Detection and Reuse of the Produced Chemicals in Chemical Enhanced Oil Recovery Operations

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in Partial Fulfillment of the Requirements for the

Degree of Master of Applied Science in

Petroleum Systems Engineering

University of Regina

By

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ABSTRACT

Chemical flood processes, especially the so-called alkaline-surfactant-polymer (ASP) floods, have been increasingly applied in the oil fields due to their high ultimate oil recovery. However, a major technical challenge is how to reduce the amount and the cost of chemicals used so that ASP floods can become cost-effective as well. On the other hand, field applications show that the concentrations of alkali, surfactant and polymer remain relatively high in the produced fluids of ASP floods. Therefore, successful detection and reuse of these produced chemicals can substantially reduce the capital cost and the environmental impact. In this thesis, several methods have been developed to detect each chemical and quantify its concentration in the produced fluids. Also re-injection of the produced chemicals is conducted for further enhancing oil recovery. More specifically, first, the total interactions of alkali, surfactant, and polymer with the oil-brine-sand system are studied. With the developed detection techniques for each individual chemical used in ASP floods, the total loss of each chemical is measured. The chemical loss is caused by its chemical reactions with the crude oil and the reservoir brine, as well as its adsorption onto the rock surface. Secondly, the dynamic interfacial tension (IFT) and equilibrium IFT as a function of alkaline concentration are studied by using the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. The synergistic effect of alkali and surfactant combinations on reducing the IFT to ultra-low value is examined. The ultra-low IFTs are measured by using a spinning drop tensiometer. Thirdly, coreflood tests are performed for alkaline floods, surfactant floods, alkaline-surfactant (AS) floods, polymer floods, and alkaline-surfactant-polymer floods

to determine their respective tertiary oil recovery. Hence, a better understanding of how each chemical contributes to enhanced oil recovery (EOR) is achieved. Fourthly, typical chemical concentrations in the produced fluids are measured and compared with their initial concentrations in the injected slugs so as to determine the potential of reusing these chemicals in practice. Finally, the follow-up coreflood tests of reusing these produced chemicals are carried out by directly re-injecting the produced fluids into new sand-packs/Berea cores. The re-injection test results show that the produced chemicals can be reused to effectively enhance oil recovery. It is anticipated that the detection techniques and reuse strategy developed in this thesis study should facilitate the design, optimization and implementation of ASP flood projects.

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TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGMENTS	iv
LIST OF TABLES	ix
LIST OF FIGURES	ix
LIST OF APPENDICES.....	xv
CHAPTER 1 INTRODUCTION.....	1
1.1 Alkaline Floods.....	2
1.1.1 EOR mechanisms of alkaline floods.....	3
1.1.2 Interfacial tension phenomena	4
1.1.3 Alkaline consumption in an alkaline flood	6
1.2 Surfactant Floods	7
1.2.1 Surfactant adsorption onto the reservoir rocks	8
1.2.2 Micellar floods	9
1.3 Alkaline-Surfactant Floods	10
1.4 Polymer Floods	12
1.4.1 EOR mechanisms of polymer floods	12
1.4.2 Polymer adsorption	13
1.4.3 Inaccessible pore volume.....	14
1.4.4 Polymer slug design.....	15
1.4.5 Field applications	15
1.5 Alkaline-Surfactant-Polymer Floods	16
1.5.1 EOR mechanisms of alkaline-surfactant-polymer floods	16

1.5.2 Field applications	18
1.6 Problem Statement	19
CHAPTER 2 EXPERIMENTAL	20
2.1 Measurements of Chemical Concentrations	20
2.1.1 Alkaline concentration	20
2.1.1.1 Acid-base titration	20
2.1.1.2 pH vs. alkaline concentration calibration method	21
2.1.2 Surfactant concentration	21
2.1.3 Polymer concentration	22
2.1.3.1 Bleach method	22
2.1.3.2 Viscosity vs. polymer concentration calibration method	23
2.2 Interactions of Chemicals with Oil-Brine-Sand Systems	24
2.2.1 Alkali and oil-brine-sand system	24
2.2.2 Surfactant and oil-sand system	24
2.2.3 Polymer and sand system	25
2.3 IFT Phenomena and Oil Shrinking Effect of Crude Oil in Alkaline Solutions	25
2.3.1 Apparatus	26
2.3.2 Pendant drop delivery system	26
2.3.3 Crude oil and aqueous solutions	26
2.3.4 Dynamic IFT measurements	27
2.3.5 Equilibrium IFT measurements	27
2.3.6 Experimental procedure	27
2.4 Coreflood Tests	28

2.4.1 Schematic diagram.....	28
2.4.2 Apparatus and materials.....	29
2.4.2.1 Coreflood setup.....	29
2.4.2.2 Sand-pack/Berea core	29
2.4.2.3 Crude oil and brine samples.....	31
2.4.2.4 Chemicals.....	31
2.4.3 Experimental procedure	32
CHAPTER 3 ALKALINE FLOODS.....	45
3.1 Interactions with Oil-Brine-Sand System	45
3.1.1 Alkali-oil system.....	45
3.1.2 Alkali-brine system.....	45
3.1.3 Alkali-sand system.....	46
3.2 IFT Phenomena and Oil Shrinking Effect	47
3.2.1. Dynamic IFT behavior.....	47
3.2.2 Equilibrium IFTs between the crude oil and alkaline solutions	50
3.2.3 Effects of monovalent and divalent ions.....	51
3.2.4 Oil shrinking effect	52
3.3 Alkaline Coreflood Tests	53
3.4 Re-injection of the Produced Alkaline Solutions.....	55
3.5 Summary.....	55
CHAPTER 4 SURFACTANT FLOODS	74
4.1 Interactions with Oil-Sand System	74
4.1.1 Surfactant-oil system	74

4.1.2 Surfactant-sand system	75
4.2 Equilibrium IFTs between Pure Surfactant Solutions and Crude Oil.....	75
4.3 Surfactant Coreflood Tests	75
4.4 Re-injection of the Produced Surfactant Solutions.....	77
4.5 Summary.....	77
CHAPTER 5 ALKALINE -SURFACTANT FLOODS.....	89
5.1 Synergistic Effect of Alkali-Surfactant System on IFT	89
5.2 Alkaline-Surfactant Coreflood Tests	90
5.3 Effect of Alkalis on Reducing the Adsorption of Anionic Surfactant	92
5.4 Pressure Drop Build-up during the Alkaline-Surfactant Floods.....	93
5.5 Re-injection of the Produced Alkaline-Surfactant Solutions.....	94
5.6 Summary.....	94
CHAPTER 6 POLYMER FLOODS.....	107
6.1 Interactions with Sand System.....	107
6.2 Alkali-Polymer Interactions.....	107
6.3 Polymer Coreflood Tests	108
6.4 Re-injection of the Produced Polymer Solutions.....	112
6.5 Summary.....	112
CHAPTER 7 ALKALINE-SURFACTANT-POLYMER FLOODS.....	127
7.1 Alkaline-Surfactant-Polymer Coreflood Tests	127
7.2 Chemical Concentrations in the Produced Fluids.....	129
7.3 Re-injection of the Produced Alkaline-Surfactant-Polymer Solutions.....	131
7.4 EOR Mechanisms of Alkaline-Surfactant-Polymer Floods.....	132

7.5 Summary	133
CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS	146
8.1 Conclusions.....	146
8.2 Recommendations.....	149
REFERENCES	151

LIST OF TABLES

Table 2.1 Physical and chemical properties of clean Instow dead oil.	33
Table 2.2 Physical and chemical properties of clean Instow brine.....	33
Table 3.1 Coreflood test results for alkaline floods (sand-packs).	57
Table 4.1 Coreflood test results for surfactant floods (Berea cores).	79
Table 5.1 Coreflood test results for AS floods (Berea cores).	96
Table 6.1 Coreflood test results for polymer floods (Sand-packs).	114
Table 6.2 Coreflood test results for polymer floods (Berea cores).....	114
Table 7.1 Coreflood test results for ASP floods (Berea cores).....	135

LIST OF FIGURES

Figure 2.1 pH vs. NaOH concentration calibration curve.	34
Figure 2.2 Absorbance vs. polymer concentration calibration curve (Flopaam 3630s, wavelength=470 nm).	35
Figure 2.3 Viscosity vs. polymer concentration calibration curve (Flopaam 3630s).	36
Figure 2.4 Experimental setup used to measure the IFT between a crude oil and an alkaline solution.	37

Figure 2.5 Flow chart of the coreflood tests.	38
Figure 2.6 Maxima plus M2C vacuum pump.	39
Figure 2.7 DBR-JEFRI positive displacement pump.	40
Figure 2.8 500 ml hydraulic cylinder purchased from DBR.	41
Figure 2.9 The sand-pack and lead sleeve used in the alkaline floods and some polymer floods.....	42
Figure 2.10 The prepared Berea cores used in the surfactant floods, alkaline-surfactant floods, some polymer floods, and alkaline-surfactant-polymer floods.....	43
Figure 2.11 A typical layout of a chemical flood.	44
Figure 3.1 NaOH loss in the oil phase vs. NaOH concentration.	58
Figure 3.2 Alkaline loss onto sand surface vs. NaOH concentration.	59
Figure 3.3 Silica loss vs. NaOH concentration.	60
Figure 3.4 Dynamic IFT vs. time at low NaOH concentrations.	61
Figure 3.5 Dynamic IFT vs. time at high NaOH concentrations.	62
Figure 3.6 The minimum IFT vs. NaOH concentration.	63
Figure 3.7 Variations of equilibrium IFT with NaOH concentration.	64
Figure 3.8 Dynamic IFT vs. time in the presence of either monovalent or divalent ions.	65
Figure 3.9 Dimensionless volume of oil drop vs. time for different aqueous solutions... ..	66
Figure 3.10 Variations of oil drop volume with time at 0.10 wt.% NaOH concentration.	67
Figure 3.11 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF1, NaOH concentration: 0.10 wt.%).	68
Figure 3.12 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF2, NaOH concentration: 0.40 wt.%).	69

Figure 3.13 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF3, NaOH concentration: 0.80 wt.%).	70
Figure 3.14 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF4, NaOH concentration: 1.20 wt.%).	71
Figure 3.15 Variations of produced NaOH concentration with injected PV during alkaline flooding (AF) and subsequent waterflooding (SWF) (Runs No. AF1-4).	72
Figure 3.16 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF5, NaOH concentration: 0.81 wt.%).	73
Figure 4.1 Anionic active substance concentration vs. surfactant weight percentage concentration calibration curve.	80
Figure 4.2 Surfactant loss in oil phase vs. surfactant concentration.	81
Figure 4.3 Surfactant loss onto sand surface vs. surfactant concentration.	82
Figure 4.4 Variations of the equilibrium IFT with surfactant concentration.	83
Figure 4.5 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF1, surfactant concentration: 0.10 wt.%).	84
Figure 4.6 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF2, surfactant concentration: 0.30 wt.%).	85
Figure 4.7 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF3, surfactant concentration: 0.50 wt.%).	86

Figure 4.8 Variations of produced surfactant concentration with injected PV during surfactant flooding (SF) and subsequent waterflooding (SWF) (Runs No. SF1-3)..	87
Figure 4.9 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF4, surfactant concentration: 0.04 wt.%).	88
Figure 5.1 Variations of equilibrium IFT with surfactant concentration at different NaOH concentrations.	97
Figure 5.2 Variations of equilibrium IFT with surfactant concentration at different Na ₂ CO ₃ concentrations.	98
Figure 5.3 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF1, surfactant: 0.30 wt.%, Na ₂ CO ₃ : 1.00 wt.%).	99
Figure 5.4 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF2, surfactant: 0.30 wt.%, Na ₂ CO ₃ : 0.40 wt.%).	100
Figure 5.5 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF3, surfactant: 0.30 wt.%, NaOH: 1.00 wt.%).	101
Figure 5.6 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF4, surfactant: 0.30 wt.%, NaOH: 0.40 wt.%).	102
Figure 5.7 Variations of produced Na ₂ CO ₃ and surfactant concentrations with injected PV during AS flooding (ASF) and subsequent waterflooding (SWF) (Runs No. ASF1-2 for Na ₂ CO ₃).	103

Figure 5.8 Variations of produced NaOH and surfactant concentrations with injected PV during AS flooding (ASF) and subsequent waterflooding (SWF) (Runs No. ASF3-4 for NaOH).	104
Figure 5.9 Variations of produced surfactant concentration with injected PV in four AS floods (Runs No. ASF1-4) in comparison with those in Run No. SF2.....	105
Figure 5.10 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF5, surfactant: 0.03 wt.%, Na ₂ CO ₃ : 0.46 wt.%).	106
Figure 6.1 Polymer loss onto sand surface vs. polymer concentration.....	115
Figure 6.2 Effects of alkali on the viscosity of alkali-polymer solutions.	116
Figure 6.3 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF1, polymer concentration: 1500 ppm).	117
Figure 6.4 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF2, polymer concentration: 1500 ppm).	118
Figure 6.5 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF3, polymer concentration: 1500 ppm).	119
Figure 6.6 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF4, polymer concentration: 1000 ppm).	120
Figure 6.7 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF5, polymer concentration: 1000 ppm).	121
Figure 6.8 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF6, polymer concentration: 1000 ppm).	122

Figure 6.9 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF7, polymer concentration: 1000 ppm).	123
Figure 6.10 Variations of produced polymer concentration with injected PV during 0.4 PV polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF6, polymer concentration: 1000 ppm).	124
Figure 6.11 Variations of produced polymer concentration with injected PV during 0.8 PV polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF7, polymer concentration: 1000 ppm).	125
Figure 6.12 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF8, polymer concentration: 354 ppm).	126
Figure 7.1 Production performance curves during AS+P flooding (ASF+PF) and subsequent waterflooding (SWF) (Run No. ASPF1).	136
Figure 7.2 Production performance curves during P + AS flooding (PF + ASF) and subsequent waterflooding (SWF) (Run No. ASPF2).	137
Figure 7.3 Production performance curves during 0.8 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF3).	138
Figure 7.4 Production performance curves during 0.4 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF4).	139
Figure 7.5 Variations of produced ASP concentrations with injected PV during AS+P flooding (ASF+PF) and subsequent waterflooding (SWF) (Run No. ASPF1).	140
Figure 7.6 Variations of produced ASP concentrations with injected PV during P+AS flooding (PF+ASF) and subsequent waterflooding (SWF) (Run No. ASPF2).	141

Figure 7.7 Variations of produced ASP concentrations with injected PV during 0.8 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF3)...	142
Figure 7.8 Variations of produced ASP concentrations with injected PV during 0.4 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF4)...	143
Figure 7.9 Production performance curves during 0.8 PV ASP Re-injection (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF5).....	144
Figure 7.10 Production performance curves during 0.8 PV ASP Re-injection (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF6).....	145

LIST OF APPENDICES

Appendix 3.1 Detailed experimental data for coreflood Run No. AF1.....	167
Appendix 3.2 Detailed experimental data for coreflood Run No. AF2.....	168
Appendix 3.3 Detailed experimental data for coreflood Run No. AF3.....	169
Appendix 3.4 Detailed experimental data for coreflood Run No. AF4.....	170
Appendix 3.5 Detailed experimental data for coreflood Run No. AF5.....	171
Appendix 4.1 Detailed experimental data for coreflood Run No. SF1.....	172
Appendix 4.2 Detailed experimental data for coreflood Run No. SF2.....	173
Appendix 4.3 Detailed experimental data for coreflood Run No. SF3.....	174
Appendix 4.4 Detailed experimental data for coreflood Run No. SF4.....	175
Appendix 5.1 Detailed experimental data for coreflood Run No. ASF1.....	176
Appendix 5.2 Detailed experimental data for coreflood Run No. ASF2.....	177
Appendix 5.3 Detailed experimental data for coreflood Run No. ASF3.....	178
Appendix 5.4 Detailed experimental data for coreflood Run No. ASF4.....	179

Appendix 5.5 Detailed experimental data for coreflood Run No. ASF5.....	180
Appendix 6.1 Detailed experimental data for coreflood Run No. PF1.....	181
Appendix 6.2 Detailed experimental data for coreflood Run No. PF2.....	182
Appendix 6.3 Detailed experimental data for coreflood Run No. PF3.....	183
Appendix 6.4 Detailed experimental data for coreflood Run No. PF4.....	184
Appendix 6.5 Detailed experimental data for coreflood Run No. PF5.....	185
Appendix 6.6 Detailed experimental data for coreflood Run No. PF6.....	186
Appendix 6.7 Detailed experimental data for coreflood Run No. PF7.....	187
Appendix 6.8 Detailed experimental data for coreflood Run No. PF8.....	188
Appendix 7.1 Detailed experimental data for coreflood Run No. ASPF1.....	189
Appendix 7.2 Detailed experimental data for coreflood Run No. ASPF2.....	190
Appendix 7.3 Detailed experimental data for coreflood Run No. ASPF3.....	191
Appendix 7.4 Detailed experimental data for coreflood Run No. ASPF4.....	192
Appendix 7.5 Detailed experimental data for coreflood Run No. ASPF5.....	193
Appendix 7.6 Detailed experimental data for coreflood Run No. ASPF6.....	194

CHAPTER 1 INTRODUCTION

Waterflooding has been in use since 1865 and is by far the simplest secondary oil recovery method. However, it is well known that a typical oil recovery for waterflooding is usually around 20-30% original oil in place (OOIP). Thus, there is still 70-80% OOIP left in the reservoirs in the form of oil ganglia. A large amount of residual oil remains in oil reservoirs due to high capillary forces and poor waterflooding sweep efficiency. Capillary forces arise from the interfacial tension (IFT) between the oil and water phases, resist externally applied hydrodynamic forces and cause the injected water to bypass the residual oil. The predominant mechanism for further recovering this unswept residual oil is to lower the IFT. Thus, additional oil can be recovered due to reduced capillary forces. On the other hand, by improving the water-oil mobility ratio, viscous fingering is reduced and water breakthrough is mitigated. Therefore the sweep efficiency of water injection can be greatly improved.

In practice, different enhanced oil recovery (EOR) technologies are widely applied to recover this residual oil. Current EOR processes may be divided into four categories: (a) thermal, (b) miscible, (c) chemical, and (d) others. The thermal process has been moderately commercialized. The mechanisms of miscible processes are reasonably well understood. It is still difficult to predict, however, whether a miscible process is effective and profitable for a given reservoir. The chemical processes are technically complex but can achieve the highest recovery efficiencies in some favorable cases. It should be noted that the applicability and potential development of any EOR process is limited not only

by technical constraints, but by economic, material, institutional and regulatory constraints as well.

Generally speaking, there are three basic chemical EOR processes: alkaline floods, surfactant floods, and polymer floods. Over the years, many new chemical EOR schemes for improving oil recovery have been developed on the basis of these three EOR processes, such as alkaline-surfactant (AS) floods, alkaline-polymer (AP) floods, surfactant-polymer (SP) floods (also known as microemulsion floods or micellar floods), and alkaline-surfactant-polymer (ASP) floods, which are the latest and most complex chemical EOR processes. A large number of chemical EOR processes have been field tested around the world. Field results show that chemical EOR processes can be considered as one of the most promising EOR techniques for recovering the residual oil from the waterflooded reservoirs.

1.1 Alkaline Floods

An alkaline flood is an EOR process in which the pH of the injected water is increased by the addition of relative inexpensive alkalis, such as sodium hydroxide, sodium carbonate, sodium silicate and potassium hydroxide. The effect of an alkaline flood (i.e., caustic flood) was recognized by Squires (1917). Later, Nutting (1927) described the principles underlying soda process and application of alkalis for improving the performance of the waterflooding process. Since the first patent on caustic flood issued to Atkinson (1927) in 1927, extensive lab studies and field tests have been carried out. There has been no record of successful field application of caustic flood described. Although Leach *et al.* (1962) showed that caustic injection water could alter wettability

and improve oil recovery in laboratory experiments, the results of a field test were somewhat inconclusive.

Emery *et al.* (1970) showed that caustic injection could cause wettability reversal and improve the waterflood recovery of crude oil from the Singleton field, Nebraska. Cooke *et al.* (1974) and Ehrlich *et al.* (1974) reported the application of alkaline flooding for enhancing oil recovery. Furthermore, Coreflood tests conducted by Flock *et al.* (1977) also showed the good potential of alkaline floods. Also, Chiwetelu *et al.* (1991) pointed out that, among the various non-thermal processes, alkaline flood appeared to be the most attractive. Also, alkaline reagents are abundant and quite cheap in comparison with conventional surfactants.

1.1.1 EOR mechanisms of alkaline floods

In the alkaline flood process, the surfactants are generated by the *in situ* chemical reactions between the alkali of the aqueous phase and the organic acids of the oil phase. The surface-active products can be adsorbed onto the rock surface to alter the wettability of the reservoir rock and/or can be adsorbed onto the oil-water interface to lower the interfacial tension. With these lowered interfacial tensions (1-10 mN/m), surface forces and/or shear-driven forces promote the formation of oil-in-water (O/W) emulsions or water-in-oil (W/O) emulsions. It should be noted that the characteristics of the emulsions depend on the pH, temperature, electrolyte type, and electrolyte concentration. Four EOR mechanisms may be involved in an alkaline flood, emulsification (Tsay and Menzie, 1985) and entrainment (Subkow, 1942), emulsification and entrapment (Jennings *et al.*, 1974), emulsification and coalescence (Schechter *et al.*, 1975), and wettability reversal

(Raimondi *et al.*, 1976 and Cooke *et al.*, 1974). The concurrence of these four mechanisms can substantially enhance oil recovery (Castor *et al.*, 1981).

In an alkaline flood, the generated surfactants can emulsify the crude oil into small oil droplets, which can be entrained and carried forwards by the shear flow. Thus, the residual oil is mobilized. On the other hand, due to its high viscosity, such an emulsion can also improve the mobility ratio. As the emulsified small oil droplets migrate to the pore throats, some smaller droplets are squeezed through the pore throats and the others are entrapped to form certain blockage. Then the subsequently injected fluids are forced to flow through the untouched zones and the sweep efficiency is improved (Wang and Gu, 2002, Wang and Gu, 2003a). In addition, the coalescence of small oil droplets with the oil ganglia can form some local regions of high oil saturation, i.e., oil bank is formed at the flood front. Finally, the generated surfactants, which are adsorbed onto the reservoir rocks, further react with them to alter their wettability and nearby distribution of the residual oil ganglia.

1.1.2 Interfacial tension phenomena

The surfactants generated by the *in situ* chemical reactions between the alkali and the organic acids of the oil phase can be adsorbed at the oil-water interface and gradually dissolved in the bulk aqueous phase and/or in the oil phase, depending on their affinities for the aqueous and oil phases. Thus, the interfacial tension (IFT) between the oil phase and alkaline solution changes during an alkaline flood and finally reaches an equilibrium value. In the literature, some efforts were made to study this dynamic IFT phenomenon. An experimental study was carried out by Reisburg and Doscher (1956), who examined the effects of interface aging and sodium hydroxide concentration on IFT. McCaffery

(1976) measured IFT between four crude oils and sodium hydroxide solutions and found that IFT increased dramatically during the interface aging, a fact that can be attributed to the migration of surfactants away from the oil-water interface after their initial generation. Rubin and Radke (1980) presented a diffusion model to explain the reduction of IFT when an acidic crude oil was made in contact with an alkaline solution. They explained this dynamic IFT behavior by postulating the existence of a desorption barrier for surface-active species at the oil-water interface. Later, Chan and Yen (1982) proposed a chemical equilibrium model to interpret IFT variations with pH, salinity, and temperature. However, they did not specify the starting time in their IFT measurements. Further, Sharma *et al.* (1984) modeled the dynamic IFT behavior by using both one-component model and two-component model, respectively. In their models, they assumed that chemical reaction of acidic species with alkali quickly generated surface-active species, which gradually diffused away from the interface. Thus a minimum IFT occurred.

In the past, relatively low IFTs (less than 1 mN/m) were usually measured by using the spinning drop method, which was first proposed by Vonnegut (1942). The spinning drop apparatus basically consists of a cylindrical glass tube that rotates about its horizontal axis. Inside the tube, oil is dispersed in the denser aqueous phase. The oil drop stays at the horizontal axis when the interfacial force is counterbalanced by the centrifugal force. Thus, the IFT can be related to the drop radius, the rotational speed, and the density difference between the two phases according to well-known Vonnegut's equation. Although this method has often been applied to study the dynamic IFT behavior, the major technical problem associated with this method is that the centrifugal

field existing in the tube may cause the convection of the both phases and affect the molecule diffusion of surface-active species into the bulk phases. Therefore, a question that naturally arises with this method is whether such measured dynamic IFTs can be used to truly represent those in real alkaline floods.

More recently, axisymmetric drop shape analysis (ADSA) technique (Rotenberg *et al.*, 1983; Cheng *et al.*, 1990; Li *et al.*, 1992) for the pendant drop case was applied to determine low IFTs (less than 1 mN/m) in many cases, such as CO₂ flood and solvent injection (Guo and Schechter, 1997). Unlike the spinning drop method, the pendant drop shape method is stationary and involves no convective motion. The ADSA technique for the pendant drop case can be used to determine the IFT with sufficient accuracy. In particular, sequential images can be taken to study the dynamic IFT phenomenon. ADSA technique for the pendant drop case has been successfully employed to measure the dynamic IFTs of crude oil in contact with a variety of aqueous solutions (Li, *et al.*, 2003).

1.1.3 Alkaline consumption in an alkaline flood

The economic success or failure of alkaline flooding may be controlled, to a large extent, by alkaline consumption because the total amount of alkali required is directly related to its consumption. It is well known that alkali reacts with the crude oil to form a low or ultra-low IFT, which is favorable for oil displacement. If the alkaline consumption is too high, then IFT may not be lowered to a desired value, which results in less oil displacement efficiency (Jennings *et al.*, 1974). Selby *et al.* (1988) surveyed 15 alkaline flood field tests in Canada and U.S., among which only one was considered successful and the majorities were abandoned. One major reason for this poor performance is due to

an inadequate understanding of the interactions among alkalis, crude oil, formation brine and matrix minerals.

Generally, alkaline consumption is due to the interactions of: (1) alkali-oil; (2) alkali-reservoir brine; (3) alkali-reservoir rock. Alkali-oil reaction is necessary and useful. The amount of alkali consumed during the alkali-oil chemical reaction is usually very small because the acid number of oil seldom exceeds 5 mg KOH/g-oil. The alkaline consumption due to alkali-brine interactions will be high in the presence of high concentration of Ca^{2+} and Mg^{2+} . Recently, fresh water pre-flush of the reservoir is widely applied in many oil fields to reduce the adverse effects of Ca^{2+} and Mg^{2+} ions on the alkaline consumption (Bunge *et al.*, 1980; Smith, 1978; Hill, 1977; Criffith, 1978; Pope *et al.*, 1978). In addition, the reactions of alkalis with clay minerals in reservoir rocks have been investigated under static conditions (Huang *et al.*, 1986).

It was reported by Cheng (1986) that field applications of alkaline flooding have been plagued with excessive alkaline loss and plugging problem due to the chemical reactions of alkalis with the reservoir rocks and the divalent ions. However, such a chemical consumption can be significantly reduced if Na_2CO_3 is used. In comparison with the other alkalis, Na_2CO_3 has less ion exchange and mineral dissolution. In addition, Na_2CO_3 reacts with hard water to form carbonate precipitates, which do not severely affect permeability as compared to the precipitates of the hydroxide or the silicates.

1.2 Surfactant Floods

The displacement of oil by surfactant is one of the methods used in enhanced oil recovery (EOR) (Poollen, 1980; Lake, 1989; Green and Willhite, 1998). The major

mechanisms of surfactant flooding rely on the injection of a surfactant solution to lower the interfacial tension to the ultra-low values, i.e., lower than 10^{-3} mN/m. Ideally, emulsions are formed during surfactant flooding. Such an emulsification process helps to mobilize the residual crude oil. The reduced IFT leads to reduced capillary forces that trap the residual oil in porous media, making displacement of the oil easier (Farouq Ali and Thomas, 1995; Wassmuth *et al.*, 1999). It should be noted that the efficiency of oil displacement at low concentration surfactant flooding depends on the partitioning of surfactant molecules in the water phase and the oil phase, which in turn may cause wettability alteration. The wettability of a porous medium has a profound effect on flow behavior (Anderson, 1987a; 1987b).

1.2.1 Surfactant adsorption onto the reservoir rocks

In practice, surfactant floods alone cannot achieve desired oil recovery due to several technical problems, such as viscous fingering, surfactant adsorption, surfactant-rock interactions. Mannhardt *et al.* (1994) pointed out that the adsorption of anionic surfactants onto the surface of the Berea sandstone was low at low salinities, but increased substantially at moderate salinities. Limited solubility of the anionic surfactants in the aqueous phase tends to drive these surfactants to the solid-liquid interface and can also lead to increased surfactant loss through precipitation. Dunning and Johansen (1957) tested 165 surfactant solutions in the laboratory and concluded that surfactant floods were ineffective, mainly due to adsorption and also because of their sensitivity to rocks. Over the years, many progresses have been made. Notable among them is the use of petroleum sulfonates as surfactants. They are more effective than conventional surfactants and less susceptible to adsorption onto the rock surface and interactions with minerals. Smith *et*

al. (1975) summarized the four laboratory methods for determining adsorption loss in the porous media. In addition, adsorption of surfactants involved in the EOR applications has been studied extensively by other researchers (Meyers and Salter, 1980; Celik *et al.*, 1979; Krumrine, *et al.*, 1980; Novosad, 1981a; Glover, *et al.*, 1979; Trogus, *et al.*, 1979). It has been convincingly shown that in principle one can develop surfactant systems to displace almost all the residual oil from a porous medium when a large amount of surfactant solution is applied. Many surfactant floods have been carried out, using both high and low concentration surfactant slugs and a polymer slug as the driving fluid in many cases. Novosad (1981b) concluded that the overall surfactant loss is attributed to surfactant adsorption at solid-liquid interface, surfactant trapping in the immobile hydrocarbon phase, surfactant precipitation by divalent ions, and poor surfactant solubility in the absence of co-surfactants.

1.2.2 Micellar floods

Generally speaking, success of surfactant floods in the fields has been limited. Use of surfactants in the form of micellar flood has been more successful (Farouq Ali and Thomas, 1994). Micellar flooding was initially developed by the Marathon Oil Company in the early 1960s (Gogarty and Tosch, 1968). Micellar or microemulsion flooding is a complex but promising EOR method for light oils and has been extensively tested in the laboratory. Many successful field tests have also been conducted. In micellar floods, a micellar solution (actually it is a microemulsion) slug (about 0.05 PV) is injected and then followed by a polymer solution slug (0.25-0.50 PV). This polymer slug is further driven by water. Usually, a pre-flush (low salinity brine, alkaline solution, or even diluted polymer solution) is injected to condition the reservoir rocks prior to the micellar slug.

The micellar solution consists of water, a suitable hydrocarbon and 5-15 wt.% surfactant, together with small amount of salt and a suitable alcohol (Farouq Ali and Thomas, 1994). Nearly thirty field tests of micellar floods have been reported and the oil recovery for those field tests has been excellent in most cases (Farouq Ali and Thomas, 1992).

1.3 Alkaline-Surfactant Floods

As mentioned above, in the alkaline flood process, the surfactants are generated *in situ* by the chemical reactions between the alkali of the aqueous phase and the organic acids of the oil phase. The surface-active products can adsorb onto the reservoir rock surface to alter its wettability and/or can adsorb onto the oil-water interface to lower its IFT. However, for a non-acidic oil reservoir, the amount of *in situ* generated surfactants is not large enough to produce ultra-low interfacial tension. Nelson *et al.* (1984) proposed the idea of using a commercial surfactant to augment the *in situ* generated surfactant. On the other hand, alkaline consumption by the rock makes propagation through the oil reservoir of such dilute alkaline solution extremely slow. Also, alkali at low concentration requires uneconomically large injection volumes because of rapid alkaline consumption by acidic oils and divalent ions in brine and ionic exchange sites (Bunge and Radke, 1981). The dilemma of having to choose between high displacement efficiency (low IFT) and satisfactory displacement rate can be resolved by adding co-surfactants to the alkaline solutions. A properly chosen co-surfactant can increase the electrolyte concentration so that a minimum IFT may be achieved. Thus, a co-surfactant can be used to obtain the conditions of "optimum salinity" of an alkaline flood (Nelson *et al.*, 1984). The primary concern in an AS flood process is how to optimize the

effectiveness of the surfactant. The performance of a surfactant is impaired by either its complexation with multivalent metal ions in the reservoir/injected water or its adsorption onto the reservoir rock surface (Krumrine and Falcone Jr., 1981). Ahearn (1969) pointed out that the addition of sodium silicate, sodium carbonate, and sodium phosphate could improve the surfactant performance by minimizing the harmful effect of multivalent metal ions. Holm and Robertson (1981) showed that the application of sodium orthosilicate as a pre-flush significantly improved the oil recovery. Similarly, Feuerbacher and Smith (1973) used NaOH as a pre-flush prior to a surfactant flood.

When surfactants are added into an alkaline solution, the interfacial tension at the crude oil-AS solution interface can be significantly reduced. Such a synergistic effect of alkali and surfactant on reducing IFT has been reported by a number of researchers. Different mechanisms have been proposed to explain this favorable effect. On the one hand, when alkaline concentration is increased, the increased ionic strength is believed to be the governing mechanism for the minimum IFT (Rudin and Wasan, 1991). The added alkali produces surface-active soaps, which lower the IFT. A further increase in alkaline concentration increases the IFT because the alkali acts as an electrolyte, which increases the ionic strength and either partitions the salt of the ionized acid into the oil or precipitates it. On the other hand, the minimum IFT is probably because of equal partitioning of a surfactant in the oil and brine phases at certain surfactant concentration (Chan and Shah, 1981; Wang and Gu, 2003a).

1.4 Polymer Floods

Muskat (1949) first pointed out that fluid mobility would affect waterflooding performance. However, it was not until 1964 that Pye (1964) and Sandiford (1964) found that the mobility of water/brine used in waterflooding could be reduced efficiently by adding small amount of a water-soluble polymer. Since then, numerous laboratory studies and field tests have been carried out. In essence, polymer flooding is a chemically augmented waterflood in which chemicals at small concentrations (250-1500 ppm), such as partially hydrolyzed polyacrylamides (HPAM) or xanthan gum, are added to the injected water to increase the effectiveness of the water in displacing oil. The oil recovery is enhanced by several different mechanisms, not all of which are well understood. Although improvement in the efficiency of waterflood recovery with the use of polymers is relatively modest, a polymer flood is effective enough for this process to be applied in limited commercial use.

1.4.1 EOR mechanisms of polymer floods

In addition to increased viscosity, HPAM also lowers the effective permeability of the injected water. When the effective permeability of the injected water is lower, a lower polymer concentration can be used to obtain equivalent mobility control. However, HPAM are salt sensitive and can be mechanically degraded by shear stress. Thus special care in surface handling is required to avoid the shear degradation. Xanthan gums are relatively insensitive to salinity and can tolerate mechanical shearing effects, which make them easier to handle in field injections. The major disadvantages of xanthan gums are formation plugging and susceptibility to bacterial attacks (Lake, 1989).

Although polymer flooding does not reduce the residual oil saturation, it improves oil recovery beyond waterflooding by increasing both the areal and vertical sweep efficiencies (Chang, 1977). This process has its greatest potential for reservoirs with viscous oils, which are moderately heterogeneous and have adverse water-oil mobility ratios. During the displacement of viscous oils, viscous fingering of the displacing water results in poor sweep efficiency. Displacement can be stabilized and sweep efficiency can be increased by adding polymer to the injected water/brine to enhance its viscosity and reduce reservoir permeability in swept zones (Allen and Boger, 1988). Early water breakthrough is a serious problem in reservoirs with fractures or with severe permeability heterogeneities. The latter are often in the form of vertically stratified layers. Poor waterflooding performance occurs in these cases, even though the oil viscosity is not too high. Preferentially plugging thief zones with a viscous polymer slug (Sorbie *et al.*, 1987a; 1987b), or a clay gum slug (Wang and Gu, 2002), or a weak gel slug (Wang *et al.*, 2002a, Wang *et al.*, 2003a, Wang *et al.*, 2003b) can significantly improve the sweep efficiency.

1.4.2 Polymer adsorption

The amount of polymer adsorbed onto the reservoir rock surface depends on the properties of the polymer and the rock surface (Broseta *et al.*, 1992). Both physical adsorption of polymer onto the solid surface and polymer retention due to mechanical entrapment play a dominant role in total polymer loss in a reservoir. In general, the following three patterns regarding polymer adsorption have been observed. First, laboratory tests often have higher adsorption than that in field performance. Secondly,

adsorption is significantly less onto consolidated cores than that onto sand-packs (Mungan, 1969). Thirdly, adsorption increases with increased brine salinity.

Typical field adsorption values range from 20 to over 500 lb/acre-ft. Laboratory adsorption values range from 30 to a few hundred $\mu\text{g/g-sand}$ (Mungan, 1969). It should be emphasized that laboratory results cannot be extrapolated to predict polymer adsorption in oil reservoirs due to the heterogeneity of the reservoir.

Polymer retention due to mechanical entrapment is also important. Maerker (1973) concluded that as a result of the lower flow rates encountered in the reservoir, polymer retention under the reservoir conditions was usually less than that measured in the laboratory.

1.4.3 Inaccessible pore volume

Polymer solutions propagate through porous media at a velocity different from that of water because of adsorption and inaccessible pore volume. Adsorption tends to move the front edge of a polymer slug at a slower velocity than that of water flow, whereas inaccessible pore volume tends to move the polymer slug at a higher velocity. The phenomenon of inaccessible pore volume was first found by Dawson and Lantz (1972). They showed that not all the pore space might be accessible to polymer molecules. This allows polymer solutions to advance and displace oil at a faster rate than the predicted rate on the basis of the total porosity. They also concluded from laboratory results that about 30% of the total pore volume in the rock samples was untouched by the polymer solution.

The inaccessible pore volume may have a beneficial effect on field performance. The actual rock surface in contact with the polymer solution will be less than the total rock

surface available. Thus the amount of polymer adsorbed onto the rock surface may be less than the predicted value. However, movable oil located in the smaller pores will not be accessed by the polymer solution in some cases and thus may not be displaced either.

1.4.4 Polymer slug design

In the 1960s, polymer slugs were injected at a constant concentration during field operations. As a polymer slug propagates through porous media, the front edge is gradually stripped of polymer due to the adsorption onto the rock surface. More importantly, when a low-mobility polymer slug is followed by a high-mobility brine injection, viscous fingering tends to occur at the polymer-brine interface as a result of the adverse mobility ratio. Thus the major purpose of a polymer slug design is to avoid a sharp change in the mobilities of the fluids before and behind the slug (Mungan, 1968; Uzoigwe *et al.*, 1974). The slug starts at a relatively high concentration and declines to a fairly low concentration. The variation in polymer concentration helps to reduce the above-mentioned viscous fingering in constant-concentration polymer injection. Currently, such designed slug is used in almost all the field operations of polymer or micellar-polymer flooding. Another modified method is to inject an initial mobility control slug with progressively increased polymer concentration, an intermediate mobility control slug, and a terminal mobility control slug with progressively decreased polymer concentration (Chang, 1977). Usually, the size of the initial slug is smaller than that of the terminal slug.

1.4.5 Field applications

Polymer flooding had been tested extensively in the fields and used commercially at a limited scale in the U.S. and elsewhere before 1980. Daqing Oil Field in China started

polymer flooding at an industrial scale in 1996 and its oil production was rapidly increased. The annual oil production in 2001 attributed to the injection of polymer was more than 70 million barrels. Polymer flooding has been applied in more than three thousand wells and the accumulative oil production has been over 300 million barrels. A total of 12.6% OOIP has been recovered by using polymer floods in the Daqing Oil Field (Wang *et al.*, 1993; 2000; 2002b; 2002c).

1.5 Alkaline-Surfactant-Polymer Floods

The alkaline-surfactant-polymer (ASP) flood technique was developed in the 1980s in an economic environment of US\$15/bbl oil (Wyatt *et al.*, 2002). This technique uses similar mechanisms as the micellar flood to mobilize the residual oil but the surfactant concentration is significantly reduced by 20 to 70 times (Wyatt *et al.*, 2002). An ASP flood combines interfacial tension-reducing chemicals (alkali and surfactant) with a mobility control chemical (polymer). The interfacial tension-reducing chemicals minimize the capillary forces that trap the residual oil while the mobility control chemical improves the sweep efficiency. ASP field tests in mature waterflooded reservoirs have shown the incremental oil recovery of over 20% OOIP (Wang *et al.*, 1996; Wang *et al.*, 1999; Sui *et al.*, 2000). Previous and some ongoing projects are mainly located in the Rocky Mountain states, USA. The ASP flood technique was also applied in China, Canada, and Venezuela (Wyatt *et al.*, 2002).

1.5.1 EOR mechanisms of alkaline-surfactant-polymer floods

Alkaline-surfactant-polymer floods have long been recognized to be one of the most effective techniques in enhanced oil recovery. The success of ASP floods depends not

only on the identification of the proper alkali, surfactant, and polymer but also on the way of how these ternary components are properly combined. Therefore, desirable crude oil emulsification, low chemical losses and favorable mobility control can be achieved. Several EOR mechanisms are proposed for this technique but not well understood. This is because of the high dependence of this process on the interactions among the injected fluid, minerals (these minerals are not chemically inert), reservoir rocks, and the crude oil. In the past, several researchers described the EOR mechanisms of ASP floods. In general, an alkaline-surfactant-polymer flood combines various EOR mechanisms into one process. First, Reisberg and Doscher (1956) pointed out that the residual oil could be saponified at high pH values. Also the alkali could increase the ionic strength, which alters the saponification pH profile (Rudin and Wasan, 1992). Thus the IFT at the crude oil-water interface can be greatly reduced. In addition, at a high alkaline concentration, the negative charge density on the reservoir rock could be increased (Krumrine *et al.*, 1980). Such negative charges not only deter the adsorption of anionic chemicals but also make the rock surface more water-wet (Mungan, 1984). Secondly, the added surfactant can be adsorbed at the crude oil-water interface to lower the IFT. Also, the added surfactant can form mixed micelles with the surfactants generated *in situ* by the chemical reactions between the injected alkali and the natural organic acids in the crude oil. Such formed micelles broaden the alkaline concentration range for minimum IFT (Rudin and Wasan, 1992). Thirdly, the injected polymer solution can significantly increase the viscosity of water. On the other hand, polymer can be adsorbed onto the reservoir rock surface to decrease the effective permeability of water. Thus the mobility of water is

substantially reduced. Finally, it should be noted that some combinations of the chemicals provide greater enhancement than each individual chemical does (Wyatt *et al.*, 2002).

1.5.2 Field applications

An alkaline-surfactant-polymer flood was developed and applied to the West Kiehl Minnelusa Field starting from 1987 (Meyers *et al.*, 1992). This was the first field-wide application of the ASP process in the U.S., which was applied as a secondary recovery operation following the primary recovery (Wyatt *et al.*, 1995; Vargo *et al.*, 2000). Other alkaline-surfactant-polymer projects include a pilot test in an Oklahoma field (French, 1999), a pilot in West Venezuela (Manrique *et al.*, 2000) and three oil fields in China (Yuan *et al.*, 1998; Arihara *et al.*, 1999; Wang *et al.*, 1997; Liu *et al.*, 2002; Wang *et al.*, 1998, Delshad *et al.*, 1998; Tong *et al.*, 1998; Qu *et al.*, 1998; Hou *et al.*, 2001a; Hou *et al.*, 2001b; Gao *et al.*, 1995; Song *et al.*, 1995). It has been reported that successful applications of ASP floods can enhance oil recovery up to 20% (Wang *et al.*, 1996; Sui *et al.*, 2000; Wang *et al.*, 1999) and the cost of chemicals per barrel of incremental oil is US\$3-4 (Wang *et al.*, 1996). Generally speaking, an ASP flood is designed for a sandstone reservoir. In 1996, Al-Hashim *et al.* (1996) also carried out a systematic study on the applicability of alkaline-surfactant-polymer processes as an enhanced oil recovery method for Saudi Arabian carbonate reservoirs, which further broadened the application range of ASP floods. Some important conclusions drawn from the above-mentioned projects are described as follows. First, good mobility control is essential to a successful ASP flood project. Secondly, thorough studies in the reservoir geology and reservoir characterization, laboratory tests, and numerical simulations can greatly help to improve the probability of success. Thirdly, injection facilities must be able to mix the injected

solution according to the project designs. Finally, quality control of injected materials and scheduled maintenance of the surface equipment are proved to be important as well.

1.6 Problem Statement

Despite the fact that ASP floods can significantly enhance oil recovery, such chemical EOR operations sometimes become unfavorable in practice because of technical complexity, large capital and operational costs and possible long-term environmental impact. Some difficult technical problems associated with chemical EOR operations remain unanswered. For example, it has long been unsolved how to accurately detect and, more importantly, how to effectively reuse the chemicals in the produced fluids. On the other hand, field applications show that the concentrations of alkali, surfactant and polymer remain relatively high in the produced fluids of ASP floods (Qiao, *et al.*, 1999; Wu *et al.*, 2001). It has been reported that 30-50% of injected polymer was produced from the producers during the field applications in Daqing oil field (Wang *et al.*, 2002c). In some cases, the produced polymer concentration can reach up to 800 ppm (Wu *et al.*, 1999). The remaining alkali, surfactant and polymer in produced liquids have resulted in extremely stable oil in water (O/W) emulsions. These chemicals not only cause great difficulty in surface treatment processes (especially in oily wastewater treatment) but also have long-term environmental effects. Thus successful detection and effective reuse of these chemicals in the produced fluids can substantially reduce the capital and operational costs and the environmental impact (Wang and Gu, 2003b).

CHAPTER 2 EXPERIMENTAL

2.1 Measurements of Chemical Concentrations

2.1.1 Alkaline concentration

Two methods, acid-base titration method and pH vs. alkaline concentration calibration method, are employed to determine the alkaline concentration in this study. The purposes of accurate determination of unknown alkaline concentration in the produced alkaline solution are to determine the alkaline consumption in the formation and to explore the potential of reusing the produced alkali in chemical EOR processes.

2.1.1.1 Acid-base titration

Titration is a chemical analytical method in which a standard solution with a known concentration is used and added into another solution whose concentration is to be determined. An acid-base titration uses the fact that base can be neutralized by acid or vice versa. In this neutralization reaction, the base and acid combine to produce a salt and water. When the neutralization is reached, the resultant solution is neutral, neither acid nor caustic. In a titration, this is known as the equivalence point or the end point. The change in pH of the solution can be monitored using an indicator or a pH meter. It is extremely important that the exact amount of each solution used be known at the end point. In this study, the standard solution is hydrochloric acid (HCl) and the indicator applied is methyl orange. At the end point, the color of the mixture of the alkaline solution and the indicator changes from orange to red.

The above balanced equation indicates that one mole of sodium hydroxide will combine with one mole of hydrochloric acid to produce one mole of sodium chloride and one mole of water. At the end point, the concentration of the standard hydrochloric acid and its volume used are known. With the known volume of the base solution used, calculations can be undertaken to determine the concentration of the base solution.

2.1.1.2 pH vs. alkaline concentration calibration method

All the alkaline (NaOH) solutions are prepared with the produced brine from the Instow oil field. A calibration curve is obtained by measuring pH of NaOH solutions with known concentrations. The calibration curve is plotted in Figure 2.1. When the pH of NaOH solution is measured, this calibration curve is then used to determine its concentration. A pH meter (Oakton pH 500 meter, Oakton Instruments, USA) is used to determine the pH values of NaOH solutions.

2.1.2 Surfactant concentration

Since the surfactant used in this study is an anionic surfactant, the anionic active material in the surfactant solution can be determined directly by two-phase titration. The titrant is a standard cationic surfactant (Hyamine 1622, Romil Pure Chemistry, UK), and the indicator is an acidic mixture of a cationic dye (dimidium bromide, Fronine, Pty, Ltd., Australia) and an anionic dye (disulphine blue, Fronine, Pty, Ltd., Australia). The titration is carried out in a water-chloroform two-phase medium. The principle of the two-phase titration method is described as follows. When a mixed indicator of dimidium bromide and disulphine blue is added into an anionic surfactant solution, a pink complex is formed due to the chemical reaction between the anionic active material and the cationic dye (dimidium bromide). The pink complex is immediately extracted into the

chloroform phase and the colorless chloroform phase is changed into pink. When this two-phase system is titrated with a cationic surfactant (Hyamine 1622), the Hyamine 1622 first reacts with the remaining anionic surfactant in the aqueous phase. When all the remaining anionic surfactant is consumed, the Hyamine 1622 starts to react with the anionic dye (disulphine blue). The freed dyestuff is water-soluble. At the end point, the pink chloroform phase gradually becomes grey, and turns to blue with one additional drop of the Hyamine. From the amount of Hyamine consumed, the anionic active substance concentration in the surfactant solution is calculated.

2.1.3 Polymer concentration

Two methods, bleach method and viscosity-polymer concentration calibration method, are adopted to determine an unknown polymer concentration, respectively.

2.1.3.1 Bleach method

Bleach method is applied to quantify the polymer concentration in the produced fluids. This method is based on the chemical reaction of polyacrylamide with sodium hypochlorite, which results in an insoluble chloramide product. The absorbance of the resultant chloramide product is measured using a spectrometer (Perkin-Elmer Lambda 40, Perkin-Elmer Corp., Connecticut, USA) and the polymer concentration is determined by using the absorbance vs. polymer concentration calibration curve. It should be noted that the polymer samples for analysis must be free of oil and any colored contaminants. In general, if the polymer concentration is greater than 200 ppm, too much insoluble chloramide product can be formed. This severely affects the accuracy of absorbance measurements. Thus measurements have to be performed for solutions containing 10 to 200 ppm polymer and the brine composition must be known. The calibration curve is

established by measuring the absorbance of polymer samples versus their known concentrations. This absorbance vs. polymer concentration curve is shown in Figure 2.2. According to the Beer-Lambert Law (Ricci *et al.*, 1994), this curve should be a straight line through the origin of the absorbance-concentration coordinate system. In the experiments, the absorbance A is calculated from:

$$A = -\ln T = -\ln (P/P_o),$$

where T is the transmittance, P is the power of light after it passes through the sample, and P_o is the initial power of light.

Once the absorbance of an unknown sample is measured, the absorbance vs. polymer concentration calibration curve is then used to determine the polymer concentration of the unknown sample.

2.1.3.2 Viscosity vs. polymer concentration calibration method

It is well known that water-soluble polymer in a dilute concentration of the order of a few hundred ppm increases the aqueous viscosity significantly. The viscosity vs. polymer concentration calibration method is based on variations of viscosity of polymer solution with its polymer concentration. With the increase in polymer concentration, the viscosity of polymer solution increases accordingly.

The viscosity of HPAM solution with different concentrations is measured and plotted in Figure 2.3. The fitted curve in this figure can be used to determine the concentration of a polymer sample if the viscosity of the polymer sample is measured. A viscometer (Brookfield LVDV-II+, Brookfield Engineering Laboratories, Inc., Massachusetts, USA) is employed to measure the viscosity of polymer solutions used in this study.

2.2 Interactions of Chemicals with Oil-Brine-Sand Systems

2.2.1 Alkali and oil-brine-sand system

First, equal amount of the crude oil and an alkaline solution with a known NaOH concentration is mixed and stirred at a typical reservoir flow rate (i.e., 1-2 ft/day) for 6h. The concentration difference before and after the stirring is measured to determine the alkaline loss into the oil phase. Secondly, the alkaline loss also occurs when alkali reacts with the divalent cations in the brine sample, such as Ca^{2+} and Mg^{2+} to form some insoluble solid precipitates. Once precipitation occurs in a brine sample, the alkaline concentration change is measured before the precipitation occurs and after the precipitation is filtered. Thus the alkaline loss into the brine is quantified. Also a brine sample is titrated to determine the initial hydroxyl ionic concentration so that NaOH concentration in the brine sample can be accurately determined. Thirdly, silica sand and NaOH solution are mixed in a proportion of 1:3 at a typical reservoir flow rate for 24 h by using a shaker (L.E.D. Orbital Shaker, Lab-Line Instruments, Inc. Illinois, USA). The alkaline concentration difference is measured to determine the alkaline loss onto the sand surfaces due to alkaline adsorption. Meanwhile, the sand mass change is also recorded to quantify the silica (possibly some clay on the silica sand) dissolution in the alkaline solution.

2.2.2 Surfactant and oil-sand system

First, equal amount of the crude oil and a surfactant solution with a known surfactant concentration is mixed at a typical reservoir flow rate (i.e., 1-2 ft/day) for 6h by using the shaker. The surfactant concentration after the mixing is measured to determine the surfactant loss into the oil phase. Secondly, silica sand and surfactant solution are mixed

in a proportion of 1:3 at a typical reservoir flow rate for 24 h. The surfactant concentration change is measured to determine the surfactant loss onto the sand surface due to surfactant adsorption.

2.2.3 Polymer and sand system

Silica sand and polymer solutions with different concentrations are mixed in a proportion of 1:3 at a typical reservoir flow rate for 24 h by using the shaker. The polymer concentration change is measured to determine the polymer loss onto the sand surface due to polymer adsorption.

2.3 IFT Phenomena and Oil Shrinking Effect of Crude Oil in Alkaline Solutions

The interfacial tension at the crude oil-alkaline solution interface is measured as a function of alkaline concentration by using the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. In the ADSA technique, an objective function is constructed to express the discrepancy between the physically observed drop profile and the theoretically predicted Laplacian curve. Then this objective function is minimized numerically so as to determine the IFT with sufficient accuracy. This technique only requires two input data: the local gravitational acceleration and the density difference between the oil and aqueous phases. The output data of ADSA technique for the pendant drop case also include the radius of the curvature, volume and surface area of the oil drop.

2.3.1 Apparatus

A block diagram of the experimental set-up for the dynamic IFT measurement is shown in Figure 2.4. As seen from this figure, the entire experimental set-up consists of three major parts: microscope and camera system, glass beaker and pendant drop delivery system, and data acquisition system. The technical details regarding the optical system and data acquisition system can be found elsewhere (Gu, 2002). Here, only the pendant drop delivery system is briefed.

2.3.2 Pendant drop delivery system

In this study, a glass beaker with an injection needle at the bottom is used to form a floating pendant oil drop in an aqueous phase for the IFT measurement. The square glass beaker is made of glass slides ($5 \times 5 \times 5 \text{ cm}^3$). A needle is installed at the bottom of the glass beaker and connected to a syringe with a 1/8 inch tube. In addition, a needle valve is inserted between the needle and the syringe to control the volume of the pendant oil drop. After the completion of a set of dynamic IFT measurements, the needle is removed and replaced by a new one. Three needles with different sizes ($\text{OD}=0.254, 0.406, 0.540 \text{ mm}$) are used, depending on the IFT values to be measured.

2.3.3 Crude oil and aqueous solutions

The crude oil used in this study is also from the Instow field. The aqueous phases used in experiments are deionized ultra-filtered (DIUF) water (Fisher Scientific, Canada), and the alkaline solutions are made up from DIUF water at different NaOH concentrations, together with NaCl and CaCl_2 . These chemicals are all reagent grade (MERCK KGaA, Germany).

2.3.4 Dynamic IFT measurements

The dynamic IFT of the crude oil against the aqueous phase is measured by using the ADSA technique for the pendant drop case. It should be noted that the ADSA technique can be used to take the sequential images with time so that the dynamic IFT phenomenon can be thoroughly examined.

2.3.5 Equilibrium IFT measurements

During the dynamic IFT measurements, the IFT at the oil-water interface is found to reach a constant value after certain time. It can be assumed that the IFT reaches the equilibrium state and no longer changes with time. The constant IFT is defined as the equilibrium IFT. The equilibrium IFT at the crude oil-alkaline solution interface is measured as a function of alkaline concentration by using the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. The synergistic effect of alkali and surfactant on achieving the ultra-low equilibrium IFT is studied by using the spinning drop tensiometer (EOR, Inc., Texas, USA). Each of the two alkalis, sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3), is tested with surfactant solutions for comparison. It should be noted that both the dynamic IFT and the equilibrium IFT measurements are conducted at the room temperature of 25 °C.

2.3.6 Experimental procedure

After the pendant drop delivery system is placed between a light source and a microscope (a Leica Wild M3B microscope mounted with a Cohu 4910 CCD monochrome camera), the dynamic IFT measurement is carried out according to the following procedure. First, the glass beaker is filled with a prepared aqueous solution and then the needle valve is turned on slightly. An oil drop is formed at the tip part of the

needle. After the oil drop is stable and its digital image is well focused, the video signal of its instantaneous image is transmitted to a videopix digital processor performing the frame grab and digitization of the image to a matrix of 640×480 pixels. Finally, such acquired images are digitized and analyzed by using a personal computer to determine the IFT (Rao, 1997; Rao and Lee, 2003).

2.4 Coreflood Tests

2.4.1 Schematic diagram

Experimental study of a waterflood or a chemical flood in a homogeneous system is usually performed in short one-dimensional sand-packs/cores. Such coreflood tests may be applied to study, e.g., linear displacement efficiency, chemical adsorption, and optimum chemical slug size. Also, the variations of pressure drop vs. flow rate in the process of a coreflood test can be used in numerical simulation (Sorbie *et al.*, 1987b). In this study, coreflood tests are conducted to study the oil recovery and to determine the chemical concentration profiles of the produced fluids in alkaline floods, surfactant floods, AS floods, polymer floods, and ASP floods. It should be noted that the alkaline floods and some of polymer floods are performed in the sand-packs, whereas surfactant, AS, ASP and the other polymer floods are conducted in the Berea cores. The schematic diagram of the setup used in coreflood tests is shown in Figure 2.5. As indicated in this figure, the entire experimental setup consists of the following major parts: vacuum pump, positive displacement pump, hydraulic cylinders, pressure gauges, and sand-pack/Berea cores.

2.4.2 Apparatus and materials

2.4.2.1 Coreflood setup

As mentioned above, the coreflood setup consists of the following major parts: vacuum pump, positive displacement pump, hydraulic cylinders, pressure gauges, and sand-pack/Berea cores. The vacuum pump (See Figure 2.6) is Maxima plus M2C (Fisher Scientific, Canada), which is used to evacuate the sand-pack or the Berea core. The DBR-JEFRI Pump (See Figure 2.7) (Model PMP-1000-1-10-M-316-M4-40, DB Robinson Group, Canada) is used to pump fluids (the crude oil, brine or chemical solutions) through the sand-pack or the Berea core. Three 500 ml hydraulic cylinders (See Figure 2.8) (DB Robinson Group, Canada) are used to deliver the crude oil, the brine, and the chemical solutions, respectively. Two pressure gauges are Ametek U.S. Gauges (Pennsylvania, USA) with pressure range of 0-30 psi and 0-200 psi, respectively.

All the coreflood tests with sand-packs are conducted at the room temperature of 25 °C, whereas all the coreflood tests with the Berea cores are carried out at a temperature of 50 °C by using a heating tape (Fisher Scientific, Canada) to wrap the core. The chosen temperature (50 °C) is equal to the reservoir temperature of the Instow oil field.

2.4.2.2 Sand-pack/Berea core

The sand used in making the sand-pack is a mixture of two different Ottawa sands (Burnside Sand & Gravel Ltd, Canada), 50 wt.% of 50-60 meshes and 50 wt.% of 100-120 meshes. The coreholder (with a sand-pack inside) and a lead sleeve are shown in Figure 2.9. The sand-packs used in this study are 6 inch long and 1.5 inch in diameter and their absolute permeabilities are in a range of 5-7 μm^2 . The procedure of packing a sand-pack is described as follows. The lead sleeve in the coreholder is first filled with certain

amount of water. Sand is added up to about one third of the total volume of lead sleeve. A vibrator is used to shake the coreholder for at least 15 min. Then additional sand (1/3 each time) is added until the lead sleeve is fully packed. Usually, it takes 45 min to pack one sand-pack. In order to remove the water remaining inside the sand-pack, about 1 pore volume (PV) of acetone is injected into the sand-pack to help vaporize the water. Afterwards, the sand-pack is connected to a pressurized air hose to blow out the remaining water and acetone in the sand-pack. Once the sand-pack is thoroughly dried, the overburden pressure can be applied so that the pore volume of the sand-pack can be measured, which will be described later on.

The Berea core is homogeneous split rock from Cleveland Quarries, USA. The Berea cores are 5 inch long and 2 inch in diameter and their absolute permeabilities are in a range of $0.05\text{-}0.08\ \mu\text{m}^2$. The Berea core is first glued together with two distributors (one at each end) by using the silica sealant for 24 h. A layer of resin is applied to fully coat the core. After this resin coating is dried, the second layer of resin is applied. In general, five to seven layers of resin are needed for a well-prepared Berea core (See Figure 2.10).

The procedure to measure the pore volume of the sand-pack/Berea core is described as follows. First, the dead volume inside the two distributors (one at each end) of the sand-pack/Berea core is measured. Secondly, the sand-pack/Berea core is evacuated by using a vacuum pump. After the evacuation, the valves at both ends of the sand-pack/Berea core are tightly closed. Thirdly, the inlet of the sand-pack/Berea core is dipped into a brine solution with known weight and density. Then the inlet valve is opened and the brine is imbibed into the sand-pack/Berea core. Fourthly, when the imbibition process is finished, the weight of the brine solution is measured. With the

measured weight difference and known density of the brine solution, the total volume of the brine imbibed into the sand-pack/Berea core can be calculated. Thus the pore volume of the sand-pack/Berea core can be determined by subtracting the dead volume from the total volume of the brine imbibed.

2.4.2.3 Crude oil and brine samples

The crude oil and the brine tested in this study are collected from the Instow oil field in Saskatchewan, Canada. At the room temperature of 25 °C, the viscosity of the crude oil is 40.3 mPa·s and its density is 903.6 kg/m³. The acid number is 0.23 mg KOH/g-oil.

The density of the brine is 1001.6 kg/m³ at 20 °C and its total dissolved solids (TDS) is 4310 mg/L. The pH of brine is 8.16. The detail physical and chemical properties of the crude oil and the brine from the Instow oil field are listed in Table 2.1 and Table 2.2, respectively.

2.4.2.4 Chemicals

The alkali used in the alkaline floods is sodium hydroxide (NaOH) (reagent grade). The surfactant (ORS-62HF, Oil Chem Technologies, Inc., Texas, USA) used in the surfactant floods and the alkaline-surfactant floods is an anionic surfactant. For comparison, two alkalis, sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃), are used and each of them is tested together with the surfactant for AS floods, respectively. The partially hydrolyzed polyacrylamide (HPAM) used in polymer floods and alkaline-surfactant-polymer floods is Flopaam 3630s (SNF Floerger, France), with molecular weight of approximately 20 million grams and hydrolysis level at 25-30 % in mole.

2.4.3 Experimental procedure

The experimental procedure for the coreflood tests is described as below. After being vacuumed, the sand-pack or the Berea core is saturated first with the brine and then with the crude oil. Three-stage tests are performed in the sequence of conventional waterflooding, chemical flooding and subsequent waterflooding at a reservoir flow rate (e.g., 1.2 ft/day). More specifically, conventional waterflooding continues until the water-cut reaches 100%. The corresponding oil recovery is noted. Chemical flooding is performed by injecting pre-specified PV of the chemical solution. At the third stage, subsequent waterflooding is followed until the water-cut reaches 100%. The amount of water injected at this stage is recorded. Figure 2.11 shows a typical layout of a chemical flood. The oil recovery of each flood is determined at the end of the three-stage test. In this thesis, all the oil recovery represents the percentage of OOIP. Also, the chemical concentrations in the produced fluids collected from the beginning of chemical flooding to the end of subsequent waterflooding are measured and monitored in each coreflood test. If the measured chemical concentrations in the produced fluids are relatively high, a further coreflood test is conducted by re-injecting the produced fluids to study the feasibility of reusing the produced chemicals for further enhancing oil recovery.

It should be noted that the error analysis for all the experiments has been carried out. The relative error is 3.0% for alkaline loss, 2.0% for silica loss and 4.0% for surfactant loss, respectively. The relative error for the oil recovery is equal to 0.8-3.0% for the sand-pack coreflood tests and 0.6-2.0% for the Berea coreflood tests, respectively.

Table 2.1 Physical and chemical properties of clean Instow dead oil.

(Well Number: 16-33-9-18 W3M)

Temperature (°C)	15	25	50
Density (kg/m ³) @ 1 atm	910.1 (23.8°API)	903.6	886.5
Viscosity (mPa.s) @ 1 atm	69.8	40.3	15.7
Molecular Weight (g/mol)	268		
Acid Number (mg KOH/g-oil)	0.23		
Asphaltene (wt.%)	8.4		

Table 2.2 Physical and chemical properties of clean Instow brine.

(Well Number: 16-33-9-18W3)

Temperature (°C)	15	20	40
Density (kg/m ³) @ 1 atm	1002.4	1001.6	995.5
Viscosity (mPa.s) @ 1 atm	1.15	1.01	0.65
pH	8.16		
Conductivity @ 25°C, mS	6.69		
Refractive Index @ 25°C	1.3338		
Chloride, mg/L	1860.00		
Sulfate, mg/L	<1.00		
Total dissolved solids, mg/L	4310.00 (110 °C)		
	4200.00 (180 °C)		
Potassium, mg/L	6.42		
Sodium, mg/L	1510.00		
Calcium, mg/L	21.70		
Magnesium, mg/L	7.92		
Iron, mg/L	<0.15		
Manganese, mg/L	<0.08		
Barium, mg/L	8.50

Figure 2.1 pH vs. NaOH concentration calibration curve.

Figure 2.2 Absorbance vs. polymer concentration calibration curve (Flopaam 3630s, wavelength=470 nm).

Figure 2.3 Viscosity vs. polymer concentration calibration curve (Flopaam 3630s).

Figure 2.4 Experimental setup used to measure the IFT between a crude oil and an alkaline solution.

Figure 2.5 Flow chart of the coreflood tests.

Figure 2.6 Maxima plus M2C vacuum pump.

Figure 2.7 DBR-JEFRI positive displacement pump.

Figure 2.8 500 ml hydraulic cylinder purchased from DBR.

Figure 2.9 The sand-pack and lead sleeve used in the alkaline floods and some polymer floods.

Figure 2.10 The prepared Berea cores used in the surfactant floods, alkaline-surfactant floods, some polymer floods, and alkaline-surfactant-polymer floods.

Figure 2.11 A typical layout of a chemical flood.

CHAPTER 3 ALKALINE FLOODS

3.1 Interactions with Oil-Brine-Sand System

3.1.1 Alkali-oil system

When an alkali is made in contact with the crude oil, the surfactants are generated *in situ* by the chemical reactions between the alkali and the natural organic acids in the crude oil. With sufficient alkali available in the alkaline solution, the amount of surfactants generated entirely depends on the total organic acids present in the crude oil, which can be represented by the so-called acid number. Figure 3.1 shows NaOH loss in the oil phase at different alkaline concentrations ranging from 0.10 to 1.20 wt.%. It is seen from this figure that NaOH loss in the oil phase generally tends to increase as the alkaline concentration increases. It is worthwhile to point out that, however, the maximum alkaline loss is only about 0.14 mg/g-oil, which is below the acid number of 0.23 mg KOH/g-oil in the present case. It is obvious that alkali cannot react with all the organic acids present in the crude oil at a typical reservoir flow rate.

3.1.2 Alkali-brine system

When a sodium hydroxide is introduced into a brine sample, some precipitation is observed. Such precipitates are the insoluble calcium hydroxide and magnesium hydroxide. The alkaline loss in the brine sample depends on its calcium and magnesium ionic concentrations. Given the low concentrations of calcium ions (21.70 mg/L) and magnesium ions (7.92 mg/L) in the brine tested (Table 2.1), the alkaline loss due to the chemical reactions between the alkali and the divalent cations in the brine, e.g., Ca^{2+} and Mg^{2+} , is small and negligible in this study.

3.1.3 Alkali-sand system

When an alkaline solution is injected into reservoir formations, the alkaline loss onto the reservoir rocks is remarkable, given the tremendous amount of surface area of sand grains in a reservoir. In fact, two processes are usually involved in the interactions in an alkali-rock system. First, adsorption of alkali onto the rock surface is considered to be major alkaline loss during an alkaline flood process. Second, the injected alkali may react with the reservoir rocks. This chemical reaction also causes alkaline loss and silica loss in the alkaline solution as well. The alkaline loss onto the sand surface at different NaOH concentrations is shown in Figure 3.2. It is found from this figure that the alkaline loss onto the sand surface increases with NaOH concentration. The alkaline loss remains almost the same when NaOH concentration is higher than 0.80 wt.%. At this concentration, it is assumed that the alkaline adsorption onto the sand surface is saturated. On the other hand, chemical reaction between alkali and silica sand is another important factor causing alkaline loss. The silica loss during an alkaline flood is also measured and shown in Figure 3.3 at different NaOH concentrations. This silica loss vs. NaOH concentration curve indicates that the silica loss monotonously increases with an increase in NaOH concentration. It should be noted that the measured silica loss is not caused merely by the chemical reaction between silica sand and alkali. This loss also includes the mass loss of sand surface impurities, which are washed away during the interaction tests.

3.2 IFT Phenomena and Oil Shrinking Effect

More recently, the ADSA technique for the pendant drop case has been applied to measure low IFTs (less than 1 mN/m) in many cases, such as CO₂ flood and solvent injection (Rao, 1997; Rao and Lee, 2003). Unlike the spinning drop method, the pendant drop shape method is stationary and involves no convection. Thus the ADSA technique for the pendant drop case can be used to measure the IFT with sufficient accuracy. In particular, sequential images can be taken to study the dynamic IFT phenomenon.

3.2.1. Dynamic IFT behavior

When an acidic crude oil is made in contact with an alkaline solution, the surfactants are generated *in situ* by the chemical reactions between the natural organic acids in the crude oil and the alkali. This process results in the dynamic IFT behavior, which may influence the performance of alkaline flood process. Figures 3.4 and 3.5 show the variations of dynamic IFT with time at two low sodium hydroxide concentrations (0.05 wt.% and 0.10 wt.%), and at two high sodium hydroxide concentrations (0.80 wt.% and 1.20 wt.%), respectively. Here, some important trends are worthwhile to note in these two figures.

First, the dynamic IFT behavior is observed once NaOH is introduced into the aqueous phase regardless of its concentration. This behavior can be explained as follows. This explanation is based on the assumption that the dynamic IFT is always inversely proportional to the interfacial concentration of the surfactants so that the minimum IFT corresponds to a maximum surfactant concentration at the oil-water interface. Once the crude oil is made in contact with the alkaline solution, the generated surfactants, which are more likely water-soluble and sometimes both water-soluble and oil-soluble, start to

diffuse into the aqueous phase and possibly into the oil phase as well. At the beginning, this diffusion process is much slower than the chemical reaction process so that the concentration of the generated surfactants at the oil-water interface keeps increasing. At certain time, the chemical reaction process diminishes and then the IFT reaches minimum value. After this minimum point, the diffusion process becomes dominant so that it causes reduction of the surfactant concentration at the oil-water interface. Thus the IFT begins to increase gradually. This dynamic IFT behavior depends on the chemical reaction and the diffusion processes. In this study, it is found that, at high alkaline concentrations (>0.80 wt.%), the IFT quickly reaches the so-called minimum point. Also, the overall IFT values between the crude oil and alkaline solution at high alkaline concentrations are relatively close to the minimum value in comparison with the results at low alkaline concentrations.

Secondly, it should be noted that the dynamic IFT behavior also varies with the NaOH concentration. At low NaOH concentrations (See Figure 3.4), the IFT gradually reaches the equilibrium value after the minimum point. The former is much larger than the latter. This means that most surfactants generated *in situ* are diffused into the alkaline solution and oil phase at low NaOH concentrations. However, this phenomenon is not observed at high NaOH concentrations (See Figure 3.5), where the IFTs after their minimum points remain almost constant. This finding is rather different from the results obtained by using the spinning drop method in the literature, where the IFT was reported to reach essentially the same value regardless of NaOH concentration (Taylor and Schramm 1990; Nasr-El-Din and Taylor 1992; Taylor and Nasr-El-Din, 1995).

Thirdly, if the minimum IFT is chosen as the representative IFT for each alkaline concentration, variations of the minimum IFT with the alkaline concentration is shown in Figure 3.6. The IFT reaches 0.20 mN/m at 0.20 wt.% NaOH concentration and above this concentration then slightly increases with NaOH concentration. However, no ultra-low IFT has been achieved due to the low acid number (0.23 mg KOH/g-oil) of crude oil sample. IFT values shown in Figure 3.6 indicate that there may exist an optimum NaOH concentration at which the lowest IFT is obtained.

Given the fact that the dynamic IFT phenomenon always occurs when the acidic crude oil with natural acids is reacted with an alkaline solution, one question that naturally arises is what IFT value should be used in characterizing an alkaline flood. McCaffery (1976) concluded that, though the initial displacement at low IFT may be possible, the rapid increase in IFT after its minimum precludes the sustained displacement. The enhanced oil recovery due to low IFT cannot be operative in an alkaline flood. It should be noted that McCaffery (1976) performed the dynamic IFT measurements by using the spinning drop tensiometer. It is speculated that the convection involved in the IFT measurements by using the spinning drop tensiometer may affect the diffusion process of the surfactants in crude oil-alkaline solution system to an unknown degree. From this point of view, the IFT of the crude oil and alkaline solution measured in this study may be closer to those under the practical reservoir conditions. Also the present experimental results show that, after their minimum points, the IFTs remain almost constant at high alkaline concentrations. Therefore, a high alkaline concentration may be needed in an alkaline flood process in order to avoid the rapid increase of IFT after its minimum point.

In addition, the dynamic IFT phenomenon plays an important role in the emulsification during an alkaline flood process in which the spontaneous emulsification is considered as a major enhanced oil recovery mechanism (Cash *et al.*, 1975; Schechter, *et al.*, 1975). The surfactants generated *in situ* by the chemical reactions between the natural organic acids in the oil and the injected alkali can effectively emulsify the residual oil into small oil droplets, which can be entrained and carried forward by the shear flow. Thus the residual oil is mobilized. It is also noted that, when the added surfactant in water is made in contact with clean oil rather than acidic oil, no emulsification is observed in this case (Rubin and Radke, 1980). Therefore, the spontaneous emulsification is essentially caused by the IFT gradient across the oil-water interface, which is called the Marangoni effect. Hence, the dynamic IFT phenomenon may significantly affect this emulsification process and thus the performance of an alkaline flood.

3.2.2 Equilibrium IFTs between the crude oil and alkaline solutions

During the dynamic IFT measurements, the IFT at the oil-water interface is found to reach a constant value after certain time. It can be assumed that the IFT reaches the equilibrium state and no longer changes with time. The constant IFT is defined as the equilibrium IFT. In this study, the effect of alkaline concentration on the equilibrium IFT is examined. Variations of the equilibrium IFT between the crude oil and the alkaline solutions at different NaOH concentrations are shown in Figure 3.7. The IFT is reduced from 21.03 mN/m for a blank brine sample to 0.80 mN/m at 0.40 wt.% NaOH concentration. The IFT remains relatively constant at higher NaOH concentrations. However, no ultra-low IFT is achieved for a pure alkaline solution (0.02-1.20 wt.%

NaOH). This is probably due to the low acid number (0.23 mg KOH/g-oil) of the crude oil sample tested.

3.2.3 Effects of monovalent and divalent ions

In this thesis study, the effects of monovalent and divalent ions on the dynamic IFT behavior are also investigated. In the reservoir, NaCl and CaCl₂ often exist in the brines. In the literature, some previous studies (Chan and Shah, 1980; Chan and Shah, 1981) examined the effects of the monovalent and divalent ions on the IFT, respectively. At low salinities, most of the surfactant molecules are in the brine phase, whereas at very high salinities, some are in the oil phase. Hence, as the salinity is increased, the surfactant molecules gradually migrate from the aqueous phase to the oil phase. At certain salinity, the surfactant concentrations in the oil and aqueous phases become equal. This leads to the partition coefficient of unity and the minimum IFT is achieved (Chan and Shah, 1981). It has also been found that divalent ions can greatly increase the IFT. However, so far the detailed effects of monovalent and divalent ions on the dynamic IFT behavior have not been studied yet.

Figure 3.8 shows the dynamic IFT behavior when 1500 ppm NaCl and 50 ppm CaCl₂ are added into the alkaline solutions, respectively. It is found that, in comparison with the results shown in Figure 3.4, addition of NaCl does not noticeably affect the dynamic IFT behavior. However, it reduces the value of IFT to certain extent. This is because 1500 ppm NaCl concentration is lower than the so-called optimum salinity of this alkaline solution. The IFT at the oil-water interface decreases with an increase in the electrolyte concentration before the optimum salinity is reached (Green and Willhite, 1998). As shown in Figure 3.4, the minimum IFT at 0.05 wt.% NaOH concentration is

9.37 mN/m and changes to 4.36 mN/m at the same NaOH concentration with addition of 1500 ppm NaCl. In the presences of CaCl_2 , however, it is seen that the dynamic IFT behaves in a rather different manner. In fact, there is no minimum IFT in Figure 3.8 for 0.10 wt.% NaOH concentration with 50 ppm CaCl_2 . In comparison with the results shown in Figure 3.4 for 0.10 w % NaOH concentration, here, the IFT increases significantly with addition of only 50 ppm CaCl_2 .

3.2.4 Oil shrinking effect

In this thesis study, an interesting phenomenon is observed when the crude oil reacts with alkali. The volume of the crude oil drop reduces in the alkaline solution. The oil shrinking effect is quantified by using the ADSA technique for the pendant drop case.

Three possible mechanisms are suggested to explain this phenomenon. These mechanisms include oil volatility in an aqueous solution, chemical reactions between the oil phase and the alkaline solution, and possible migration of micro-water droplets from inside the oil drop to the bulk aqueous phase.

Furthermore, the effects of oil volatility and possible migration of micro-water droplets can be easily examined by testing the crude oil with DIUF water in which there are no chemical reactions involved. In this case, the oil shrinking is solely attributed to oil volatility and possible migration of micro-water droplets. Figure 3.9 shows the variations of dimensionless oil drop volume (dimensionalized by its initial volume) with time when the oil drop is in DIUF water and in alkaline solutions at NaOH concentrations of 0.05, 0.10, 0.80 and 1.20 wt.%, respectively. It is seen from this figure that the dimensionless volume of the oil drop decreases to 0.960 at 50 min in the pure DIUF water. For the same duration, however, the dimensionless oil drop volume decreases to 0.945 at 0.05 wt.%

NaOH concentration and to 0.881 at 0.10 wt.% NaOH concentration, respectively. It is also found that the dimensionless oil drop volume can decrease to approximately 0.525 at 1.20 wt.% NaOH concentration when $t=18$ min. A sequence of oil drop images is shown in Figure 3.10 for 0.10 wt.% NaOH concentration. It can be seen from these digital drop images that the oil shrinking effect is obvious. The above experimental results also indicate that the chemical reactions between the crude oil and the alkaline solution play a predominant role in the oil shrinking effect. This effect becomes more pronounced at high NaOH concentrations. By using the ADSA technique for the pendant drop case, the oil shrinking effect is quantified.

3.3 Alkaline Coreflood Tests

The alkaline coreflood tests have been performed to determine the oil displacement efficiency. Table 3.1 lists the results of four alkaline coreflood tests (Run No. AF1-4) and one re-injection test (Run No. AF5). The corresponding detailed coreflood data are given in Appendices 3.1-3.5. In Table 3.1, K_a stands for the absolute permeability of the sand-pack; ϕ stands for the porosity of sand-packs; OOIP is the original oil in place; S_{wi} is the irreducible water saturation; R_{WF} stands for oil recovery of waterflooding; AF stands for alkaline flooding, and SWF stands for subsequent waterflooding. The production performance curves at low alkaline concentrations, 0.10 and 0.40 wt.%, are shown in Figures 3.11 and 3.12, respectively. The corresponding enhanced oil recovery of alkaline floods is 7.0% and 7.1%, respectively, as given in Table 3.1. The water-cut is reduced from 100% to the lowest 94.8% for 0.10 wt.% and 93.7% for 0.40 wt.%, respectively. During subsequent waterflooding, 100% water-cut is reached after 1.9 PV of water is

injected for Runs No. AF1-2. The production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) for Runs No. AF3 and AF4 are shown in Figure 3.13 and 3.14, respectively. It is seen from these two figures that, when the injected alkaline concentration is increased to 0.80 wt.% (Run No. AF3), the oil recovery is apparently enhanced by 12.4% and the water-cut is reduced from 100% to the lowest 96.6%. Also, during subsequent waterflooding, the volume injected to reach 100% water-cut is increased up to 3.4 PV. However, if the alkaline concentration is further increased to 1.20 wt.% (Run No. AF4), marginal improvement of oil recovery is achieved. The oil recovery is only enhanced by 12.7% and the water-cut is reduced from 100% to the lowest 96.2%. The volume injected to reach 100% water-cut during subsequent waterflooding is further increased up to 3.7 PV. These four coreflood test results indicate that pure alkaline flood can enhance oil recovery up to approximately 12%. Nevertheless, the oil recovery in an alkaline flood may not be further enhanced by merely increasing the alkaline concentration. In fact, there may exist an optimum alkaline concentration for an alkaline flood process, e.g., in the range of 0.80-1.20 wt.% in this study.

The alkaline concentration of the produced fluids is monitored from the beginning of alkaline flooding for each alkaline coreflood test. Figure 3.15 shows the alkaline concentration curves of the produced fluids during the coreflood tests (Runs No. AF1-4). These curves clearly show the concentration variations at each flooding stage at four different injected NaOH concentrations. It is found that the highest alkaline concentration in the produced fluids reaches approximately 90% of the injected alkaline concentration at about 0.5 PV of subsequent waterflooding. As a large amount of alkali remained in the

produced fluids, a coreflood test is conducted by re-injecting the produced alkaline solutions collected from coreflood test Run No. AF4 (1.20 wt.% NaOH) to study the feasibility of reusing the produced alkali for further EOR.

3.4 Re-injection of the Produced Alkaline Solutions

As given in Table 1 for the re-injection test AF5, the average NaOH concentration of the produced fluids is found to be 0.81 wt.%. A total of 1.0 PV of the produced fluids is re-injected into the sand-pack as an alkaline slug. The production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) for Run No. AF5 are shown in Figure 3.16. As indicated in this figure, the enhanced oil recovery is equal to 10.8% and the water-cut is reduced from 100% to the lowest 94.7%. It is noted that the oil recovery for re-injecting the produced alkaline solutions (0.81 wt.%) is slightly lower than 12.4% obtained by directly injecting freshly made 0.80 wt.% alkaline solution.

3.5 Summary

In this chapter, an experimental study of alkaline flood process is carried out. First, the detailed experimental data for the total interactions of alkaline solutions with oil-brine-sand system are obtained and discussed. The alkaline loss into oil, into brine and onto sand surface is quantified, respectively. It is found that NaOH loss in the oil phase generally tends to increase as the alkaline concentration increases. However, the NaOH cannot react with all the organic acids in the crude oil at a typical reservoir flow rate. The NaOH loss due to the chemical reactions between the alkali and the divalent cations in the brine, i.e., Ca^{2+} and Mg^{2+} , is small and negligible in this study. The NaOH loss onto the sand surface increases with NaOH concentration. At certain concentration (0.80 wt.%)

NaOH), it is assumed that the alkaline adsorption onto the sand surface is saturated. The silica loss due to the chemical reactions between alkali and silica sand monotonously increases with an increase in NaOH concentration. Secondly, a series of measurements of the dynamic IFTs between the crude oil and different aqueous solutions are performed by using the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. It has been found that the measured IFT changes with time. This dynamic IFT phenomenon is interpreted in terms of the surfactant generation and distribution at the oil-water interface, as well as the diffusion processes in the bulk phases. Meanwhile, it has also been observed that the volume of the pendant oil drop in an alkaline solution decreases with time. The so-called oil shrinking effect has been quantified and three possible mechanisms for this effect have been proposed. These mechanisms include oil volatility in an aqueous solution, chemical reactions between the oil phase and the alkaline solution, and possible migration of micro-water droplets from inside the oil drop to the alkaline solution. Thirdly, alkaline coreflood test results show that a pure alkaline flood may enhance oil recovery up to 12.7%. However, the oil recovery in an alkaline flood may not be further enhanced by merely increasing the alkaline concentration. There might be an optimal alkaline concentration, above which the oil recovery cannot be significantly enhanced. Also, it has been found that the produced alkaline solutions can be effectively reused for further oil recovery.

Table 3.1 Coreflood test results for alkaline floods (sand-packs).

Run No.	k_a (μm^2)	ϕ (%)	OOIP (ml)	S_{wi} (%)	NaOH (wt.%)	R_{WF} (%)	AF (PV)	SWF (PV)	EOR (%)
AF1	6.68	33.0	48.5	10.0	0.10	52.6	1.0	1.9	7.0
AF2	7.11	33.1	46.5	13.7	0.40	49.5	1.0	1.9	7.1
AF3	7.18	32.6	45.5	14.3	0.80	49.9	1.0	3.4	12.4
AF4	7.26	32.6	46.5	12.4	1.20	46.5	1.0	3.7	12.7
AF5	7.18	32.7	47.5	10.9	0.81	50.5	1.0	3.4	10.8

Figure 3.1 NaOH loss in the oil phase vs. NaOH concentration.

Figure 3.2 Alkaline loss onto sand surface vs. NaOH concentration.

Figure 3.3 Silica loss vs. NaOH concentration.

Figure 3.4 Dynamic IFT vs. time at low NaOH concentrations.

Figure 3.5 Dynamic IFT vs. time at high NaOH concentrations.

Figure 3.6 The minimum IFT vs. NaOH concentration.

Figure 3.7 Variations of equilibrium IFT with NaOH concentration.

Figure 3.8 Dynamic IFT vs. time in the presence of either monovalent or divalent ions.

Figure 3.9 Dimensionless volume of oil drop vs. time for different aqueous solutions.

Figure 3.10 Variations of oil drop volume with time at 0.10 wt.% NaOH concentration.

Figure 3.11 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF1, NaOH concentration: 0.10 wt.%).

Figure 3.12 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF2, NaOH concentration: 0.40 wt.%).

Figure 3.13 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF3, NaOH concentration: 0.80 wt.%).

Figure 3.14 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF4, NaOH concentration: 1.20 wt.%).

Figure 3.15 Variations of produced NaOH concentration with injected PV during alkaline flooding (AF) and subsequent waterflooding (SWF) (Runs No. AF1-4).

Figure 3.16 Production performance curves during alkaline flooding (AF) and subsequent waterflooding (SWF) (Run No. AF5, NaOH concentration: 0.81 wt.%).

CHAPTER 4 SURFACTANT FLOODS

4.1 Interactions with Oil-Sand System

In this thesis study, the interactions between surfactant and the crude oil are investigated. The surfactant used is ORS-62HF, a free sample supplied by the Oil Chem Technologies, Inc. (Texas, USA), which is a commercial product composed of anionic surfactant and some co-surfactants. Since the specifications of this surfactant, e.g., the molecular weight, is not provided by the supplier, the anionic active substance concentration is first determined by titrating the known weight percentage concentration of surfactant solutions. A standard cationic reagent with known molar concentration is employed to titrate the surfactant solution with a known weight percentage concentration. At the end point, the molar concentration of this surfactant sample can be accurately determined because the mole numbers of the two solutions should be the same. Thus a calibration curve of anionic active substance concentration vs. surfactant weight percentage concentration is established and plotted in Figure 4.1. As seen from this figure, this calibration curve is close to a straight line.

4.1.1 Surfactant-oil system

The surfactant used in this study has both oil-soluble and water-soluble species. When a surfactant solution is made in contact with the crude oil, the water-soluble species stay in the aqueous phase (brine) while the oil-soluble species are in the oil phase, both of which can be absorbed at the oil-brine interface. The solubilization of surfactant species in the oil phase and their adsorption at the oil-brine interface result in the mass transfer of surfactant from the aqueous phase. Figure 4.2 shows the solubilization and the

adsorption, which are called surfactant loss in the oil phase, at different surfactant concentrations. It is found from this figure that the surfactant loss in the oil phase increases with an increase in surfactant concentration. The surfactant loss remains essentially the same when the surfactant concentration is higher than 0.20 wt.%. At this surfactant concentration, it is assumed that the oil phase is saturated with the oil-soluble surfactant species.

4.1.2 Surfactant-sand system

The surfactant loss onto the sand surface at different surfactant concentrations is shown in Figure 4.3. This figure indicates that the surfactant loss onto the sand surface increases with surfactant concentration. When the surfactant concentration reaches 0.40 wt.%, the adsorption of surfactant onto the sand surface assumedly reaches the saturation state.

4.2 Equilibrium IFTs between Pure Surfactant Solutions and Crude Oil

Figure 4.4 shows the equilibrium IFTs between pure surfactant solutions and crude oil at different surfactant concentrations. It is found that, in the tested surfactant concentration range (0.05-1.00 wt.%), the ultra-low IFT cannot be obtained for a pure surfactant solution.

4.3 Surfactant Coreflood Tests

The surfactant coreflood tests have been performed to determine the oil recovery of surfactant floods. Table 4.1 lists the results of three surfactant flood tests (Runs No. SF1-3) and one re-injection test (Run No. SF4). The detailed coreflood data are given in

Appendices 4.1-4. It is found that the enhanced oil recovery of a surfactant flood increases with the concentration of injected surfactant. The production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) for Runs No. SF1, SF2 and SF3 are shown in Figures 4.5, 4.6, and 4.7, respectively. As indicated in these figures and Table 4.1, when a total of 0.8 PV of 0.10 wt.% surfactant slug is injected into the Berea core, the oil recovery is enhanced by 17.2% and the water-cut is reduced from 100% to the lowest 92.4%. When the surfactant concentration is increased to 0.30 wt.%, the oil recovery is enhanced by 21.6% and the water-cut is reduced from 100% to the lowest 88.3%. If the surfactant concentration is further increased to 0.50 wt.%, the oil recovery is apparently enhanced by 27.3% and the water-cut is reduced from 100% to the lowest 86.2%. Also, it is seen from these figures that the volume injected to reach 100% water-cut is increased accordingly with the concentration of injected surfactant during subsequent waterflooding. This is because the higher the injected surfactant concentration is, the more the residual oil is displaced by the surfactant slug.

The surfactant concentration of the produced fluids is measured from the beginning of surfactant flooding for each surfactant coreflood test. Figure 4.8 shows the variations of produced surfactant concentration with injected PV during surfactant flooding and subsequent waterflooding for Runs No. SF1-3. It is seen from these curves that the peak surfactant concentrations in the produced fluids reach only about 10% of the injected concentration at about 0.8 PV of subsequent waterflooding. This fact indicates that there is a large amount of surfactant loss onto the core surface, in the oil phase and/or at the oil-water interface.

4.4 Re-injection of the Produced Surfactant Solutions

A coreflood test is conducted by re-injecting the produced surfactant solution collected from coreflood test Run No. SF3 (0.50 wt.% surfactant) to study the feasibility of reusing the produced surfactant. As shown in Table 4.1 for the re-injection test Run No. SF4, the average surfactant concentration of the produced fluids is measured to be 0.04 wt.%. A total of 0.8 PV of the produced fluids is re-injected into the Berea core. The production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) for Run No. SF4 are shown in Figure 4.9. It is found from Table 4.1 that the oil recovery for re-injecting the produced surfactant solutions is equal to 8.3% and the water-cut is reduced from 100% to the lowest 93.5%.

4.5 Summary

In this chapter, an experimental study of surfactant flood processes is conducted. First, the detailed experimental data for the total interactions of surfactant solutions with oil-rock system are presented and discussed. The surfactant loss in oil and onto rock surface is quantified, respectively. The surfactant loss in the oil phase increases with an increase in surfactant concentration. At certain concentration (0.20 wt.%), it is assumed that the oil phase is saturated with the oil-soluble surfactant species. Also the surfactant loss onto the sand surface increases with surfactant concentration. When the surfactant concentration reaches 0.40 wt.%, the adsorption of surfactant onto the sand surface assumedly reaches the saturation state. Secondly, the equilibrium IFT data show that pure surfactant solution cannot result in the ultra-low IFT. Thirdly, surfactant coreflood tests

show that oil recovery of a surfactant flood increases with the surfactant concentration. It is noted that surfactant flooding can enhance oil recovery by up to 27.3% at the surfactant concentration of 0.50 wt.%. Finally, the re-injection coreflood test shows that, even though the produced surfactant solution has a concentration of as low as about 10 % of the injected surfactant concentration, it can still enhance the oil recovery by 8.3%.

Table 4.1 Coreflood test results for surfactant floods (Berea cores).

Run No.	k_a (μm^2)	ϕ (%)	OOIP (ml)	S_{wi} (%)	R_{WF} (%)	Surfactant (wt.%)	SF (PV)	SWF (PV)	EOR (%)
SF1	0.070	18.4	30.2	35.1	20.5	0.10	0.8	1.6	17.2
SF2	0.075	18.6	30.0	36.2	20.0	0.30	0.8	2.0	21.6
SF3	0.052	18.6	30.8	34.5	23.4	0.50	0.8	2.4	27.3
SF4	0.052	18.5	30.0	35.9	20.0	0.04	0.8	1.6	8.3

Figure 4.1 Anionic active substance concentration vs. surfactant weight percentage concentration calibration curve.

Figure 4.2 Surfactant loss in oil phase vs. surfactant concentration.

Figure 4.3 Surfactant loss onto sand surface vs. surfactant concentration.

Figure 4.4 Variations of the equilibrium IFT with surfactant concentration.

Figure 4.5 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF1, surfactant concentration: 0.10 wt.%).

Figure 4.6 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF2, surfactant concentration: 0.30 wt.%).

Figure 4.7 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF3, surfactant concentration: 0.50 wt.%).

Figure 4.8 Variations of produced surfactant concentration with injected PV during surfactant flooding (SF) and subsequent waterflooding (SWF) (Runs No. SF1-3).

Figure 4.9 Production performance curves during surfactant flooding (SF) and subsequent waterflooding (SWF) (Run No. SF4, surfactant concentration: 0.04 wt.%).

CHAPTER 5 ALKALINE -SURFACTANT FLOODS

5.1 Synergistic Effect of Alkali-Surfactant System on IFT

In this study, the synergistic effect of alkali-surfactant system on reducing IFT is examined. Figure 5.1 shows variations of the equilibrium IFT with surfactant concentration at different respective NaOH concentrations. It is found that, in the tested surfactant concentration range (0.05-1.00 wt.%), the ultra-low IFT cannot be achieved for a pure surfactant solution. Once alkali is added into the surfactant solution, however, the IFT is reduced significantly and the ultra-low IFT can be achieved. In particular, the measured IFT reaches the order of 10^{-3} mN/m at 0.15 wt.% surfactant concentration, in conjunction with 1.0 wt.% NaOH. Figure 5.2 shows variations of the equilibrium IFT with surfactant concentration at different respective Na_2CO_3 concentrations. In comparison with the results shown in Figure 5.1, Na_2CO_3 shows a stronger ability to reduce IFT to the ultra-low values. For example, at the concentration of 0.3 wt.% surfactant together with 1.0 wt.% Na_2CO_3 , the measured IFT reaches 5.0×10^{-5} mN/m. All the ultra-low IFT data reported in this thesis are measured by using the spinning drop tensiometer.

As shown in Figures 5.1 and 5.2, it is found that there always exists a minimum IFT in each IFT curve. This fact is probably because of equal partitioning of surfactant in the oil and the brine phases at certain surfactant concentration (Chan and Shah, 1981; Wang and Gu 2003a). The surfactant used in this study has both oil-soluble and water-soluble species. At a lower surfactant concentration, the water-soluble species remain in the aqueous phase and the oil-soluble species stay in the oil phase, both of which can be

absorbed at the oil-brine interface. At certain concentration, partitioning of surfactant becomes equal in both the oil and the aqueous phases and the minimum IFT is achieved. As the surfactant concentration increases, the concentrations of both oil-soluble species and water-soluble species increase. Finally, the water-soluble species in the aqueous phase reach their critical micelle concentration (CMC) and begin to form micelles. In this case, the oil-soluble species can partition more into the oil phase or can be solubilized in the micelles in the aqueous phase. The solubilization of the oil-soluble species in the micelles decreases the CMC and the surfactant monomer concentration as well. The reduction in monomer concentration leads to a decrease in the interfacial concentration of the water-soluble species and thus to an increase in IFT. Hence, the IFT increases after the minimum value.

On the other hand, the chemical reactions between the organic acids in the oil phase and the alkalis in the aqueous phase for alkali-surfactant system may shorten the oil chain. Once the oil chain is shortened, partitioning of the surfactant in the oil phase increases and consequently the surfactant concentration in the brine phase decreases (Chan and Shah, 1981). Thus, when a proper oil chain length is achieved, the surfactant concentrations in both the oil and the aqueous phases become equal. Thus, the minimum IFT occurs at this specific oil chain length.

5.2 Alkaline-Surfactant Coreflood Tests

Table 5.1 lists the results of four AS coreflood tests (Run No. ASF1-4) and one re-injection test (Run No. ASF5). The detailed coreflood data are given in Appendices 5.1-5. In the tests, the initial surfactant concentration is kept the same at 0.30 wt.%. Two

alkalis, Na_2CO_3 and NaOH , are used for comparison at concentrations of 1.00 wt.% and 0.40 wt.%, respectively. A total of 0.8 PV of AS slug is injected after waterflooding. The production performance curves for Run No. ASF1 is shown in Figure 5.3. The surfactant concentration is 0.30 wt.% and the Na_2CO_3 concentration is 1.00 wt.% in the AS slug in ASF1. It is seen from this figure that the water-cut is reduced from 100% at the end of waterflooding to the lowest 86.4%. The oil recovery is enhanced by 27.3%. The production performance curves for Run No. ASF2 is shown in Figure 5.4. The surfactant concentration is 0.30 wt.% and the Na_2CO_3 concentration is 0.40 wt.% in the AS slug in ASF2. The water-cut is reduced from 100% at the end of waterflooding to the lowest 86.5%. The oil recovery is enhanced by 24.3%. The production performance curves for Run No. ASF3 is shown in Figure 5.5. The surfactant concentration is 0.30 wt.% and the NaOH concentration is 1.00 wt.% in the AS slug in Run No. ASF3. The water-cut is reduced from 100% at the end of waterflooding to the lowest 72.7%. The oil recovery is enhanced by 27.3%. The production performance curves for Run No. ASF4 is shown in Figure 5.6. The surfactant concentration is 0.30 wt.% and the NaOH concentration is reduced to 0.40 wt.% in the AS slug. It is seen from this figure that the water-cut is reduced from 100% at the end of waterflooding to the lowest 85.0%. The oil recovery is enhanced by 24.2%. It is worthwhile to note that, although the combinations of Na_2CO_3 and surfactant result in much lower IFTs than those for NaOH and surfactant combinations, the former yield essentially the same EOR results as the latter. For example, the IFT of 1.00 wt.% Na_2CO_3 and 0.30 wt.% surfactant combination is around 5.0×10^{-5} mN/m, whereas the IFT of 1.00 wt.% NaOH and 0.30 wt.% surfactant combination is about 7.1×10^{-3} mN/m. However, the EOR results of both AS floods

(ASF1 and ASF3) are equal to 27.3%. It is speculated that, as long as the IFT is lowered to certain level, the oil recovery in an AS flood cannot be significantly enhanced by merely further reducing IFT.

5.3 Effect of Alkalis on Reducing the Adsorption of Anionic Surfactant

Both alkaline and surfactant concentrations of the produced fluids are monitored from the beginning of AS flooding for each AS coreflood test. Figures 5.7 and 5.8 show the variations of produced alkaline and surfactant concentrations with injected PV during AS flooding and subsequent waterflooding for Runs No. ASF1-2 (Na_2CO_3) and Runs No. ASF3-4 (NaOH), respectively. These two figures show that the highest surfactant concentration in the produced fluids reaches over 12% of the injected surfactant concentration and the highest alkaline concentration reaches about 90% of the injected alkaline concentration at about 0.4-0.8 PV of subsequent waterflooding. These data are rather consistent with the results obtained from pure alkaline floods in Chapter 3 and pure surfactant floods in Chapter 4.

In order to clearly show the effects of alkalis on the produced surfactant concentration in an AS flood, the variations of produced surfactant concentration with injected PV in the four AS coreflood tests (Runs No. ASF1-4) are plotted in Figure 5.9 in comparison with the results for a pure surfactant flood Run No. SF2 at the same injected surfactant concentration (0.30 wt.%). It is worthwhile to point out that the produced surfactant concentrations in AS coreflood tests are slightly higher than those in a pure surfactant coreflood test. Moreover, the higher the alkaline concentration in an AS slug is, the higher the produced surfactant concentration is. These two facts are because the core

surface becomes more negatively charged at higher hydroxyl ionic concentrations in an AS flood. These anionic ions are adsorbed onto the rock surface to effectively deter the subsequent adsorption of anionic surfactants. In addition, in comparison with the oil recovery of SF2, the effects of the addition of alkalis on EOR are obvious. The higher the alkaline concentration in an AS slug is, the higher the oil recovery is. This is probably because the synergistic effect of alkali and surfactant combination results in the ultra-low IFT. The ultra-low IFT helps to more readily emulsify the residual oil and thus achieve higher oil recovery.

5.4 Pressure Drop Build-up during the Alkaline-Surfactant Floods

During an AS flooding process, it is noted that the pressure drop across the Berea core is increased to 50-60 psi, much higher than 20-35 psi in pure surfactant floods. There may be three possible major reasons for the pressure drop to increase. First, when alkali is made in contact with brine, the chemical reactions occur and result in certain precipitation, which may block some pore throats. Secondly, due to the ultra-low IFT, some residual oil is emulsified by the shear flow and broken into small oil droplets. These small oil droplets are entrained and carried forward by the AS slug until they are entrapped at the pore throats. Accordingly, there is a pressure build-up that forces the displacing phase to enter the untouched zones. Thirdly, the emulsified oil droplets are accumulated in front of the AS slug and gradually an oil bank may be formed. Thus, the pressure drop required to displace the oil bank is much higher than that required to displace sporadically distributed oil ganglia (Wang *et al.*, 2000; 2001a; 2001b).

5.5 Re-injection of the Produced Alkaline-Surfactant Solutions

In order to study the feasibility of reusing the produced AS solutions for further enhancing oil recovery, a re-injection coreflood test is conducted by re-injecting the produced alkaline and surfactant solutions collected from coreflood test Run No. ASF1. As shown in Table 5.1 for the re-injection test Run No. ASF5, the average alkaline and surfactant concentrations of the produced fluids collected from Run No. ASF1 are found to be 0.46 wt.% Na_2CO_3 and 0.03 wt.% surfactant, respectively. A total of 0.8 PV of the produced fluids is re-injected into the Berea core. The production performance curves are shown in Figure 5.10. It is seen from this figure that the water-cut is reduced from 100% at the end of waterflooding to the lowest 94.2% and the oil recovery is enhanced by 10.0%.

5.6 Summary

In this chapter, an experimental study of alkaline-surfactant flood processes is carried out. First, it has been found in Chapter 4 that a pure surfactant solution cannot result in the ultra-low IFT. Once alkali is added into the surfactant solution, however, the IFT is reduced significantly and the ultra-low IFT can be achieved. In addition, Na_2CO_3 shows a stronger ability to lower IFT to the ultra-low values in comparison with NaOH . The mechanisms of the synergistic effect of alkali and surfactant on reducing the equilibrium IFT are examined. It is found that equal partitioning of surfactant in the oil and the brine phases at certain surfactant concentration will result in a minimum IFT. The addition of alkalis may shorten the oil chain length, which also promotes the equal partitioning of surfactant in the oil and the brine phases. Secondly, coreflood test results show that

alkaline-surfactant floods can effectively enhance oil recovery, e.g., by up to 27.3%. Also, it is inferred that IFT plays an important but not dominant role in enhancing oil recovery. As long as the IFT is lowered to certain level, the oil recovery in an alkaline-surfactant flood cannot be effectively enhanced by merely further reducing IFT. Thirdly, the addition of alkalis into a surfactant solution can effectively reduce the adsorption of surfactant onto the reservoir rocks and significantly enhance oil recovery. Fourthly, the ultra-low IFTs resulted from alkaline-surfactant combinations promote the formation of the oil-in-water emulsions, which partially increase the displacement pressure drop across the Berea core. Therefore, the sweep efficiency is improved. Finally, re-injection coreflood test shows that the produced alkaline-surfactant fluids from alkaline-surfactant coreflood test can still enhance oil recovery by 10.0%. This fact suggests that the produced alkaline-surfactant fluids can be effectively reused for further EOR, though the concentration of the produced surfactant is rather low.

Table 5.1 Coreflood test results for AS floods (Berea cores).

Run No.	k_a (μm^2)	ϕ (%)	OOIP (ml)	S_{wi} (%)	R_{WF} (%)	Alkali (wt.%)	Surfactant (wt.%)	ASF (PV)	SWF (PV)	EOR (%)
ASF1	0.072	18.9	30.8	35.6	21.1	1.00 (Na_2CO_3)	0.30	0.8	2.4	27.3
ASF2	0.076	19.0	30.5	36.7	21.3	0.40 (Na_2CO_3)	0.30	0.8	2.0	24.3
ASF3	0.080	18.5	30.0	35.9	23.3	1.00 (NaOH)	0.30	0.8	1.6	27.3
ASF4	0.076	19.7	32.7	34.6	22.0	0.40 (NaOH)	0.30	0.8	1.6	24.2
ASF5	0.060	19.0	30.0	37.5	23.3	0.46 (Na_2CO_3)	0.03	0.8	1.6	10.0

Figure 5.1 Variations of equilibrium IFT with surfactant concentration at different NaOH concentrations.

Figure 5.2 Variations of equilibrium IFT with surfactant concentration at different Na_2CO_3 concentrations.

Figure 5.3 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF1, surfactant: 0.30 wt.%, Na_2CO_3 : 1.00 wt.%).

Figure 5.4 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF2, surfactant: 0.30 wt.%, Na_2CO_3 : 0.40 wt.%).

Figure 5.5 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF3, surfactant: 0.30 wt.%, NaOH: 1.00 wt.%).

Figure 5.6 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF4, surfactant: 0.30 wt.%, NaOH: 0.40 wt.%).

Figure 5.7 Variations of produced Na₂CO₃ and surfactant concentrations with injected PV during AS flooding (ASF) and subsequent waterflooding (SWF) (Runs No. ASF1-2 for Na₂CO₃).

Figure 5.8 Variations of produced NaOH and surfactant concentrations with injected PV during AS flooding (ASF) and subsequent waterflooding (SWF) (Runs No. ASF3-4 for NaOH).

Figure 5.9 Variations of produced surfactant concentration with injected PV in four AS floods (Runs No. ASF1-4) in comparison with those in Run No. SF2.

Figure 5.10 Production performance curves during AS flooding (ASF) and subsequent waterflooding (SWF) (Run No. ASF5, surfactant: 0.03 wt.%, Na_2CO_3 : 0.46 wt.%).

CHAPTER 6 POLYMER FLOODS

6.1 Interactions with Sand System

Application of polymer floods provides an effective way to increase the viscosity of the injected water and thus its sweep efficiency. However, Broseta *et al.* (1992) pointed out that polymer floods are sometimes uneconomical due to excessive retention in the reservoir. This retention includes the adsorption of polymer onto the rock system and the physical retention of polymer at the pore throats. In this study, the adsorption tests of the polymer solutions onto the sand system at different polymer concentrations are conducted. Figure 6.1 shows the variation of polymer loss onto the rock surface vs. polymer concentration. As indicated in this figure, for example, the adsorption of polymer onto the sand surface reaches 73.5 $\mu\text{g/g}$ -sand after the silica sand and 100 ppm polymer solution are mixed in a proportion of 1:3 and stirred at a typical reservoir flow rate (1.2 ft /day) for 24 h. The amount of this adsorption remains almost unchanged as polymer concentration increases up to 1500 ppm. This fact may suggest that after the polymer solutions and silica sand are mixed for 24 hours, the sand surface is already fully covered with polymer. Given the limited sand surface area, the amount of polymer consumed on the adsorption is almost the same for different polymer concentrations.

6.2 Alkali-Polymer Interactions

It has been reported that addition of alkalis into a polymer solution can slightly increase its viscosity (Krumrine and Falcone Jr., 1983). However, the opposite trends are found in the present viscosity measurements. Figure 6.2 shows effects of alkali on the

viscosity of polymer solutions. It is seen from these curves that the higher the alkaline concentration is, the lower the viscosity of an alkali-polymer solution is. For example, the viscosity of a 1200 ppm polymer solution prepared with the brine is equal to 15.7 mPa·s. It becomes 13.2 mPa·s at 0.1 wt.% NaOH, 12.0 mPa·s at 0.4 wt.% NaOH, and 10.3 mPa·s at 1.0 wt.% NaOH. It is speculated that addition of NaOH helps to increase the hydrolysis of polyacrylamide, which introduces negative charges, i.e., carboxyl groups, on the backbone of polymer chain. These carboxyl groups repel each other and cause the polymer chain to stretch. This process can slightly increase the viscosity of a polymer solution. On the other hand, the presence of sodium ions in the polymer solution can electrically neutralize these carboxyl groups. Thus, the repulsive forces among carboxyl groups are shielded and the polymer chains begin to coil up. This shielding causes a significant decrease in the viscosity of polymer solution (Lake, 1989). The competition of these two processes determines the overall effects of alkali on the viscosity of alkali-polymer solutions.

6.3 Polymer Coreflood Tests

Table 6.1 lists the results of five polymer coreflood tests (Runs No. PF1-5) conducted in the sand-packs. The detailed coreflood data are given in Appendices 6.1-5. In Run No. PF1, an attempt to determine the maximum oil recovery of polymer flooding is carried out. A total of 1 PV polymer slug with concentration of 1500 ppm is injected into a sand-pack. The production performance curves during polymer flooding and subsequent waterflooding are shown in Figure 6.3. It is found that the ultimate oil recovery is as high as 81.8% and that the oil recovery is significantly increased by 27.5% at polymer

flooding stage and then remains almost unchanged at subsequent waterflooding stage. Also, the water-cut is greatly reduced from 100% to the lowest 70.4% at polymer flooding stage and quickly reaches 100% again at subsequent waterflooding stage. This fact suggests that the highly viscous polymer slug sweeps through the sand-pack in a manner of a piston-like displacement because little oil is produced at subsequent waterflooding stage and the corresponding water-cut increases sharply at this stage.

In practice, however, polymer solution cannot be injected in the order of 1 PV due to its high cost. Coreflood tests with reduce-sized polymer slugs are conducted. In Runs No. PF2 and PF3, polymer slugs of 0.6 and 0.4 PV are injected, respectively, but at the same polymer concentration. The production performance curves of these two floods are shown in Figures 6.4 and 6.5, respectively. These results show that during the course of polymer flooding, the oil recovery is apparently reduced in comparison with that of Run No. PF1. However, oil recovery picks up quickly at subsequent waterflooding stage if a smaller slug is injected during the polymer flooding. These processes indicate that the polymer flood front will not breakthrough at polymer flooding stage if the slug size is around 0.4-0.6 PV. The major contribution to the ultimate oil recovery is from subsequent waterflooding stage at which the subsequently injected water keeps displacing the polymer slug forward to the outlet of the sand-pack. Compared with the ultimate oil recovery of Run No. PF1, the ultimate oil recovery for 0.4 PV polymer slug is not reduced remarkably. This suggests that the oil recovery of a homogenous sand-pack is not proportional to the injected polymer slug size.

To further confirm the above-mentioned pattern, the polymer concentration is reduced to investigate the effect of polymer concentration on oil recovery. Run No. PF4

is carried out by injecting 0.6 PV of 1000 ppm polymer and Run No. PF5 is conducted by injecting 0.4 PV of polymer slug at the same concentration. The production performance curves of these two corefloods are shown in Figures 6.6 and 6.7, respectively. As indicated in these two figures, the oil recovery follows the same trend as shown in the above-mentioned higher concentration polymer floods (Runs No. PF2-3) at the same injected pore volume. However, the oil recovery of lower concentration polymer floods is much lower than those of higher concentration polymer floods.

In order to more closely simulate the oil recovery of polymer floods in real reservoirs, two polymer coreflood tests (Runs No. PF6-7) and one re-injection test (Run No. PF8) are conducted in the Berea cores and the corresponding results are listed in Table 6.2. The detailed coreflood data are given in Appendices 6.6-8. Two different-sized polymer slugs, 0.4 PV and 0.8 PV, are injected for comparison at the same polymer concentration, 1000 ppm. It should be noted that such a polymer concentration, 1000 ppm, is chosen on the basis of literature review. In Run No. PF6, a total of 0.4 PV polymer slug is injected into the Berea core to determine its oil recovery. The production performance curves for Run No. PF6 are shown in Figure 6.8. It is found that at polymer flooding stage the oil recovery is enhanced by 4.0% only, whereas at subsequent water flooding stage the oil recovery is apparently enhanced by 16.9% and the water-cut is effectively reduced from 100% to 86.8%. The lower oil recovery achieved during this polymer flooding is consistent with the result obtained in the sand-pack (Run No. PF5), which is mainly due to its smaller slug size. Such a polymer slug is too small to push the accumulated oil bank to the outlet of the Berea core at polymer flooding stage. However, the oil recovery at subsequent waterflooding stage is still as high as approximately 15-20%. This fact again

verifies the piston-like displacement of polymer flooding. Although the concentration of polymer slug is diluted by the subsequently injected water, the oil displacement efficiency is still relatively high.

It should be noted that the EOR of Run No. PF6 in the Berea core is slightly higher than that of Run No. PF5 conducted at the same injected concentration and with the same injected PV in the sand-pack. This difference can be explained as follows. As the permeability of the Berea core is about two orders lower than that of the sand-pack, the flow behavior of polymer slug through the porous media is rather different. When the polymer slug flows through the sand-pack, the flow resistance is rather small and the large polymer molecules can pass the high permeability sand-pack. However, when the polymer slug flows through the low permeability Berea core, the polymer molecules can be entrapped at some small pore throats and thus certain blockage can be formed. Such blockage will force the subsequently injected polymer to flow through the untouched zones. Thus, the sweep efficiency is greatly improved in the Berea core. The above-mentioned entrapment is also confirmed by the pressure drop build-up during the polymer flooding in the Berea core. The pressure drop across the Berea core is around 80 psi during the polymer flooding, whereas the pressure drop across the sand-pack is around 15 psi during the same flooding.

In Run No. PF7, a total of 0.8 PV of 1000 ppm polymer slug is injected into the Berea core. The production performance curves for Run No. PF7 are shown in Figure 6.9. As indicated in Table 6.2 and in this figure, the oil recovery is significantly enhanced by 27.4%, which is almost the same as the EOR of injecting 1 PV of 1500 ppm polymer slug

in the sand-pack (Run No. PF1). The water-cut is effectively reduced from 100% to 85.3%. Such high oil recovery is attributed to the improved sweep efficiency.

6.4 Re-injection of the Produced Polymer Solutions

The produced polymer concentrations for the polymer floods performed in the Berea cores (Runs No. PF6 and PF7) are monitored and shown in Figures 6.10 and 6.11, respectively. It is seen from Figure 6.10 that the peak concentration for produced polymer from Run No. PF6 reaches 199 ppm at 1.6 PV of subsequent waterflooding. Similarly, as shown in Figure 6.11, the peak concentration for produced polymer from Run No. PF7 reaches 541 ppm at 0.8 PV of subsequent waterflooding. A re-injection coreflood test (Run No. PF8) is conducted by directly re-injecting 0.8 PV of produced fluids collected from Run No PF7. The average polymer concentration of the produced solutions is measured to be 354 ppm. The production performance curves during polymer re-injection and subsequent waterflooding are shown in Figure 6.12. Although the re-injected polymer concentration is rather low, the oil recovery of Run No. PF8 is still enhanced by 13.0% and the water-cut is reduced from 100% to 93.6%.

6.5 Summary

This chapter presents an experimental study of polymer flood processes in two different porous media. First, the interactions between polymer solution and sand system are investigated. It is found that the adsorption of polymer does not increase with polymer concentration in the range of 100-1500 ppm. Given the limited sand surface area, the polymer loss due to the adsorption is around 73.5 $\mu\text{g/g-sand}$. Secondly, the

addition of alkali into a polymer solution can slightly reduce its viscosity. Thirdly, coreflood test results show that the piston-like displacement of a polymer slug can greatly enhance oil recovery. Also, it is found that polymer flooding achieves higher oil recovery in the Berea cores than that in the sand-packs. The major reason is that some blockage is formed due to the entrapment of polymer molecules at some small pore throats so that the sweep efficiency in the low permeability Berea core is significantly improved. Finally, a re-injection coreflood test shows that the produced polymer solutions can be reused to effectively enhance oil recovery.

Table 6.1 Coreflood test results for polymer floods (Sand-packs).

Run No.	k_a (μm^2)	ϕ (%)	OOIP (ml)	S_{wi} (%)	R_{WF} (%)	Polymer (ppm)	PF (PV)	SWF (PV)	EOR (%)
PF1	7.15	35.2	51.5	10.1	54.2	1500	1.0	1.0	27.6
PF2	7.03	34.4	52.0	12.1	57.7	1500	0.6	1.2	25.7
PF3	7.18	32.7	48.5	13.8	55.7	1500	0.4	1.6	20.6
PF4	7.50	37.9	53.5	13.4	54.2	1000	0.6	1.5	22.4
PF5	5.23	34.4	51.0	12.9	61.8	1000	0.4	2.0	15.9

Table 6.2 Coreflood test results for polymer floods (Berea cores).

Run No.	k_a (μm^2)	ϕ (%)	OOIP (ml)	S_{wi} (%)	R_{WF} (%)	Polymer (ppm)	PF (PV)	SWF (PV)	EOR (%)
PF6	0.082	18.8	30.2	36.4	26.5	1000	0.4	2.0	20.9
PF7	0.077	18.9	30.2	36.8	27.2	1000	0.8	2.0	27.4
PF8	0.077	18.8	30.0	37.0	26.7	354	0.8	1.6	13.0

Figure 6.1 Polymer loss onto sand surface vs. polymer concentration.

Figure 6.2 Effects of alkali on the viscosity of alkali-polymer solutions.

Figure 6.3 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF1, polymer concentration: 1500 ppm).

Figure 6.4 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF2, polymer concentration: 1500 ppm).

Figure 6.5 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF3, polymer concentration: 1500 ppm).

Figure 6.6 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF4, polymer concentration: 1000 ppm).

Figure 6.7 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF5, polymer concentration: 1000 ppm).

Figure 6.8 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF6, polymer concentration: 1000 ppm).

Figure 6.9 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF7, polymer concentration: 1000 ppm).

Figure 6.10 Variations of produced polymer concentration with injected PV during 0.4 PV polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF6, polymer concentration: 1000 ppm).

Figure 6.11 Variations of produced polymer concentration with injected PV during 0.8 PV polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF7, polymer concentration: 1000 ppm).

Figure 6.12 Production performance curves during polymer flooding (PF) and subsequent waterflooding (SWF) (Run No. PF8, polymer concentration: 354 ppm).

CHAPTER 7 ALKALINE-SURFACTANT-POLYMER FLOODS

7.1 Alkaline-Surfactant-Polymer Coreflood Tests

On the basis of the studies of alkaline floods, surfactant floods, AS floods, and polymer floods, a series of ASP coreflood tests are performed to determine the oil recovery of ASP floods. Table 7.1 lists the results of four ASP coreflood tests (Runs No. ASPF1-4) and two re-injection tests (Runs No. ASPF5 and ASPF6). The detailed coreflood data are given in Appendices 7.1-6. A total of four different ASP injection schemes are employed for comparison in these coreflood tests. As given in Table 7.1, the injection scheme for Run No. ASPF1 is 0.8 PV AS slug (1.00 wt.% NaOH + 0.30 wt.% surfactant) followed by 0.4 PV polymer slug (1000 ppm polymer). The production performance curves for Run No. ASPF1 during 0.8 PV AS flooding, 0.4 PV polymer flooding and subsequent waterflooding are shown in Figure 7.1. As indicated in this figure, at AS flooding stage, the oil recovery is significantly enhanced by 24.8% and the water-cut is sharply decreased from 100% to 72.2%. At polymer flooding stage, the oil recovery is further enhanced by 10.3% and the water-cut is gradually increased to 83.9%. In summary, the oil recovery for Run No. ASPF1 during 0.8 PV AS flooding, 0.4 PV polymer flooding and subsequent waterflooding is enhanced by up to 43.4%.

Run No. ASPF2 is conducted by injecting 0.4 PV polymer slug (1000 ppm polymer) followed by 0.8 PV AS slug (1.00 wt.% NaOH + 0.30 wt.% surfactant). The major purpose of this coreflood test is to study the effect of chemical slug sequence on the oil recovery. The production performance curves for Run No. ASPF2 during 0.4 PV polymer flooding, 0.8 PV AS flooding and subsequent waterflooding are shown in Figure 7.2. It is

found that at polymer flooding stage, the oil recovery is increased by 3.4% only and the water-cut is slightly reduced from 100% to 94.3%. At AS flooding stage, the oil recovery is further enhanced by 22.4% and the water-cut is further reduced to 80.9%. In summary, the oil recovery for Run No. ASPF2 during 0.4 PV polymer flooding, 0.8 PV AS flooding and subsequent waterflooding is enhanced by up to 40.4%.

In comparison with the EOR result obtained in Run No. ASPF2, Run No. ASPF1 achieves a higher EOR. It can be interpreted in terms of the major EOR mechanisms of an AS slug injection followed by a polymer slug injection. The functions of an AS slug injection are to emulsify the crude oil into oil droplets and to mobilize the residual oil. The follow-up polymer slug injection is applied mainly to improve the mobility ratio so that a piston-like displacement can be established. However, when the polymer slug is injected before the AS slug in ASPF2, the residual oil is neither emulsified nor mobilized during the polymer flooding. Thus the polymer slug sweeps through the Berea core with relatively lower oil displacement efficiency. Although the follow-up AS slug can still emulsify and mobilize the residual oil to some extent, the oil recovery is lower due to its lower slug viscosity.

Runs No. ASPF3 and ASPF4 are carried out by simultaneous injection of either 0.8 PV or 0.4 PV of alkali, surfactant, and polymer solution. The production performance curves during 0.8 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) for Run No. ASPF3 are shown in Figure 7. 3. It is seen from this figure that the oil recovery is greatly enhanced by 26.1% at ASP flooding stage and the water-cut is remarkably reduced from 100% to 72.5%. In addition, at subsequent waterflooding stage, the oil recovery is further enhanced by 25.5% and the water-cut remains relatively low and then

gradually increases. It is noted that a total of 51.6% of OOIP is recovered during ASP flooding and subsequent waterflooding in Run No. ASPF3. Such a high oil recovery is attributed to the piston-like displacement of the emulsified and mobilized residual oil in the ASP flood. Also the homogeneity of the Berea core promotes the uniform displacement of the ASP slug with reduced water channeling and viscous fingering.

The production performance curves during 0.4 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) for Run No. ASPF4 are shown in Figure 7.4. The oil recovery is increased by 4.7% and the water-cut is reduced from 100% to 92.7% during the ASP flooding. However, the oil recovery is significantly enhanced by 32.3% and the water-cut is effectively reduced to 67.8% during subsequent waterflooding. When 0.4 PV ASP slug is injected into the Berea core, it recovers only a little amount of the residual oil due to its small slug size and its adsorption onto the Berea core surface. However, there are a large number of oil droplets accumulated in front of the ASP slug and gradually an oil bank is formed. During subsequent waterflooding, the subsequently injected water keeps pushing the ASP slug and the oil bank in front of it until they reach the outlet of the Berea core. Therefore, a sharp decrease in the water-cut is observed up to 0.4 PV during subsequent waterflooding.

7.2 Chemical Concentrations in the Produced Fluids

The produced chemical concentrations for each ASP coreflood test are monitored from the beginning of chemical flooding to the end of subsequent waterflooding. The produced chemical concentration profiles for Run No. ASPF1 are shown in Figure 7.5. It is seen from this figure that the peak concentrations for alkali, surfactant, and polymer are

0.75 wt.%, 0.02 wt.%, and 297 ppm, respectively. Figure 7.6 shows the variations of each produced chemical concentration with injected volume in Run No. ASPF2. The peak concentrations for alkali, surfactant, and polymer in ASPF2 are 0.80 wt.%, 0.03 wt.%, and 277 ppm, respectively. In comparison with the results obtained in ASPF1, the produced alkaline and surfactant concentrations in Run No. ASPF2 are slightly higher, whereas the produced polymer concentration in Run No. ASPF2 is slightly lower than that in Run No. ASPF1. These results suggest that if alkali and surfactant are injected first (ASPF1), they are adsorbed onto the Berea core surface. Their adsorption makes the rock surface more negatively charged and deters the subsequent adsorption of the anionic polymer. Similarly, if an anionic polymer is injected first (ASPF2) and adsorbed onto the core surface, its adsorption can reduce the subsequent adsorption of alkali and anionic surfactant due to the electrostatic repulsion.

Figure 7.7 shows the variations of the produced ASP concentrations with injected PV for Run No. ASPF3, which is carried out by injecting 0.8 PV of alkali, surfactant, and polymer solution simultaneously. The peak concentrations of alkali, surfactant, and polymer in Run No. ASPF3 reach 0.74 wt.%, 0.04 wt.%, and 642 ppm, respectively. In comparison with the peak surfactant concentration achieved in AS coreflood test Run No. ASF3 and the peak polymer concentration achieved in polymer coreflood test Run No. PF7, it is found that Run No. ASPF3 produces slightly higher surfactant and polymer concentrations. These results again suggest that the interactions among these ternary components (alkali, surfactant and polymer) and reservoir rocks can counteract each other and reduce the consumption of each chemical. Thus, the adsorption of alkali and anionic surfactants onto the reservoir rocks is reduced due to the electrical repulsion.

Figure 7.8 shows the variations of the produced ASP concentrations with injected PV for Run No. ASPF4, which is carried out by injecting 0.4 PV of alkali, surfactant, and polymer solution simultaneously. The peak concentrations of alkali, surfactant, and polymer in Run No. ASPF4 reach 0.42 wt.%, 0.02 wt.%, and 67 ppm, respectively. The produced chemical concentrations in this case are rather lower due to its smaller ASP slug and its adsorption onto the Berea core surface.

7.3 Re-injection of the Produced Alkaline-Surfactant-Polymer Solutions

Two re-injection coreflood tests (Runs No. ASPF5 and ASPF6) are conducted by directly re-injecting 0.8 PV of produced fluids collected from ASPF2 and ASPF3, respectively. The average concentrations of produced ASP solutions are given in Table 7.1. The viscosities of these two slugs are found to be 1.46 and 2.75 mPa·s, respectively. Such low viscosities are resulted from the chemical and mechanical degradations when the ASP solutions flow through the Berea cores. Obviously, these degradations are adverse to utilize the produced ASP fluids to improve the mobility of displacing phase. In addition, the IFT measurements show that the IFTs between the crude oil and the produced ASP fluids are in a range of 1-15 mN/m. The possible reason for such high IFTs is that most of the injected surfactant is consumed during the ASP flooding processes. The major component remaining in the produced fluids is alkali, which alone cannot result in low or ultra-low IFTs. A total of 0.8 PV of the produced fluids is re-injected into the Berea core. The production performance curves for Runs No. ASPF5 and ASPF6 are shown in Figures 7.9 and 7.10, respectively. It is found that the oil recovery of Run No. ASPF5 is enhanced by 16.8% and the water-cut is reduced from

100% to 92.2%. In addition, the oil recovery of Run No. ASPF6 is enhanced by 19.7% and the water-cut is reduced from 100% to 88.5%. The re-injection coreflood test data indicate that the produced ASP fluids collected from the ASP floods can be effectively reused and re-injected for further enhancing oil recovery.

7.4 EOR Mechanisms of Alkaline-Surfactant-Polymer Floods

The above-mentioned experimental data show that an ASP flood is a promising EOR technique for recovering the residual oil in an oil reservoir. The major EOR mechanisms of ASP floods can be summarized as follows. In conjunction with the added surfactant, the surfactants generated *in situ* by the chemical reactions between the injected alkali and the natural organic acids in the crude oil can result in ultra-low IFT. The ultra-low IFT at the oil-brine interface helps to emulsify and mobilize the residual oil in a reservoir. In addition, the reservoir rock surface becomes more negatively charged at higher hydroxyl ion concentrations. These negatively charged ions not only prevent the adsorption of anionic chemicals (Krumrine *et al.*, 1980), such as anionic surfactants and polyacrylamide, but also change the wettability of the rock surface (Mungan, 1984). Meanwhile, the added surfactant can increase the salinity tolerance of the alkalis (Gao *et al.*, 1995). To achieve the same displacement efficiency, the surfactant concentration required in the ASP flood can be one order lower than that in the micellar-polymer flood (Tong *et al.*, 1998). Finally, the injected polymer in ASP floods can significantly improve the mobility ratio and thus enhance the areal and vertical sweep efficiencies.

7.5 Summary

In this chapter, an experimental study of ASP flood processes is conducted. First, four different ASP injection schemes are employed to study the effect of chemical slug sequence and size on the oil recovery. It is found that the injection scheme of AS flooding followed by a polymer slug achieves a higher oil recovery than the injection scheme of polymer flooding followed by an AS slug. This is because AS slug can effectively emulsify and mobilize the residual oil in the core. Once the residual oil is mobilized, the follow-up polymer slug can cause a piston-like displacement to sweep through the core with higher displacement efficiency. In addition, simultaneous injection of alkali, surfactant and polymer can significantly enhance oil recovery. Secondly, the measured chemical concentrations in the produced fluids show that if alkali and surfactant are injected first, their adsorption onto the core surface will deter the subsequent adsorption of the anionic polymer. Similarly, if an anionic polymer is injected first and adsorbed onto the core surface, its adsorption can reduce the subsequent adsorption of alkali and anionic surfactant. Thirdly, re-injection coreflood tests show that, even though the viscosity of the produced ASP fluids from the ASP coreflood tests is rather low and the IFT between the crude oil and the produced ASP fluids cannot reach the ultra-low value, the produced ASP fluids can still be effectively reused for further enhancing oil recovery. Finally, the EOR mechanisms of ASP flood processes are discussed. The combinations of alkali and surfactant can result in the ultra-low IFTs at the crude oil and brine interface. Such ultra-low IFTs help to emulsify and mobilize the residual oil in a reservoir. In addition, the reservoir rock surface becomes more

negatively charged at higher hydroxyl ionic concentrations. These negatively charged ions not only prevent the adsorption of anionic chemicals but also change the wettability of the rock surface. Moreover, the injected polymer in ASP floods can significantly improve the mobility ratio and the sweep efficiency.

Table 7.1 Coreflood test results for ASP floods (Berea cores).

Run No.	k_a (μm^2)	ϕ (%)	OOIP (ml)	S_{wi} (%)	R_{wf} (%)	Injection Scheme	SWF (PV)	EOR (%)
ASPF1	0.080	18.5	29.0	38.0	24.1	0.8 PV AS (NaOH: 1.00 wt.%, S: 0.30 wt.%) + 0.4 PV 1000 ppm polymer	1.6	43.4
ASPF2	0.076	19.2	32.2	33.7	21.7	0.4 PV 1000 ppm polymer + 0.8 PV AS (NaOH: 1.00 wt.%, S: 0.30 wt.%)	1.6	40.4
ASPF3	0.086	19.1	32.2	33.3	28.6	0.8 PV ASP (NaOH: 1.00 wt.%, S: 0.30 wt.%, 1000 ppm polymer)	2.0	51.6
ASPF4	0.062	19.1	30.0	37.9	23.3	0.4 PV ASP (NaOH: 1.00 wt.%, S: 0.30 wt.%, 1000 ppm polymer)	2.0	37.0
ASPF5*	0.076	19.0	31.5	34.4	27.0	0.8 PV ASP (NaOH: 0.43 wt.%, S: 0.031 wt.%, 192 ppm polymer)	1.6	16.8
ASPF6**	0.074	19.0	32.0	33.3	27.2	0.8 PV ASP (NaOH: 0.51 wt.%, S: 0.033 wt.%, 387 ppm polymer)	1.6	19.7

Notes:

ASPF5* is conducted by re-injecting the produced solutions from ASPF2.

ASPF6** is conducted by re-injecting the produced solutions from ASPF3.

Figure 7.1 Production performance curves during AS+P flooding (ASF+PF) and subsequent waterflooding (SWF) (Run No. ASPF1).

Figure 7.2 Production performance curves during P + AS flooding (PF + ASF) and subsequent waterflooding (SWF) (Run No. ASPF2).

Figure 7.3 Production performance curves during 0.8 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF3).

Figure 7.4 Production performance curves during 0.4 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF4).

Figure 7.5 Variations of produced ASP concentrations with injected PV during AS+P flooding (ASF+PF) and subsequent waterflooding (SWF) (Run No. ASPF1).

Figure 7.6 Variations of produced ASP concentrations with injected PV during P+AS flooding (PF+ASF) and subsequent waterflooding (SWF) (Run No. ASPF2).

Figure 7.7 Variations of produced ASP concentrations with injected PV during 0.8 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF3).

Figure 7.8 Variations of produced ASP concentrations with injected PV during 0.4 PV ASP flooding (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF4).

Figure 7.9 Production performance curves during 0.8 PV ASP Re-injection (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF5).

Figure 7.10 Production performance curves during 0.8 PV ASP Re-injection (ASPF) and subsequent waterflooding (SWF) (Run No. ASPF6).

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This thesis studies the experimental techniques for detecting and reusing the produced chemicals in alkaline floods, surfactant floods, alkaline-surfactant floods, polymer floods and alkaline-surfactant-polymer floods. The chemical loss into the crude oil, into the brine, and onto the rock surface is quantified, respectively. The synergistic effect of alkali and surfactant combinations on reducing the interfacial tension (IFT) to the ultra-low value has been investigated. Coreflood tests for each type of chemical flood are performed to determine its oil recovery. The chemical concentrations in the produced solutions for each coreflood test are measured to examine the feasibility of reusing these produced chemicals. A total of six re-injection coreflood tests are conducted to reuse the produced chemicals for further enhancing oil recovery. On the basis of the experimental results obtained from this thesis study, the following specific conclusions can be made.

1. NaOH loss in the oil phase is below the acid number of the crude oil. NaOH loss in the brine is small and negligible in this study. NaOH loss onto the sand surface tends to increase with the alkaline concentration. At certain NaOH concentration, the alkaline adsorption onto the sand surface is assumed to reach the saturation state. In addition, the sand loss in the alkaline solution monotonously increases with an increase in NaOH concentration.
2. Dynamic IFT phenomenon is attributed to the chemical reactions between alkali and the crude oil and the diffusion processes of the generated surfactants into the aqueous phase and the oil phase. In addition, the oil shrinking effect observed during the

dynamic IFT measurements is probably due to oil volatility in an aqueous solution, chemical reactions between the oil phase and the alkaline solution, and possible migration of micro-water droplets from the oil drop to the bulk aqueous phase.

3. Alkaline coreflood test results indicate that a pure alkaline flood has reasonably good EOR potential. It is found that, however, the oil recovery in an alkaline flood cannot be further enhanced by merely increasing the alkaline concentration. In addition, the alkaline concentration in the produced solutions can reach approximately 90% of the injected alkaline concentration. Thus the produced alkaline solutions can be reused for further oil recovery.
4. The respective surfactant loss into the oil phase and onto the sand surface increases with an increase in surfactant concentration. The surfactant loss in both cases can reach its maximum at respective surfactant concentration.
5. Surfactant coreflood tests show that the oil recovery of a surfactant flood increases with the surfactant concentration. Even though the produced surfactant concentration is as low as 10% of the injected concentration, the re-injection of the produced surfactant solutions can still enhance the oil recovery to certain extent.
6. The ultra-low IFT cannot be achieved if either a pure alkaline solution or a pure surfactant solution is used. If alkali and surfactant are used together, however, the IFT is reduced significantly and the ultra-low IFT can be obtained. In addition, Na_2CO_3 and surfactant combinations show a stronger ability to lower the IFT in comparison with NaOH and surfactant combinations.

7. Alkaline-surfactant coreflood test results show that AS floods can greatly enhance oil recovery and the produced AS solutions can be effectively reused to enhance oil recovery.
8. The adsorption of polymer onto the sand surface does not vary with the polymer concentration in the range of 100-1500 ppm. Given the limited sand surface area, the polymer loss due to the adsorption is around 73.5 $\mu\text{g/g-sand}$.
9. Polymer coreflood test results show that the piston-like displacement of a polymer slug can greatly enhance oil recovery. Re-injection of the produced polymer solutions can effectively enhance oil recovery.
10. The injection scheme of AS flooding followed by a polymer slug achieves a higher oil recovery than that for the injection scheme of polymer flooding followed by an AS slug. Simultaneous injection of alkali, surfactant and polymer can significantly enhance oil recovery.
11. If alkali and surfactant are injected first, their adsorption onto the core surface deters the subsequent adsorption of the anionic polymer. Similarly, if an anionic polymer is injected first and adsorbed onto the core surface, its adsorption can reduce the subsequent adsorption of alkali and anionic surfactant.
12. ASP re-injection coreflood tests show that, even though the viscosity of the produced ASP solutions is rather low and the IFT between the crude oil and the produced ASP solutions does not reach the ultra-low value, the produced ASP fluids can still remarkably enhance oil recovery.

8.2 Recommendations

How to accurately detect and effectively reuse the produced chemicals in chemical EOR operations is a relatively new topic. So far, there have been few studies on the techniques for detecting and reusing the produced fluids in the chemical EOR operations. Recent field applications show that there is great potential of reusing the produced fluids for further enhancing oil recovery so that the capital cost and, more importantly, the negative environmental impact is reduced. This thesis study should serve as a basis for further development of these techniques. In this regard, some recommendations for future research are made as follows.

1. The produced alkaline-surfactant-polymer fluids may be re-injected together with natural gas as an ASP foam system to displace the residual oil. Such an ASP foam system should have low IFT, high viscosity and high sweep efficiency as well. This may be an excellent research topic.
2. Parallel coreflood tests of alkaline floods, surfactant floods, alkaline-surfactant floods, polymer floods, and alkaline-surfactant-polymer floods may be performed to simulate the production performance of these chemical floods in the heterogeneous reservoirs.
3. The mechanisms of the synergistic effect of alkali and surfactant combinations on reducing the IFTs to the ultra-low values are still not understood yet. It has been reported that the minimum IFT corresponds to the maximum electrophoretic mobility, i.e., the maximum ζ -potential at the oil-brine interface (Chan and Shah, 1981). A

comprehensive mechanism study can be conducted to correlate the IFT and the ζ -potential at the oil-brine interface.

4. Coreflood tests can be conducted by using the produced fluids either as a pre-flush prior to or as a driving fluid after a chemical slug. In these two cases, the produced chemicals can function either as a sacrificing agent to reduce the adsorption of subsequently injected chemical slug or as an oil displacement agent to improve the sweep efficiency.

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Appendix 3.1 Detailed experimental data for coreflood Run No. AF1.

Water saturated (ml)^a	71.8
Total dead volume (ml)^b	18.0
Pore volume (ml)^c	53.8
Movable dead volume (ml)^d	2.5
OOIP (ml)^e	48.5

	ΔP (Pa)	Q (ml/s)
K_a	10100	32.0
K_o	26600	2.0
K_w	5000	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	98.5	25.5
Subtotal	98.5	25.5
AF		
No.1	25.0	1.3
No.2	28.8	0.7
Subtotal	53.8	2.0
SWF		
No.1	25.0	0.6
No.2	25.0	0.3
No.3	25.0	0.3
No.4	25.0	0.2
Subtotal	100.0	1.4

Notes:

^a Total volume available inside the sand-pack after the evacuation;

^b Total dead volume inside the two distributors;

^c $PV = a - b = \text{total volume available} - \text{total dead volume}$;

^d Movable dead volume inside the two distributors;

^e The original oil in place.

Appendix 3.2 Detailed experimental data for coreflood Run No. AF2.

Water saturated (ml)	71.9
Total dead volume (ml)	18.0
Pore volume (ml)	53.9
Movable dead volume (ml)	2.5
OOIP (ml)	46.5

	ΔP (Pa)	Q (ml/s)
K_a	9500	32.0
K_o	8700	0.4
K_w	4500	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	97.5	23.0
Subtotal	97.5	23.0
AF		
No.1	27.0	1.7
No.2	26.9	0.8
Subtotal	53.9	2.5
SWF		
No.1	25.0	0.5
No.2	25.0	0.3
No.3	25.0	0.2
No.4	25.0	0.2
Subtotal	100.0	1.2

Appendix 3.3 Detailed experimental data for coreflood Run No. AF3.

Water saturated (ml)	71.1
Total dead volume (ml)	18.0
Pore volume (ml)	53.1
Movable dead volume (ml)	2.5
OOIP (ml)	45.5

	ΔP (Pa)	Q (ml/s)
K_a	9400	32.0
K_o	9000	0.4
K_w	4700	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	106.0	22.7
Subtotal	106.0	22.7
AF		
No.1	26.8	0.9
No.2	26.3	0.9
Subtotal	53.1	1.8
SWF		
No.1	25.7	0.8
No.2	25.4	0.7
No.3	25.3	0.7
No.4	30.0	0.6
No.5	25.4	0.4
No.6	25.4	0.4
No.7	25.4	0.2
Subtotal	182.6	3.8

Appendix 3.4 Detailed experimental data for coreflood Run No. AF4.

Water saturated (ml)	71.1
Total dead volume (ml)	18.0
Pore volume (ml)	53.1
Movable dead volume (ml)	2.5
OOIP (ml)	46.5

	ΔP (Pa)	Q (ml/s)
K_a	9300	32.0
K_o	25300	1.5
K_w	5500	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	104.0	23.0
Subtotal	104.0	23.0
AF		
No.1	26.6	1.0
No.2	26.5	1.0
Subtotal	53.1	2.0
SWF		
No.1	26.0	0.4
No.2	25.2	0.5
No.3	25.5	0.5
No.4	25.3	0.5
No.5	25.2	0.6
No.6	25.8	0.5
No.7	44.0	0.9
Subtotal	197.0	3.9

Appendix 3.5 Detailed experimental data for coreflood Run No. AF5.

Water saturated (ml)	71.3
Total dead volume (ml)	18.0
Pore volume (ml)	53.3
Movable dead volume (ml)	2.5
OOIP (ml)	47.5

	ΔP (Pa)	Q (ml/s)
K_a	9400	32.0
K_o	24300	1.5
K_w	5600	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	99.5	24
Subtotal	99.5	24
AF		
No.1	26.3	1.4
No.2	27.0	1.1
Subtotal	53.3	2.5
SWF		
No.1	27.0	0.5
No.2	25.3	0.7
No.3	25.3	0.2
No.4	25.4	0.3
No.5	25.2	0.2
No.6	25.2	0.4
No.7	26.0	0.3
Subtotal	179.4	2.6

Appendix 4.1 Detailed experimental data for coreflood Run No. SF1.

Water saturated (ml)^a	53.3
Dead volume (ml)^b	6.8
Pore volume (ml)^c	46.5
OOIP (ml)^d	30.2

	ΔP (Pa)	Q (ml/s)
K_a	29600	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	51.0	6.2
Subtotal	51.0	6.2
SF		
No.1	18.6	0.9
No.2	18.6	1.1
Subtotal	37.2	2.0
SWF		
No.1	18.6	1.4
No.2	18.6	0.9
No.3	18.6	0.8
No.4	18.6	0.1
Subtotal	74.4	3.2

Notes:

^a Total volume available inside the sand-pack after the evacuation;

^b Total dead volume inside the two distributors;

^c $PV = a - b$ = total volume available – total dead volume;

^d The original oil in place.

Appendix 4.2 Detailed experimental data for coreflood Run No. SF2.

Water saturated (ml)	57.0
Dead volume (ml)	10.0
Pore volume (ml)	47.0
OOIP (ml)	30.0

	ΔP (Pa)	Q (ml/s)
K_a	27600	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	54.0	6.0
Subtotal	54.0	6.0
SF		
No.1	18.8	1.2
No.2	18.8	1.3
Subtotal	37.6	2.5
SWF		
No.1	18.8	2.2
No.2	18.8	0.8
No.3	18.8	0.2
No.4	18.8	0.6
No.5	18.8	0.2
Subtotal	94.0	4.0

Appendix 4.3 Detailed experimental data for coreflood Run No. SF3.

Water saturated (ml)	53.8
Dead volume (ml)	6.8
Pore volume (ml)	47.0
OOIP (ml)	30.8

	ΔP (Pa)	Q (ml/s)
K_a	40000	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	59.0	7.2
Subtotal	59.0	7.2
SF		
No.1	18.8	1.1
No.2	18.8	2.0
Subtotal	37.6	3.1
SWF		
No.1	18.8	2.6
No.2	18.8	1.2
No.3	18.8	0.8
No.4	18.8	0.3
No.5	18.8	0.3
No.6	18.8	0.1
Subtotal	112.8	5.3

Appendix 4.4 Detailed experimental data for coreflood Run No. SF4.

Water saturated (ml)	56.8
Dead volume (ml)	10.0
Pore volume (ml)	46.8
OOIP (ml)	30.0

	ΔP (Pa)	Q (ml/s)
K_a	40000	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	54.0	6.0
Subtotal	54.0	6.0
SF		
No.1	18.7	0.6
No.2	18.7	0.0
Subtotal	37.4	0.6
SWF		
No.1	18.7	1.3
No.2	18.7	0.0
No.3	18.7	0.6
No.4	18.7	0.0
Subtotal	74.8	1.9

Appendix 5.1 Detailed experimental data for coreflood Run No. ASF1.

Water saturated (ml)	54.6
Dead volume (ml)	6.8
Pore volume (ml)	47.8
OOIP (ml)	30.8

	ΔP (Pa)	Q (ml/s)
K_a	29000	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	58.5	6.5
Subtotal	58.5	6.5
ASF		
No.1	19.1	1.4
No.2	19.1	2.1
Subtotal	38.2	3.5
SWF		
No.1	19.1	2.6
No.2	19.1	1.0
No.3	19.1	0.4
No.4	19.1	0.5
No.5	19.1	0.3
No.6	19.1	0.1
Subtotal	114.6	4.9

Appendix 5.2 Detailed experimental data for coreflood Run No. ASF2.

Water saturated (ml)	55.0
Dead volume (ml)	6.8
Pore volume (ml)	48.2
OOIP (ml)	30.5

	ΔP (Pa)	Q (ml/s)
K_a	27600	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	66.0	6.5
Subtotal	66.0	6.5
ASF		
No.1	19.3	1.2
No.2	19.3	1.7
Subtotal	38.6	2.9
SWF		
No.1	19.3	2.6
No.2	19.3	1.3
No.3	19.3	0.5
No.4	19.3	0.1
No.5	19.3	0.0
Subtotal	96.5	4.5

Appendix 5.3 Detailed experimental data for coreflood Run No. ASF3.

Water saturated (ml)	56.8
Dead volume (ml)	10.0
Pore volume (ml)	46.8
OOIP (ml)	30.0

	ΔP (Pa)	Q (ml/s)
K_a	26200	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	60.0	7.0
Subtotal	60.0	7.0
ASF		
No.1	18.7	1.9
No.2	18.7	5.1
Subtotal	37.4	7.0
SWF		
No.1	18.7	1.0
No.2	18.7	0.2
No.3	18.7	0.0
No.4	18.7	0.0
Subtotal	74.8	1.2

Appendix 5.4 Detailed experimental data for coreflood Run No. ASF4.

Water saturated (ml)	56.8
Dead volume (ml)	6.8
Pore volume (ml)	50.0
OOIP (ml)	32.7

	ΔP (Pa)	Q (ml/s)
K_a	27600	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	64.0	7.2
Subtotal	64.0	7.2
ASF		
No.1	20.0	0.9
No.2	20.0	2.2
Subtotal	40.0	3.1
SWF		
No.1	20.0	3.0
No.2	20.0	1.0
No.3	20.0	0.6
No.4	20.0	0.2
Subtotal	80.0	4.8

Appendix 5.5 Detailed experimental data for coreflood Run No. ASF5.

Water saturated (ml)	58.0
Dead volume (ml)	10.0
Pore volume (ml)	48.0
OOIP (ml)	30.0

	ΔP (Pa)	Q (ml/s)
K_a	34500	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	58.0	7.0
Subtotal	58.0	7.0
ASF		
No.1	19.2	1.1
No.2	19.2	0.2
Subtotal	38.4	1.3
SWF		
No.1	19.2	1.1
No.2	19.2	0.1
No.3	19.2	0.1
No.4	19.2	0.4
Subtotal	76.8	1.7

Appendix 6.1 Detailed experimental data for coreflood Run No. PF1.

Water saturated (ml)	75.3
Total dead volume (ml)	18.0
Pore volume (ml)	57.3
Movable dead volume (ml)	2.5
OOIP (ml)	51.5

	ΔP (Pa)	Q (ml/s)
K_a	9440	32.0
K_o	23500	1.0
K_w	5000	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	48.5	21.4
No.2	48.5	4.0
No.3	50.0	2.5
Subtotal	147.0	27.9
PF		
No.1	28.7	8.5
No.2	28.7	5.2
Subtotal	57.4	13.7
SWF		
No.1	28.7	0.5
No.2	28.7	0.0
Subtotal	57.4	0.5

Appendix 6.2 Detailed experimental data for coreflood Run No. PF2.

Water saturated (ml)	74.0
Total dead volume (ml)	18.0
Pore volume (ml)	56.0
Movable dead volume (ml)	2.5
OOIP (ml)	52.0

	ΔP (Pa)	Q (ml/s)
K_a	9600	32.0
K_o	23600	1.0
K_w	5000	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	99.2	30.0
Subtotal	99.2	30.0
PF		
No.1	16.7	1.1
No.2	16.7	3.8
Subtotal	33.4	4.9
SWF		
No.1	16.7	6.8
No.2	16.7	1.1
No.3	16.7	0.6
No.4	16.7	0.0
Subtotal	66.8	8.5

Appendix 6.3 Detailed experimental data for coreflood Run No. PF3.

Water saturated (ml)	71.2
Total dead volume (ml)	18.0
Pore volume (ml)	53.2
Movable dead volume (ml)	2.5
OOIP (ml)	48.5

	ΔP (Pa)	Q (ml/s)
K_a	9400	32.0
K_o	43400	2.0
K_w	4800	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	98.5	27.0
Subtotal	98.5	27.0
PF		
No.1	21.5	1.5
Subtotal	21.5	1.5
SWF		
No.1	21.5	6.5
No.2	21.5	1.0
No.3	21.5	0.8
No.4	21.5	0.2
Subtotal	86.0	8.5

Appendix 6.4 Detailed experimental data for coreflood Run No. PF4.

Water saturated (ml)	79.8
Total dead volume (ml)	18.0
Pore volume (ml)	61.8
Movable dead volume (ml)	2.5
OOIP (ml)	53.5

	ΔP (Pa)	Q (ml/s)
K_a	9000	32.0
K_o	39000	2.0
K_w	5500	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	100.8	29.0
Subtotal	100.8	29.0
PF		
No.1	18.4	0.6
No.2	18.4	2.6
Subtotal	36.8	3.2
SWF		
No.1	18.4	5.5
No.2	18.4	2.2
No.3	18.4	0.7
No.4	18.4	0.2
No.5	18.4	0.2
Subtotal	92.0	8.8

Appendix 6.5 Detailed experimental data for coreflood Run No. PF5.

Water saturated (ml)	74.0
Total dead volume (ml)	18.0
Pore volume (ml)	56.0
Movable dead volume (ml)	2.5
OOIP (ml)	51.0

	ΔP (Pa)	Q (ml/s)
K_a	12900	32.0
K_o	64500	2.0
K_w	9800	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	97.5	31.5
Subtotal	97.5	31.5
PF		
No.1	22.5	0.1
Subtotal	22.5	0.1
SWF		
No.1	22.5	5.6
No.2	22.5	0.2
No.3	22.5	1.9
No.4	22.5	0.1
No.5	22.5	0.2
Subtotal	112.5	8.0

Appendix 6.6 Detailed experimental data for coreflood Run No. PF6.

Water saturated (ml)	54.3
Dead volume (ml)	6.8
Pore volume (ml)	47.5
OOIP (ml)	30.2

	ΔP (Pa)	Q (ml/s)
K_a	25500	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	64.0	8.0
Subtotal	64.0	8.0
PF		
No.1	19.0	1.2
Subtotal	19.0	1.2
SWF		
No.1	19.0	2.5
No.2	19.0	1.1
No.3	19.0	0.8
No.4	19.0	0.5
No.5	19.0	0.2
Subtotal	95.0	5.1

Appendix 6.7 Detailed experimental data for coreflood Run No. PF7.

Water saturated (ml)	54.6
Dead volume (ml)	6.8
Pore volume (ml)	47.8
OOIP (ml)	30.2

	ΔP (Pa)	Q (ml/s)
K_a	26900	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	63.5	8.2
Subtotal	63.5	8.2
PF		
No.1	19.1	1.2
No.2	19.1	2.8
Subtotal	38.2	4.0
SWF		
No.1	19.1	1.7
No.2	19.1	1.2
No.3	19.1	0.8
No.4	19.1	0.4
No.5	19.1	0.2
Subtotal	95.5	4.3

Appendix 6.8 Detailed experimental data for coreflood Run No. PF8.

Water saturated (ml)	57.6
Dead volume (ml)	10.0
Pore volume (ml)	47.6
OOIP (ml)	30.0

	ΔP (Pa)	Q (ml/s)
K_a	26900	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	67.0	8.0
Subtotal	67.0	8.0
PF		
No.1	19.0	1.0
No.2	19.0	1.2
Subtotal	38.0	2.2
SWF		
No.1	19.0	0.5
No.2	19.0	0.7
No.3	19.0	0.4
No.4	19.0	0.1
Subtotal	76.0	1.7

Appendix 7.1 Detailed experimental data for coreflood Run No. ASPF1.

Water saturated (ml)	56.8
Dead volume (ml)	10.0
Pore volume (ml)	46.8
OOIP (ml)	29.0

	ΔP (Pa)	Q (ml/s)
K_a	26200	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	60.0	7.0
Subtotal	60.0	7.0
ASPF		
No.1	18.7	2.0
No.2	18.7	5.2
Subtotal	37.4	7.2
SWF		
No.1	18.7	3.0
No.2	18.7	3.0
No.3		
No.4	18.7	1.3
Subtotal	18.7	0.4

Appendix 7.2 Detailed experimental data for coreflood Run No. ASPF2.

Water saturated (ml)	55.4
Dead volume (ml)	6.8
Pore volume (ml)	48.6
OOIP (ml)	32.2

	ΔP (Pa)	Q (ml/s)
K_a	27600	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	58.0	7.0
Subtotal	58.0	7.0
ASPF		
No.1	19.4	1.1
No.2	19.4	1.1
Subtotal		
SWF	19.4	3.5
No.1	19.4	3.7
No.2	38.8	7.2
No.3		
No.4	19.4	2.0
Subtotal	19.4	2.0

Appendix 7.3 Detailed experimental data for coreflood Run No. ASPF3.

Water saturated (ml)	55.1
Dead volume (ml)	6.8
Pore volume (ml)	48.3
OOIP (ml)	32.2

	ΔP (Pa)	Q (ml/s)
K_a	24100	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	63.0	9.2
Subtotal	63.0	9.2
ASPF		
No.1	19.3	3.1
No.2	19.3	5.3
Subtotal	38.6	8.4
SWF		
No.1	19.3	4.1
No.2	19.3	2.6
No.3	19.3	1.0
No.4	19.3	0.4
No.5	19.3	0.1
Subtotal	96.5	8.2

Appendix 7.4 Detailed experimental data for coreflood Run No. ASPF4.

Water saturated (ml)	58.3
Dead volume (ml)	10.0
Pore volume (ml)	48.3
OOIP (ml)	30.0

	ΔP (Pa)	Q (ml/s)
K_a	33800	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	70.0	7.0
Subtotal	70.0	7.0
ASPF		
No.1	19.3	1.4
No.2	19.3	1.4
Subtotal		
SWF	19.3	6.2
No.1	19.3	2.6
No.2	19.3	0.6
No.3	19.3	0.2
No.4	19.3	0.1
No.5	96.5	9.7
Subtotal	70.0	7.0

Appendix 7.5 Detailed experimental data for coreflood Run No. ASPF5.

Water saturated (ml)	58.0
Dead volume (ml)	10.0
Pore volume (ml)	48.0
OOIP (ml)	31.5

	ΔP (Pa)	Q (ml/s)
K_a	27600	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	63.5	8.5
Subtotal	63.5	8.5
ASPF		
No.1	19.2	1.4
Subtotal	19.2	0.9
SWF	38.4	2.3
No.1		
No.2	19.2	1.2
No.3	19.2	1.5
No.4	19.2	0.1
Subtotal	19.2	0.2

Appendix 7.6 Detailed experimental data for coreflood Run No. ASPF6.

Water saturated (ml)	54.8
Dead volume (ml)	6.8
Pore volume (ml)	48.0
OOIP (ml)	32.0

	ΔP (Pa)	Q (ml/s)
K_a	28300	2.0

WF	Volume of produced fluids (ml)	Oil volume (ml)
No.1	62.5	8.7
Subtotal	62.5	8.7
ASPF		
No.1	19.2	1.1
No.2	19.2	2.2
Subtotal	38.4	3.3
SWF		
No.1	19.2	2.0
No.2	19.2	0.6
No.3	19.2	0.2
No.4	19.2	0.2
Subtotal	76.8	3.0