure 7.3abcd show the raw image captured by the DSLR camera (Nikon D5600), enhanced image, segmented image (binarized) and the colored image, respectively. The image segmentation separated the crude oil phase (black) from aqueous phase and grains using thresholding method “Otsu” function as shown in Figure 7.3c. The oil saturation in each binarized image was calculated. Red color was assigned to oil phase by adjusting the LUT (Look-Up Table for color mapping) value in the binarized grey scale image (Figure 7.3d).

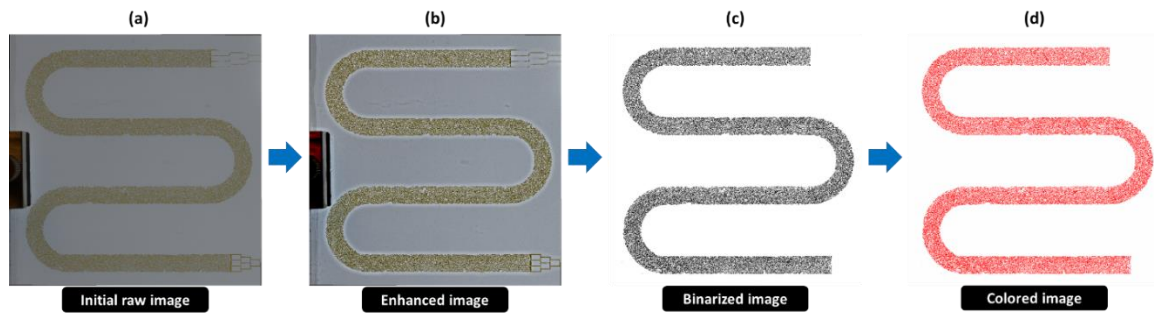


Figure 7.3: Image processing procedures for the results presented in Chapter 7. Oil phase is in brown in (a) and (b). (c) Grey scale image in black (oil) and white. (d) Image with adjusted color in red (oil) and white.

7.3 RESULTS

7.3.1 Qualitative results

Figure 7.4 shows the oil distribution initially (Figure 7.4a) and at the end of secondary (Figure 7.4b), tertiary (Figure 7.4c) and post-tertiary floods (Figure 7.4d) in experiments 1-8. The four images in each column are from the same experiment. Experiments 1-4 are high elasticity and experiments 5-8 are low elasticity; experiments 1-

3 and 7-8 are low salinity and experiment 4-6 are high salinity. No unswept regions or fingering were observed in all experiments (Figure 7.4), as the invading fluids used in secondary floods are much more viscous than the defending fluid, which leads to stable displacement.

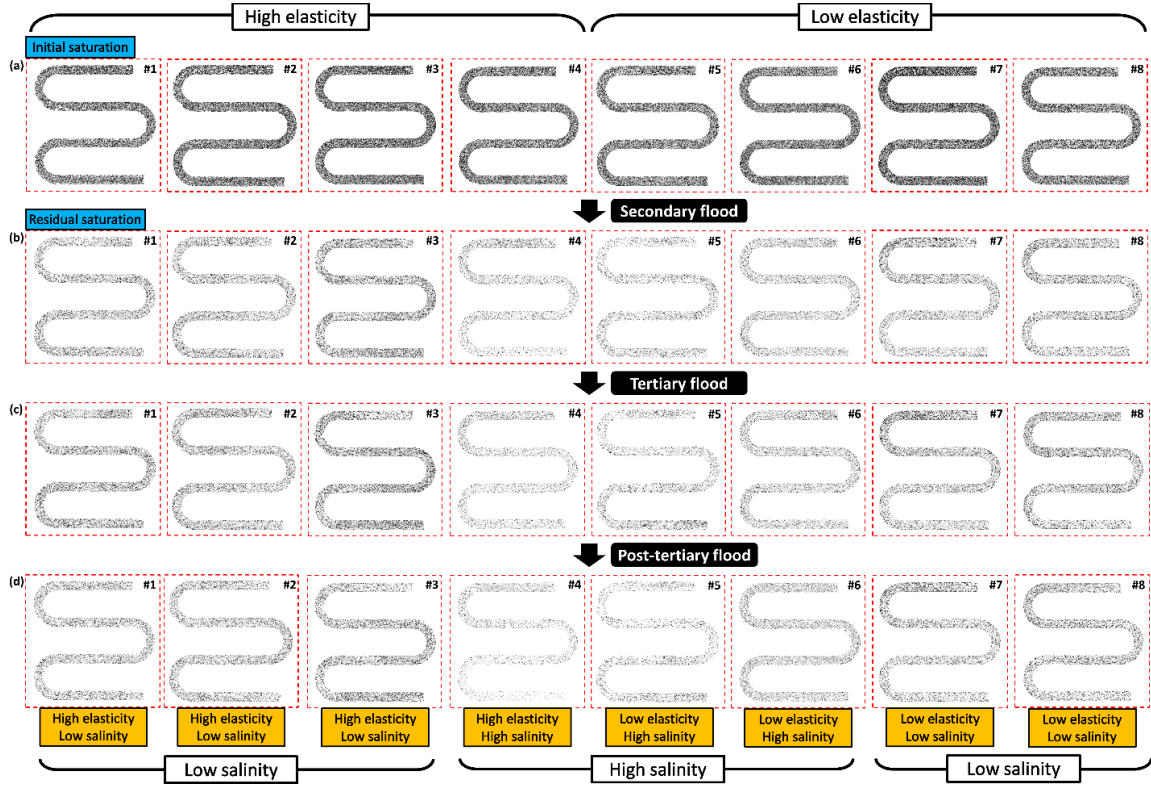


Figure 7.4: Oil (black) distribution in the micromodel at (a) initial oil saturation, (b) residual oil saturation at the end of secondary flood, (c) end of tertiary polymer flood, and (d) end of post-tertiary flood. Experiment number (#) is labeled at the top right corner in each image.

It is important to ensure that residual oil saturation was achieved in the micromodel by the secondary flood. Water is commonly used as the saturating aqueous fluid and the secondary flooding phase in such experiments to mimic the real-world conditions and operations. However, fingering occurs when water is the connate aqueous phase due to

adverse viscosity ratio between the invading and the invaded phases and the mobilization of trapped aqueous phase (Mejia et al., 2020), making the remaining oil saturation significantly higher than residual saturation. This unswept, remaining oil impedes the observation of the microscopic displacement dynamics. Therefore, viscous glycerol solutions (inelastic and Newtonian) were used as the aqueous phase instead of water for the secondary and post-tertiary flood and fingering was not observed. The displacement fronts were stable, and the entire porous medium behind the fronts was swept by the invading glycerol solutions (Figure 7.5). This is consistent with the favorable mobility ratio between the displacing phase (glycerol solution) and the displaced phase (oil).

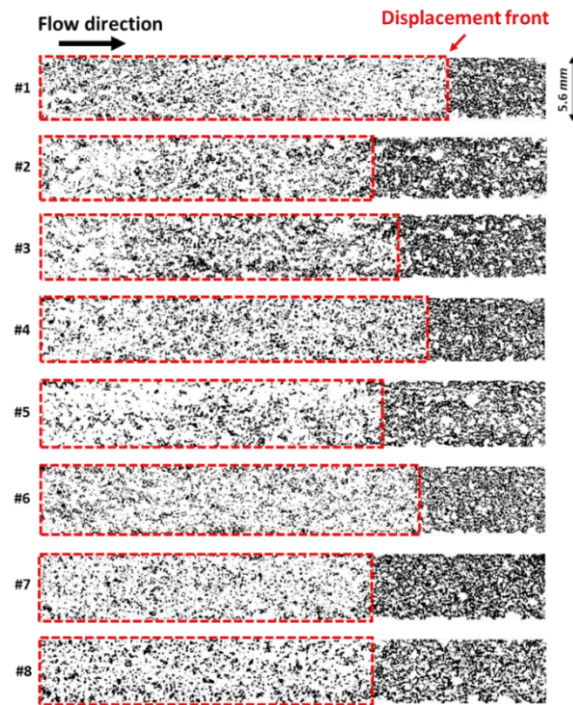


Figure 7.5: Displacement fronts during secondary glycerol flood in experiments 1-8 with oil phase (black) and aqueous glycerol solution phase (white). Swept regions are marked within red dashed rectangles.

7.3.2 Quantitative results

Oil saturations from the binarized images are quantitatively analyzed by the image analysis software (ImageJ). Oil saturation versus injected pore volumes in experiments 1-8 are shown in separate plots numbered #1-#8 in Figure 7.6, with high elasticity cases (#1-#4) in Figure 7.6a and low elasticity cases (#5-#8) in Figure 7.6b. The saturation and changes are also summarized in Table 7.4. The variation in the initial and residual oil saturations in parallel experiments 1-8 were largely due to technical reasons, and does not compromise the reproducibility and conclusions of this work. In each plot in Figure 7.6, there are three stages marked with three colors (blue, red and green), representing the secondary, tertiary and post-tertiary floods, respectively.

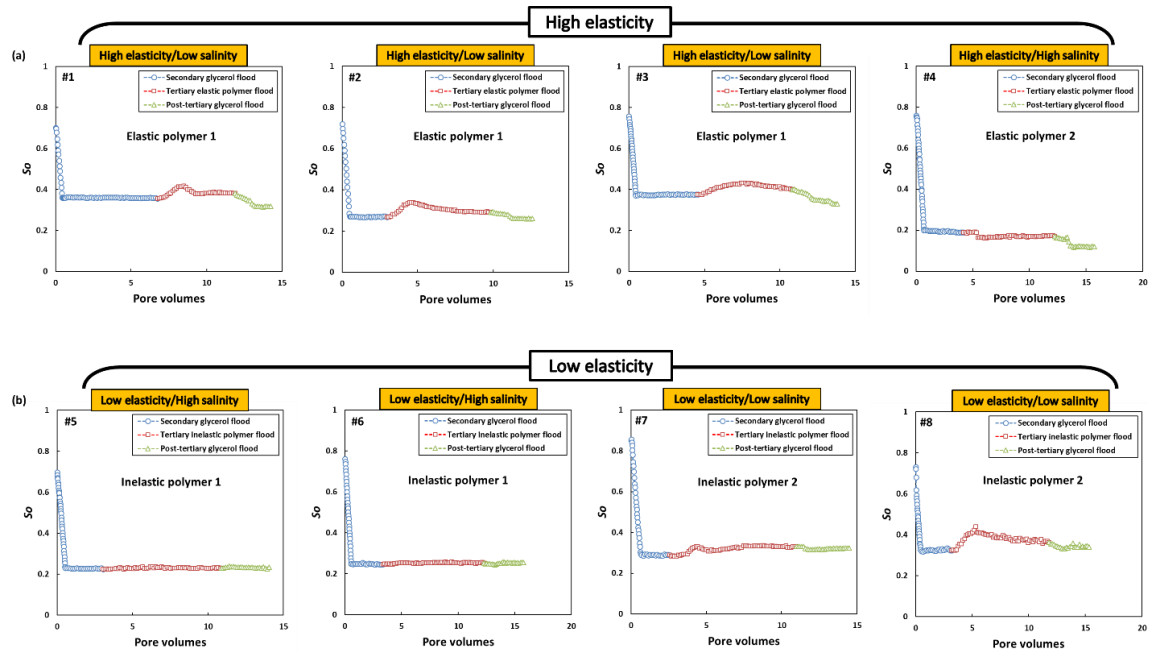


Figure 7.6: Oil saturation curves in each experiment for experiments 1-8 with (a) high elasticity in tertiary flood and (b) low elasticity in tertiary flood. Experiment number (#) is labeled at the top left corner in each image.

Table 7.4: Oil saturation and changes in each flood in Experiments 1-8

Experiment	1	2	3	4	5	6	7	8
Elasticity of 2 nd flood	Elastic polymer 1	Elastic polymer 1	Elastic polymer 1	Elastic polymer 2	Inelastic polymer 1	Inelastic polymer 1	Inelastic polymer 2	Inelastic polymer 2
Salinity of 2 nd flood	High	High	High	High	Low	Low	Low	Low
Salinity	Low	Low	Low	High	High	High	Low	Low
Soi	0.70	0.72	0.76	0.76	0.70	0.76	0.85	0.73
So after 1 st flood	0.357	0.270	0.375	0.19	0.23	0.25	0.290	0.327
ΔSo in 1 st flood	-0.343	-0.450	-0.375	-0.57	-0.47	-0.50	-0.560	-0.403
So after 2 nd flood	0.381	0.290	0.400	0.17	0.23	0.25	0.330	0.365
ΔSo in 2 nd flood	+0.024	+0.020	+0.027	-0.02	0	0	+0.040	+0.038
So after 3 rd flood	0.317	0.260	0.327	0.12	0.23	0.25	0.320	0.343
ΔSo in 3 rd flood	-0.064	-0.030	-0.073	-0.05	0	0	-0.008	-0.022
$\Delta So_{(net)}$ from 2 nd and 3 rd floods	-0.040	-0.010	-0.048	-0.07	0	0	+0.032	+0.017

Note: the saturation change at each step (ΔSo) is calculated by subtracting the post-flood saturation by the pre-flood saturation

7.3.2.1 Residual saturation after secondary aqueous flood:

Secondary flood decreases the oil saturation from the initial saturation of 70 – 85% to the residual saturation of 19 – 37%, where a plateau is reached with additional pore volumes injected in each of the eight experiments.

7.3.2.2 Saturation increase in tertiary polymer flood

Unexpected saturation increase is observed during tertiary polymer flood in all cases that the polymer salinity is low (#1-#3, #7 and #8). In plots #1-#3, the saturation increases during the first several pore volumes of injection and then decreases, but is still higher by 2.0 – 2.7% at the end of the tertiary floods than before them. In plots #7 and #8, similar to the trend in #1-#3, the saturation increases and then decreases with an increase of 3.8% and 4.0%, respectively, at the end of the tertiary floods. In plot #4, the saturation

decreases by 2% and no saturation increase is observed at any point during the flood. In plots #5 and #6 the saturation curves remain flat during the entire flood.

7.3.2.3 Saturation reduction in post-tertiary aqueous flood

Saturation reduction is obtained in several cases (#1-#4, #7 and #8) during the post-tertiary flood. In plots #1-#4, the oil saturation decreases by 3.0 – 7.3% to the final saturation which is lower than the saturation at the end of the secondary flood. In plots #5 and #6 the curves remain almost flat during the entire flood. In plots #7 and #8, the saturation decreases by 0.9 – 2.2% to the final saturation which is still higher than the saturations at the end of the secondary flood.

Importantly, despite of the saturation changes, oil was only produced in high elasticity cases (#1-#4) during post tertiary flood in #1-#3 and both tertiary and post-tertiary floods in #4, determined from the produced fluids. This observation and the saturation increase from the low-salinity tertiary flood are discussed in Chapter 7.3.

7.3.3 Schematic summary

Elasticity and salinity of the polymers are the two factors shown to affect the flow dynamics and the reduction of residual saturation. The key findings with regards to these two factors are subsequently summarized in Figure 7.7 schematically, and are discussed in Chapter 7.3. When the elasticity was high, residual ganglia recovery and ultimate residual saturation reduction were obtained. No recovery or residual saturation reduction was obtained when elasticity was low. Most of the recovery was obtained from post-tertiary inelasticity flood which was also observed in corefloods (Erincik et al., 2018; Jin et al., 2020). Oil saturation increase was observed when polymer salinity was low (1000 ppm

NaCl) regardless of elasticity, and was not observed when polymer salinity was relatively high (20000 ppm NaCl).

(a)

Elasticity of 2 nd flood	Salinity of 2 nd flood	Tertiary polymer flood		Post-tertiary flood
		Saturation increase	Recovery	Recovery
High	Low	Yes	No	Yes
	High	No	Yes	Yes
Low	Low	Yes	No	No
	High	No	No	No

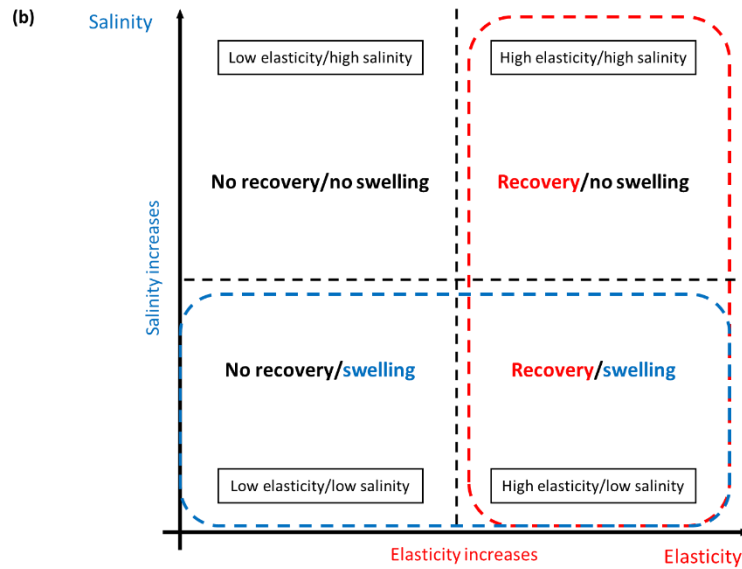


Figure 7.7: Schematic summary of the results presented in Chapter 7.3.2. (a) Summary of behaviors using different polymer solutions. (b) Conceptual diagram based on polymer elasticity and salinity conditions.

7.4 ANALYSIS AND DISCUSSION

7.4.1 Microscopic observation

Unexpected oil saturation increase during low salinity tertiary polymer flood was observed in experiments 1-3, 7 and 8, despite the salinity of the previous flood (glycerol solutions) was also low. To explore the underlying reason for the saturation increase, pore-

scale observations were conducted in experiments 9 and 10 under a microscope using the fluids shown in Table 7.3. A fixed view of an area of $2\text{mm} \times 2.6\text{mm}$ was captured during experiments and the visualizations are presented.

7.4.1.1 Residual ganglia swelling in tertiary polymer flood

After the secondary flood, residual oil ganglia distributed in the captured area in the middle of individual pores or occupying multiple pores (left column of Figure 7.8a). Upon the start of the low salinity, high elasticity polymer flood (elastic polymer 1), emulsions (dark phase within oil ganglia) began to form inside the oil ganglia (middle column of Figure 7.8a). The emulsions caused ganglia swelling that lead to the saturation increase and contributed to ganglia reconnection. The peak amount of emulsions occurred during the first several pore volumes of injection (middle column of Figure 7.8a), after which point emulsions began to subside and the oil ganglia partially de-swelled as a consequence. The observed non-monotonic oil swelling explains the oil saturation increase followed by decrease shown in Figure 7.6. In this process, some oil ganglia moved in the transverse direction but did not move out in the longitudinal direction. The transverse movement was not (at least not mainly) caused by low salinity induced swelling, although swelling assisted the movement (see Appendix C2).

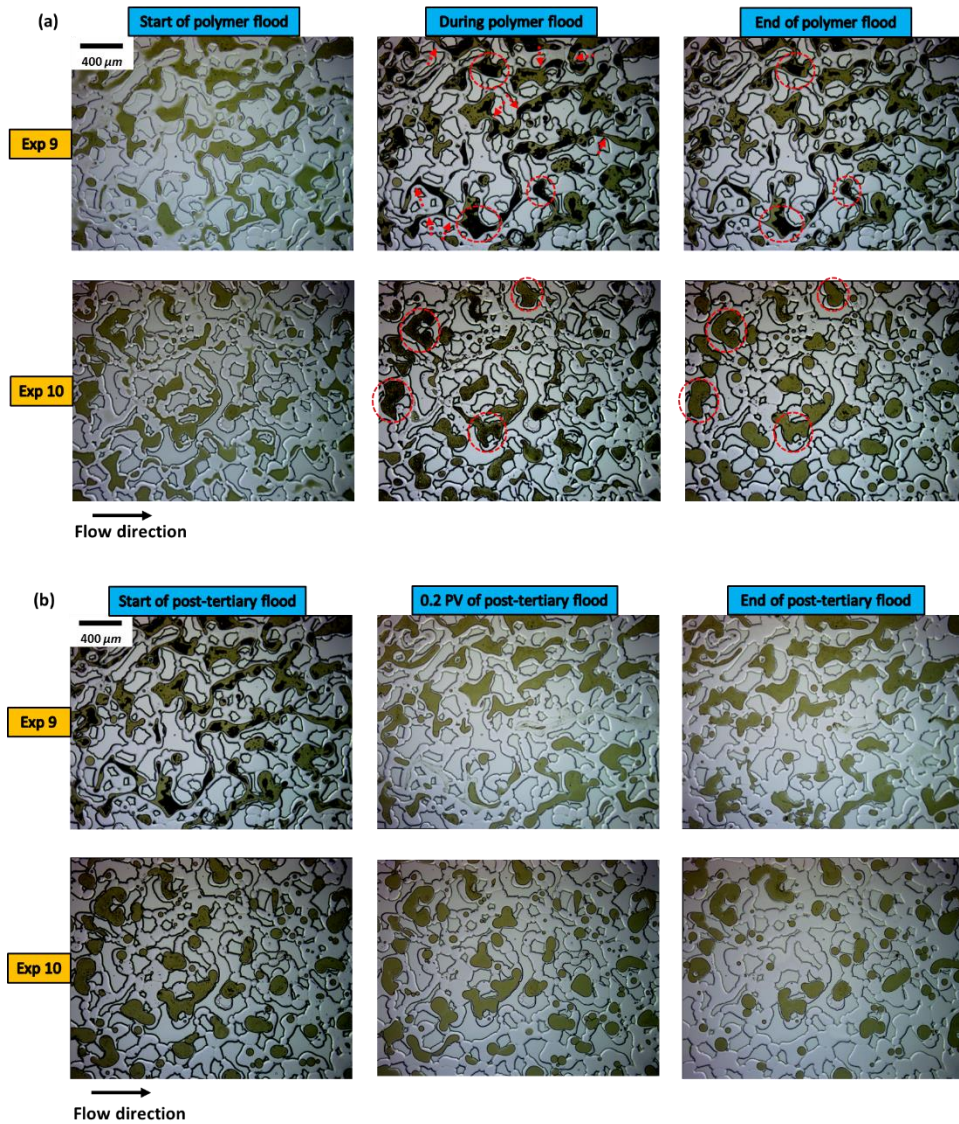


Figure 7.8: Pore-scale visualization of residual oil ganglia in experiments 9 (top row) and 10 (bottom row) during (a) tertiary polymer flood (high elasticity and low salinity), and (b) post-tertiary glycerol flood with oil (brownish) and glycerol (white). Red circles in (a) highlight the emulsifications (dark) inside the oil phase; red arrows in (a) point to locations where oil interfaces change and oil ganglia reconnect.

7.4.1.2 Residual ganglia mobilization in post-tertiary aqueous phase flood

During the post-tertiary glycerol flood the emulsions quickly subsided and eventually almost disappeared after a short period of injection (0.1 – 0.2 pore volumes), despite the salinity of the glycerol solutions were also low. Meanwhile, the residual oil ganglia left behind in previous two floods became mobilized and flowed out of the observed area in the longitudinal direction. Ganglia de-swelling and break-up were also observed in the captured area (Figure 7.8b). The observation agreed with the macroscopic observation from experiments 1-3, and further confirmed that the decrease in saturation in the post-tertiary flood in these experiments were from oil mobilization in addition to de-swelling.

7.4.2 Ganglia analysis in single cross-sections

Low polymer salinity induced swelling explains the observed saturation increase, but does not have a determinant impact on the residual oil recovery (Figure 7.7). Instead, saturation reduction and residual oil recovery were obtained only when the tertiary flood had high elasticity as in experiments 1-4. To reveal the role of elasticity on saturation reduction and residual oil recovery, ganglia analysis in single cross-sections zoomed-in from the macroscopic visualizations was performed.

7.4.2.1 Residual ganglia swelling, redistribution and mobilization in tertiary polymer flood

A negligible (if any) amount of oil was produced (determined from the produced fluids) in experiments 1-3 where elastic polymer 1 (low salinity) was used for the tertiary flood. The oil saturation increase of 2.0 – 2.7% at the end of the tertiary flood (Figure 7.6 - #1-#3) was caused by the oil swelling (non-monotonic) due to the emulsion generation in the oil ganglia. The swelling and saturation increase are visually demonstrated in the

zoomed-in cross-section (in the middle of the chip to avoid entrance/end effects) in Figure 7.9cde. Oil ganglia redistribution in the transverse direction was observed, as indicated by the locations of the green (mobilized) and blue colors (newly occupied) in Figure 7.9e. Ganglia swelling and redistribution reduced the ganglia number and changed the ganglia morphology. In the cross-section from Figure 7.9c to Figure 7.9d, the oil saturation increased from 30% to 32% due to ganglia swelling, and the number of oil ganglia decreased by 7.7% as a result of redistribution and reconnection induced by swelling. Obvious ganglia transverse redistribution and swelling were repeatedly observed from experiments 2 and 3 which are included in Appendix C4.

Due to the oil swelling and the later partial de-swelling in experiments 1-3, the oil saturation increased then decreased. The peak saturation increase was 5.6%, 7.0% and 5.8%, higher than the saturation increase at the end of tertiary flood was 2.4%, 2.0% and 2.7%, respectively (Figure 5 - #1-#3). The number of oil ganglia first decreased then increased but was lower than the prior to the polymer flood. Supplemental analysis and discussion regarding this non-monotonic saturation change are included in Appendix C3.

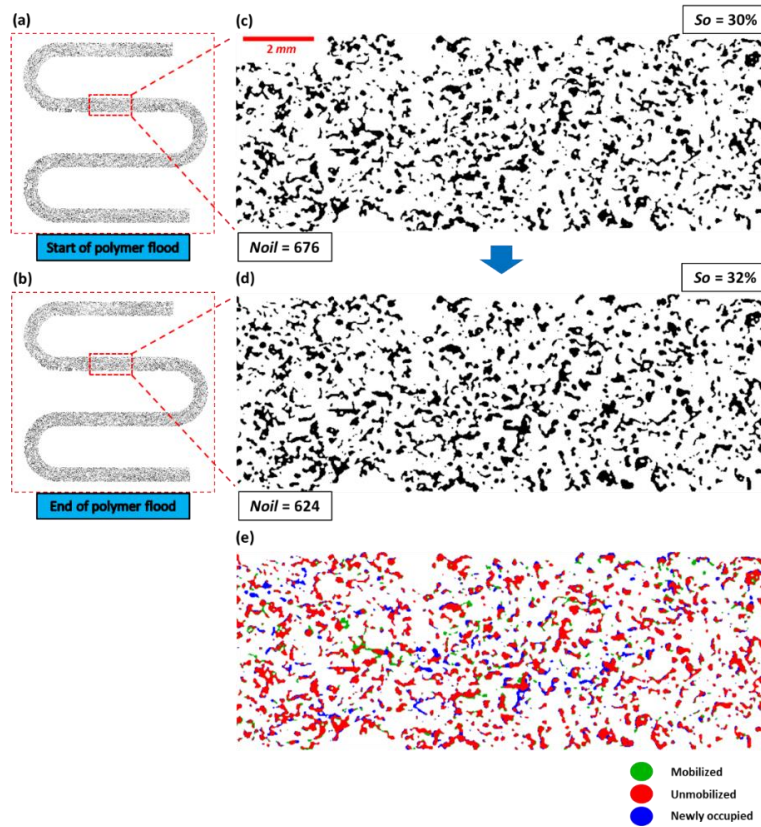


Figure 7.9: Oil swelling and redistribution during tertiary polymer flood in experiment 1 (high elasticity and low salinity). Entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.

In experiment 4 where elastic polymer 2 (high salinity) was used for the tertiary flood, oil started to mobilize and was produced upon switching to polymer flood, and a saturation reduction of 2% was obtained (Figure 7.6 - #4). The oil saturation did not change at any point except the decrease due to oil production, and no ganglia swelling was observed (Figure 7.10cde). Many small to moderate oil ganglia were entirely recovered, while some larger ones were broken down and/or partially recovered (Figure 7.10e). In the cross-section from Figure 7.10c to Figure 7.10d, the oil saturation decreased from 21% to

17% due to mobilization, and the ganglia number increased by 7.8% as a result of ganglia break-up. More details regarding the oil mobilization process (not relevant to the mechanisms discussed in this paper) are included in Appendix C5.

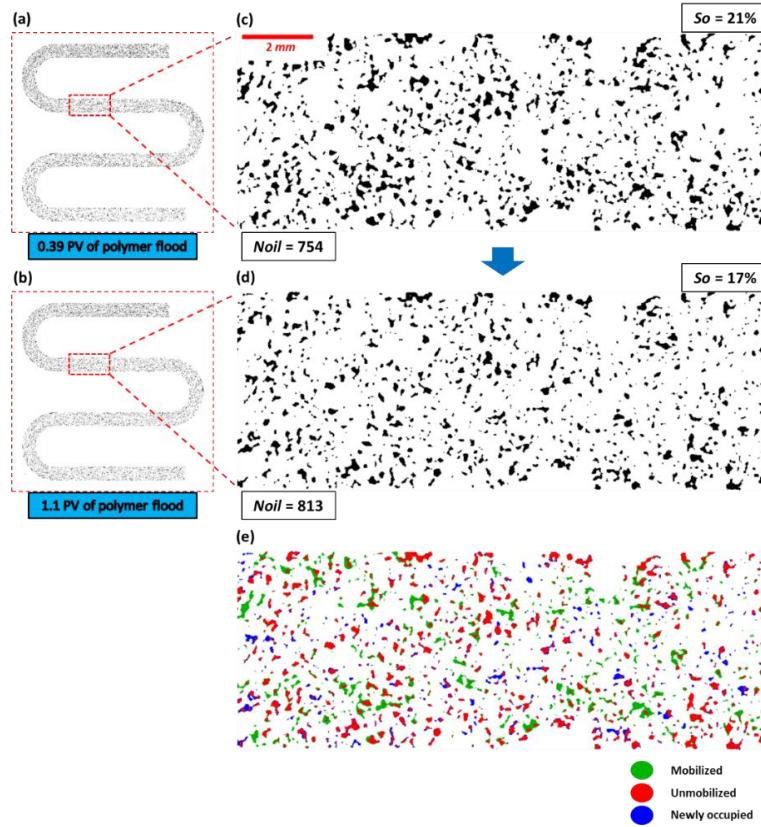


Figure 7.10: Oil mobilization during tertiary polymer flood in experiment 4 (high elasticity and high salinity). Entire domain is shown at (a) 0.39 pore volumes of polymer flood (before oil mobilization) and (b) 1.1 pore volumes of polymer flood (after oil mobilization). (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.

In experiments 5 and 6 where inelastic polymer 1 (high salinity) was used for the tertiary flood, no oil was produced from the outlet of the micromodel. The oil saturation remained unchanged as seen from the saturation plots (Figure 7.6 - #5, #6) and from the

cross-section from Figure 7.11c to Figure 7.11d. The oil in the micromodel was already at residual saturation resulting from the secondary glycerol flood, therefore a conventional inelastic polymer flood cannot recover residual oil by improving macroscopic sweep efficiency which agrees with fractional flow theory (Lake, 2015). No ganglia swelling or mobilization was observed. Slight difference between the two images was observed in Figure 7.11e, which is commonly encountered when changing fluids as additional pressure may cause certain effect. In addition, a slight resolution variation adds to the difference in the smallest droplets (green) in Figure 7.11e.

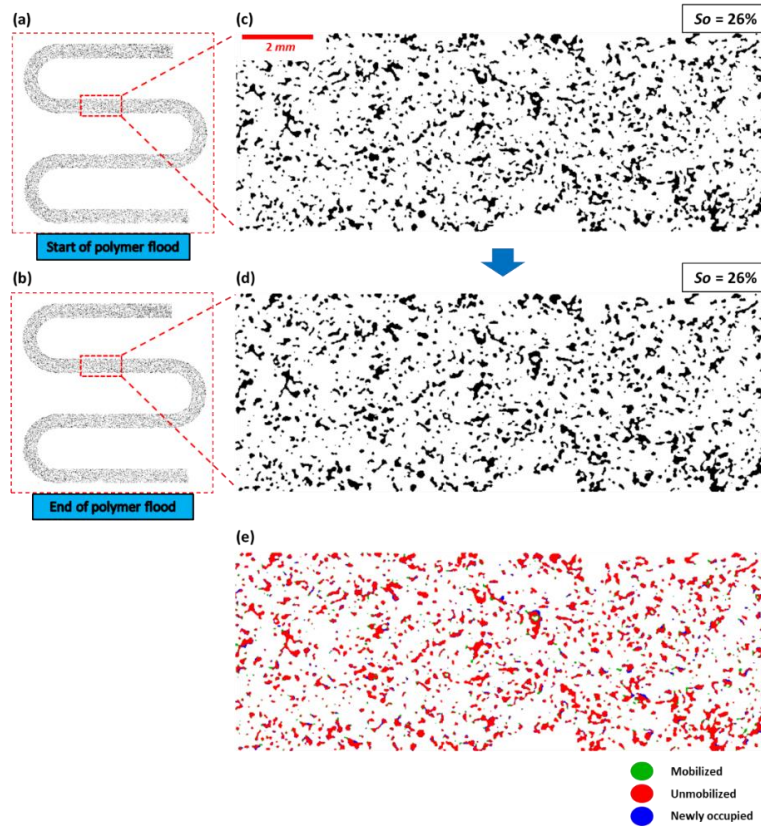


Figure 7.11: Oil distribution during tertiary polymer flood in experiment 6 (low-elasticity and high salinity). Entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.

In experiments 7 and 8 where inelastic polymer 2 (low salinity) was used for the tertiary flood, no oil was produced from the outlet of the micromodel. Similar to experiments 1-3, oil saturation increased by 4.0% and 3.8% for experiments 7 and 8 (Figure 7.6 - #7, #8), respectively, which was caused by ganglia swelling (Figure 7.12cde). Unlike experiments 1-3, redistribution of oil was not observed, as residual oil ganglia enlarged around their original locations and barely moved indicated by the lack of green color (mobilized) (Figure 7.12e). In the cross-section from Figure 7.12c to Figure 7.12d, the oil

saturation increased from 30% to 36% due to ganglia swelling, and the ganglia number slightly decreased by 3.6% as a result of the ganglia reconnection induced by swelling.

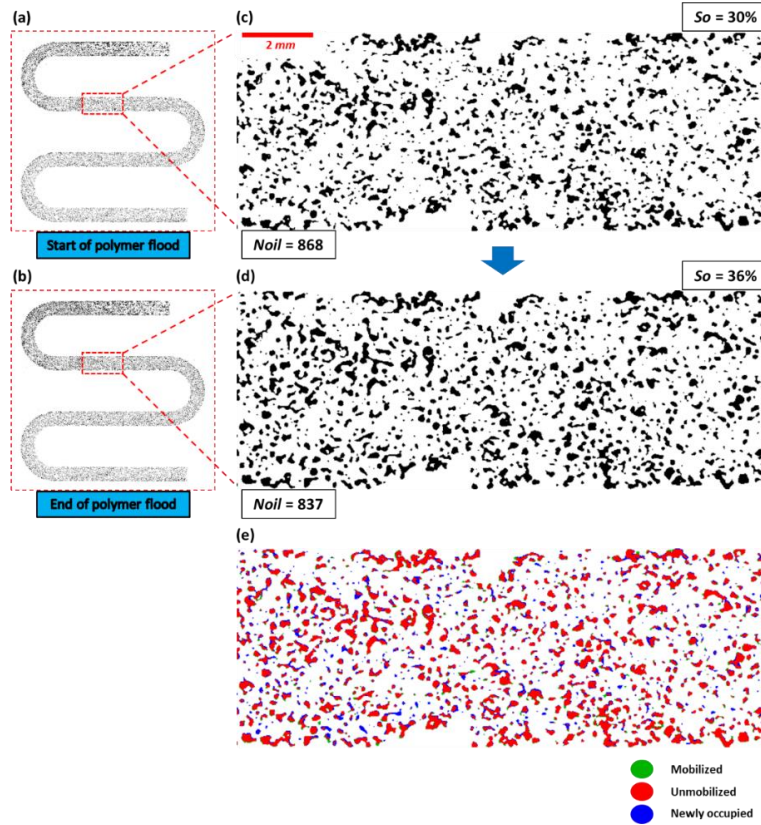


Figure 7.12: Oil swelling during tertiary polymer flood in experiment 7 (low elasticity and low salinity). Entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.

7.4.2.2 Residual ganglia mobilization in post-tertiary viscous aqueous phase flood

In experiments 1-3 where elastic polymer 1 was used in the previous tertiary flood, saturation decrease (of 6.4%, 3.0% and 7.3%, respectively) with oil mobilization (Figure 7.13a) and recovery were observed. The saturation decrease and oil mobilization both

began immediately after starting the flood. The saturation decrease continued for ~ 1.0 pore volume of injection, starting with a gradual decrease followed by a more abrupt decline. The combined oil saturation changes in the tertiary and the post-tertiary floods indicated a net oil saturation decrease (of 4.0%, 1.0% and 4.8%, respectively). The actual net oil recovery due to elasticity should be higher than the net saturation reduction, because the oil de-swelling cannot completely compensate the prior swelling (see experiments 7 and 8), therefore the remaining oil saturation was higher than its original state.

In experiment 4 where elastic polymer 2 was used in the previous tertiary flood, saturation decrease (of 5%) entirely from residual oil mobilization and recovery, and not de-swelling, were observed (Figure 7.13b). The saturation decrease and oil mobilization both began immediately after starting the flood. The decline trend was similar to that in experiments 1-3, as the saturation decrease continued for ~ 1.0 pore volume of injection, starting with a gradual decrease followed by a more abrupt decline. The combined oil saturation changes in the tertiary and the post-tertiary floods indicated a net oil saturation decrease (of 7.0%), which is the total saturation reduction caused by elasticity.

In experiments 5 and 6 where inelastic polymer 1 was used in the previous tertiary flood, no saturation decrease or oil recovery were observed. The oil saturation remained almost unchanged (Figure 7.6 - #5, #6) and no oil production from the outlet was observed.

In experiments 7 and 8 where inelastic polymer 2 was used in the previous tertiary flood, a slight, gradual saturation decrease (of 0.8% and 2.2%, respectively) without oil recovery or mobilization were observed. The oil saturation decrease was completely from the oil ganglia de-swelling and negligible mobilization was observed (Figure 7.13c). The final oil saturation was higher than before the tertiary polymer flood, described by a net saturation increase (of 3.2% and 1.7%, respectively), indicating that the de-swelling did not completely compensate for the prior swelling.

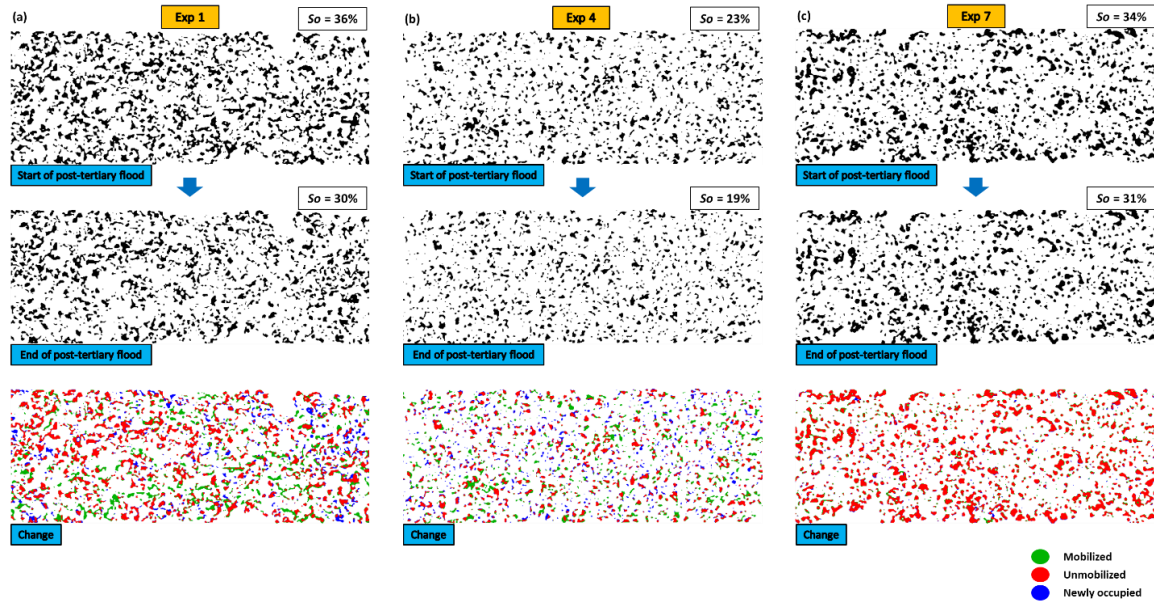


Figure 7.13: Oil saturation and distribution changes in a cross-section during post-tertiary glycerol flood in (a) experiments 1 (high elasticity and low salinity) in the left column, (b) experiment 4 (high elasticity and high salinity) in the middle column, and (c) experiment 7 (low elasticity and low salinity) in the right column. The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.

7.4.3 Mechanistic discussion

7.4.3.1 Elasticity induced redistribution/mobilization & salinity related ganglia swelling

With either high or low salinity, the high-elasticity polymers redistribute the residual ganglia and ultimately lead to residual oil recovery mainly through the post-tertiary flood. Low salinity plays a role supplemental to elasticity, but did not significantly impact the relationship between the ultimate oil recovery and elasticity (Figure 7.7b). Low salinity polymers cause ganglia swelling which contribute to reconnection. Swelling and reconnection, which reduce the capillary trapping force and make mobilization relatively easier, are minor effects on residual saturation reduction compared with redistribution.

Swelling may add to redistribution through morphology changes, but is a minor effect on redistribution compared to elasticity (Appendix C3).

The low polymer salinity induced non-monotonic ganglia swelling has not been revealed in previous works. The observed water-in-oil emulsions are not shear-induced where the emulsion stability increases with salinity (Ling et al., 2018), but are generated spontaneously during the oil/water contact at low flow/shear and static conditions as shown in Appendix C2. In the static experiment (Figure C.2), the crude oil was directly contact with inelastic polymer 1 (low salinity), and water-in-oil emulsions and oil swelling were observed. The swelling rate versus time of the oil ganglion when contacting the low salinity polymer solution is analyzed. We did not investigate the emulsion stability after the spontaneous formation of the emulsions in this work.

The low polymer salinity induced non-monotonic ganglia swelling has not been revealed in previous works. It is not the traditional low salinity effects (improved recovery due to low invading aqueous phase salinity) described in previous studies (Du et al., 2019; Tetteh et al., 2020) in terms of occurrence, process and consequences. For the occurrence, low salinity aqueous solutions flood did not cause emulsions or swelling before or after the polymer flood (Figure 7.8) but could have with traditional low salinity effects. In addition, the emulsions and swelling occurred immediately after switching to polymer flood which contradict previous observations of the slow process that takes tens of hours to days to progress (Sandengen et al., 2016; Sohrabi et al., 2017; Du et al., 2019). In the process, chemical potential difference (between water components) induced spontaneous mass transfer between phases may occur (de Gennes and Taupln, 1982; Lemaire et al., 1983), but cannot sufficiently explain the non-monotonicity. As to the consequences, no recovery was obtained when the low salinity, low elasticity polymer was used, and the initial wettability with oil and glycerol solutions was already water-wet. Both evidences exclude

the occurrence of low salinity effects and their wettability alteration (from oil-wet to water-wet) induced saturation reduction. In summary, this salinity related swelling is a combined effect of the salinity and the specific polymer properties, which needs further investigation.

The in-situ contact angle between oil and the glycerol solution before secondary flood and after post-tertiary flood with different polymers used in the tertiary floods in between are demonstrated in Figure 7.14. No significant contact angle difference was observed before and after each of the cases regardless of different salinity and elasticity of the polymers used. Therefore, the wettability of the system (water-wet) was the same in the secondary flood and the post-tertiary flood, regardless of the elasticity, salinity or IFT differences of the polymers used in the prior tertiary flood. These observations exclude wettability's impact on residual saturation reduction and improved recovery.

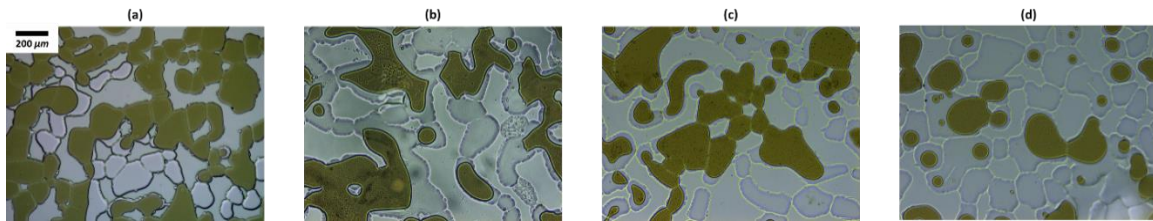


Figure 7.14: Contact angle between oil and glycerol solutions (a) before secondary flood and after tertiary flood when (b) elastic polymer 1, (c) inelastic polymer 1, and (d) elastic polymer 2 was used, respectively.

Polymer salinity appears to affect the interfacial tension (IFT) with crude oil, as the interfacial tension of the high salinity polymer/oil is an order of magnitude lower than that of low salinity polymers/oil (Table 7.2), but IFT is not a significant contributor to the elasticity induced residual saturation reduction. The two polymers with similar, low IFT values (elastic polymer 2 and inelastic polymer 1) show qualitatively different behaviors because of the elasticity difference.

7.4.3.2 Comparison and discussion with existing studies

A considerable amount of residual oil recovery was obtained in the post-tertiary flood that followed the high elasticity polymer floods (regardless of the polymer salinity) in the “*coreflood-on-a-chip*” model. Post-tertiary low elasticity polymers also further reduce the residual oil saturation in corefloods (Erincik et al., 2018; Jin et al., 2020). It is clear that the microscopic ganglia redistribution and morphology changes, although occur immediately, have long-term effects on mobilization and residual saturation reduction. It can be inferred that residual saturation is affected by microscopic distribution and fluid morphology, which play the dominant role in further saturation reduction after the high elasticity flood. Existing analyses of the microscopic redistribution and morphology changes of the NAPL/oil ganglia in rock samples during fluid-fluid displacement have provided enormous amount of related evidence (Berg et al., 2013; Reynolds et al., 2017; Lin et al. 2019; Gao et al. 2020).

The observed residual fluid redistribution can be related to the flow field fluctuation or ganglia oscillation during viscoelastic flow as demonstrated in 2D micromodel experiments (Clarke et al., 2015) and by pore-scale simulation in a pore-throat geometry (Xie et al., 2020). The correlation of neighbouring pores (e.g., the pore spacing) may contribute to the ganglion redistribution and mobilization, within and between pores, by forming unstable eddies in the corners of the pore bodies under unstable flow with proper pore spacing (Browne et al., 2020). In this paper, we did not measure the flow field in the coreflood-on-a-chip model as conducted in the mentioned works (Clarke et al., 2015; Browne et al., 2020), which could be an important component in our future study.

In this work, residual oil reduction was mainly obtained from the post-tertiary flood although the redistribution occurred in tertiary high-elasticity flood. Previous microfluidic studies rarely reported reduction in residual oil saturation, and corefloods obtained

considerable amounts of saturation reduction in tertiary high-elasticity polymer flood (Vermolen et al., 2014; Qi et al., 2017). Geometric differences (e.g., cross-section topology) may explain the different observations, by affecting the transverse redistribution and impacting on flow dynamics. The limited amount of redistribution restricted by the cross-sectional dimension of micromodels caused the lack or delay of the mobilization/recovery, but can lead to residual recovery when redistribution is high in real rocks.

A concern with traditional microfluidics is whether the observations in a small geometry are applicable to larger scales. For example, capillary end effects may impact the distribution of fluids and the displacement efficiency (Huang and Honarpour, 1998; Kang and Yun, 2018; Tanino and Christensen, 2019), and can be significant in the study of viscoelasticity's effects on flow behaviors in water-wet porous media (e.g., glass micromodels). In addition, the redistribution, mobilization and re-trapping of capillary trapped residual oil are also impacted by the spatial scale and topology of the flow geometries, which explains the lack of direct evidence in previous microfluidic studies.

7.5 LIMITATION DISCUSSION

7.5.1 Micromodel

Certain 3D features are included in the 2.5D micromodel by having pore-scale connectivity of grains; however, there are still quantitative and some qualitative differences with three-dimensional spaces in real rocks. The lack of connectivity in the third dimension of the two-dimensional pore arrays potentially affect the pore-scale behavior especially under complex multiphase flow conditions. The effects of such topographical difference on the residual oil remobilization, re-trapping and recovery is not well known yet.

Glass micromodels, despite having similar surface properties as the quartz component of sandstones, are still different in surface mineralogy (e.g., lacking in clays) and morphology (e.g., lacking in surface roughness), which may affect the flow patterns.

7.5.2 Fluids

Only HPAM polymers with different molecular weights were tested in this work and were simply categorized as “high elasticity” and “low elasticity”. Their compositions and therefore properties such as elasticity and salinity, etc., may not be optimal combination. More types of polymers with properties (elasticity, salinity) of wider range are to be considered in future researches.

7.5.3 Rheology and viscoelasticity estimation

Some of the parameters used for estimating the properties (e.g., De) that distinguish the experiments are taken from the empirical data from real rocks. By this, we try to quantitatively show the relative differences among fluids and experiments for better understanding. This can be improved in future with more understanding/data obtained in the porous media/micromodel.

Moreover, our estimation of the polymers’ elasticity in porous media using De is relatively accurate. The rheological behaviors of polymers in porous media are complex, and the parameters including De are defined using empirical methods in an average manner. The actual values can be different from the estimations and in wider ranges. Using the estimation method presented in this paper, we try to quantitatively show the relative difference between high and low elasticity fluids for better understanding. This can be improved in future with more understanding obtained in the porous media.

7.5.4 Image analysis

An open sourced image processing software (ImageJ) was used to process the images acquired in all experiments. The image processing procedure results in systematic error defined by the processing function plugged in the software which is difficult to decode. In addition, the error generated in this process also depends on the geometry heterogeneity, fluid distribution and image quality during the image acquisition process, which makes it more convoluted. These factors always superpose together. A variation of several percent by each factor may add up to a bigger difference in the ultimate results. Therefore, compromises are inevitable although efforts were made during data acquisition and image processing to reasonably reflect the actual experimental processes. Despite of the limitations, the quantitative analysis presented in the study are still significant, as the relative changes in each experiment are the key focus, which are quantitatively consistent among experiments.

7.6 CONCLUSIONS

In this chapter, systematic “*Coreflood-on-a-chip*” experiments were conducted to explore the role of viscoelasticity in reducing residual fluid saturation, which has been observed, but not well explained, in literature studying NAPL/oil recovery. The effects of viscosity and salinity were isolated from elasticity by conducting a secondary flood and a post-tertiary flood with high viscosity Newtonian fluid before and after polymer flood, respectively. This work overall demonstrates that (1) viscoelasticity does help in reducing the residual NAPL/oil saturation without posing extraordinary large viscous force, as flow instabilities resulted from viscoelastic flow induce reconnection and redistribution of residual ganglia; and (2) low salinity enhances the residual fluid reconnection and

redistribution by swelling residual ganglia, therefore enhances the residual fluid recovery when elasticity is high. Systematic screening experiments indicate:

- Recovery of residual fluid occurs only when tertiary flood is of high elasticity. In addition, the recovery is mainly observed after the tertiary flood, during the post-tertiary, inelastic flood. No recovery of residual fluid is observed during tertiary or post-tertiary flood when the polymer is of low elasticity.
- Microscopic observation and ganglia-scale statistics reveal that high elastic polymer flood triggers the redistribution and reconnection of residual ganglia, which allows additional recovery of residual fluid in the post-tertiary flood by viscous Newtonian fluid. The reconnection and redistribution of residual fluid are attributed to flow instabilities during the viscoelastic fluid flood.
- An increase of apparent residual fluid saturation during tertiary flood is always observed under low salinity condition. Microscopic observation reveals that low salinity induces spontaneous emulsification and therefore apparent “swelling” of oil. This swelling effect makes the reconnection of residual ganglia easier, and also contributes to the increase of apparent residual fluid saturation.
- Low salinity enhances the recovery of residual fluid when high elasticity polymer flood is performed. However, low salinity does not impact recovery when the tertiary flood is conducted with low-elasticity polymer.

Chapter 8: Conclusions and Recommendations for Future Directions

8.1 CONCLUSIONS

Microfluidics/micromodels are applied in this work to investigate several important several important multiphase flow phenomena in the enhanced/improved oil recovery processes. The investigated research topics include low salinity effects on improving oil recovery, impacts of microfractures on displacement efficiency, and viscoelasticity's effects on reducing residual oil saturation. Several types of 2.5D (pore-scale 3D) microfluidics/micromodels are fabricated and utilized, including dead-end pore, single channel microfluidics, inch-long, homogeneous micromodels, and foot-long, heterogenous micromodels. Experiments are performed and the obtained results are then analyzed at the pore-scale ($10^0 - 10^1$), meso-scale ($10^1 - 10^2$), inch-scale (10^4), and foot-scale (10^4) geometries.

In the study of the low salinity effects in Chapter 4, the key role of the polar compounds/natural surfactants in oil is demonstrated. First, the adsorption of polar compounds on the solid surface (glass or sandstone rocks) in the high salinity environment causes the system to be oil-wet at the initial state, and the initial oil-wet state is crucial for the subsequent wettability alteration and the improved recovery. Second, when the salinity is low, water in oil emulsions are generated which is attributed to the interplay of the polar compounds and the water diffusion. Oil then begins to de-wet the surface because of the desorption of polar compounds at the interfaces. Experiments in the dead-end pores demonstrated the oil de-wetting and swelling in contact with low salinity water, in support of the interplay between polar components and water diffusion. Flow experiments on the pore-network scale and “*reservoir-on-a-chip*” models both show that the oil de-wetting and swelling under low salinity water flooding leads to a re-direction of flooding liquid

from the swept region to un-swept region, thus help to recover originally un-swept oil. The response time after low-salinity water injection remains at the same order of tens of hours, regardless of that the experiment is scaled-up from 1 to $\sim 10^4$ pores. This time-dependency agrees with the estimated characteristic time of the water in oil diffusion process. A 10% – 18% incremental oil recovery is obtained during tertiary low salinity waterfloods in this model system.

Chapter 5 demonstrates that low salinity effects are significant when there is a sufficient amount of surfactant in the oil because surfactant causes the water-in-oil emulsion and the wettability alteration to a more water-wet state, which are critical for the occurrence of low salinity effects. Wettability alteration and oil swelling significantly change the established steady state from the prior high salinity waterflooding, and cause additional oil mobilization either by sudden decreases due to local instability, or by gradual, capillarity dominant imbibition. The process shows a time-dependency trend, and a delay of $\sim 10^2$ hours is repeatedly observed before any changes occur. The delay is dominated by the polar compounds/surfactant components in oil, and the delay time increases with the decrease of surfactant concentration. The improved oil recovery from low salinity waterflooding, however, does not change monotonically with the surfactant concentration, because of the competition between the wetting tendency of the original resident oil and the later oil-water interactions. The incremental recovery of oils (10 – 20%) with moderate surfactant concentration agrees with the findings in Chapter 4 and literature.

In the study of the impacts of microfracture (Chapter 6), the impacts of microfracture, connected and dead-end, on the displacement efficiency and invasion dendrites and invaded ganglia generation mechanisms are revealed. The experiments show that when the viscosity ratio is unfavorable ($M = \mu_i/\mu_d \ll 1$), a connected microfracture significantly inhibits the invasion of water into the porous matrix and results in low

displacement at low to medium capillary number ($10^{-7} - 10^{-6}$), regardless of whether it is water- or oil-wet. The dead-end microfracture does not inhibit water invasion or dendrites generation as the connected fracture does under both wettability at all capillary numbers in the investigated range ($10^{-7} - 10^{-5}$). On contrary, dead-end microfracture promotes dendrites invasion in regions near the fracture tip due to the sudden change in the geometry. The resulting displacement in the porous matrix is therefore qualitatively different where the connected microfracture greatly decreases the displacement efficiency and the dead-end fracture does not change the overall recovery in the entire geometry, compared to porous matrix without the presence of any microfractures.

In the study of the viscoelastic effects (Chapter 7), the effects of viscoelasticity and salinity on reducing the residual fluid saturation were explored. High viscoelasticity floods ultimately reduce the residual oil saturation after high viscosity Newtonian fluid (low elasticity) floods, regardless of salinity. Most residual saturation reduction, however, was obtained from the post-tertiary low elasticity floods compared to the tertiary high elasticity floods. Ganglia analysis in cross-sections reveals a trend of residual fluid ganglia redistribution/mobilization in the transverse direction which attributes to the viscoelastic flow instabilities. The ganglia redistribution/mobilization subsequently leads to long-term remobilization in the following low elasticity post-tertiary flood. Furthermore, low salinity polymer causes significant oil swelling due to the water emulsion generated inside of the oil. The swelling is not shown when the polymer solution salinity is high or when polymer is not present in the injected aqueous phase (the Newtonian fluids). The oil swelling is non-monotonic, characterized by an initial saturation increase and a subsequent decrease. The mechanism is different from the low salinity effects discussed in Chapters 4 and 5, because of the non-monotonicity and the lack of wettability alteration.

Importantly, this dissertation demonstrated a complete, high efficiency workflow, combining the design, experiments and analysis, of using the microfluidic platform and the “*reservoir-on-a-chip*” technique to investigated complex multiphase flow processes encountered in geologic porous formation in the high capillarity environments. Through systematic experiments and qualitative and quantitative analysis at multiple scales, fundamental details were revealed. Mechanistic descriptions were presented Chapter 4 to Chapter 7. The work also serves as a connecting link between previous studies and future developments in the engineering’s application of microfluidics. The efficiency, reproducibility and representativeness of using the micromodels and the “*reservoir-on-a-chip*” and “*coreflood-on-a-chip*” techniques, as well as the robustness of the post-experiment analysis are continuously demonstrated throughout this dissertation. Overall, this work aims to provide an example of using the workflow of microfluidics/micromodel and to promote future research in the related area, in addition to providing benchmark opportunities for specific studies (Chapter 4 – 7) using similar or different methods.

8.2 RECOMMENDATION FOR FUTURE DIRECTIONS

8.2.1 Microfluidic platform improvement

In future studies, more features and equipment can be incorporated to the present microfluidic platform presented in this dissertation to allow for experiments at elevated temperature and higher pressure. All work presented in this dissertation are performed at ambient conditions (room temperature and atmosphere pressure) to provide benchmark experimental evidences. However, a typical reservoir conditions are usually at higher pressure and elevated temperature, and it is desired to perform experiments at the same or similar conditions. In addition, some phenomena occur only at high pressure, such as the sequestration of supercritical CO₂.

To achieve high pressures, a pressure controller, pressure maintenance box, and pressure monitor are needed. The pressure controller should be able to provide an adjustable, stable back pressure, similar to those equipped with the coreflood experiments. The pressure maintenance box should be robust at high pressure, and allows for observation and visualization by having transparent windows. The pressure monitor can record the in-time pressure of the environment inside the pressure resistant box, and coreflood pressure sensors can be utilized here for the large pressure range.

To also obtain high temperatures, the heating elements and temperature monitor are needed. The heating elements should be able to be installed inside the pressure maintenance box. The temperature monitor units consist of temperature sensor and monitoring software can be implemented for instantaneous temperature recording and monitoring.

8.2.2 Future work on low salinity effects

- The role of surfactant is qualitatively well described and some quantitative analyses are presented. Experiments can be performed to quantitatively identify the effects of surfactant types and concentration, brine salinity, oil viscosity and temperature. The effective surfactant concentration range depends on other factors including the surfactant characteristics, the oil viscosity, temperature, brine salinity, and needs to be determined with experiments. The impacts of these factors are convoluted and the impacts are to be estimated with preliminary experiments.
- The importance of other mechanisms as discussed in Chapter 2.2 can be investigated using microfluidics with different designs. For example, by coating the micromodel surface with saline or calcite to alter the original wettability.
- Coreflood experiments using the same or similar oil (crude oil and mineral oil with surfactant) and brines (salinity varies from 0 ppm to 100000 ppm) can provide more

data from the real rocks during the low salinity waterflooding. Sandstones should be used because they have similar properties to glass and can serve as a good comparison for the proposed mechanisms in this work. Homogeneous cores are preferred to be tested first which eliminates complexities from the geometry heterogeneity and provides a baseline for further experiments.

- Simulations can be performed at the pore-scale to simulate the fluid-fluid interactions and the de-wetting process observed in the microfluidic experiments. For pore-scale simulation, lattice Boltzmann method can be used because it can efficiently simulate the behaviors of small droplets at pore-scale and which also involves fluids interactions. The time scale of the reactions can be obtained and compared with the microfluidic experiments and the other experimental results in literature.
- Reservoir scale simulations using in-house reservoir simulation (e.g., UTCHEM) can be performed to predict oil recovery improvement from low salinity waterflooding. A dynamic wettability alteration model can be developed where the relative permeabilities of the oil and water are functions of the water salinity, oil components (active components content in oil) and reaction time. It is expected that the changes in the relative permeability and therefore the wettability gradually improve the recovery efficiency in the reservoir.

8.2.3 Future work on viscoelasticity effects

- Previous rheological measurements were mostly performed in the rheometers and rock cores and data from micromodels are lacking. The rheological behaviors of the polymers in the 2.5D micromodels and the “*coreflood-on-a-chip*” models can be obtained by measuring the pressure drop at different flow rates and calculating

- the viscosity – shear rate relationship. The results can then be compared with the measurements in the rheometers and cores, and can be used to develop an empirical description of the rheological behaviors of polymer in this type of micromodels.
- In this work, only HPAM polymers with three molecular weights are tested, and the tested elasticity is in a limited range ($1 < De < 10$ and $De \sim 100$). In future study, other types of viscoelastic polymers, such as polyethylene oxide (PEO), should be tested to clarify the effects of polymer characteristics on the residual fluids' mobilization process. The salinity and concentration of the polymer solution should be varied to obtain different viscoelasticity in a wider range ($0.1 < De < 500$), which can be used to reveal the quantitative relationship between the elasticity and reduction of residual saturation.
 - The non-monotonic oil swelling induced by the low salinity polymer flood is a very interesting phenomenon not revealed before. It is still unsure how the polymer properties, the salinity and the flows impact the dynamics of the non-monotonic swelling. In future work, both dynamic (flooding experiments) and static experiments (contacting the polymer with oil at static state) are needed with different type of polymers and different salinities to characterize the swelling trend. The swelling and emulsion generation rates can be quantitatively related to the salinity and polymer concentration in the solution at both static and dynamic conditions with each type of polymer tested. The underlying mechanisms can be discussed when more observations and analysis are obtained.
 - REV scale to core-scale simulations of inch- to foot-long geometry can be performed to predict the effect of the residual oil reduction caused by the viscoelastic flood using computational fluid dynamic method. The model should be able to capture the residual ganglia mobilizations and redistribution during the high

viscoelastic flood. The connection between the ganglia mobilizations and redistribution and further residual saturation reduction should be delineated through simulation.

Appendices

A SUPPLEMENTAL DISCUSSION FOR THE STUDY OF LOW SALINITY EFFECTS

A1 Crude oil viscosity

The crude oil (220cp) was used in this work because it is active and is more likely to contain polar compounds. In the literature, high viscosity oil has been used to study the low salinity effect. For example, Song and Kovscek (2015) used an oil with a viscosity of 105.7 cp at 22°C, Emadi and Sohrabi (2013) used an oil with a viscosity of 93 cp at 50°C.

The single-pore experiments (Experiments 4 and 5) with diluted crude oils with much lower viscosity (2-5 cp) show similar pore-scale effect. We discussed the effect of oil viscosity on the oil swelling dynamics in section 3.1.3 (Line 226-252). Based on our observations and hypotheses, we think that using a lighter active oil could produce qualitatively similar results as we saw in this work, although the lower viscosity can lead to higher recovery from secondary water flooding, which may affect the tertiary flooding performance. However, more work is needed to reveal how oil viscosity affects the overall flow behaviors besides the oil swelling.

A2 Ageing time

The ageing time in our experiments was 10 hours. In the literature, investigators have used longer ageing time from days to weeks to mimic the real reservoir conditions. In our systems, 10 hours of ageing was enough to establish a pre-condition. We want to focus on simple and first-order effect resulted from the reaction between the oil and the solids. Longer ageing time might trigger more complicated chemical or physical reactions between oil and grain, which may lead to longer reaction time during the tertiary low salinity flood.

We observed the low salinity effect and its related phenomena (oil swelling, de-wetting, etc.) consistently at all three scales. However, we did not exclude the possibility that longer ageing time could have changed the results to higher order degree and did not perform tests on longer ageing times. We have not yet performed optimization of ageing time, which is very meaningful work but requires specific and systematic investigations. For the current stage, our goal of aging is simply to (1) establish an oil-wet condition that cannot be changed by high-salinity flooding and (2) ensure consistency of all our micromodel experiments.

A3 Micromodel cleaning

We used a standard procedure to clean the used micromodels for reuse. To clean the micromodel containing crude oil and brine, we first injected hexanes until crude oil is completely dissolved and washed out of the micromodel. Then we injected acetone to clean the remaining hexanes and any oil-soluble components dissolved in hexanes. Finally we injected DI water to clean any water-soluble components like salts. After cleaning procedures, we placed the micromodels on a hot plate at 110 degree Celsius until they are dry. By cleaning, the micromodels are cleaned close to the original state. During the cleaning, we checked under the microscope to make sure no residual was left from the previous cleaning procedure.

Additionally, we used fresh new micromodel chips and used each chip limited times (usually less than 3 times) to minimize any possible effect of repeated cleanings. During all the experiments, we did not notice the effect of the cleaning chemicals, as the wettability consistently changed from water-wet to more oil-wetting.

A4 In-situ contact angle measurement

For the in-situ contact angle measurement, we analyzed a higher magnification image, drew lines along the oil-water and the water-solid interfaces and measured the angle between the two lines. Considering the uncertainty of this method we included the error bars ($\pm 10^\circ$) in the plot. The goal was not to precisely measure the contact angle, but to show the time-dependent process of wettability change by simple quantifications. The in-situ contact angle measurements are debatable and errors are generated (Andrew et al., 2014; Deglint et al., 2017; Fassi-Fihri et al., 1995; Schmatz wt al., 2017). This is because (1) the observation scale (nm, μm or mm), the image resolutions and the light intensity affect the image analysis accuracy, (2) the measurement in a 2D projection lacks the information in the third dimension, and (3) the geometry, combined with the observation scale, affect the determination of the contact locations. These effects can be more significant when the liquid is not wetting the surface. Therefore, the value of the measured angles are only partially quantitative. The goal was not to precisely measure the contact angle, but to show the time-dependent process of wettability change by simple quantifications.

A5 Microscopic details of crude oil de-wetting and W/O emulsion generation during DI water injection in pore-network scale experiments

Higher magnification observations of crude oil droplets before and after 3 days of DI water injection in Experiment 5 are shown in Figure A.1ab. In Figure A.1a (captured before low salinity waterflood), it can be seen that the residual oil droplets occupied the pore throats while there were many small oil droplets adhered to the glass surface. Both observations strongly indicate an oil-wetting state before the low salinity waterflood.

As shown in Figure A.1b (captured after DI waterflood), the oil droplets de-wetted the on small oil droplets remained on the glass surface. The crude oil shown here after the

low salinity waterflood was the non-wetting phase. The many ‘dark dots’ dispersed in the yellow crude oil phase can only be water droplets since the system only contained water and oil components. The small water droplets appeared to be darker than the surroundings under the transparent light because they reflected some amount of the light. The size of the water droplets in our study is on the order of microns after ~10 hours of contact with low salinity water.

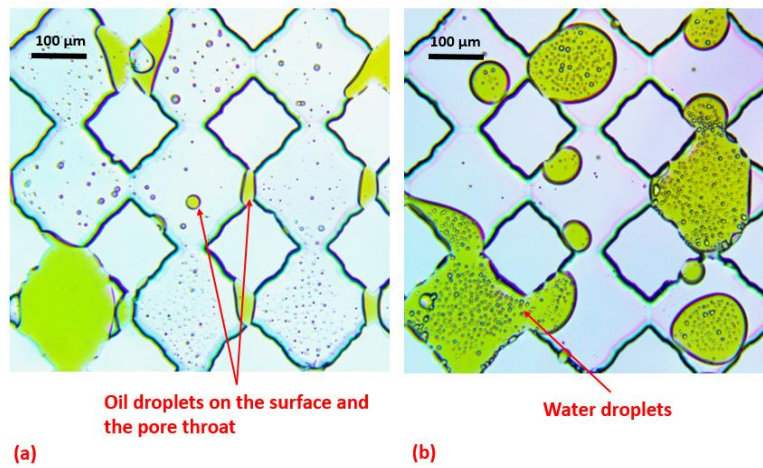


Figure A.1: Higher magnification images of crude oil droplets in pore networks in Experiment 3 (a) before DI water injection (oil was the wetting phase) and (b) after 3 days of DI water injection (oil was the non-wetting phase).

A6 De-wetting and water in oil emulsification behaviors of model oil (dodecane) mixed with surfactant (0.1% Span 80)

The oil swelling (due to water in oil emulsions) and wettability alteration were also observed when DI water came into contact with dodecane oil with 0.1% surfactant (Span80). Contrary to a pure dodecane-water system which is water-wet, the system with a mixture of dodecane and oleic surfactant (e.g. 0.1%) was initially oil-wet. During the DI water injection, water emulsions gradually formed inside the oil droplets (dark dots in the red circles), and oil in the dead-end pores gradually de-wetted the surface and swelled

(Figure A.2). We zoomed in the images captured during the process and roughly plotted the contact angle with time as shown in Figure A.3. There was a trend of a contact angle decrease, indicating the de-wetting of the dodecane droplets. After three days of DI water injection, the system changed from oil-wet to slightly water-wet. The uncertainty of our estimation was considered by including the error bars ($\pm 15^\circ$) in the plot. Compared to the crude oil-water system, the de-wetting trend in the dodecane-water system was less significant, possibly caused by the concentration and/or composition differences between the artificial surfactant and the polar compounds in crude oil. More work needs to be done to account for the different performance between the natural polar compounds and the artificial surfactant.

For a pure dodecane-water-glass system, water is the wetting phase and water-in-oil emulsification is not significant (Armstrong and Wildenschild, 2012; Bartels et al., 2016). Dodecane droplets escapes from the pores quickly because of its low viscosity, therefore time-lapse images of similar time-scale was unable to be captured.

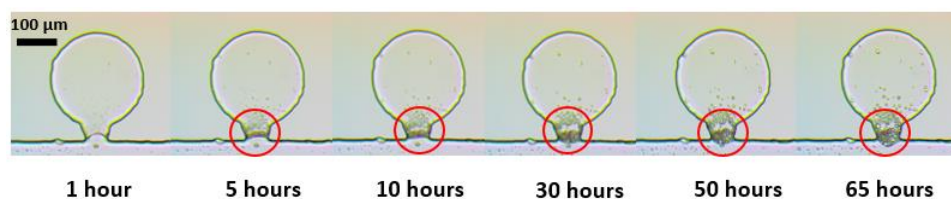


Figure A.2: Dodecane with 0.1% surfactant (Span 80) in dead-end pores during DI water injection at different times. Dodecane was in the pores and DI water was in the main channel. Circled dark areas contain water in oil emulsions.

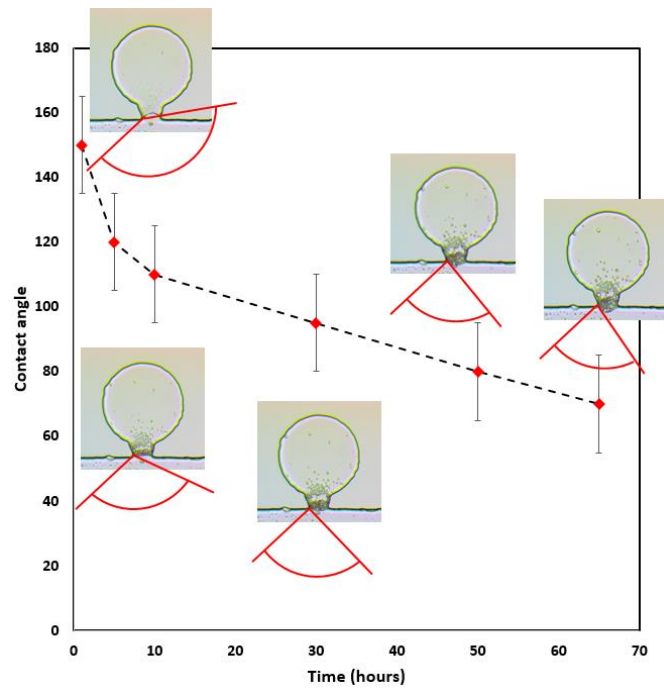


Figure A.3: Contact angle between dodecane with 0.1% surfactant (Span 80) and DI water in dead-end pores vs. time.

A7 Limitations of microfluidics in this study

- The pores are artificially designed and homogeneous. This can be improved by using pore structure patterns taken from a real rock.
- The surface properties are different from real rocks. This can be addressed by surface modifications to achieve desirable properties.
- The design is 2D (with some 3D features) and lacks the connectivity in a true 3D space.
- The size is limited to up to several inches. This can be addressed by upscaling methods.

B SUPPLEMENTAL RESULTS FOR THE STUDY OF MICROFRACTURE'S IMPACTS

B1 Pore-Scale Visualizations of wettability

Immediately after flow experiments, we checked the wettability under the microscope and documented the wettability. Pore-scale images captured immediately after flow experiments are shown in Figure B.1.

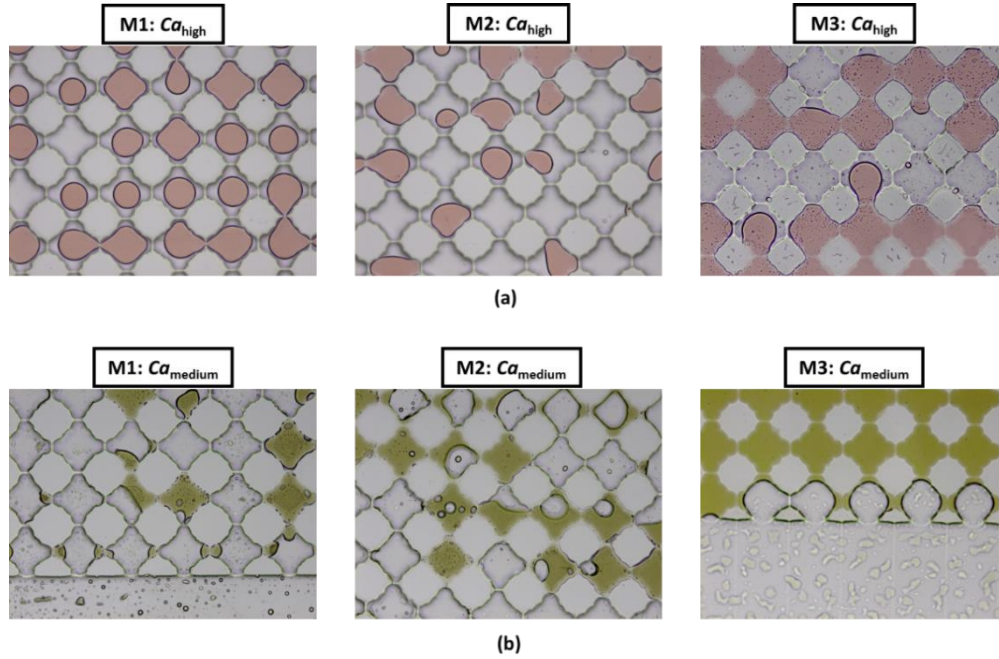


Figure B.1: Pore-scale images of (a) mineral oil (red) remaining after water injection in M1, M2 and M3, and (b) crude oil (beige) remaining after water injection in M1, M2 and M3. Mineral oil and crude oil are the non-wetting and wetting phase, respectively.

B2 Fractal Dimension Analysis

The fractal dimension of a viscous fingering pattern provides a quantification of its complexity. We have implemented a box-counting method in which an image of a viscous fingering pattern is discretized into meshes (boxes) with equal size (ℓ). The number of

boxes (s) that fall into the pixels of the invading phase are then plotted with respect to the box size (ℓ) in a log-log plot, with the slope providing the fractal dimension. Figure B.2 illustrates utilizing box-counting method.

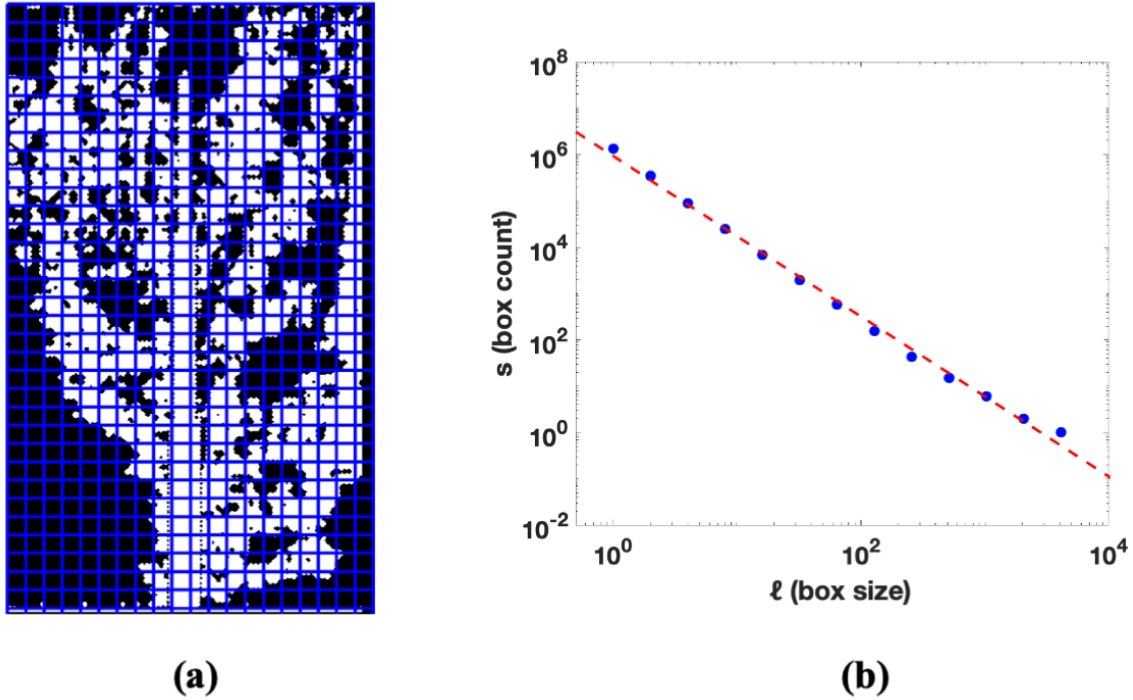


Figure B.2: Example of (a) an image divided into boxes with size ($\ell = 64$ pixels) and (b) log-log plot of the box numbers that contain an invading phase pixel. The slope of the plot is the fractal dimension (D_f) – in this case 1.73. The smallest box sizes are limited to the voxel resolution (approximately $12 \mu m$).

B3 Reproducibility Study

Repeated experiments (shown in Figure B.3a-f) demonstrate qualitative consistency in viscous fingering generation mechanisms that were conceptualized in Figure 5.1c. Viscous fingering is inherently a random phenomenon; however, we observe that channeling due to microfractures creates a non-random dendrite in the middle of the porous

domain. Oil saturation curves in case (a) - (e) also show good quantitative consistency between replicate experiments with a small variant of less than 5%. In case (f) where the repeated experiment (run #2) was conducted in a different mix-wet micromodel, the oil saturation falls in-between the oil-wet case (run #1) and oil-wet case (# 3), while the fingering patterns are qualitatively similar. Further Monte Carlos type investigations are required to establish uncertainty intervals for the quantitative analysis conducted in this work. We have shown the invasion patterns along with the $S_o(t)$ plots in 6 replicate experiments (a-f) in Figure B.3. The 6 cases include:

- a) mineral oil - low Ca - M1
- b) crude oil - low Ca - M2
- c) mineral oil - medium Ca - M2
- d) mineral oil - high Ca - M2
- e) emineral oil - low Ca - M3
- f) mineral oil - high Ca - M3

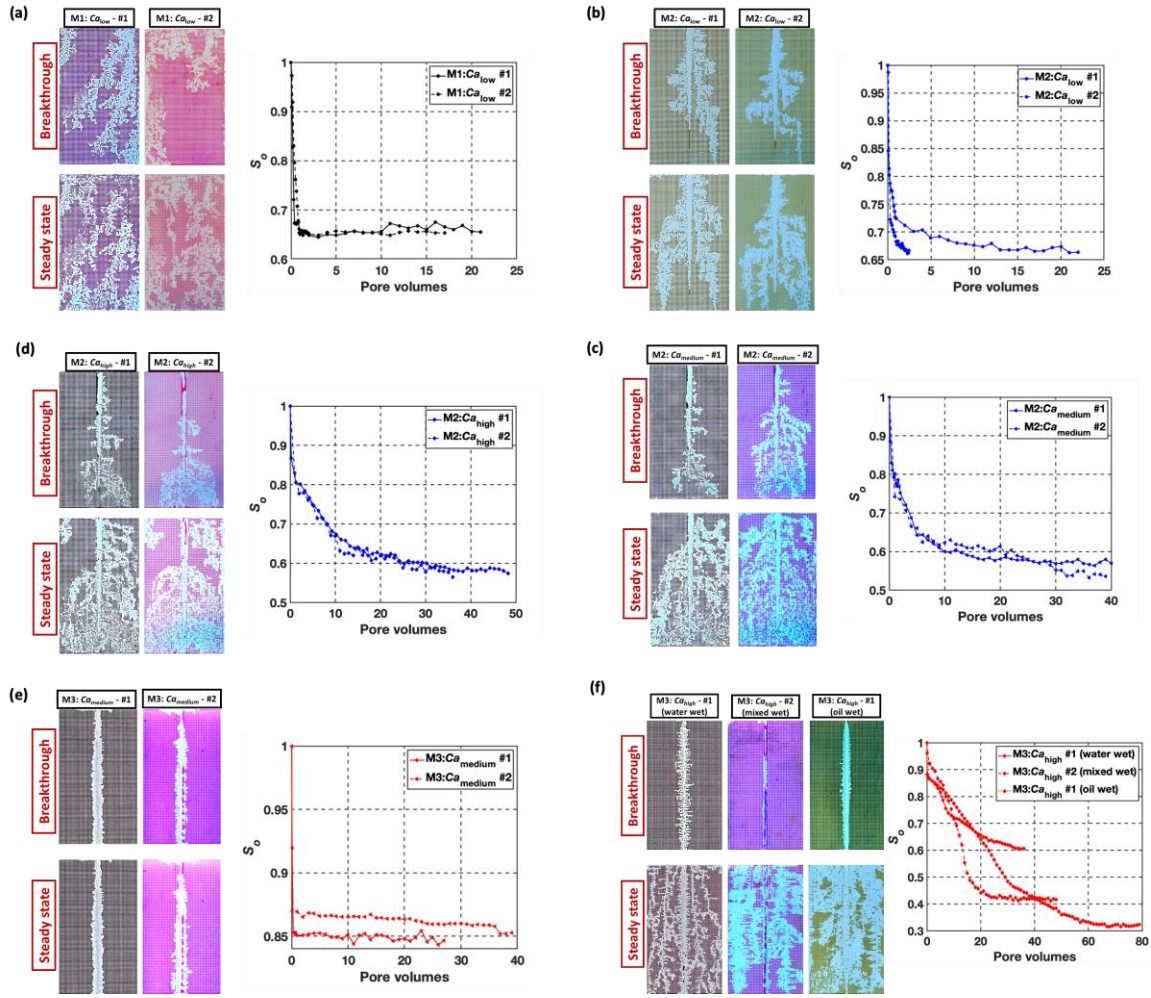


Figure B.3: Repeated experiments (run #2) in 6 cases are shown in (a) - (f). Note that case (f) run #2 was conducted in a different micromodel which tended to be “mixed-wet” instead of water-wet compared with #1 in (f), therefore the oil saturation curve falls in-between the mineral oil case (water-wet) and crude oil case (oi-wet).

C SUPPLEMENTAL RESULTS AND ANALYSIS FOR THE STUDY OF VISCOELASTICITY’S EFFECTS

C1 Micromodel permeability

The permeability of the micromodel was determined by measuring the steady state pressure drop across the flow domain by injecting deionized water at constant flow rates.

Figure C.1 demonstrate pressure data measured in one case. At each flow rates, the pressure value was recorded after a steady state was reached. The slope represents the pressure drop (kPa) per unit flow rate (ul/hour) and is used for permeability calculation using Darcy's law.

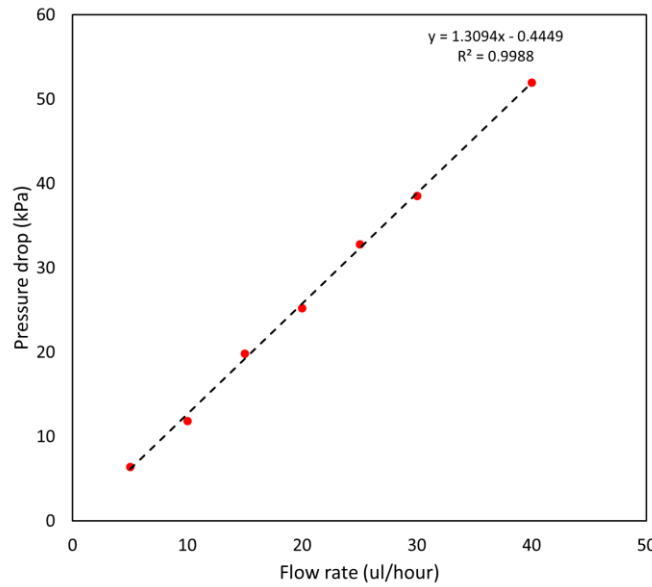


Figure C.1: Pressure drop at different water injection rates

C2 Ganglia swelling during static experiment with high elasticity, low salinity polymer

To separate the effect of low salinity from flow induces changes, a static experiment observing the fluid-fluid interaction between oil and low salinity, high elasticity polymer (elastic polymer 1) was performed in a simple homogeneous pore-network. The static experiment lasted for 60 hours which was at similar time scale with the dynamic experiments (about 70 hours). Oil ganglia became darker and swelled as emulsions generated (Figure C.2a). No ganglia coalesce/reconnection or movement was observed in the captured area at completely static condition despite of the swelling, indicating that the redistribution was not (at least not mainly) caused by swelling.

The swelling rate versus time of one of the ganglia in the captured images is analyzed and presented in Figure C.2b. The ganglion size increased rapidly in the first 40 mins by 2.5%, afterwards, the increase slowed down and the swelling rate at 60 hours was 2.8%. The swelling trend in the static experiment was monotonic which was different from the non-monotonic trend in the dynamic experiments, indicating that the elasticity induced flow instabilities also had great impact on the ganglia morphology changes in addition to redistribution. This further proves that low polymer salinity by itself is not sufficient to cause residual saturation reduction and oil mobilization and recovery, which is consistent with the observations in experiments 7 and 8.

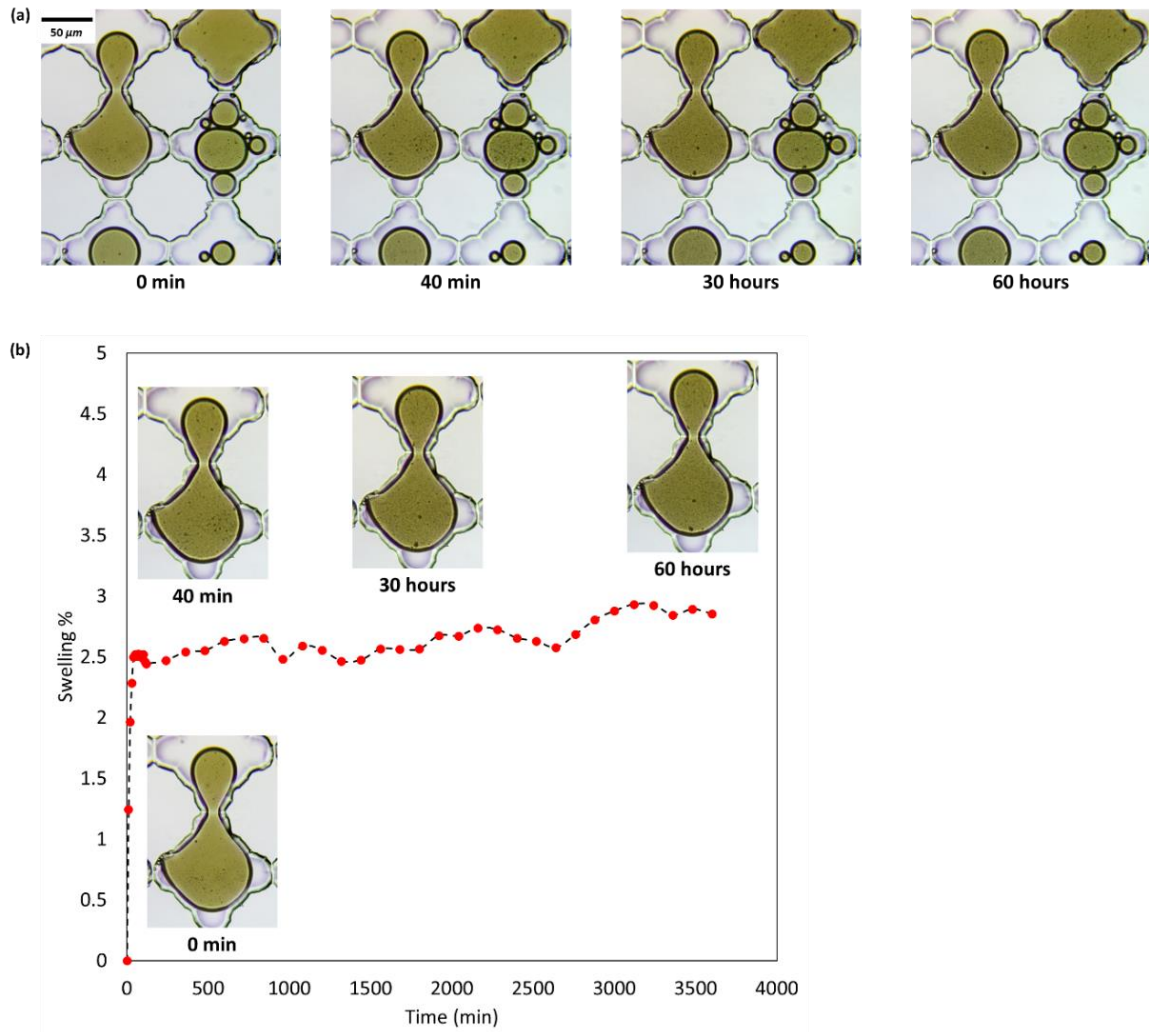


Figure C.2: (a) Oil ganglia at 0 min, 40 min, 30 hours and 40 hours during static experiment with elastic polymer 1 (low salinity and high elasticity). (b) Ganglion swelling percentage versus time.

C3 Non-monotonic ganglia swelling during tertiary high elasticity, low salinity polymer flood in experiment 1

During the tertiary flood in experiment 1 where elastic polymer 1 (low salinity) was used, oil saturation initially increased in the first 1-2 pore volumes of injection and then decreased gradually during further injection but was still higher after than before tertiary flood, corresponding to the swelling and partial de-swelling observed at the pore-scale. The

peak saturation increase was 5.6%, 7.0% and 5.8%, and the ultimate saturation increase at the end of tertiary flood was 2.4%, 2.0% and 2.7% for experiments 1-3, respectively.

The non-monotonic swelling and saturation changes are visually demonstrated in the zoomed-in cross-section in Figure C.3. Oil ganglia redistribution in the transverse direction was observed, as indicated by the locations of the green (mobilized) and blue colors (newly occupied) in Figure C.3gh. As a result of the swelling and the later partial de-swelling, the oil saturation increased from 30% to 35% and then decreased to 32% in the cross-section in Figure C.3def. As a result of redistribution and reconnection, the number of oil ganglia decreased by 13.3% from Figure C.3d to Figure C.3e and 7.7% from Figure C.3d to Figure C.3f. Significant more redistribution with lower saturation and more ganglia number are presented at the end of polymer flood (Figure C.3h) than at peak oil saturation (Figure C.3g). Therefore, swelling (higher saturation) mainly contributes to reconnection which may add to redistribution, but is a minor effect to redistribution compared with elasticity.

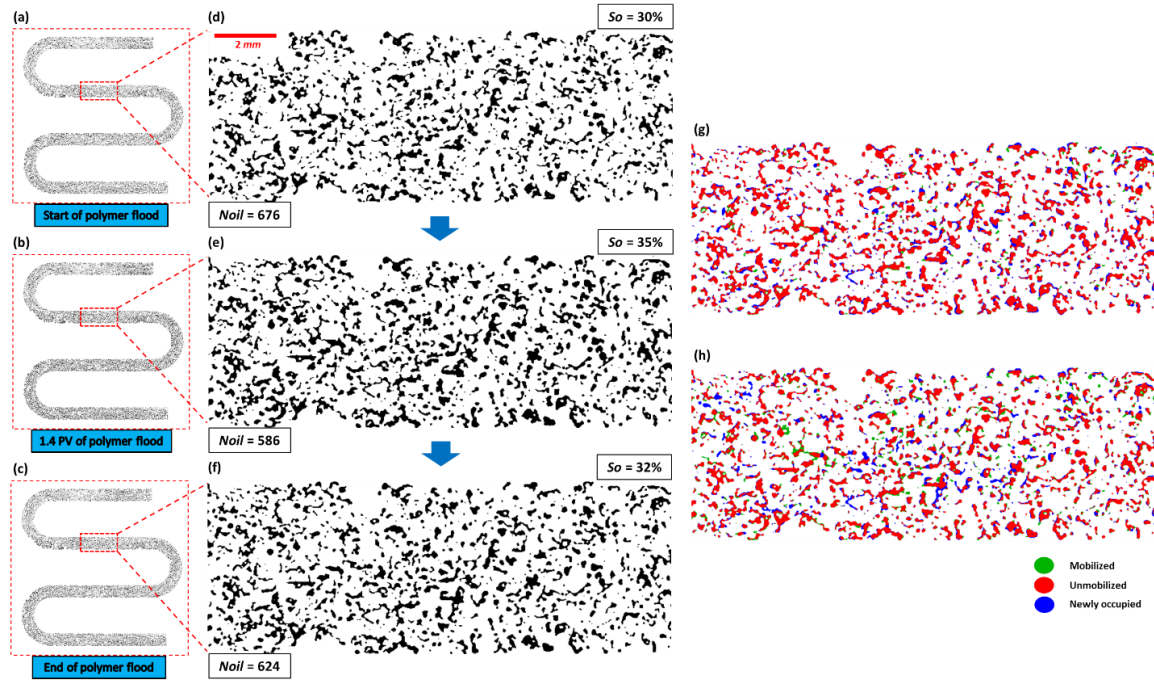
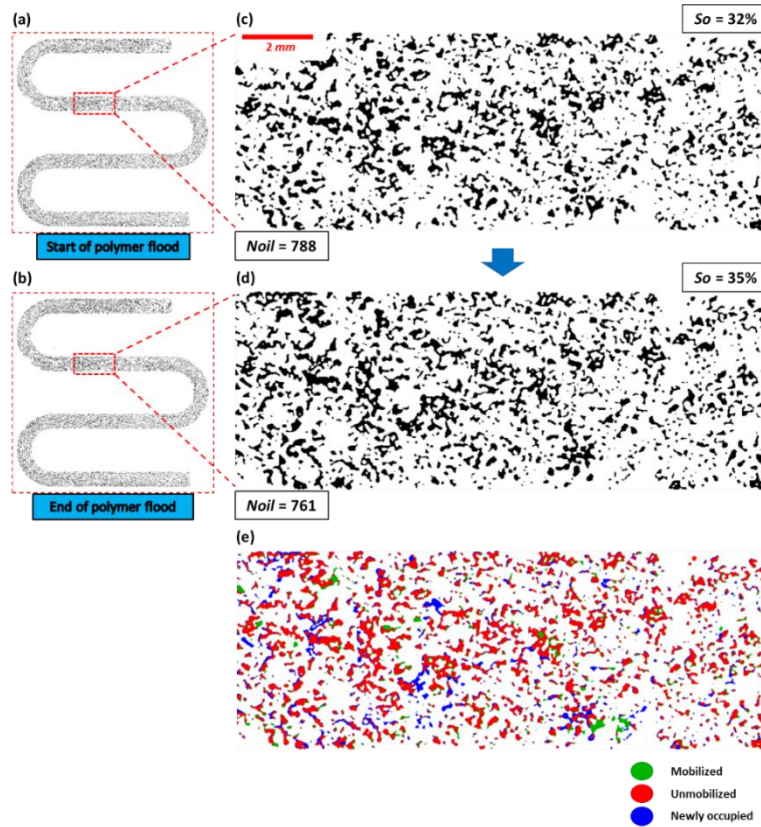


Figure C.3: Oil swelling and redistribution during tertiary polymer flood in experiment 1 (high elasticity and low salinity). Entire domain is shown at (a) the beginning of polymer flood, (b) 1.4 pore volumes of polymer flood at peak oil saturation, and (c) the end of polymer flood. (d), (e), and (f) are the same cross-section zoomed-in from (a), (b) and (c), respectively. (g) Changes from (d) to (e). (h) Changes from (d) to (f). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.

C4 Ganglia swelling and redistribution during tertiary high elasticity, low salinity polymer flood in experiments 2 and 3

Ganglia swelling, reconnection and transverse redistribution were also observed from experiment 2 (Figure C.4A) and experiment 3 (Figure C.4B) during the tertiary flood where elastic polymer 1 (low salinity) was used. In the zoomed-in cross-section from Figure C.4A-c to Figure C.4A-d, the oil saturation increased from 32% to 35% due to swelling, and the number of oil ganglia decreased by 3.4% as a result of redistribution and reconnection. In the zoomed-in cross-section from Figure C.4B-c to Figure C.4B-d, the oil

saturation increased from 37% to 41% due to swelling, and the number of oil ganglia decreased by 8.8% as a result of redistribution and reconnection.



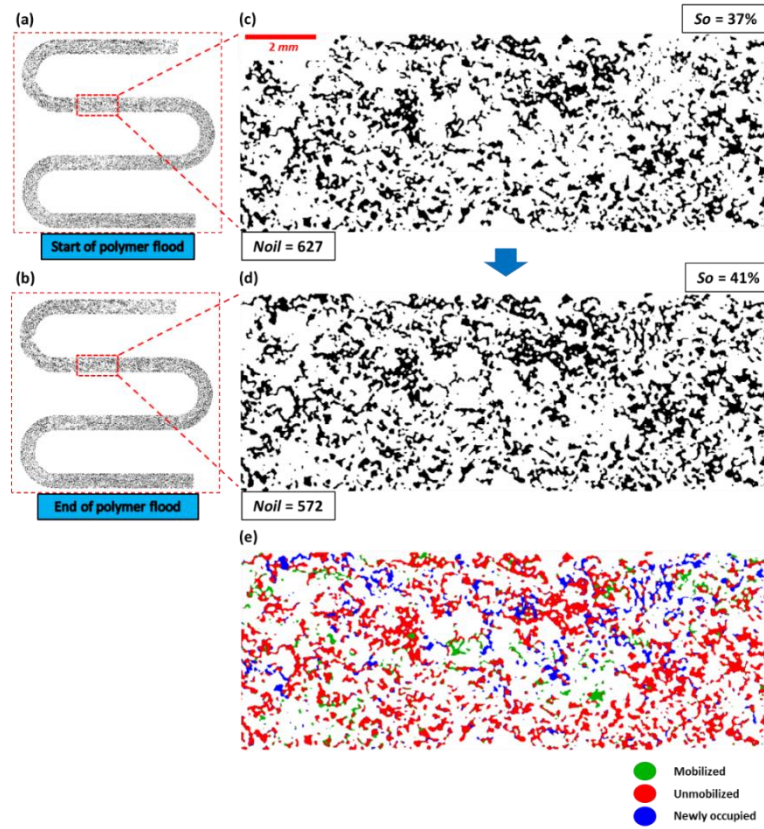


Figure C.4: Oil swelling and redistribution during tertiary polymer flood (high elasticity and low salinity) in experiment 2 (A) and experiment 3 (B). In both (A) and (B), entire domain is shown at (a) the beginning of polymer flood and (b) the end of polymer flood. (c) and (d) are the same cross-section zoomed-in from (a) and (b), respectively. (e) Changes from (c) to (d). The green, red and blue colors represents the mobilized, unmobilized, and newly occupied oil ganglia, respectively.

C5 Oil cluster mobilization process during tertiary high elasticity polymer flood in experiment 4

During the tertiary flood in experiment 4 where elastic polymer 2 (high salinity) was used, the volume of mobilized oil increased along moving towards the outlet, which indicated the recovery was from the entire micromodel. The length of mobilized oil cluster, however, first increased and then decreased (Figure C.5). Initially, the increase of mobilized oil cluster length was solely contributed to the accumulation of mobilized oil

along the flow pathway (e.g., Point 1 to Point 2). After that, there was a period when the mobilized oil cluster stretched and accumulated and the same time (e.g., Point 3). Finally, the cluster length decreased as the mobilized oil cluster became more compact (Point 4). Shortly after point 4, the mobilized oil cluster flew out of the geometry.

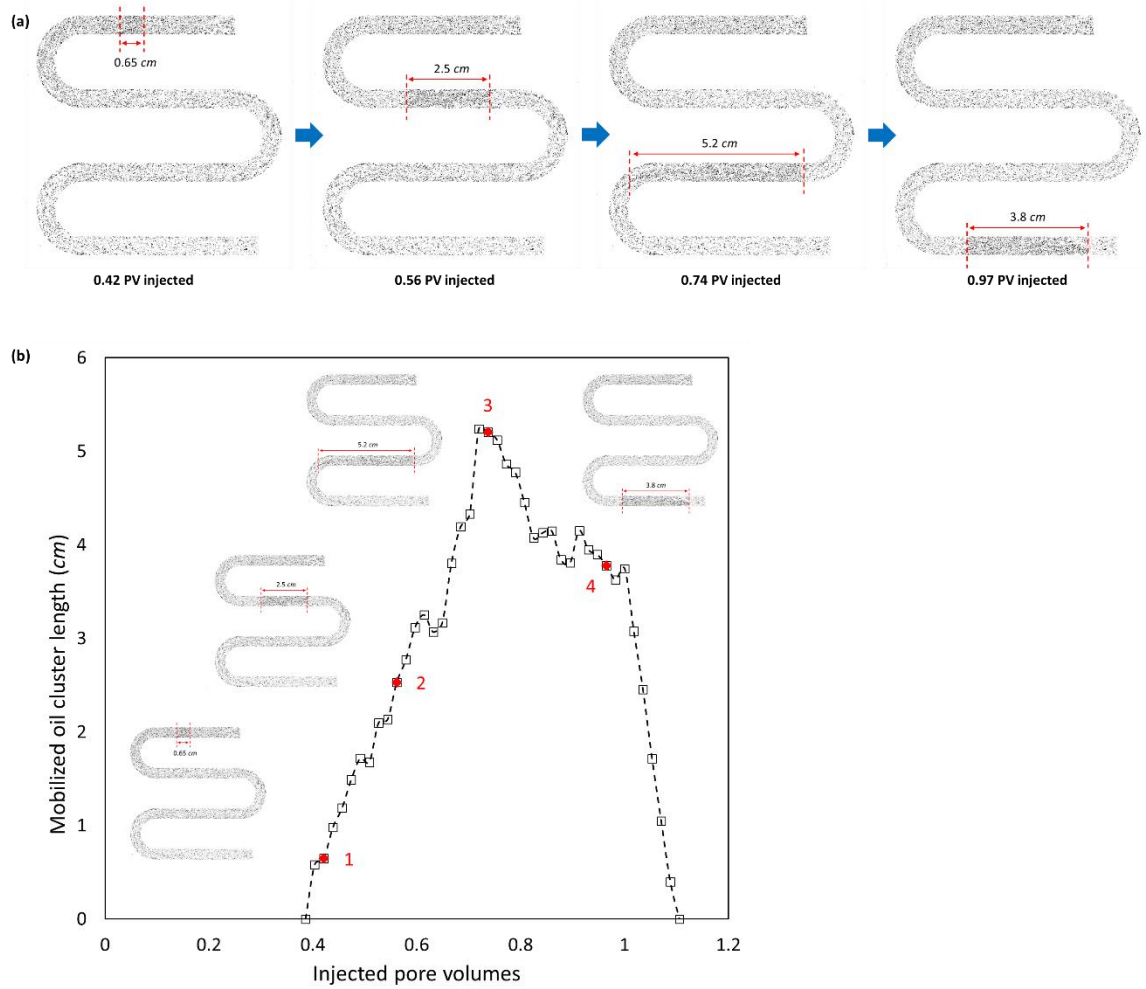


Figure C.5: (a) Oil mobilization process at different times during tertiary polymer flood in experiment 4 (high elasticity and high salinity). (b) Mobilized cluster's length versus injected pore volumes.

D SENSITIVITY ANALYSIS OF THE IMAGE ANALYSIS METHODS

In this section, the sensitivity analysis of the image analysis performed in this dissertation is presented and the uncertainty generated during the image analysis is discussed. A series of images with different fluid distributions and saturations (mineral oil and water) from one experiment in Chapter 6 are used in the sensitivity analysis. The image histograms after image enhancement and segmentation using different thresholding algorithms are presented. The saturations measured from the binarized images using different thresholding algorithms are compared.

D1 Histogram and threshold in image segmentation

Five images and their histogram charts before and after the enhancement of the raw images captures in Experiment 4 in Chapter 6 are shown in Figure D.1. In the experiment, water and mineral oil distribute in a “*reservoir-on-a-chip*” micromodel geometry as shown in Table 6.3. The enhancement was performed using “Enhanced Local Contrast (CLAHE)” function in ImageJ to enhance the separation of phase boundaries (Figure D.1ab). The histogram represents the color intensity distribution in the images which is used to distinguish different phases when thresholds are identified and applied. Two peaks are distinguished in the histogram charts in Figure D.1b and c and the peaks on the right correspond to the oil phase. The enhancement widens the distribution band in the process.

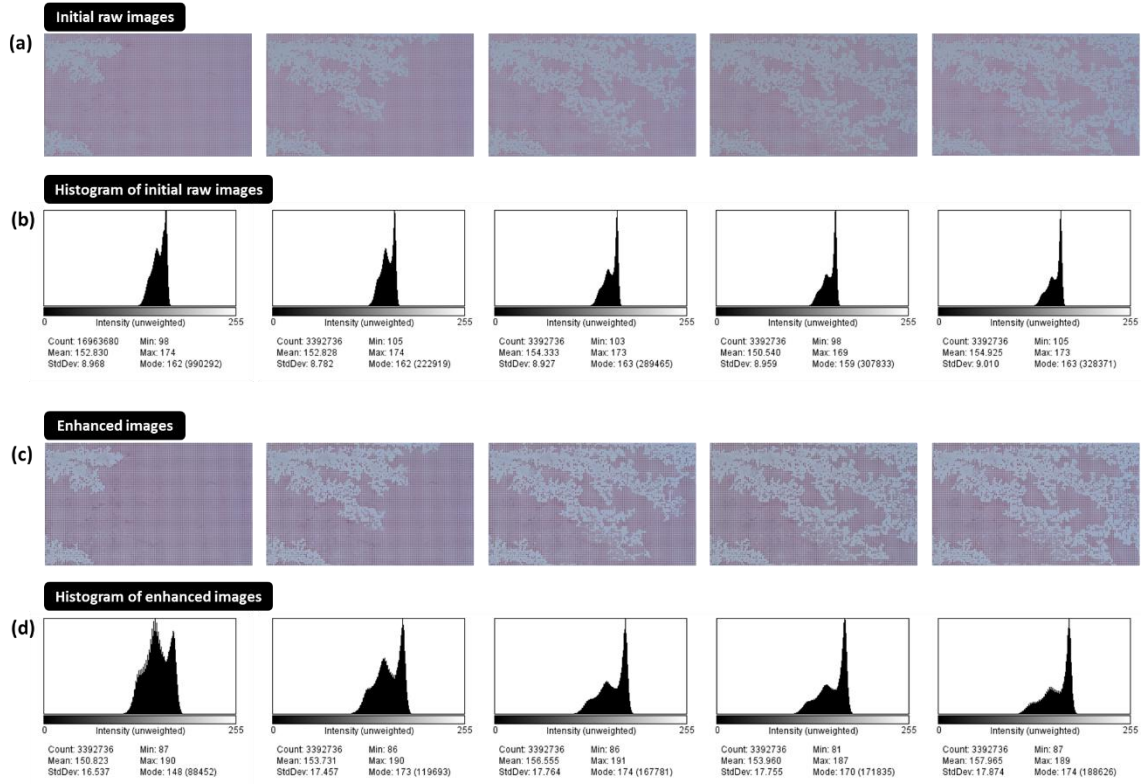


Figure D.1: Histogram changes during image enhancement procedure. (a) Initial raw images. (b) Histogram of the raw images. (c) Enhanced images. (d) Histogram of the enhanced images. The pink phase is mineral oil and the light phase is DI water.

In image segmentation, five different algorithms are used to binarize the images into black (oil) and white (water and grains) as shown in Figure D.2. Different algorithms choose threshold values differently (Table D.1) which lead to slightly different binarizing results. Before the segmentation, the histogram values in each image are distributed in a continuous range as shown in Figure D.1d. In the segmentation, if the histogram at a pixel is larger than the chosen threshold value, the histogram value is reassigned to 255 which corresponds to the black color in binarized images; if the histogram at a pixel is smaller than the chosen threshold value, the histogram value is reassigned to 0 which corresponds to the white color.

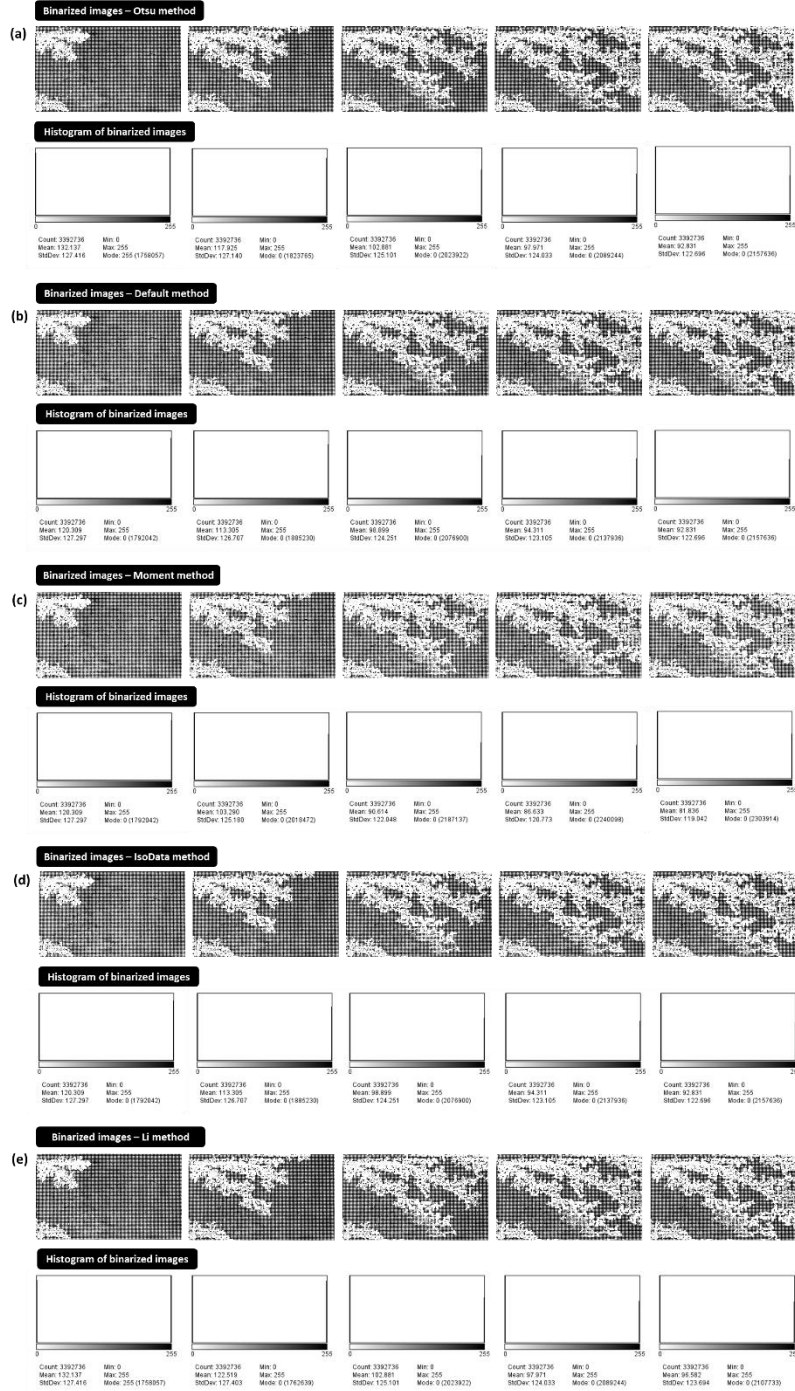


Figure D.2: Histogram changes during image segmentation using five different thresholding algorithms with (a) Otsu, (b) Default, (c) Moment, (d) IsoData and (e) Li methods. Oil is in black (histogram value = 255) and water and grains are in white (histogram value = 0).

Table D.1: Threshold values for segmentation in different methods

Image #	Threshold				
	Otsu	Default	Moment	IsoData	Li
1	151	149	149	149	151
2	152	151	149	151	153
3	153	152	150	152	153
4	150	149	147	149	150
5	153	153	150	153	154

After the segmentation, each image contains two values (0 and 255) at both ends of the histogram charts (Figure D.2). The peak heights represent the fractions of the segmented phases, which are sometimes different in the same images because of the different threshold choices. The peak height at the right side decreases as the oil saturation (black phase) decrease in the image sequence.

D2 Saturation measurement through image analysis

The oil saturation (the black phase) is then measured directly from the binarized images by calculating the areal fractions. The results using different methods are shown in Figure D.3a. Among the five methods, Moment method gives the lowest saturation for all five images at different saturations, and Li method gives the highest saturation at all conditions. Saturations calculated using other three methods, Default, Otsu, and IsoData, are between the Moment and Li methods. The average saturation and standard deviation resulted from different thresholding methods are shown in Figure D.3b and Table D.2. In addition, the saturation change (decrease in this case) and the standard deviation using different methods are reported in Figure D.3c and Table D.2. At some conditions, the saturation changes can be smaller than the analysis uncertainty; for example, the saturation change at interval 3 and 4 are 0.033 and 0.020, respectively, smaller than the uncertainty

resulted from image analysis which is $\sim 0.03 - 0.04$. However, the saturation change, though can be small, is relatively consistent using different methods. The trend of change in each of the saturation curves using different methods are consistent, and the uncertainty calculation of the saturation change shown in Figure D.3c is smaller than the relative change in each interval.

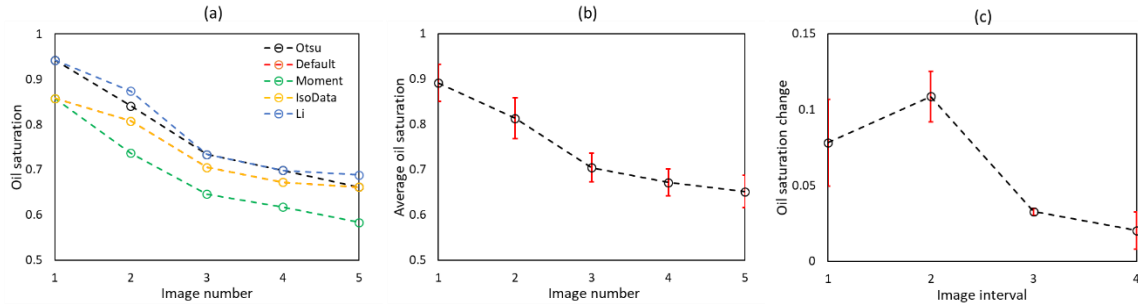


Figure D.3: (a) Oil saturation measured from the image sequence (1-5) after binarizing using different thresholding methods. (b) Average oil saturation (black dash line) and the standard deviation of saturation (red bars) using different methods. (c) Saturation decrease of an image compared to the next one (black dash line) and the standard deviation of the saturation change (red bars) using different methods. E.g., image interval 1 is the saturation difference between image 1 and image 2.

Table D.2: Average oil saturation and saturation decrease using different thresholding methods

Image / Interval #	Average saturation	Standard deviation of saturation	Average saturation change	Standard deviation of saturation change
1	0.892	0.041	0.078	0.029
2	0.813	0.046	0.109	0.017
3	0.705	0.032	0.033	0.002
4	0.672	0.030	0.020	0.012
5	0.652	0.036	—	—

D3 Codes (ImageJ) of the image analysis procedure in Appendix D

```
run("Image Sequence...", "open=[D:/PhD dissertation_2021/Figures_ApendixD/Cropped  
image_ch6/Aligned02.tif] number=5 sort");  
run("Enhance Local Contrast (CLAHE)", "blocksize=127 histogram=256 maximum=3  
mask=*None*");  
setOption("BlackBackground", false);  
run("Make Binary", "method=Otsu background=Light calculate");  
run("Measure");  
saveAs("Tiff", "D:/PhD dissertation_2021/Figures_ApendixD/Binarized  
image_ch6/Binarized image_ch6.tif");  
close()
```

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