

6-2002

Low Salinity Flooding in a Selected Carbonate Reservoir: Experimental Approach

Mohamed Yehia Mohamed Mahmoud

Follow this and additional works at: https://scholarworks.uaeu.ac.ae/all_theses

Part of the [Petroleum Engineering Commons](#)

Recommended Citation

Mohamed Mahmoud, Mohamed Yehia, "Low Salinity Flooding in a Selected Carbonate Reservoir: Experimental Approach" (2002). *Theses*. 514.

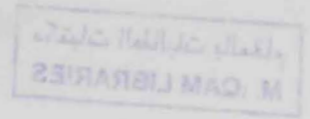
https://scholarworks.uaeu.ac.ae/all_theses/514

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Scholarworks@UAEU. It has been accepted for inclusion in Theses by an authorized administrator of Scholarworks@UAEU. For more information, please contact fadl.musa@uaeu.ac.ae.



جامعة الإمارات العربية المتحدة
United Arab Emirates University

UAEU



**Low Salinity Flooding in a Selected Carbonate Reservoir:
Experimental Approach**

By

Mohamed Yehia Mohamed Mahmoud

Department of Chemical and Petroleum Engineering
Faculty of Engineering
United Arab Emirates University

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Petroleum Engineering

Master Program of Petroleum Engineering
Department of Chemical and Petroleum Engineering
Faculty of Engineering
United Arab Emirates University

June 2012



جامعة الإمارات العربية المتحدة
United Arab Emirates University

UAEU

Master Program of Petroleum Engineering
Department of Chemical and Petroleum Engineering
Faculty of Engineering
United Arab Emirates University

Thesis Title:

Low Salinity Flooding in a Selected Carbonate Reservoir: Experimental Approach

Author's Name:

Mohamed Yehia Mohamed Mahmoud

Supervisors:

Dr. Hazim AL-Attar

Associate Professor of Petroleum Engineering
Department of Chemical and Petroleum Engineering
Faculty of Engineering
United Arab Emirates University

Prof. Abdulrazag Y. Zekri

Professor of Petroleum Engineering
Department of Chemical and Petroleum Engineering
Faculty of Engineering
United Arab Emirates University

U.A.E LIBRARIES



1000486114

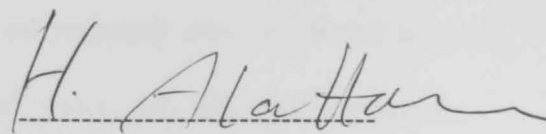


مكتبات الطالبات بالمقام
M. QAM LIBRARIES

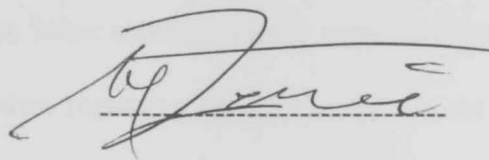
June 2011

Thesis of **Mohamed Yehia Mohamed**
Submitted in Partial Fulfillment for the Degree of
Master of Petroleum Science and Engineering

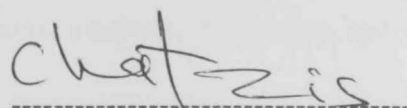
Chair of Examination Committee
Dr. Hazim Al-Attar
Chemical & Petroleum Engineering Department
United Arab Emirates University



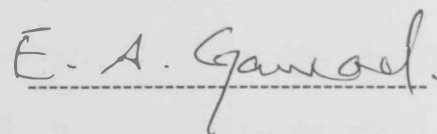
Co. Supervisor
Prof. Abdulrazag Zekri
Chemical & Petroleum Engineering Department
United Arab Emirates University



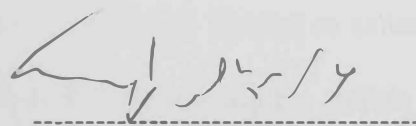
External Examiner
Prof. John Chatzis
Department of Chemical Engineering
University of Waterloo, Ontario, Canada



Internal Examiner
Dr. Essam Ahmed Abdelgawad Mohd.
Geology Department
United Arab Emirates University



Associate Dean, Research and Graduate Studies
Dr. Ali H. Hassan Al-Marzouqi



United Arab Emirates University
2011/2012

ABSTRACT

Low-salinity water flooding *LoSal*TM has been used to improve oil recovery for many decades. Historically, the mechanisms behind this improvement in oil recovery were attributed to the pressure maintenance and displacement of oil by injected water, i.e. physical mechanism. Recently, evidence from laboratory and field tests indicated that water flooding also involves chemical processes and that modifying of the injection brine salinity and its ionic composition can significantly impact the oil recovery. Several theories regarding the mechanism of *LoSal*TM flooding have been discussed in the literature. These include interfacial tension reduction, wettability alteration (cation exchange), change in pH (increase), emulsion formation, and clay migration. It is clear from the literature that there is no agreement among the researchers regarding the mechanism of *LoSal*TM flooding and although limited work has been done on carbonates, some studies have concluded that *LoSal*TM have no effect on oil recovery.

This work presents the results of core flooding tests with sea water, and two of Abu Dhabi oil field injection waters UER (197,584 ppm) and SIM (224,987 ppm) to evaluate the effects of brine salinity and ionic composition on the possible interactions of limestone rock/ brine/ and oil, and to identify the recovery mechanism. The original injection waters were diluted to salinities of 5000 and 1000 ppm and the optimum salinity system was modified by varying the sulfate and calcium ion concentrations. Wettability alteration is determined by contact angle measurements. Interfacial tensions measurements of the studied systems were also performed in an attempt to evaluate the flow mechanism with *Lowsal*TM flooding.

The experimental results revealed that a significant improvement in the oil recovery can be achieved through alteration of the injection water salinity. Reducing the salinity of UER water from 197,362 ppm to 5000 ppm resulted in an improvement of oil recovery from 63% to 84.5%

of OOIP, respectively. Therefore, the salinity of 5000 ppm UER was considered as the optimum salinity to evaluate the effect of sulfate and calcium ion concentrations. Results also indicated that sulfate concentration has a significant effect on the process and increasing the sulfate concentration beyond the optimum concentration (47 ppm) resulted in a negative effect. Contact angle measurements indicated that lowering the solution salinity could shift the wettability of the system toward intermediate wettability levels and that the UER water exhibits higher shift toward intermediate wettability compared to other waters. Results also indicated that there is no clear correlation between the improvements in oil recovery and interfacial tension and the pH of the studied systems.

ACKNOWLEDGEMENTS

I would like to express my sincerest thanks and appreciation to all those who were involved in this significant period of my life. I owe my deepest gratitude and gratefulness to my thesis supervisors, Dr. Hazim AL-Attar and Prof. Abdulrazag Y. Zekri, for their continuous encouragement, inestimable guidance, precious support and constructive assistance they offered me throughout the course of this study. It would have been next to impossible to complete this thesis without the time and effort they have allocated to it. I would like to thank them for the friendly environment they have created for me and the invaluable pieces of advice I received from them which played a major role in making some crucial decisions in my career and social life. Also, I would like to express my gratitude to the examination committee members Dr. Essam Ahmed Abdeljawad and Prof. Ioannis (John) Chatzis for their input on the work and their time.

My appreciation also goes to the faculty and staff members in the department of chemical and petroleum engineering at UAE University for their precious support and encouragement. I would like to extend special gratitude to my colleagues Eng. Mohamed Elwy and Eng. Rashid Sher for the valuable assistance they offered and the sweet memories they left through the experimental phase of the study. I would like to express my gratitude to Eng. Issa Louiseh, Eng. Sami Abdallah and Mr. Hassan Kamal Ahmed from the chemical and petroleum engineering laboratories at UAEU for their great efforts and help during the experimental work.

Finally, special recognition goes out to the people who brought me to existence and devoted their life to my well-being and happiness. I would like to thank my parents and my brother, Mustafa, and my lovely sister, Omnia, for the invaluable encouragement and unlimited support that I have received from them in all aspects. I would like to express them my deepest gratitude for believing in me, sharing their life experience with me, and helping me to overcome the obstacles that I have faced. I am truly thankful to their blessing which have always been the source of motivation in achieving any success in my life.

TABLE OF CONTENTS

Contents

Abstract	2
ACKNOWLEDGEMENTS	4
TABLE OF CONTENTS	5
LIST OF TABLES	8
LIST OF FIGURES	9
Chapter 1: INTRODUCTION	14
Chapter 2: LITERATURE REVIEW	16
2.1 Early Work with Fresh Water:	16
2.2 Recovery mechanisms:.....	17
2.2.1 Primary recovery:.....	17
2.2.2 Secondary recovery:.....	18
2.2.3 Tertiary recovery/EOR processes:	18
2.3 Wettability:	19
2.4 Focused Low Salinity Research Begins:.....	24
2.5 Focused Low Salinity in carbonate rocks:	28
2.6 Different proposed low salinity mechanisms:	30
2.6.1 Migration of fines:.....	30
2.6.2 PH increase:	31

2.6.3 MIE (multicomponent ionic exchange):	32
2.6.4 Double layer effects:	35
2.6.5 Salting-in effect:	35
2.6.6 Desorption by pH increase:	37
2.7 LOWSAL Field Scale:	39
2.8 The objective of this work:	41
 Chapter 3: EXPERIMENTAL APPARATUS AND PROCEDURE	 42
3.1 Bu Hasa Field:	42
3.2 Materials Used In the Experiments:	42
3.2.1 Crude Oil:	42
3.2.2 Brines:	43
3.2.3 Core Samples:	44
3.2.4 Safety precaution:	45
3.3 Experimental setup and procedures:	45
3.3.1 Cutting, trimming and cleaning of core samples:	45
3.3.2 Pressure Saturation of the Cores:	48
3.4 Liquid permeability:	51
3.5 Core Flooding Experiment and Setup:	53
3.5.1 Oil Flooding:	53
3.5.2 Water Flooding:	54

3.6 Contact Angle Measurements:.....	55
--------------------------------------	----

3.7 Interfacial Tension (IFT) measurements:	56
---	----

Chapter 4: RESULTS AND DISCUSSION	58
-----------------------------------	----

4.1 Results of Core Flooding Experiments:	58
---	----

4.1.1 Flooding with UER Water:	58
--------------------------------------	----

4.1.2 Flooding with SIM Water:	59
--------------------------------------	----

4.1.3 Flooding with Sea Water:.....	60
-------------------------------------	----

4.2 Discussion of results of core flooding experiments:	61
---	----

4.3 Results of changing ionic composition of the brine:.....	62
--	----

4.4 contact angle measurements:.....	65
--------------------------------------	----

4.5 IFT measurements:.....	70
----------------------------	----

4.6 PH Measurements:.....	73
---------------------------	----

Chapter 5: CONCLUSIONS AND RECOMMENDATIONS	75
--	----

5.1 Summary:	75
--------------------	----

5.2 Conclusions:	75
------------------------	----

5.3 Recommendations:	76
----------------------------	----

References	77
------------	----

Appendix A: Results of Core Flooding Experiments	86
--	----

Appendix B: Results of Contact Angle Measurements	102
---	-----

LIST OF TABLES

Table		Page
2.1	Wettability preference for a water-oil system	21
2.2	Mechanisms of organic matter adsorption onto clay mineral	34
3.1	Compositional analysis of the oil up to C ₁₀₊	43
3.2	Analysis of the different types of Water	44
3.3	Properties of the selected core samples	45

LIST OF FIGURES

Figure		Page
2.1	Displacement of oil by water a) Oil-wet rock, b) Water-wet rock.	20
2.2	Measurement of the contact angle θ , through the water phase.	21
2.3	Typical water/oil relative permeability curves based on the effective permeability to oil at the reservoir connate water saturation: a) strongly water-wet rock, b) strongly oil-wet rock.	22
2.4	Typical capillary pressure curve, capillary pressure vs. water saturation, for a two-phase flow system	23
2.5	Detachment of clay particles and mobilization of oil.	31
2.6	Attraction between clay surface and crude oil by divalent cations.	33
2.7	System containing crude oil components, Ca^{2+} -ions in the water and clay. a) Salting-out effect, b) Salting-in effect.	37
2.8	Adsorption of quinoline onto kaolinite and montmorillonite.	38
2.9	Proposed mechanism for LowSal EOR effects. Upper: Desorption of basic material. Lower: Desorption of acidic material. The initial pH at reservoir conditions may be in the range of 5.	39
2.10	Schematic of Omar field.	40
3.1	Core Number 31.	45
3.2	(a) Diamond Tooled Drill Press (b) Core Trimming Machinery.	46
3.3	Soxhlet Extraction Apparatus.	47
3.4	Core Saturating Cylinder.	48
3.5	The Liquid Permeameter.	52

Figure	Page
3.6	A schematic diagram of the core flooding setup. 53
3.7	The core holder assembly. 54
3.8	Block diagram showing the test various runs performed in this work. 55
3.9	Schematic diagram of apparatus used for contact angle measurements. 56
3.10	The interfacial tensiometer apparatus. 57
4.1	Oil recovery % of OOIP vs. pore volume injected of UER water with different salinity concentrations. 58
4.2	Oil recovery % of OOIP vs. pore volume injected of SIM water with different salinity concentrations. 60
4.3	Oil recovery % of OOIP vs. pore volume injected of SW water with different salinity concentrations. 61
4.4	Oil recovery vs. pore volume injected, different SO_4^{2-} concentrations. 63
4.5	Oil recovery vs. pore volume injected, different Ca^{2+} concentrations. 64
4.6	Results of contact angle measurements for UER water and its corresponding diluted solutions. 65
4.7	Results of contact angle measurements for Sim water and its corresponding diluted solutions. 66
4.8	Results of contact angle measurements for SW water and its corresponding diluted solutions. 66
4.9	Contact angle measurements for different SO_4^{2-} concentration. 68
4.10	Contact angle measurements for different Ca^{2+} concentration. 69

Figure		Page
4.11	Results of IFT measurements for UER brines and its diluted samples.	70
4.12	Results of IFT measurements for SIM brines and its diluted samples.	71
4.13	Results of IFT measurements for SW brines and its diluted samples.	71
4.14	Results of IFT measurements for UER, SIM and SW brines at 5000 ppm dilution.	72
4.15	Results of IFT measurements for different SO_4^{2-} concentration.	72
4.16	Results of IFT measurements for different Ca^{2+} concentration.	73
4.17	PH values for different brines.	74

NOMENCLATURE

A: core sample cross sectional area, cm^2

bbl: barrel

L: length of core sample, cm

t : time for effluent collection, sec

vb: bulk volume of the core sample, cc

Vol: volume of collected brine effluent, ml

w_d : dry weight of core sample, gm

w_s : 100% saturated weight of core sample with with FW, gm

Δp : pressure differential across the core, psig

Abbreviations:

AN: Acid number

BN: Base number

EOR: Enhanced oil recovery

IFT: Interfacial tension

LowSal: Low Salinity

MIE: Multicomponent ionic exchange

OOIP: Original Oil in Place

Pv: pore volume of core sample, cc

RB: Reservoir barrel

SCF: Standard cubic feet

SIM: Simsima water

STB: Stock tank barrel

SW: Sea water

UER: Um-Radhuma water

Greek Symbols:

μ : brine viscosity, cp

ρ_w : density of FW brine, gm/cc

ϕ : porosity of core sample, dimensionless.

CHAPTER 1

INTRODUCTION

Waterflooding is dominant among fluid injection methods and is without question responsible for maintaining production rate and reserves in North America (Craig, F. F. Jr, 1971). As the world's oil fields mature, waterflooding will continue to be applied to unlock the enormous endowment of oil reserves left behind by primary recovery.

The first water flood occurred as a result of accidental water injection in Pithole City, Pennsylvania in 1865 (Lewis, J.A, 1961). Indeed many early water floods occurred accidentally by leaks from shallow water sands or by surface water entering drilled wells. The first water flood in Texas was initiated in Brown County in 1936 and within 10 years waterflooding was in operation in most North American oil regions (Craig, F. F. Jr, 1971). By the early 50's water flood engineering had been improved by Buckley and Leverett (1942) and Welge (1952) pioneering papers.

When a water flood is designed, the injected brine is normally chosen because it is readily available and because it is similar to the native reservoir brine and therefore will not damage the formation. However many researchers have demonstrated that injecting low salinity brine can increase oil recovery efficiency in some cases (Agbalaka et al, 2008).

Low salinity water flooding was discovered by researchers at The University of Wyoming in the 90's (Morrow, N.R, 1991) doing experiments to determine the effect of brine, crude oil,

mineralogy and experimental procedure on wettability. In the subsequent decade the technology of low salinity flooding was repeatedly implemented in the laboratory and in the field.

Over the past decade low-salinity water flooding has emerged as a viable enhanced oil recovery (EOR) method. Both laboratory tests and field trials have shown that injecting chemically modified water instead of seawater can lead to incremental oil recoveries. Although much research has been conducted, the governing physical and chemical mechanisms for this increase in recovery are not yet agreed upon, but are generally believed to involve some form of interaction between the rock, oil, and brine leading to changes in wettability, oil/water interfacial tension, or both.

In this work, core flooding experiments were conducted to study the effect of low salinity water flooding on ultimate oil recovery in selected core samples collected from a selected carbonate field in the UAE. Three types of waters were used in this study, namely, sea water and two formation waters available from the selected field. The effect of the different types of waters on contact angle and Interfacial Tension (IFT) were investigated. Finally, the effects of Ca^{2+} and SO_4^{2-} on the performance of low salinity were investigated.

CHAPTER 2

LITERATURE REVIEW

Several studies have been undertaken to investigate potential mechanisms and the results from these studies have been used to understand potential mechanisms for increased oil recovery with low salinity water flooding.

2.1 Early Work with Fresh Water:

Researchers began injecting fresh water into core samples almost a half century ago. Researchers hoped to better understand the effect of authigenic clay content and studied the impact of fresh water on permeability and oil recovery.

Martin (1957) injected fresh water into Maracaibo Basin and East Texas Woodbine reservoir cores to study the effects of clay content on recovery efficiency and relative permeability. Several cores were flooded with cycles of toluene and fresh water to remove clay materials. The cores were flooded with heavy oil then the oil was displaced with fresh water. The pre-treated cores had lower irreducible water saturations and higher water relative permeabilities. The treated and untreated cores had similar residual oil saturations and oil relative permeabilities. Permeability to fresh water decreased over the course of several hours or days after the fresh water injection was initiated. The original water permeability could be restored momentarily by reversing the flow direction, suggesting pore throat plugging by migrating fines. Martin proposed that in the clay-rich cores clay-water dispersion was created with a higher apparent viscosity and lower water relative permeability than the fresh water.

Bernard (1967) injected NaCl brine and distilled water into sandpacks, Berea cores and outcrop cores from Wyoming. Initial oil saturation was established with oil then NaCl brine or distilled water was injected. In constant flow rate experiments, injecting distilled water increased recovery in both the secondary and tertiary modes. The increased recovery was always accompanied by a massive increase in pressure drop; three orders of magnitude in one case. NaCl brine and distilled water produced similar recoveries in constant pressure drop experiments. Bernard attributed the increased recovery to improved microscopic sweep efficiency induced by clay swelling and plugging of pore throat by migrating fines.

2.2 Recovery Mechanisms:

Oil recovery has traditionally been divided into three chronologically stages: primary, secondary and tertiary recovery. However, in many situations, oil recovery operations are not conducted in this specific order. The so-called tertiary recovery process might be applied as a secondary process in a chronologically sense. The term tertiary recovery is therefore replaced by the more accepted term "Enhanced Oil Recovery" (EOR). Another commonly used expression is "Improved Oil Recovery" (IOR). This term includes EOR but also a broader range of activities, e.g., reservoir characterization, improved reservoir management and infill drilling (Green, 1998).

2.2.1 Primary Recovery:

Primary recovery is the initial production stage resulting from the displacement energy naturally existing in the reservoir. The natural energy sources are solution gas drive, gas cap drive, natural water drive, connate water expansion and pore compaction and gravity drainage (Green, 1998). The primary recovery classification also includes gas lift and pumping. The recovery factor for this period is usually relatively low, around 5-30% on average of the original oil in place (Bavière, 1991).

2.2.2 Secondary Recovery:

Secondary recovery is usually implemented when the primary recovery starts to decline. Since there is not enough energy naturally occurring in the reservoir to produce at an economic rate, energy needs to be supplied from the surface. To produce more oil, the pressure in the reservoir can be maintained by injection of other fluids.

Traditional secondary recovery processes involve injection of fluids which already exist in the reservoir, such as water and gas. These fluids are injected to ensure pressure support and displacement of oil toward the production wells (Robertson, 2007). The most applied secondary recovery process is waterflooding. The recovery factor for a reservoir which has undergone primary production followed by waterflooding may reach 35 to 50% of the original oil in place (Green, 1998).

2.2.3 Tertiary Recovery/EOR Processes:

The target for the tertiary recovery is the residual oil saturation left behind after the secondary recovery process and that has become uneconomical to produce. An EOR process may involve injection of miscible gases, chemicals or thermal energy into the reservoir to displace additional oil - thereby the classification enhanced oil recovery. In miscible processes the objective is to inject fluids that are directly miscible with the oil or that generate miscibility in the reservoir through composition alteration. Examples are injection of hydrocarbon solvents or carbon dioxide, CO₂, at miscible conditions. Chemicals applied in an EOR process may be surfactants or alkaline agents, which are injected to use a combination of phase behavior change and reduction of interfacial tension (IFT) to displace oil. So-called mobility-control processes are primarily based on maintaining favorable mobility ratios to improve the displacement efficiency. Thickening of water with

polymers is one example. Thermal processes rely on the injection of thermal energy or in-situ generation of heat to lower the viscosity of the oil so it can flow easier toward the production wells. Steam injection or in-situ combustion from air or oxygen injection are examples (Green, 1998).

Bavières (1991) definition of enhanced oil recovery is: "EOR consists of methods aimed at increasing ultimate oil recovery by injecting appropriate agents not normally present in the reservoir, such as chemicals, solvents oxidizers and heat carriers, in order to induce new mechanisms for displacing oil". This definition excludes the pressure maintenance by water or gas injection, which uses physical energy alone (Bavière, 1991). But according to the definition, low salinity water injection is an EOR process since the chemical composition of the injected water is different from the initial formation brine, and because the wetting conditions of the surface is changed in the process.

2.3 Wettability:

Wettability can be defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of another immiscible fluid. When two immiscible phases are in contact with a solid surface, one phase usually will be attached to the solid more strongly than the other. The more strongly attracted phase is called the wetting phase (Green, 1998). The reservoir rock wettability is an important property which determines the success of water flooding, because it has great influence on the location, flow, and distribution of the fluids in the reservoir (Punternold, 2008). In a system at equilibrium, the wetting fluid is located on the pore walls and occupies the smallest pores, while the non-wetting fluid is located in the pore bodies (Ahmed, 2000). This phenomenon is illustrated in Figure 2.1.

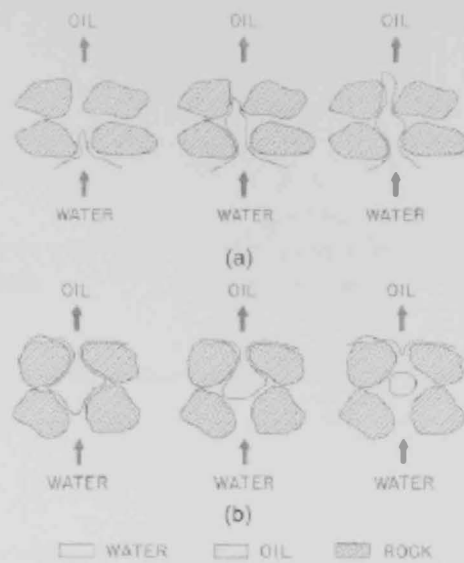


Figure 2-1 Displacement of oil by water (Strand, 2005). a) Oil-wet rock, b) Water-wet rock.

The evaluation of reservoir wettability can be made through measurements of IFT and contact angle θ , as illustrated in Figure 2.2 (Ursin, 1997). This angle can be defined as the tangent to the oil-water surface in the triple-point solid-water-oil, measured through the water phase (wetting phase) (Strand, 2005). In a system containing a reservoir rock, oil and water, as shown in Figure 2.3, the rock is typically preferentially water-wet if water occupies the smaller pores and is the spreading fluid ($\theta < 90^\circ\text{C}$). If oil is the spreading fluid ($\theta > 90^\circ\text{C}$), the rock is preferentially oil-wet (Punternvold, 2008). The rock is intermediate-/neutral-wet when both fluid phases tend to wet the solid, but one phase is only slightly more attracted to the rock than the other ($\theta = 90^\circ\text{C}$) (Green, 1998). If the formation is strongly water-wet, the oil can be trapped in the middle of the largest pores. The link between contact angle and wettability preference is given in Table 2.1.

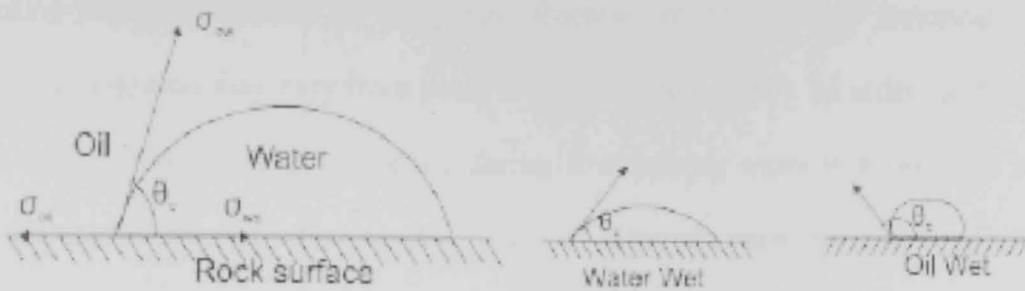


Figure 2.2 Measurement of the contact angle θ , through the water phase (Strand, 2005).

Table 2.1 Wettability preference for a water-oil system (Ursin, 1997).

Contact angle values	Wettability preference
0-30	Strongly water wet
30-90	Preferentially water wet
90	Neutral wettability
90-150	Preferentially oil wet
150-180	Strongly oil wet

Not all reservoirs have uniform/homogenous wettability throughout the reservoir, but rather a heterogeneous wettability. Fractional, spotted or dalmatian wettability are terms that are often seen representing heterogeneous wetted reservoirs (Anderson, 1986b). In this type of rock wettability, some areas of the rock are oil-wet, while the rest is water-wet. Mixed wettability is a special type of fractional wettability. Under this wetting condition small pores and grain contacts are preferentially water-wet and contain no oil, whereas the oil-wet surface form continuous paths through the largest pores and contain all of the oil (Punternvold, 2008). Mixed wettability results from a variation or heterogeneity in chemical composition of exposed rock surfaces or

cementing-material surfaces in the pores. Because of this mixed chemical exposure, the wettability condition may vary from point to point (Green, 1998). In order to observe a LowSal effect, the increased recovery obtained during low salinity water injection, the reservoir rock must be mixed-wet. In other words, organic material must be adsorbed onto the rock (Punternold, 2010).

The wettability affects the relative permeability, the ability of the porous system to conduct one fluid when one or more fluids are present, and the capillary pressure (Anderson, 1987a; Anderson, 1987c). Relative permeability curves, shown in Figure 2.3, and capillary pressure curves, illustrated in Figure 2.4, may therefore be used to measure the wettability of a system (Anderson, 1986a).

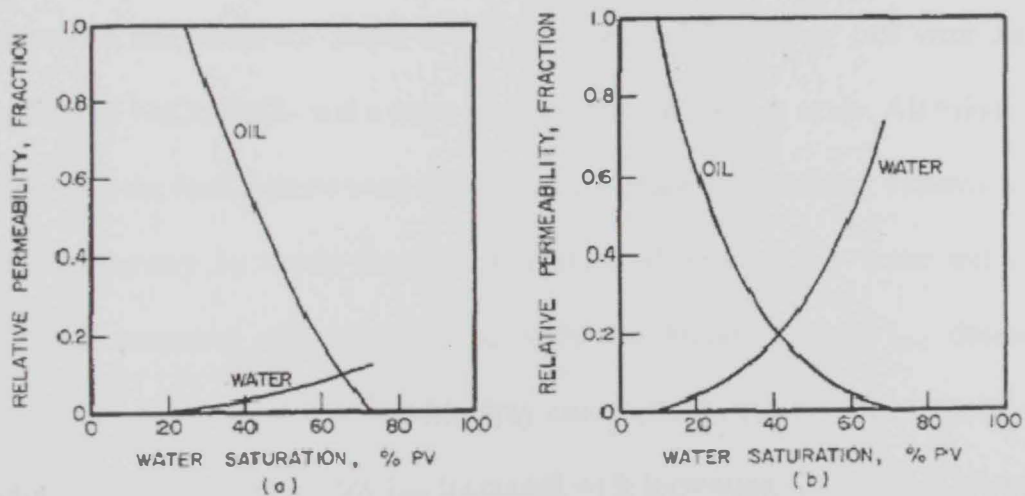


Figure 2.3 Typical water/oil relative permeability curves based on the effective permeability to oil at the reservoir connate water saturation: a) strongly water-wet rock, b) strongly oil-wet rock (Anderson, 1986a).

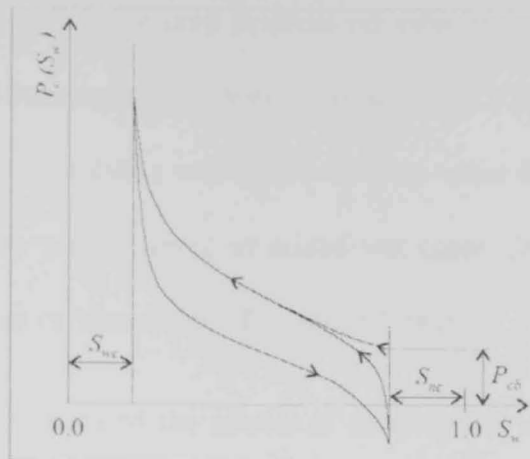


Figure 2.4 Typical capillary pressure curve, capillary pressure vs. water saturation, for a two-phase flow system (Ursin, 1997).

Jadhunandan and Morrow (1991) studied the relationship between water flood oil recovery and wettability. Wettability was modified by adjusting the aging temperature, initial water saturation, brine composition and crude oil. Berea sandstone cores and 3 different oils were used. Brines were composed of NaCl, CaCl₂ and a trace concentration of sodium azide. All brines possessed high salinity, only the Na/Ca ratios were adjusted. Fifty crude oil/brine/rock systems were tested. Maximum oil recovery by water flooding was obtained at very low water-wet conditions. Wettability was measured after water flood with the Amott method. I_{w-o} decreased with increasing calcium-ion content with the Moutray crude oil. Wettability was insensitive to Ca²⁺ with the other oils. With both crudes I_{w-o} increased with increasing S_{wi} , and I_{w-o} decreased with increasing aging temperature.

Yildiz and Morrow (1996) conducted core floods using Berea sandstone, Moutray crude oil and either sodium based brine composed of 4% NaCl + 0.5% CaCl₂ or calcium based brine composed of 2% CaCl₂. Recovery was higher with the calcium brine when the connate and injected brines were identical. The highest recovery was achieved by initially saturating the core

with calcium brine, injecting Na brine until residual oil saturation was achieved, then injecting calcium brine. Almost 13% incremental recovery was achieved about 1 PV after the start of the tertiary calcium brine flood. Wettability was measured after water flood with the Amott method. Greater water flood recovery was achieved in mixed-wet cores. Spontaneous imbibition of Na brine was 4 times greater than calcium brine after about 2 days.

Tang and Morrow (1997) investigated the effects of connate and injection brine salinity, aging time and temperature on water flooding and imbibition with 3 different crude oils and 3 different brines. In imbibition experiments with identical connate and invading brines, decreasing the salinity of both brines produced higher final recovery. In experiments with constant connate brine salinity and variable invading brine salinity, decreasing invading brine salinity increased recovery. In experiments with variable connate brine salinity and constant invading brine salinity, decreasing connate brine salinity increased recovery. In water floods with identical connate and injected brines, decreasing the salinity of both brines produced higher recovery primarily by delaying breakthrough. In water floods with constant connate brine salinity and variable injected brine salinity, diluting injected brine 100 times produced ~5% incremental oil recovery. In water floods with variable connate brine salinity and constant injected brine salinity, decreasing connate brine salinity dramatically improved recovery - about 40% incremental oil recovery was achieved by diluted the connate brine 100 times.

2.4 Focused Low Salinity Research Begins:

Based on the above findings, researchers began to focus on the only variable that can be manipulated in a reservoir - the injection brine salinity. Researchers noticed that improved recovery by injection of low salinity brine only occurred when crude oil and clay bearing

sandstone mineralogy were present. Based on this observation, Tang and Morrow (1999) offered the first theoretical interpretation of the mechanism responsible for the recovery improvement.

Tang and Morrow (1999) observed an increase in water flood and spontaneous imbibition recovery with a decrease in salinity in numerous cases. The authors used Berea cores, CS crude and refined oil and 7 different brines ranging from 35,960 ppm TDS to 151.5 ppm TDS.

Recovery improved significantly in the CS reservoir and Berea cores when low salinity brine was injected instead of high salinity, but recovery improved only marginally in the more clay free cores. Berea cores that were fired and acidized, to stabilize fines, were insensitive to brine salinity. Cores that were repeatedly water flooded produced fines and were sensitive to brine salinity in early water floods, but stopped producing fines and were insensitive to brine salinity in late water floods. Cores initially 100% saturated with crude oil - with fines completely immersed in the oil phase - were insensitive to brine salinity. And lastly, cores saturated with refined mineral oil, rather than crude oil, were insensitive to salinity. Tang and Morrow concluded that heavy polar components in the crude oil adsorb onto fine particles along the pore walls and that these mixed-wet fines are stripped by low salinity brine, altering wettability and increase oil recovery.

Zhang and Morrow (2006) conducted water flood and spontaneous imbibition experiments using 4 different samples of Berea sandstone and three different crude oils. These authors observed improved recovery by injecting low salinity brine in secondary and tertiary modes. The impact of low salinity brine varied significantly between the different samples of Berea, suggesting that mineralogy was the most important variable affecting improved recovery. The lowest permeability block of Berea ($k_{\text{nitrogen}} \sim 60$ to 140 md) showed no sensitivity to salinity. The lack

of response was attributed to the presence of chlorite. In several cases, cores responded to low salinity brine in the secondary but not the tertiary mode. Low salinity effects become more dramatic as the initial water saturation increased. In all cases, injection of low salinity brine was accompanied by an increase of pressure followed by a gradual decrease. Effluent pH also increased.

Some publications indicated that there is no benefit of low salinity water flooding, also present in the literature. Sharma and Filoco (2000) investigated the impact of connate and injection brine salinity and crude oil on oil recovery, residual saturations and wettability using Berea cores, 3 different oils and NaCl brine in various concentrations. In imbibition experiments decreasing connate brine salinity increased recovery and significantly affected relative permeability. The salinity of the displacing brine had no significant impact. Drainage experiment's recovery and relative permeability were insensitive to salinity. During waterflooding of crude oil, oil recovery increased with decreasing connate brine salinity. However, during waterflooding of mineral oil, recovery was insensitive to connate brine salinity. In all cases, waterflood recovery was insensitive to the salinity of the injected brine. Sharma and Filoco suggested that low salinity connate brine changes the wetting properties of the rock surface from water-wet to mixed-wet and thereby increase the recovery.

Webb et al. (2003) observed a reduction in residual oil saturation in the near wellbore region by injecting low salinity brine. Three different brines were injected into a clastic formation from a producing well. Saturation was measured after each injection using a pulsed neutron capture log. A base line S_{or} was established with a synthetic native brine (250,000 ppm). Synthetic sea water (120,000 ppm), injected second, did not reduce oil saturation further. A low salinity brine (3,000 ppm), injected last, reduced S_{or} significantly in two sand intervals and slightly in another.

Zhang et al. (2007) reported increased recovery in the tertiary mode by reducing reservoir brine salinity 20 times. Two consolidated reservoir sandstone cores were used. X-ray diffraction indicated that each of the cores were rich in chert and kaolinite. Two different crudes and a mineral oil were used. Almost 70% incremental oil recovery was achieved in the secondary mode. Both the high and low salinity secondary floods were conducted in the same core. Tertiary recovery was also quite large; 25% incremental recovery in the best case. The recovery was achieved slowly, taking more than 10 injected pore volumes. In several cases the pH fell upon injection of low salinity brine; contrary to other researcher's observations. Pressure drop was closely tied to incremental recovery. In all cases where significant incremental recovery was achieved pressure drop increased significantly then fell gradually.

Pu et al. (2008) observed low salinity tertiary recovery from an almost clay free core for the first time. Researchers injected coalbed methane (CBM) water into 3 sandstone reservoir cores composed of quartz, feldspar, dolomite and anhydrite cements but which had very little clay. The CBM water's salinity was about 1,316 ppm TDS. Cores were first waterflooded with high salinity formation brine (38,651 ppm). When oil production to high salinity brine ceased CBM water was injected. In all cases CBM water liberated additional oil. In each core the benefit of tertiary low salinity flooding became less dramatic after each flood and restoration. A core was acidized to remove dolomite crystals and subsequently its recovery became insensitive to low salinity flooding. Pu et al. proposes that dolomite crystals play an important role in the low salinity recovery mechanism. Some of the dolomite crystals become mixed-wet as they contacted the oil phase during aging. During the low salinity flood the dolomite crystals may detach from the pore walls releasing oil from the rock surface. The detached dolomite crystals

will then reside at the crude oil/brine interface increasing resistance to flow of brine at the interface, delay snap-off at pore-throats and preventing the collapse of oil lamella.

2.5 Focused Low Salinity in Carbonate Rocks:

Bagci et al. (2001) studied the effect of brine composition on oil recovery by water flooding using limestone cores. Ten different brine compositions were examined for injection through the study. The brines were NaCl, CaCl₂, KCl, and binary mixtures of them at two different concentrations (2 and 5 wt%). The highest oil recovery was 35.5% of OOIP for 2 wt% KCl. The authors concluded that any adjustment to the injected brine composition of a mature waterflood can offer a possible and economically feasible approach to increase oil production. Wettability alteration was mentioned as a reason for recovering more oil but without any further explanation. This paper mainly showed coreflood experiments using long core samples (20 inches) and at a reservoir temperature of 122°F. Low salinity effluent brine samples showed higher pH and that was caused by ions exchange reaction.

Høgnesen et al. (2005) concluded that any modification to the injection water ions can impact rock wettability and that can result in additional oil to be recovered. They presented an imbibition study at high temperature condition using reservoir limestone, outcrop chalk cores, seawater and formation water. The results showed that increasing the sulfate ion concentration at high temperature can act as a wettability modifying agent in carbonates, and increased the oil recovery. Scale and souring problems will be enhanced as increasing the sulfate concentration in the injected water. Moreover, this strategy has limitations with regard to initial brine salinity and temperature. At low temperature condition, cationic surfactant was mixed with the aqueous solution and that increased the spontaneous imbibition through the cores.

Webb et al. (2005) presented a study that compared oil recovery from a North Sea carbonate core samples using sulphate free formation simulated brine, with seawater, which contains sulphate. The imbibition capillary pressure experiments were performed at reservoir conditions using live crude oil and brine. The final results showed that the simulated seawater was able to modify the wettability of the carbonate system, changing the wettability of the rock to a more water-wet state. This conclusion was made based on the saturation change noted in the spontaneous imbibition tests between simulated formation and seawater.

Most of the low salinity water flood studies were conducted on limestone; seawater, also, was recommended as an injection fluid in chalk formations. Strand et al. (2008) explained in preliminary experimental studies the chemical mechanism for the wettability alteration in fractured limestone after injecting seawater, sodium chloride brine, and formation water. Synthetic seawater with and without sulfate ions was used to determine the sulfate ions effect on wettability. Spontaneous imbibitions results at 248°F showed 15% increase in the oil recovery when limestone core was imbibed with seawater compared to seawater free of sulfate ions. Seawater has the lowest TDS compared to the other examined brines, but it did not include any brine test that has lower salinity than seawater. More details on reaction mechanism will be explained in the next section.

Fjelde (2008) presented results on low salinity water that increased oil recovery in limestone formation. Spontaneous imbibition experiments were conducted using formation water and low salinity water. Low salinity water showed similar oil recovery results to seawater experiments. No further details were mentioned in this work.

2.6 Different Proposed Low Salinity Mechanisms:

Several different hypotheses have been proposed on the mechanism of LowSal waters in porous media. "Migration of fines" by Tang and Morrow, "pH increase" by McGuire et al.(2005), "Multicomponent Ionic Exchange" (MIE) by Lager et al.(2006) and "Double layer effects" by Ligthelm et al.(2009) are among the best known proposed LowSal mechanisms. None of these mechanisms have so far been generally accepted as the main contributor to the observed LowSal effect. Austad et al.(2010) have suggested a new hypothesis; desorption by pH increase.

2.6.1 Migration of fines:

An attempt to explain the LowSal mechanism was put forward by Tang and Morrow (1999). In the presence of high salinity brine, clays are undisturbed and retain their oil-wet nature leading to poorer displacement efficiency. But during low salinity water flooding, Tang and Morrow observed that fines (mainly kaolinite clay fragments), were released from the rock (sandstone/clay) surface this findings was confirmed by Lager A., (2006). They suggested that the mobilization of the fines resulted in exposure of underlying surfaces, which increased the water wetness of the system. In addition, the released clay particles could block pore throats and divert the flow of water into non-swept pores to improve the microscopic sweep efficiency this findings was confirmed by RezaeiDoust (2009b). The mobilization of fines with flowing fluid are also associated with a permeability reduction and formation damage resulting from plugging of pores. The migration of fines is illustrated in figure 2.5.

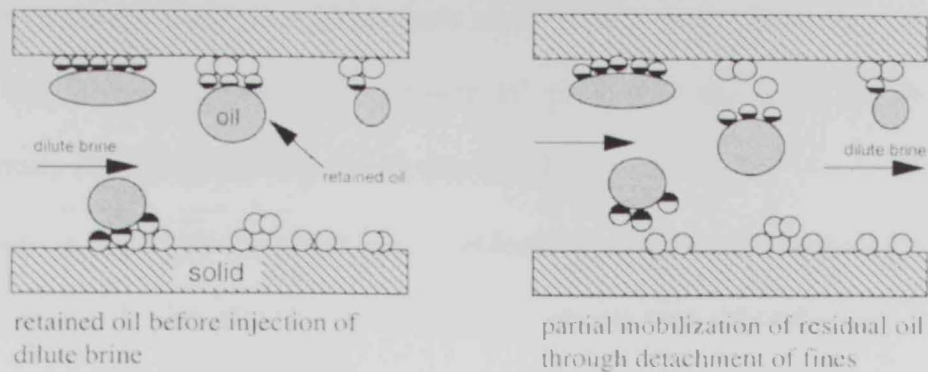


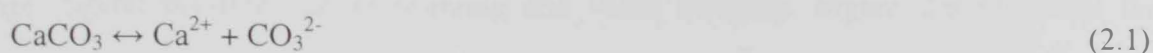
Figure 2.5 Detachment of clay particles and mobilization of oil (Tang and Morrow, 1999).

Although Tang and Morrow have shown that it is possible to have migration of fines during low salinity water flooding, BP has done numerous LowSal floods showing increase in oil recovery, without any observations of fines migration or significantly permeability reduction (Lager A., 2006). These results question the link between fines migration and oil recovery. The migration of fines may just be an effect of LowSal water flooding, and not the direct cause of the additional oil recovery observed by LowSal flooding. But migration of fines might still play a positive role in the increased oil recovery process.

2.6.2 PH increase:

McGuire et al. (2005) suggested the LowSal effect could be related to a type of alkaline waterflooding. If the pH level increases to above 9 inside a petroleum reservoir, the flooding process would be equivalent to an alkaline flood. High pH values also enable a reaction of crude oil acid compounds which results in in-situ generation of surfactants (Boussour, 2009). McGuire et al. suggested that a higher pH can increase the oil recovery by generation of surfactants and reduction in IFT. The rise in pH is due to the following chemical reactions (Lager A., 2006):

- Cation exchange between clay minerals and invading water. This reaction is relatively fast. The mineral surface will exchange H^+ present in the liquid phase with cations previously adsorbed. Thereby an increase in pH.
- Dissolution of carbonate (calcite and/or dolomite), which results in an excess of OH^- and increase in pH. The dissolution reactions is slower and dependent on the amount of carbonate material present in the rock;



To generate in-situ surfactants from carboxylic acids, the acid number (AN) of the crude oil should be larger than 0.2 mg KOH/g. But low salinity effects have been observed for crude oils with AN less than 0.05 mg KOH/g. Furthermore, the increase in pH of produced water/effluent is in many cases not more than 1 pH unit, which causes the water to become only slightly basic. It is doubtful that the small increase in pH can decrease the IFT enough to promote LowSal effects (RezaeiDoust, 2009b). Equivalent experiments have also shown a reduction in pH during LowSal flooding. High pH is more likely not responsible for the increase in oil recovery by injection of LowSal water, but rather an effect. But as migration of fines, a pH increase might play a positive role when it occurs.

2.6.3 MIE (multicomponent ionic exchange):

Lager et al. (2008) describe multicomponent ionic exchange as the basis for geochromatography. MIE involves the competition of all the ions in pore fluid for the mineral matrix exchange sites. Natural exchangers, like clay and carbonate minerals, show different selectivity for different cations or anions. Important documentation of the MIE mechanism came from effluent analysis

of a low salinity waterflood of cores from a reservoir in Alaska (North Slope). The injected brine and the connate water had similar Mg^{2+} concentrations (88 ppm). However, the effluent analysis showed a sharp decrease in Mg^{2+} concentration. This indicates that Mg^{2+} was strongly adsorbed by the rock matrix. Lager et al. claim that four mechanisms, out of eight proposed mechanisms of organic matter adsorption onto clay mineral given in Table 2.2, will be strongly affected by cation exchange occurring during a low salinity brine injection. These mechanisms are cation exchange, ligand bonding, cation bridging and water bridging. Figure 2.6 illustrates these mechanisms.

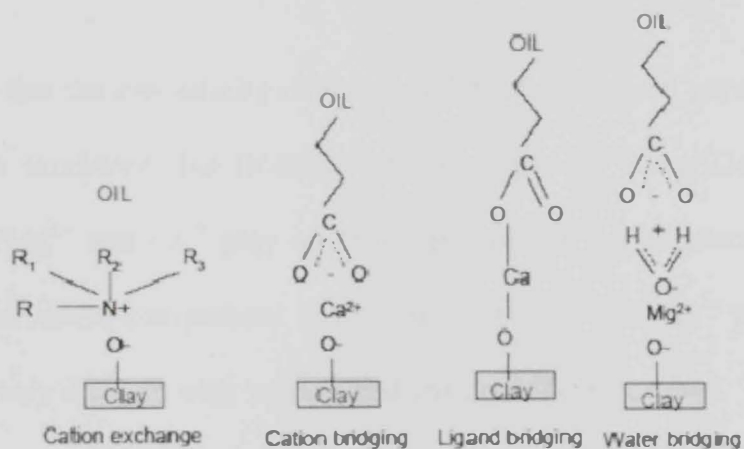


Figure 2.6 Attraction between clay surface and crude oil by divalent cations (Lager A., 2008).

Table 2.2 Mechanisms of organic matter adsorption onto clay mineral (Lager A., 2008)

Mechanism	Organic functional group involved
Cation exchange Protonation	Amino, ring NH, heterocyclic N (aromatic ring)
Anion exchange	Amino, heterocyclic N, carbonyl, carboxylate Carboxylate
Water bridging	Amino, carboxylate, carbonyl, alcoholic OH
Cation bridging	Carboxylate, amines, carbonyl, alcoholic OH
Ligand exchange	Carboxylate
Hydrogen bonding	Amino, carbonyl, carboxyl, phenolic OH
Van der Waals interaction	Uncharged organic units

Lager et al. assume that the low salinity effect was related to increased water wetness of the clay minerals present in sandstone this findings was confirmed by RezaeiDoust (2009b). It was suggested that the Mg^{2+} and Ca^{2+} play an important role in the interaction between the clay minerals and surface active components in the crude oil. Ca^{2+} and Mg^{2+} may act like a bridge between the negatively charged clay surface and the carboxylic material. The organic material was supposed to be removed by cation exchange between the mineral surface and the invading low salinity brine. Expansion of the electrical double layer due to low salinity flooding enables desorption of polar compounds from the surface (Lager A., 2007).

Computer simulations and laboratory tests performed by Tor Austad et al.(2010) have shown that a change in the effluent Ca^{2+} concentration is not necessarily caused by a MIE process. It can also be explained by precipitation of $Mg(OH)_2$ as a result of a local increase in pH in the injected low saline water. In addition, there are no chemical reasons why the strongly hydrated Mg^{2+} ion should have a superior reactivity toward the active sites on the clay surface compared to Ca^{2+} . In

recent laboratory tests it has also been observed that LowSal effects can be obtained without any divalent cations present in the LowSal fluid (Austad, 2010).

2.6.4 Double layer effects:

Ligthelm et al. (2009) proposed that the LowSal effect was due to double layer effects. They suggested that a decrease in salinity results in an expansion of the ionic electrical double layer between the clay and the oil interfaces (Ligthelm et al., 2009). Thus, oil is desorbed from the surface and the water wetness increase. This is a pure physical explanation. It was illustrated by supposing a Ca^{2+} bridge between the negatively charged clay and oil, similar to the illustrations put forward by Lager et al. in Figure 2.6. But, polar oil components may adsorb onto clay minerals without a bridge of divalent cations (Austad, 2010).

2.6.5 Salting-in effect:

Salting-in effect was the first LowSal working proposal by Austad et al. (2008). The proposal is related to changes in the solubility of polar organic components in the aqueous phase, described as salting in and out effects. In water, the organic material is solvated by the formation of a structure created by hydrogen bonds around the nonpolar part of the organic compounds. The organic components are in that way structure makers. Inorganic ions, such as Ca^{2+} , Mg^{2+} and Na^+ , break up the water structure around the organic molecules and decrease the solubility, and are thereby called structure breakers (RezaeiDoust, 2009).

Salting-out effect: Decrease in the solubility of organic material in water by adding salt to the solution.

Salting-in effect: Increase in the solubility of organic material in water by removing salt from the water.

The thermodynamic equilibrium between the crude oil, brine and rock, which has been established during geological time, is disturbed when injecting water with a different salinity than the initial formation water. The solubility of polar organic components in water is affected by ionic composition and salinity, as illustrated in figure 2.7. The terms salting-out and salting-in effects have been used in the chemical literature, and there is a large number of examples where these effects have been observed (Li, 1997; RezaeiDoust, 2009).

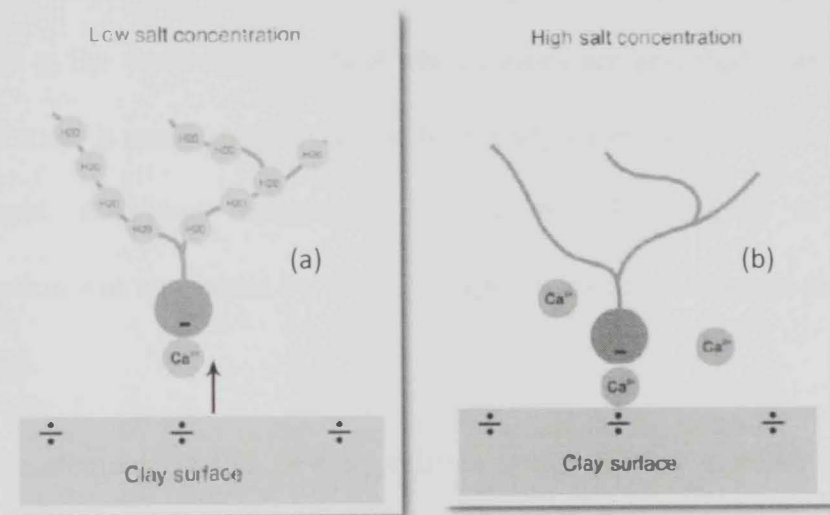


Figure 2.7 System containing crude oil components, Ca^{2+} -ions in the water and clay. a) Salting-out effect, b) Salting-in effect.

Recent studies indicate that adsorption of the base quinoline onto kaolinite clay in the presence of brine seem to increase with a decrease in salinity (Punternold, 2010). These observations are in direct contradiction to the salting-in mechanism and to the fact that oil components are released in a low salinity waterflood.

2.6.6 Desorption by pH increase:

Desorption of acids and bases by pH increase is the latest proposed LowSal mechanism by Austad et al. (2010) Desorption of initially adsorbed cations onto the clay is the key process in increasing the pH of the water at the clay surface. This pH increase cause desorption of organic material from the surface by an acid-base interaction. In order to observe tertiary LowSal effects in sandstone, there must be an initial balanced adsorption of organic material and active cations onto the negatively charged clays present in sandstone. In other words, enough organic material must be present to make the clay oil-wet, and enough cations must be present to create an increase in the pH at the water-clay interface when cations are desorbed from the clay surface. The adsorption process is completely reversible by pH adjustment and the reactions are very fast because of rapid acid/base reactions. The strong dependence of pH regarding adsorption/desorption was confirmed by static adsorption studies of a model base onto kaolinite (Punternvold, 2010).

One of the main statements in this new hypothesis is that a local increase in pH at the clay surface, promoted by desorption of cations, is necessary to release oil components from the rock and thus see LowSal effect. The adsorption of the organic material onto the clay surface is very sensitive to changes in pH. Both acidic and basic crude oil material are released from the surface as the pH is increased from 5-6 to about 8-9 (Austad, 2010). Adsorption of the base quinoline onto kaolinite and montmorillonite versus different pH values is shown in figure 2.8. The adsorption decreases as the pH increases. In lab experiments, increase in pH is usually verified, but due to buffering effects in field situations (due to CO_2 and H_2S), an increase in pH is seldom observed (Punternvold, 2010).

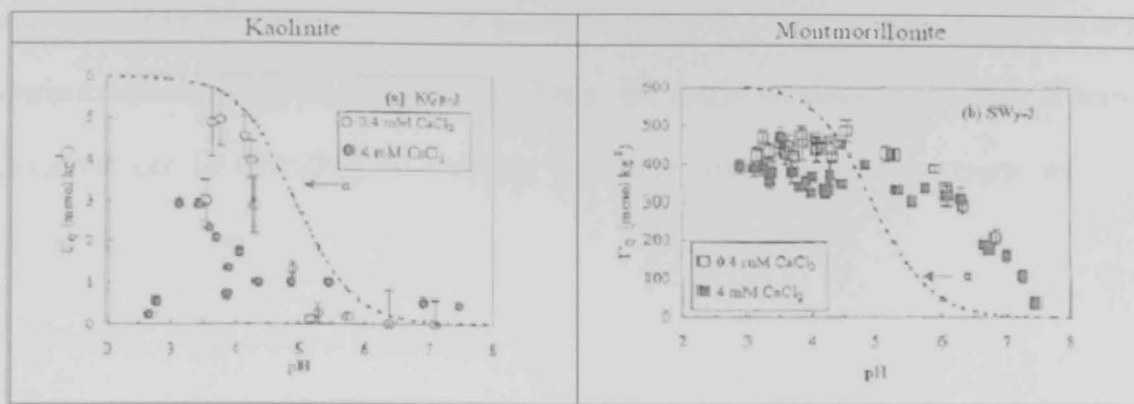


Figure 2.8 Adsorption of quinoline onto kaolinite and montmorillonite (Burgos, 2002).

The suggested mechanism is schematically illustrated in Figure 2.9 for adsorbed basic and acidic material. The clay acts as a cation exchanger with relatively large surface area. Initially, both acidic and basic organic materials are adsorbed onto the negatively charged clay surface together with inorganic cations, especially Ca^{2+} , from the formation water. A chemical equilibrium is then established at actual reservoir conditions regarding pH, temperature, pressure etc. It is important to remember that the initial pH of the formation water may be even below 5 due to dissolved CO_2 and H_2S . The crude oil should therefore be saturated with CO_2 at lab. When the low saline water is injected into the reservoir with an ion concentration much lower than the initial formation brine, the equilibrium associated with the brine-rock interaction is disturbed, and a net desorption of cations, especially of Ca^{2+} , occurs. To compensate for the loss of cations, protons (H^+) from the water close to the clay surface, adsorb onto the clay. Substitution of Ca^{2+} by H^+ is taking place. This creates a local increase in pH close to the clay surface as illustrated by the following equation, using Ca^{2+} as an example:



A fast reaction between OH^- and the adsorbed acidic and basic material will cause desorption of organic material from the clay surface. Thus, the water wetness of the rock is improved. The reactions can be described by ordinary acid-base proton transfer reactions, as shown by the following equations:

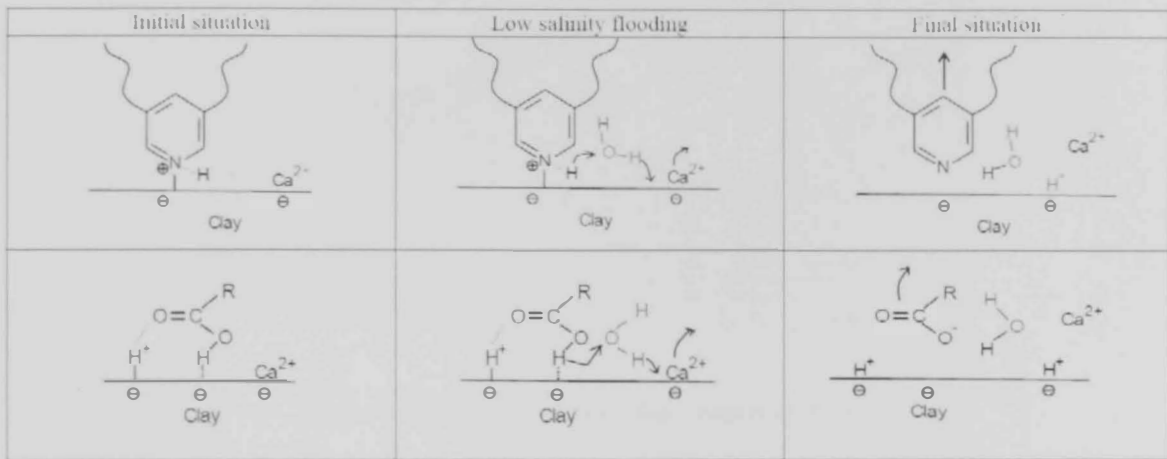
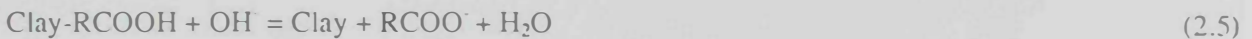


Figure 2.9: Proposed mechanism for LowSal EOR effects. Upper: Desorption of basic material. Lower: Desorption of acidic material. The initial pH at reservoir conditions may be in the range of 5 (Austad, 2010).

2.7 LOWSAL Field Scale:

Paul Vledder et al. (2010) studied the effect of low salinity flooding in Omar field in Syria. A LowSal secondary flood application in the Omar field in Syria showed a change of wettability from oil wet to a water-wet system. This change in wettability is supported by the observation of dual steps in watercut development. In between the two steps the watercut was constant. This behaviour is a known indicator of changing wettability. Moreover, direct connate water banking

measurements confirm the change. The field observations are supported by spontaneous imbibition experiments in core material and a single well Log-Inject-Log test in an analogue field.

The field is an elongated, high relief, tilted horst block, which is internally compartmentalized. The field is delimited by two main boundary faults and sealed by an erosional unconformity. A schematic cross section is shown in Figure 2.10.

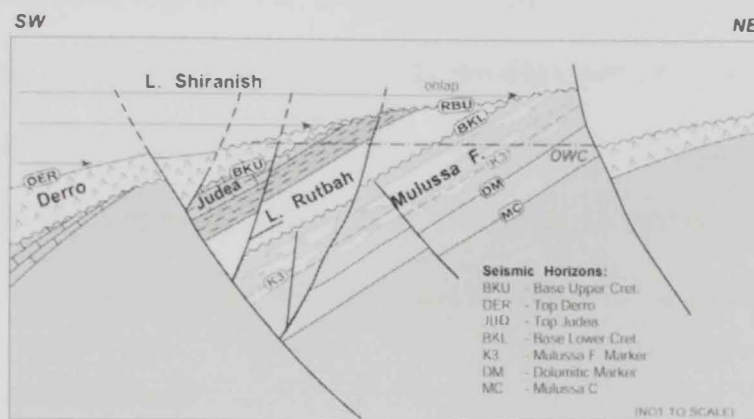


Figure 2.10 schematic of Omar field (Paul et al. 2010).

The field was discovered in 1987 and production started in 1989. After an initial peak production of 80kbopd, production plummeted to only 25kbopd within a year. The reservoir pressure declined rapidly and wells were closed in at the bubble point pressure to avoid shrinkage losses and an irreversible loss in oil recovery. This early data confirmed the absolute lack of any active aquifer (Neidhart et al. 2008).

In order to revive production, water injection was implemented in January 1991 using river water, which was the only water source available at that time. The quality of the injection water lifted from the Euphrates river varied over time, but salinity is about 500 mg/L and bivalent cations \ll 100 mg/L. Water was injected in the oil leg, mainly in the RUL but also in the MUF formation. The Omar field was converted to a produced water injection scheme around 2004

after injection of around 0.4 Pore Volume (PV) of low-salinity water. The current (2009) cumulative injection is approximately 0.6 PV.

Paul Vledder et al. (2010) work shows that the wettability can be changed at a reservoir scale, similar to more controlled experiments such as laboratory experiments and Log-Inject-Log tests. A large number of observations consistently prove this change in wettability that is shown to lead to an increased recovery factor. The incremental recovery due to the change in wettability on a field wide scale is 5-15%. This range mostly overlaps with the range obtained from the experimental data (9-23%) and therefore the final conclusion is that the incremental recovery due to low-salinity injection in Omar Field amounts to 10-15% of the STOIP. The main issues to be managed are water sourcing, water disposal and water mixing in the reservoir.

2.8 The Objective of This Work:

1. Investigate the merits of using Low Salinity flooding techniques to enhance oil recovery in a Bu Hasa reservoir.
2. Better understanding of the mechanism involved in the additional recovery of oil by low salinity flooding.
3. Study the effect of LowSal on contact angle and IFT.
4. Investigate the effect of different ions (SO_4^{2-} and Ca^{2+}) on the recovery process.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Bu Hasa Field:

The Bu Hasa field is located south west of Abu Dhabi city in sand dunes and intervening plains between the areas of Saruq Qufa and Bida Al Qemzan. The field was first discovered in 1962 and oil production commenced in 1965. It has the highest installed production capacity of any of ADCO's fields. In terms of proven oil reserves, it is one of the top twenty fields in the world. The current average reservoir pressure is about 3300 psig and the bubble point is found to be 2502 psig. The current reservoir formation volume factor is 1.531 RB/STB and the current solution gas oil ratio is 761 SCF/bbl.

3.2 Materials Used In the Experiments:

3.2.1 Crude oil:

Reservoir crude oil from the Bu Hasa field field was used in all experiments. The oil was filtered through a 5.0 μm filter paper (with a vacuum pump) to remove any possible particles. The oil is sweet oil that has no H_2S and about 2.6 mole % CO_2 which is very low. The oil density and viscosity are 0.825 g/cc and 3.08 cp measured at room temperature (25°C), respectively. The compositional analysis of the crude oil is illustrated in Table 3.1.

Table 3.1 compositional analysis of the oil up to C₁₀₊.

Components	Mole%
H ₂	0
H ₂ S	0
CO ₂	2.59
N ₂	0.12
C ₁	34.16
C ₂	6.72
C ₃	6.36
iC ₄	1.54
nC ₄	4.05

Components	Mole%
C ₅	0.01
iC ₅	1.99
nC ₅	2.66
C ₆	4.78
C ₇	3.82
C ₈	6.11
C ₉	2.58
C ₁₀₊	22.51
Total	100

3.2.2 Brines:

In this study, five types of water were used. The first type is the original formation water (FW) which was used to saturate the core samples. This water was prepared in the laboratory with salinity of about 163,071 ppm and density of 1.11 g/cc. The second type is Um- Radhuma (UER) water which is the formation water that has been used in flooding of the reservoir for many years. A live sample of this water was filtered, degased, then used in the experiments. This water has a salinity of about 197,584 ppm and density of 1.15 g/cc. The third type is Simsima (SIM) water which is formation water that has been used in water flooding the reservoir for many years. A live sample from of this water was filtered, degased, then used in the experiments. Its salinity is about 224,987 ppm and its density is 1.16 g/cc. The forth type is sea water (SW) which was collected from the one Arabian Gulf beaches in Abu Dhabi. It was filtered, degased, then used in

the experiments. Its salinity is about 43,980 ppm and its density is 1.029 g/cc. The fifth type is distilled water which was prepared in the laboratory.

Table 3.2 shows the analysis of Um- Radhuma (UER) water, Simsima (SIM) water, formation water (FW) and sea water (SW).

Table 3.2 Analysis of the different types of Water.

Type	mg/L								TDS salinity (ppm)
	Ca ⁺⁺	K	Mg ⁺⁺	Na ⁺	CO ₃	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁼⁼	
SIM	20808	---	3047	68214	---	119	150617	350	224987
UER	14033	---	3024	57613	---	244	122023	420	197584
FW	15992	---	1282	51820	---	391	111852	272	163071
SW	600	---	1560	13900		200	24300	420	34980

3.2.3 Core samples:

Five core samples were selected from well number 589 in Bu Hasa field. The properties of these cores are listed in Table 3.3. Four of these core samples were used in the flooding experiments, namely, numbers 31, 39, 40 and 42. The fifth core sample (no.46) was used for contact angle measurements. Figure 3.1 shows an image of one of the core samples which has no vuggs or fractures.

Table 3.3 Properties of the selected core samples.

SAMPLE NO	DEPTH ft	L cm	D cm	Kw md	DRY WT gm	SAT WT gm	PV cc	ϕ frac.
31	8694.90	7.090	3.843	8.7	164.080	186.700	20.423	0.248
39	8695.10	7.032	3.850	8.5	163.470	184.960	19.402	0.237
40	8697.30	7.247	3.853	8.7	170.210	192.370	20.007	0.237
42	8701.80	7.272	3.855	8.8	190.160	205.030	13.425	0.158
46	8702.10	7.160	3.860	7.7	190.800	204.130	12.035	0.144



Figure 3.1 core # 31.

3.2.4 Safety precaution:

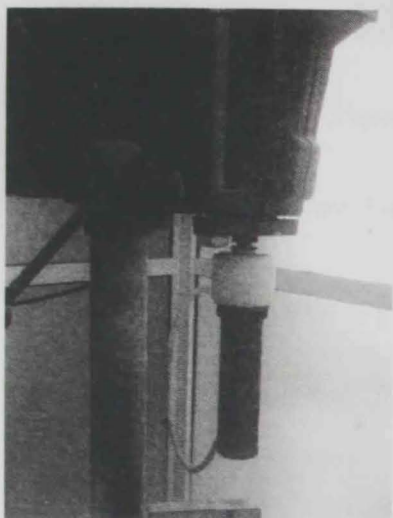
Core analysis work involves high risk and it is mandatory to wear lab coat, gloves and goggles at all times. Organic solvents (toluene, n-hexane etc.) must be used under the fume hood and when using them fume mask must be used. Face shield and ear plugs must be used while drilling and trimming of core samples.

3.3 Experimental Setup and Procedures:

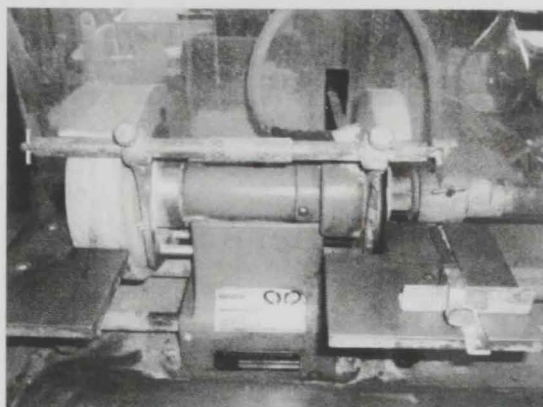
3.3.1 Cutting, trimming and cleaning of core samples:

Standard core lab procedures were implemented in cutting, trimming and cleaning the core samples. In order to conduct core flooding experiments, core plugs of size 1.5 in diameter is

needed. Diamond Tooled Drill Press is used to cut the plugs from the whole core that we received from the company. It is adapted to cut plug cylinders from selected core samples, a drill bit with a cutting surface of small diamond chips is utilized in the drilling process. Using tap water or air as drilling fluids, this machinery can drill all types of rocks to produce plug samples with 1.5 inches in diameter and up to 3.0 inches in length.



(a)



(b)

Figure 3.2 (a) Diamond Tooled Drill Press (b) Core Trimming Machinery.

After the cutting of the cores, a core trimming machinery was used to trim and fine trim the plug samples and give them a cylindrical shape. Figure 3.2 shows the Diamond Tooled Drill Press machine and core trimming machine.

Soxhlet Extraction Apparatus was used to extract oil and salts and clean the core samples as shown in Figure 3.3. This unit can handle 6 samples at a time. Usually toluene is recommended to extract hydrocarbons, and methanol is recommended to extract salts, but they may be replaced with any other solvents.

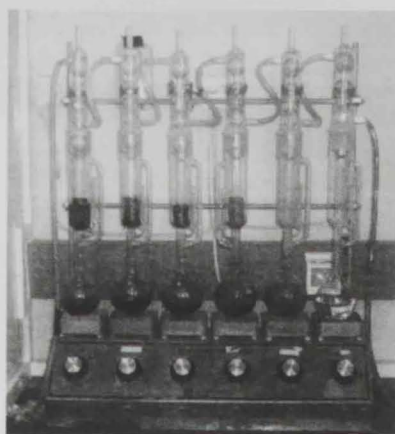


Figure 3.3 Soxhlet Extraction Apparatus.

The cleaning process that was used is the core lab standards procedures and it's as follow:

1. The cores are placed like in Figure 3.3 in the upper part of the Soxhlet.
2. Toluene is placed in the flasks in the lower part of the Soxhelt.
3. Start the water flow through the water condenser.
4. Start the heaters under the flasks.
5. The cores are to be leaved in the Soxhelt for three days under observation.
6. After the three days, cores are removed from the Soxhelt and placed in open air for at least two hour to dry.
7. The cores are to be exposed to ultraviolet light source. If it start to glow (fluorescent) then there is some residual organic materials present then step 1 to 6 is repeated if not, the core is organic free.
8. Step 1 to step 7 is repeated by instead of using toluene the flasks is be filled with methanol and to be leaved for three days also under observation.
9. After the three days, cores are removed from the Soxhelt and placed in open air for at least two hour to dry.

10. A drop of AgNO_3 is to be placed on the core. If a precipitate of white color is formed there are salts in the core and step 8 and 9 is repeated if not, is core is salt cleaned.
11. Cores are placed in open air for at least two hour to dry. Then placed in oven for eight hours.

3.3.2 Pressure saturation of the cores:

The purpose of this experiment is to evacuate and pressure saturate core samples with brine. This is a preparation stage prior to many advanced rock properties analyses. Core saturating cylinder is used to saturate core samples with brine under pressure. This cylinder is attached to a vacuum pump so air is pulled out of the samples before saturating pressure is applied; pressure may be elevated up to 10,000 psi. Figure 3.4 shows the Core Saturating Cylinder.

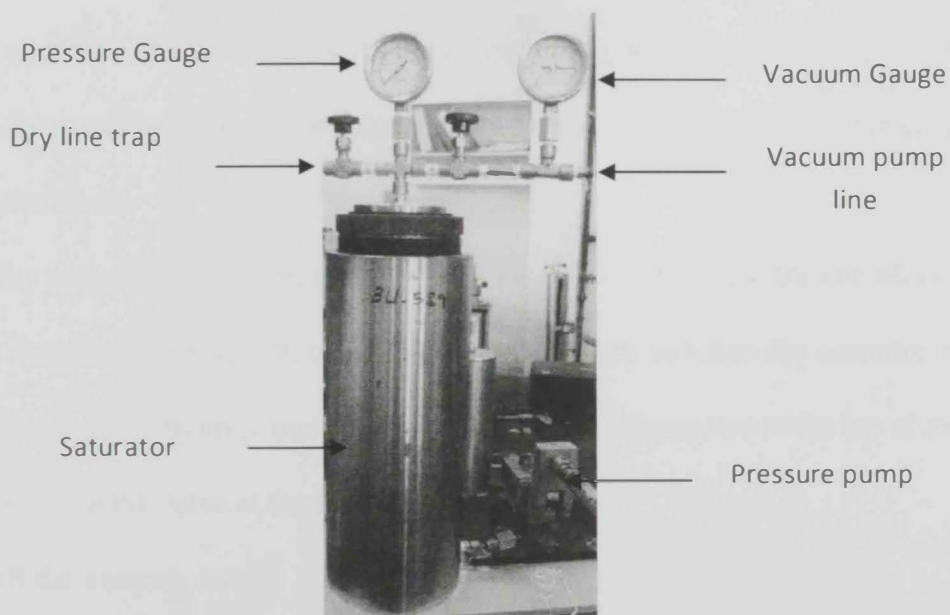


Figure 3.4 Core Saturating Cylinder.

Again, core lab procedures were implemented in the core Saturation process and as follow:

1. Measure the dry weight of each sample and record.

2. Ensure that saturator cylinder is clean and dry.
3. Carefully place the core sample(s) into the saturator. Take care not to dislodge grains from the samples.
4. Include clean spacers (e.g. rubber plugs) to minimize unused volume in the saturator (the plug closest to the outlet port shall be placed with its curved edge next to the port). Close the saturator.
5. Connect the vacuum source to the top of the saturator. Ensure that a clean, dry liquid trap is in-line close to the saturator and a vacuum gauge is connected.
6. Close the valve at the bottom of the saturator, open the valve at the top of the saturator, switch on the vacuum and monitor the vacuum gauge. A vacuum, equivalent to 29 inches of mercury or more, shall be maintained for a minimum period of 4 hours.
7. Prime and flush the pressure pump, including the bypass line, with brine (or the saturant fluid). Connect the pump to the bottom valve on the saturator and bleed the connecting line to remove all air.
8. Open the pump bypass valve, open the bottom valve of the saturator and allow brine to be drawn from the brine source, through the pump bypass and into the saturator. Continue to fill the saturator with brine until brine appears in the vacuum line at the top of the separator, and then close the valve at the top of the separator.
9. Turn off the vacuum supply.
10. Close the pump bypass valve, operate the pump and increase the pressure in the saturator to 2000 psig. Monitor the pressure regularly for approximately 30 minutes and top-up to 2000 psig if required

11. Clean the liquid trap in the vacuum line and the line that connected the trap to the saturator. Leave them clean and dry.
12. Close the valve at the bottom of the separator. Disconnect the pressure pump and thoroughly flush it with de-ionized water to clean out brine.
13. Maintain a pressure of 2000 psig in the separator for a minimum of 4 hours for permeable samples (>50md), and a minimum of 8 hours for impermeable samples (<50md).
14. Place the clean plastic sample storage container under the saturator and carefully crack open the bottom valve of the separator. Let the pressure in the saturator decrease slowly to minimize pressure differential within the core samples.
15. When the pressure in the saturator has reached 0 psig add fresh brine (or saturant fluid) to the storage container. Open the saturator, drain off the brine (or saturant fluid) and immediately place the saturated core samples in the storage container fully submerged under fluid.
16. Clean the saturator and work area thoroughly.
17. Remove a core sample from storage under fluid; wipe off excess fluid by firmly rolling the sample sides and both ends on hard (low absorbency) paper towel. Weigh the sample. Immediately replace the sample under fluid in the storage container. Record the weight on under Saturated Weight.

The pore volume of the core was calculated from equation 3.1. The calculation is based upon the weight difference between dry and wet core 100% saturated with FW of known density. The porosity was then determined from equations 3.1 and 3.2.

$$pv = \frac{w_s - w_d}{\rho_w} \quad (3.1)$$

$$\phi = \frac{pv}{v_b} \cdot 100 \quad (3.2)$$

Where:

P_v = pore volume of core sample, cc

w_s = 100% saturated weight of core sample with with FW, gm

w_d =dry weight of core sample, gm

ρ_w = density of FW brine, gm/cc

v_b = bulk volume of the core sample, cc

ϕ = porosity of core sample, dimensionless.

3.4 Liquid Permeability:

The LP-401L Liquid Permeameter is designed for measurement of liquid permeability. The fluid can be injected into and through the core sample. Data is read by the software and the permeability is calculated, this data can be stored in excel file. The Liquid Permeameter is supplied with a core holder that accomodates cores of 1.5 inch diameter, of maximum 3-inch length. It is also supplied with a pump to flow the fluid through the core and to provide overburden pressure. It has a flow rate range from 0 to 10 ml/min, and a maximum pressure rating of 6000 psig. A differential-pressure transducer is provided to monitor the differential pressure across the core; it has a full-scale range of 125 psig. Figure 3.5 shows the Liquid Permeameter apparatus.

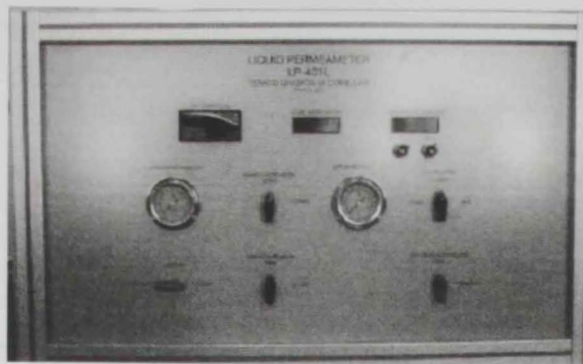


Figure 3.5 The Liquid Permeameter.

The permeability of the core to brine was then calculated by Darcy's law as expressed in equation 3.3. Since the experiments only involve single phase, the brine permeability is equal to the absolute permeability.

$$K = \frac{\mu \cdot L \cdot Vol \cdot 14600}{\Delta p \cdot A \cdot t} \quad (3.3)$$

Where:

μ = brine viscosity, cp (at measured temperature)

L = length of core sample, cm

Vol = volume of collected brine effluent, ml

Δp = pressure differential across the core, psig

A = core sample cross sectional area, cm^2

t = time for effluent collection, sec

14600 = conversion factor to convert psig to atmospheres and to convert Darcys to milliDarcys

3.5 Core Flooding Experiment and Setup:

3.5.1 Oil flooding:

Oil floods were conducted at constant injection pressure of 100 psia and at room temperature of 25 °C. The cores positioned in a vertical configuration and oil was injected at the top. Oil was injected using the oil reservoir arrangement described in Figure 3.6. Produced oil and water were collected in a burette. Oil-water and air-oil interfaces were recorded to calculate saturation. Flowrate was regularly measured with a stop watch and pressure drop was measured continuously.

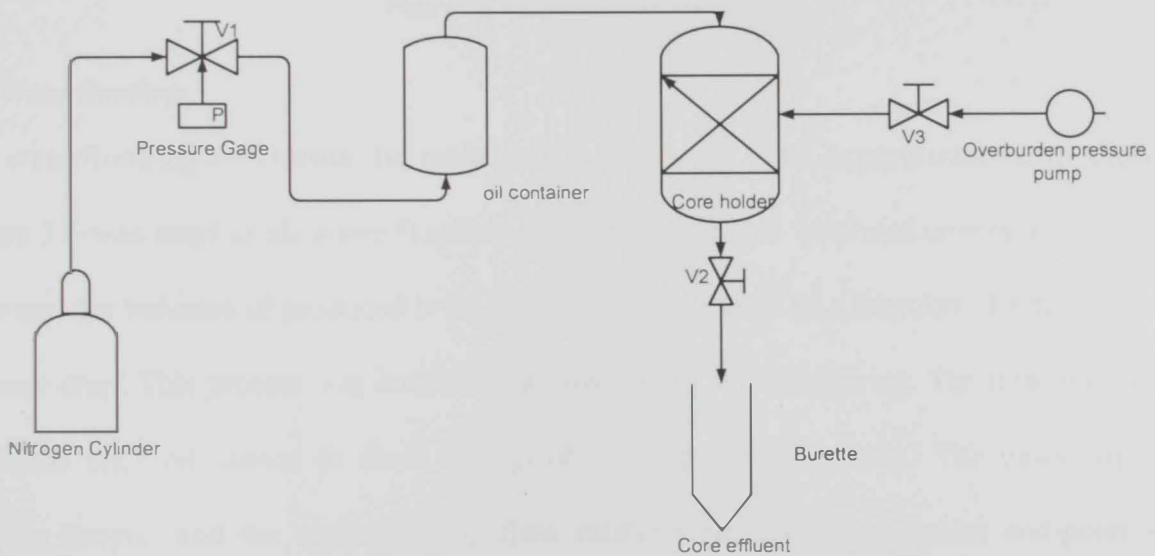


Figure 3.6 A schematic diagram of the core flooding setup.

The core holder is designed for high pressure flood tests. It is supplied with a core holder that accommodates cores of 1.5 inch diameter, of maximum 3-inch length as shown in Figure 3.7.

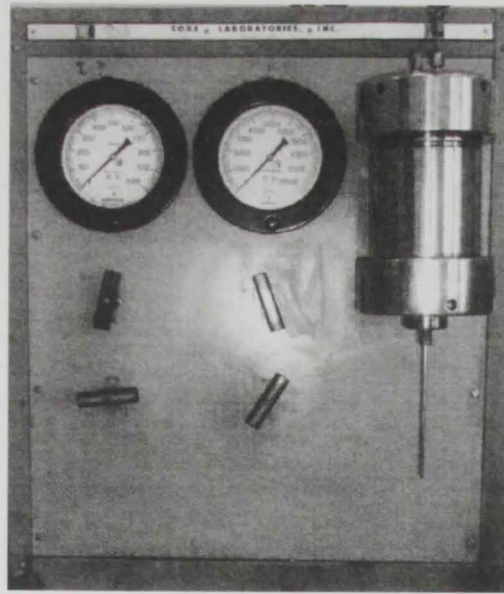


Figure 3.7 The core holder assembly.

3.5.2 Water flooding:

The waterflooding represents the main test in this work. The experimental setup shown in Figure 3.6 was used in all water flooding tests. The crude oil-saturated core was flooded with brine and the volumes of produced brine and oil were recorded as a function of time at constant pressure drop. This process was conducted at low rate to avoid fingering. The injection of brine continued until oil ceased to show any production at the core outlet. The measured stable pressure drop(s) and the corresponding flow rate(s) were used to calculate end-point water permeability to water $(k_{rw})_{Sor}$ using Darcy's law. The material balance was then applied to calculate the residual oil saturation (S_{or}). Figure 3.8 illustrates a block diagram of all test runs performed in this work. Experiments were conducted with the original UER, SIM, SW and distilled water. Then, Experiments were conducted using the dilutions of each water to find the optimum salinity water. The ionic concentration of sulfate and calcium ions was studied using the optimum salinity water.

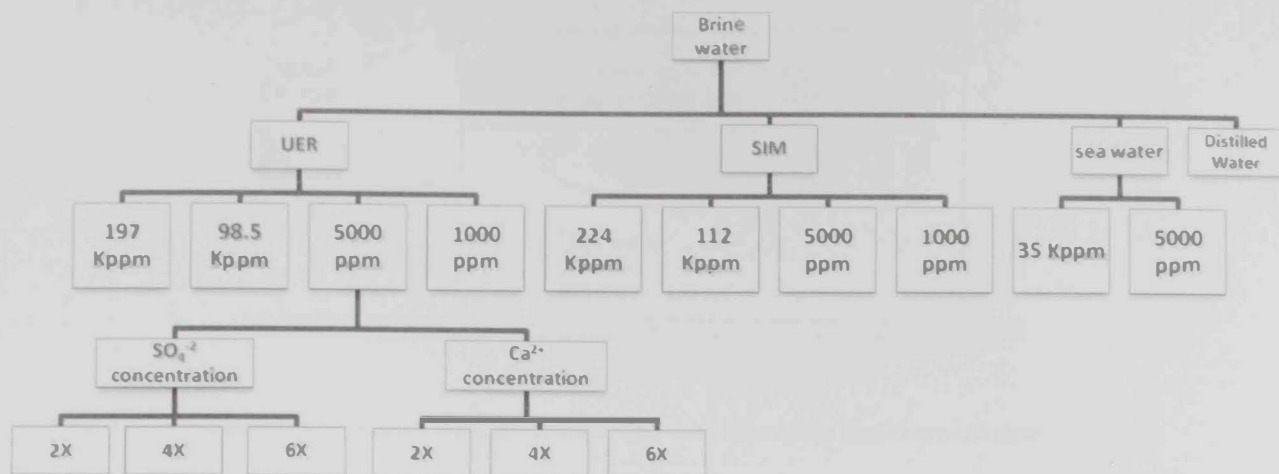


Figure 3.8 Block diagram showing the test various runs performed in this work.

3.6 Contact Angle Measurements:

In an attempt to evaluate the effect of water salinity on wettability, contact angles were measured with the sessile drop method. The device consists of a box made of glass with dimensions of 10 cm × 10 cm × 13.5 cm. A circular limestone disk (Diameter 3.6 cm) was placed on the top of the open side of the table as shown schematically in Fig. 3.9. The box was filled with the specified saline solution. Then a small drop of oil was allowed to rest at the bottom of the limestone disk. The change in the drop size as function of time was monitored using a digital camera. Different runs were performed to assess the effect of brine salinity on the contact angle of the studied system. A photo of the oil drop as function of time was taken every minute. The change in rock surface wettability with time in the presence of brine solutions was measured. These runs were analyzed for contact angle determination using Sigma Scan Pro image analysis software.

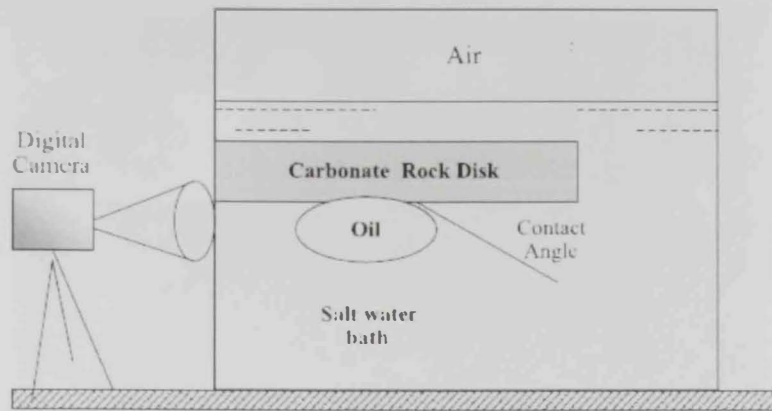


Figure 3.9 Schematic diagram of apparatus used for contact angle measurements.

3.7 Interfacial Tension (IFT) Measurements:

The interfacial tensiometer was used to determine the tension occurring at the interface of contact between a less dense fluid and a more dense fluid. The spinning drop apparatus shown in Figure 3.10 includes a capillary tube, into which an aqueous fluid was injected, followed by a small drop of oil. The tube was placed in a rotating device to make the tube spins. A microscope and strobe (lamp) light were used to observe the elongation process of the oil drop. Measurements of the oil drop elongation were then taken and the interfacial tension was calculated from these measurements.



Figure 3.10 The interfacial tensiometer apparatus.

The interfacial tension (IFT) measurement using the spinning drop tensiometer can be calculated from the equation below, as described by Cayias et al (1975).

$$\gamma = \frac{\pi(\rho_w - \rho_o)R_d^3\omega^2}{4} \quad (3.4)$$

Where:

γ = interfacial tension (dyne/cm)

ρ_w = density of water (gm/cc)

ρ_o = density of oil (gm/cc)

R_d = diameter of the droplet (cm)

ω = rotation speed (rpm)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results of Core Flooding Experiments:

4.1.1 Flooding with UER water:

In order to evaluate the effect of different salinities on the recovery eleven core flooding tests were conducted. UER brine with its original salinity of 197584 ppm was diluted to the half of its salinity 98792 ppm then to 5000 ppm and 1000 ppm. The original brine and its dilution were used in flooding the core at ambient temperature and a pressure difference of 100 psi. The flooding results was plotted as percent oil recovery from the original oil in place (OOIP) versus pore volumes injected of brine as shown in Figure 4.1.

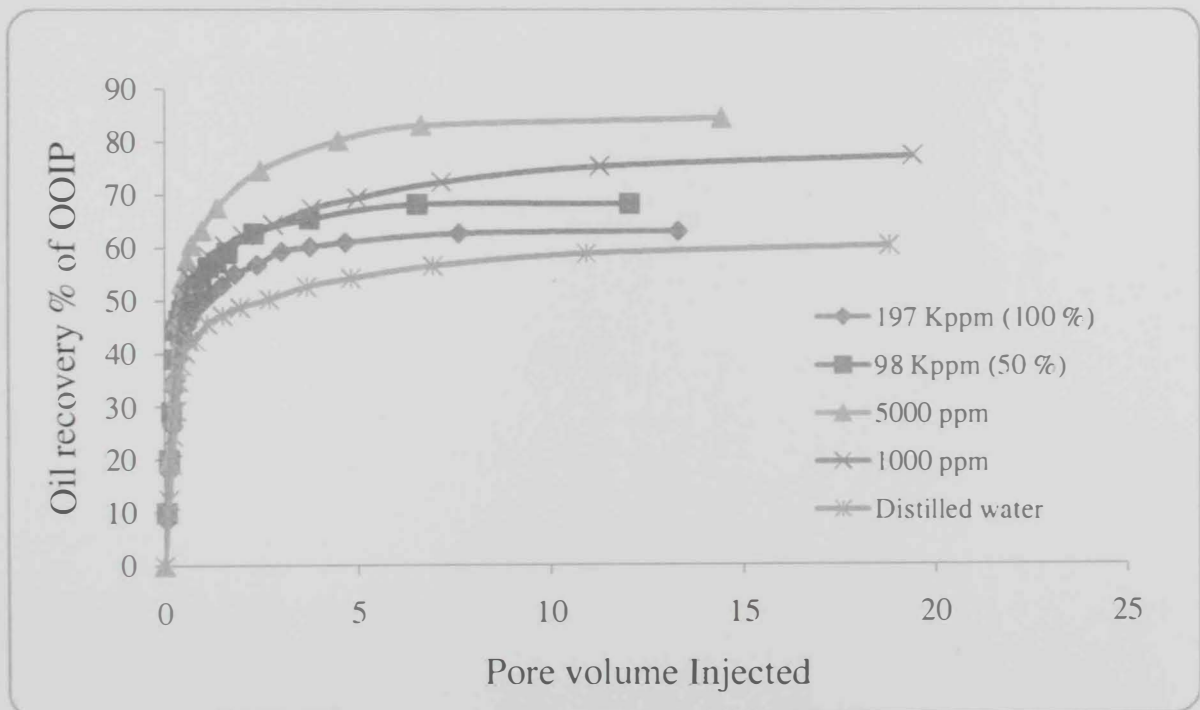


Figure 4.1 Oil recovery % of OOIP vs. pore volume injected of UER water with different salinity concentrations; figures between brackets represent percent of dilution of original salinity concentration.

Figure 4.1 shows that the highest recovery percent was obtained from the 5000 ppm dilution which was about 84.5 % of the OOIP. The lowest recovery percent was obtained from the diluted water which was about 60.5 % of the OOIP. The 1000 ppm dilution was the lowest salinity of UER water used and its gives a lower recovery from the 5000 ppm dilution which was 77.4 % of the OOIP. All the UER water dilution resulted in a higher recovery than the distilled water. Therefore, the salinity of 5000 ppm was considered as the optimum salinity for further evaluation.

4.1.2 Flooding with SIM water:

SIM brine with its original salinity of 224987 ppm was first diluted by 50% (salinity of 112493 ppm) then to 5000 ppm and finally to 1000 ppm. The original brine and the diluted solutions were used in flooding the core at ambient temperature and a pressure difference of 100 psi. The results of this part are illustrated Figure 4.2.

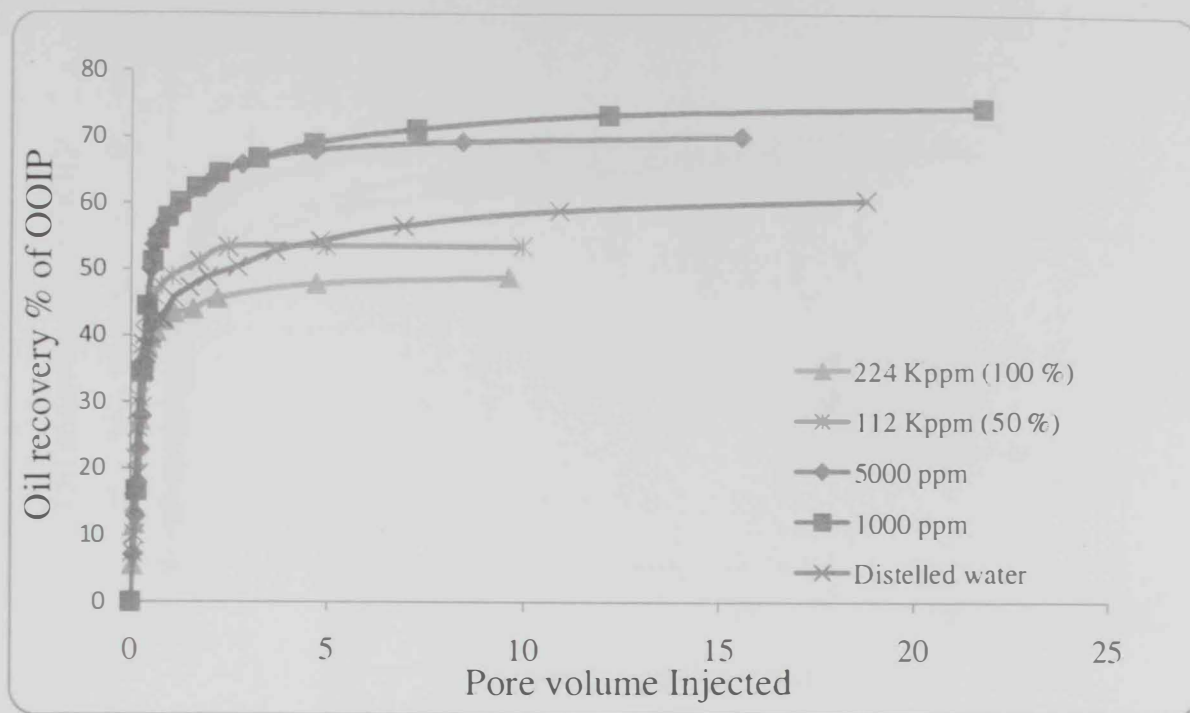


Figure 4.2 Oil recovery % of OOIP vs. pore volume injected of SIM water with different salinity concentrations: figures between brackets represent percent of dilution of original salinity concentration.

Figure 4.2 shows that the highest recovery percent was obtained from the 1000 ppm dilution which was about 74.4 % of the OOIP. The lowest recovery percent was obtained from the original SIM water which was about 48.9 % of the OOIP. The 50% dilution resulted in a recovery percent of 53.5 % of the OOIP then the 5000 ppm dilution resulted in a recovery of 70.0 % of the OOIP.

4.1.3 Flooding with Sea Water:

Sea water brine of original salinity equal 43980 ppm was diluted to 5000 ppm. The original brine and its diluted solution were used in flooding the core at ambient temperature and a pressure difference of 100 psi. The results of this part are shown in Figure 4.3.

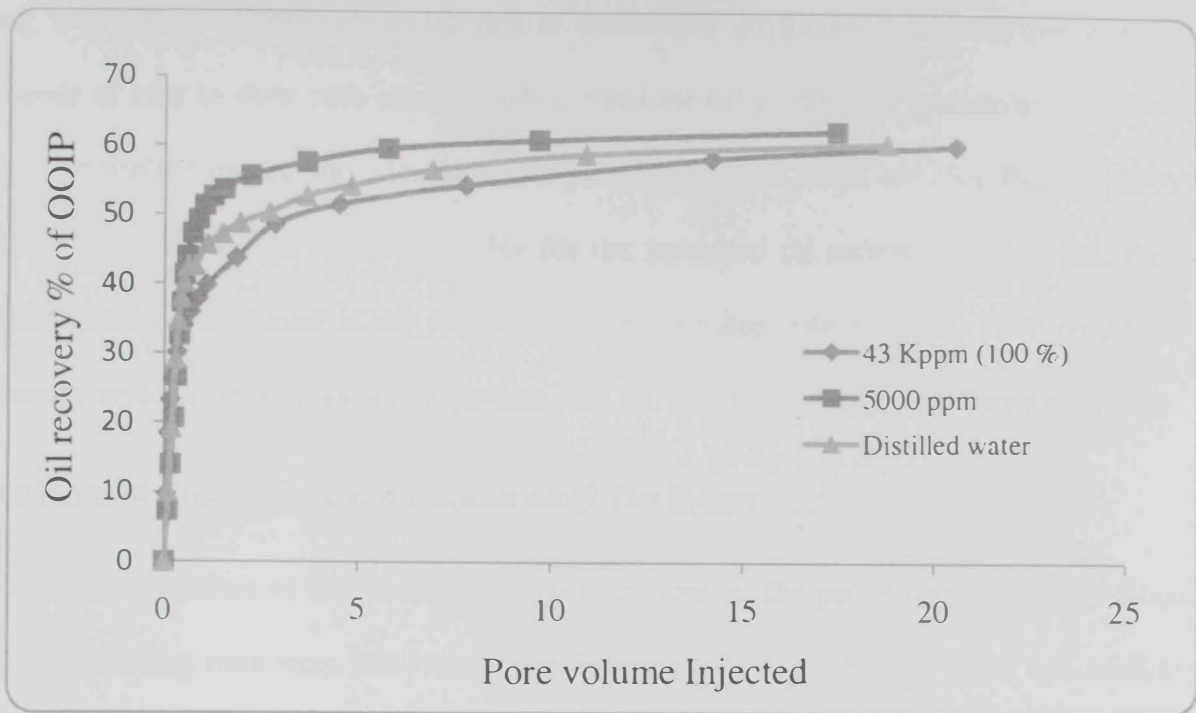


Figure 4.3 Oil recovery % of OOIP vs. pore volume injected of SW water with different salinity concentrations; figure between brackets represent percent of dilution of original salinity concentration.

Figure 4.3 shows that original SW resulted in a recovery percent of 60.2 % of the OOIP and the 5000 ppm brine gives a recovery of 62.2 % of the OOIP and the distilled water resulted in a recovery of 60.5 % of the OOIP. The three waters resulted in comparable results as there is no significant increase by dilution.

4.2 Discussion of Results of Core Flooding Experiments:

Figure 4.1, 4.2 and 4.3 show that flooding core samples with the three different brines at their original salinities resulted in the lowest ultimate oil recoveries. Also, by diluting these brines to lower salinities the oil recovery increased dramatically expect for SW as its original salinity is not high as in UER and SIM brines. The highest oil recovery of 84% of OOIP recovery was achieved by flooding with UER brine which at 5000 ppm.

Tang and Morrow (1999) observed similar trends and attributed these improvements to the presence of clay in their core samples. They concluded that the flow mechanism in LowSal is highly controlled by the clay. The core samples used in this work are clay free and therefore another flow mechanism was responsible for the increased oil recovery by LowSal. Pu et al. (2008) observed increased in oil recovery but in clay-free core samples. They proposed that dolomite crystals could play an important role in the low salinity recovery mechanism.

4.3 Results of Changing Ionic Composition of The Brine:

To evaluate the effect of Ca^{2+} and SO_4^{2-} concentrations on the performance of LoSal flooding, ten core flooding runs were conducted. The 5000 ppm dilution of UER brine was used as the base water for evaluating the effect of ionic composition because the highest oil recovery was achieved by the 5000 ppm dilution of UER brine which was about 84%. The first five cores were flooded with water UER at 5000 ppm and sulfate concentrations of 11.7 ppm, two times, four times, and six times the original sulfate concentration of the UER water at 5000 ppm, and the results are shown in Figure 4.4.

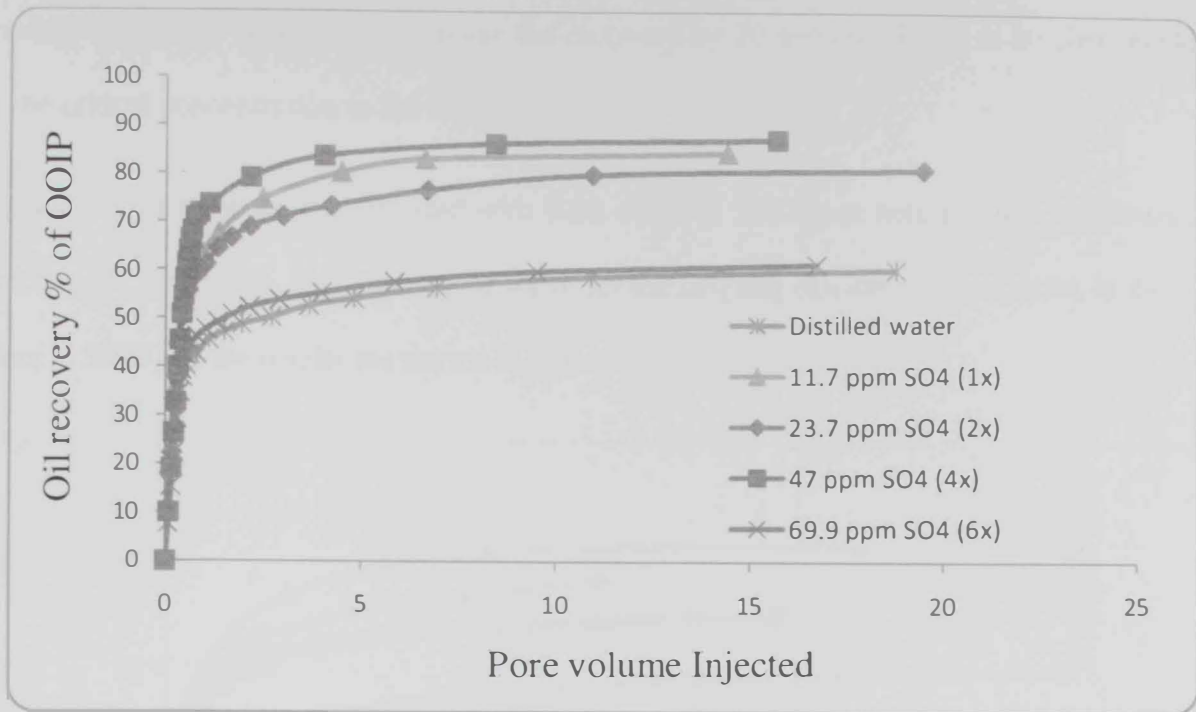


Figure 4.4 Oil recovery vs. pore volume injected brine at different SO_4^{2-} concentrations.

The concentrations of the sulfate were 11.7, 23.7, 47 and 69.7 ppm and these concentrations represent the original sulfate content (1x), two times (2x), four times (4x), and six times (6x), respectively. Figure 4.4 shows that four times the original sulfate content resulted in the highest oil recovery of about 87.2 % of the OOIP. The six times the sulfate content resulted in the lowest oil recovery of about 61.5 % of the OOIP which is comparable to the distilled water of about 60.5 % of the OOIP. Figure 4.4 also shows that increasing the sulfate concentration in the brine solution the recovery could increase until a critical value is reached then it starts to decrease again. This behavior was observed in this work and that the critical value of SO_4^{2-} was equal to 4 times its original value. These results confirm Webb et al. (2005) findings. In their study they compared oil recovery from a North Sea carbonate core samples using sulfate free formation simulated brine with seawater, which contains sulfate. The final results showed that the

simulated seawater was able to increase the recovery by 20 percent. There is no clear evidence on the critical concentration in the literature.

The second set of cores were flooded with UER water at 5000 ppm with calcium concentrations of 332 ppm, two times, four times, and six times the original calcium concentration in the UER water at 5000 and the results are shown in Figure 4.5.

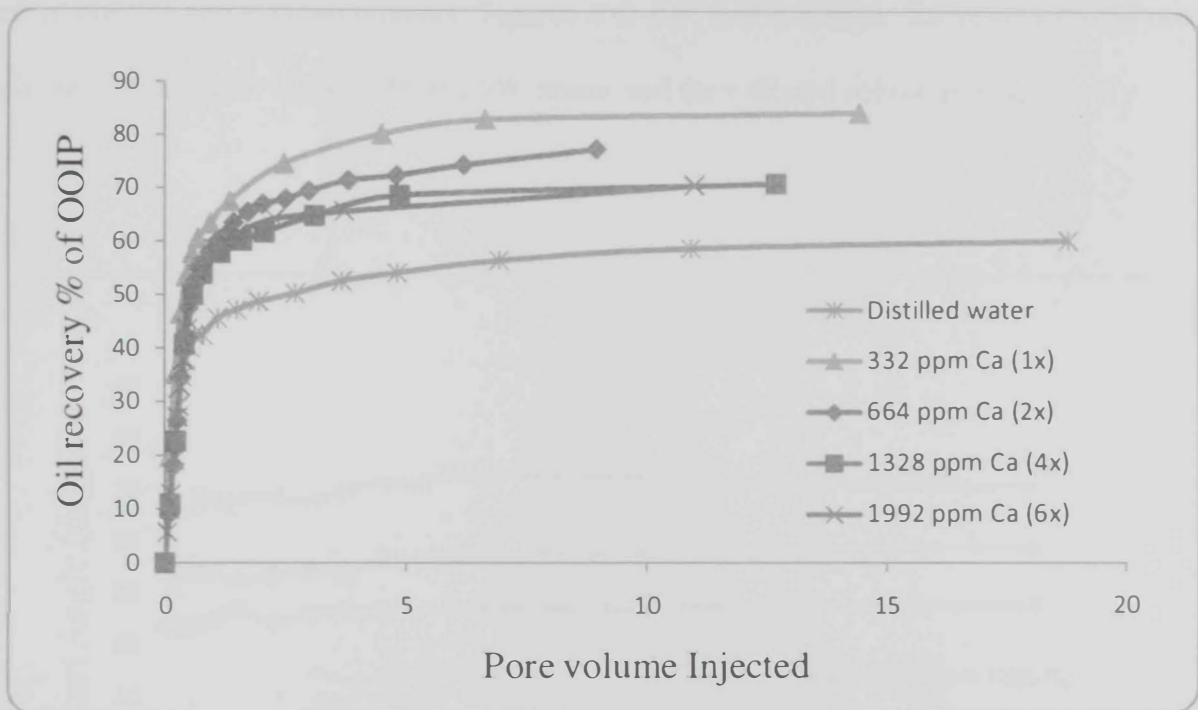


Figure 4.5 Oil recovery vs. pore volume injected brine at different Ca^{2+} concentrations

Figure 4.5 shows that calcium concentration has a negative effect on the recovery. Flooding with the original calcium concentration yields the highest recovery and by increasing the calcium concentration the recovery decreases. The MIE (multicomponent ionic exchange) concept that was proposed by Lager A., et al. (2008) and the Double layer effect that was suggested by Ligthelm et al. (2009) indicate that calcium plays a key role in the oil recovery process in the presence of clay. In this work, however, it is shown that in clay-free core samples, flooding with

calcium could have a negative effect on oil recovery. A complete listing of the results of this section is presented in appendix A.

4.4 Contact Angle Measurements:

The contact angle measurements were conducted to investigate the wettability change as part of the recovery mechanism in LowSal flooding. The brines addressed in the previous sections, were used in contact angle measurements. Figures 4.6, 4.7, and 4.8 show the results of the contact angle measurements for UER, SIM and SW brines and their diluted solutions, respectively.

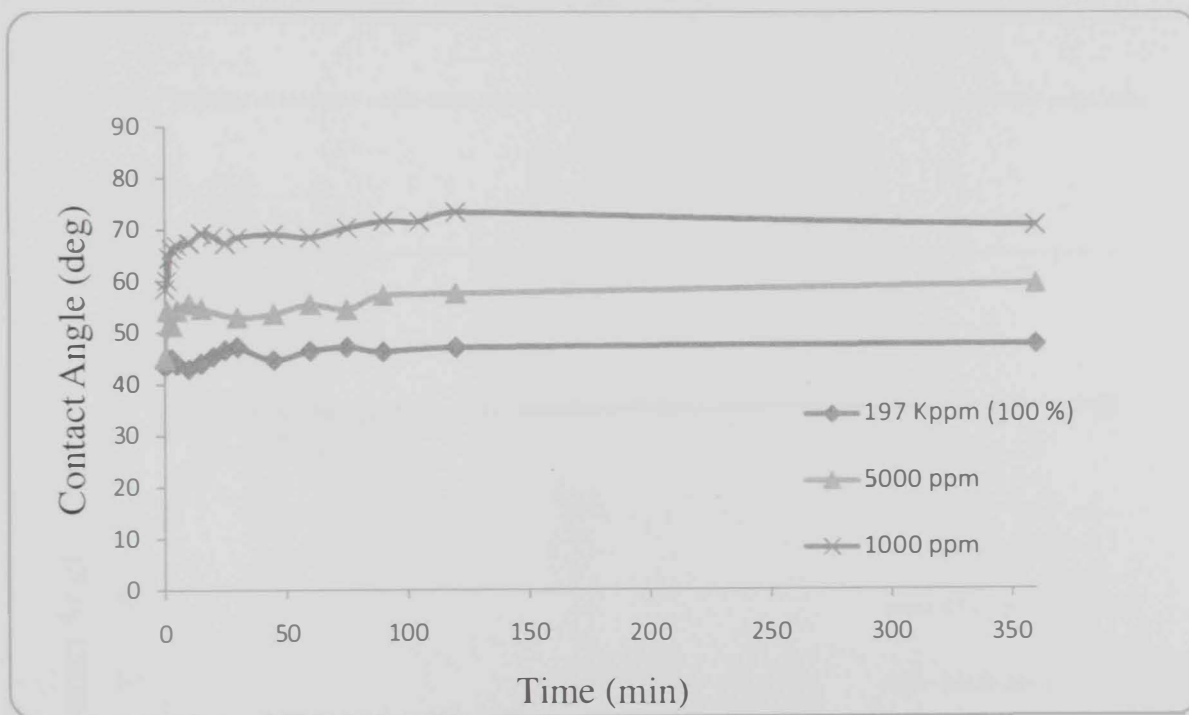


Figure 4.6 Results of contact angle measurements for UER water and its corresponding diluted solutions.

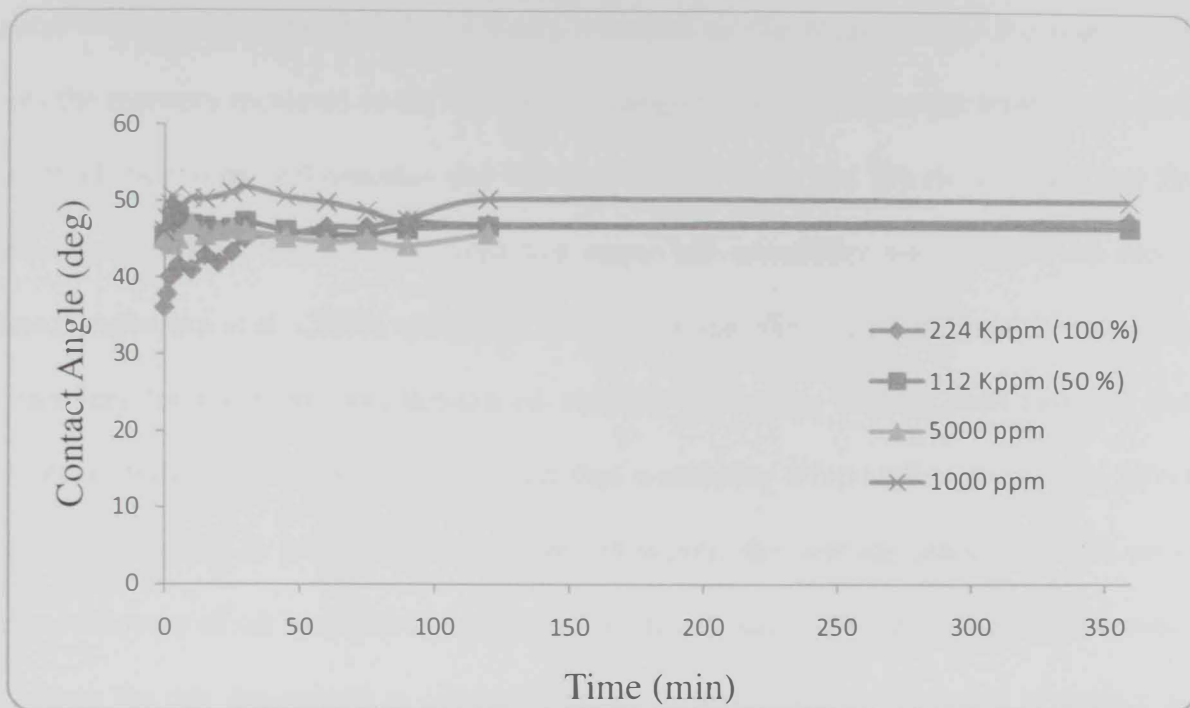


Figure 4.7 Results of contact angle measurements for Sim water and its corresponding diluted solutions.

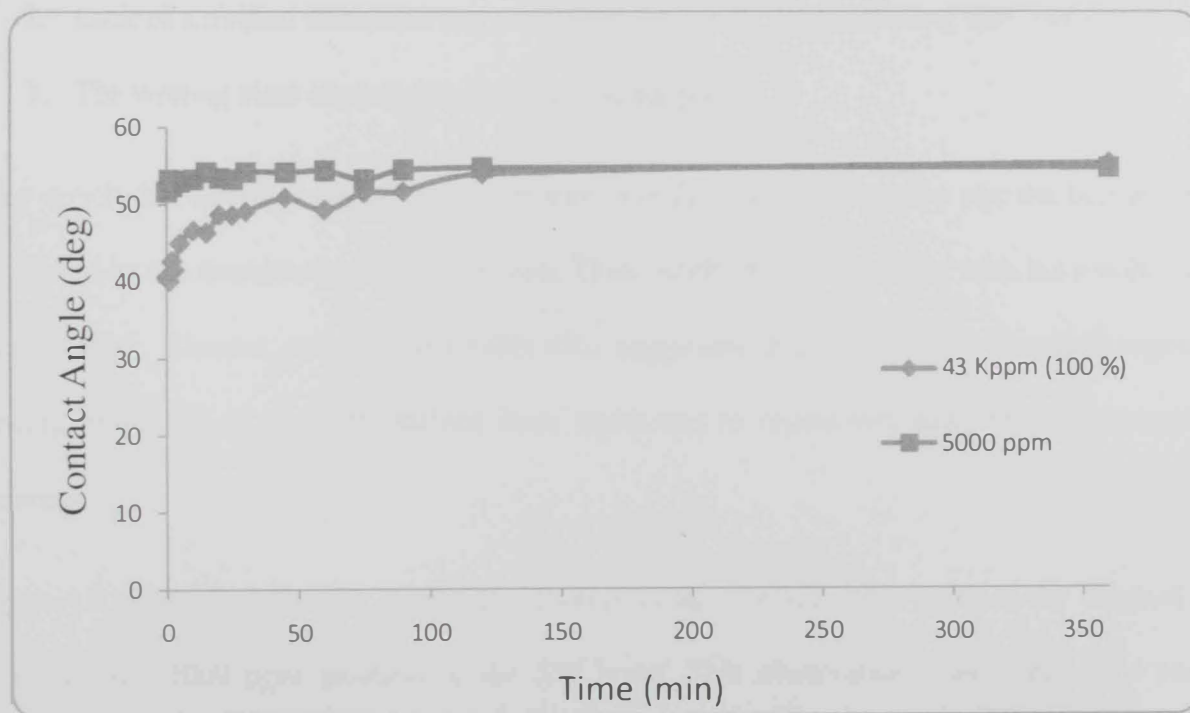


Figure 4.8 Results of contact angle measurements for SW water and its corresponding diluted solutions.

Figures 4.7 and 4.8 show that the recovery increases as the contact angle increases. In other words the recovery increases as the wettability change to more intermediate level. This results is in contradiction with Jadhunandan and Morrow (1991), Tang and Morrow (1999) and Zhang and Morrow (2006); they all concluded that water wet wettability yields higher oil recovery. Chinedu Agbalaka et al. (2008) conducted a review on the effect of reservoir rock wettability on oil recovery for secondary and tertiary oil recovery processes. Several field cases as well as laboratory studies were discussed. The fact that wettability affects oil recovery can affect oil recovery efficiency is widely acknowledged. However, the wetting phase that will result in optimal recovery of oil has been the subject of intense debate. Chinedu Agbalaka observed that the reason for this divergence in observed reports is attributable to a number of factors which includes:

1. Difficulty in wetting state reproducibility.
2. Lack of a unified standards and procedure for coring, core handling and core storage.
3. The wetting state characterization method adopted.

They concluded that strongly oil wet reservoirs give the least oil recovery and the best recovery appears to be the intermediate wet reservoirs. These findings are consistent with the results of the present work. Sharma and Filoco (2000) also suggested that low salinity brine changes the wetting properties of the rock surface from water-wet to mixed-wet and thereby increase the recovery.

Figure 4.8 shows that there is hardly any change in the contact angle between the original SW brine and the 5000 ppm solution of the SW brine. This observation may explain the results presented earlier in Figure 4.3 where flooding with LowSal SW has no effect on the oil recovery.

Also shown in Figure 4.3 that the oil recovery performances in the three runs, including distilled water are comparable.

In order to investigate the changing the ionic composition on wettability, eight brines with different concentration of Ca^{2+} and SO_4^{2-} were used. The Ca^{2+} concentration ranges from 332 ppm to 1992 ppm. The SO_4^{2-} concentration ranges from 11.7 ppm to 69.9 ppm. Figure 4.9 and 4.10 shows the results of the contact angle measurements for the different SO_4^{2-} and Ca^{2+} concentration, respectively. A complete listing of contact angle measurements can be found in the appendix B.

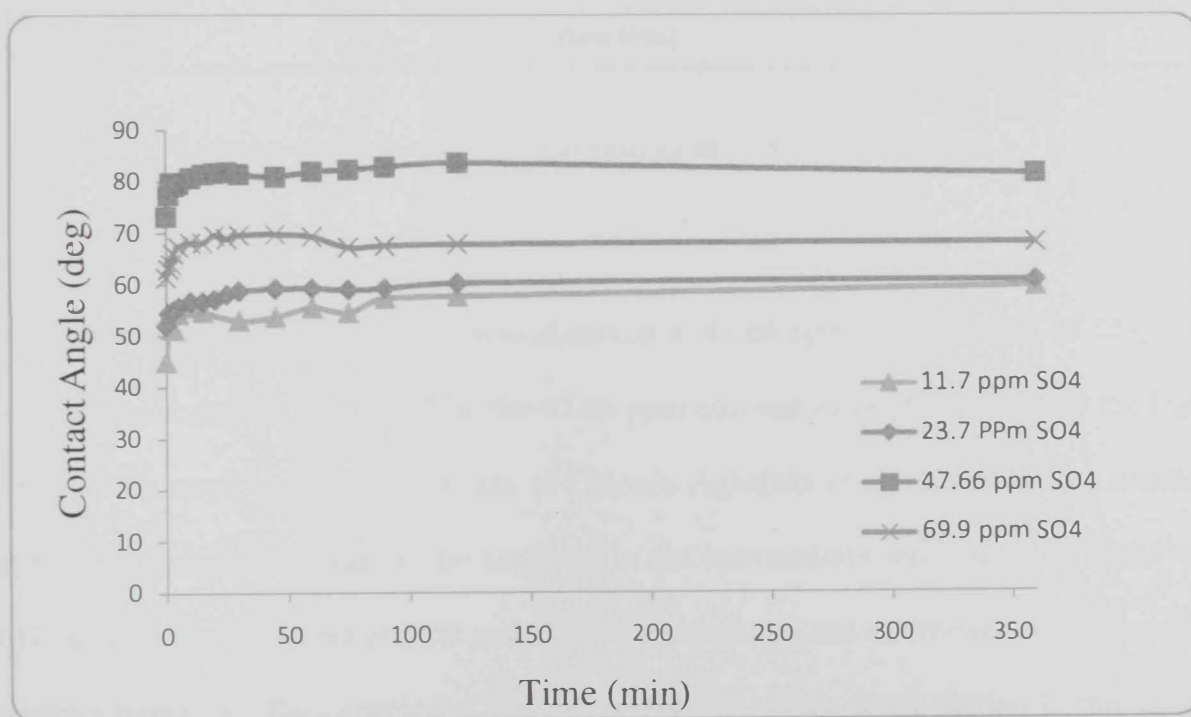


Figure 4.9 Contact angle measurements for different SO_4^{2-} concentration.

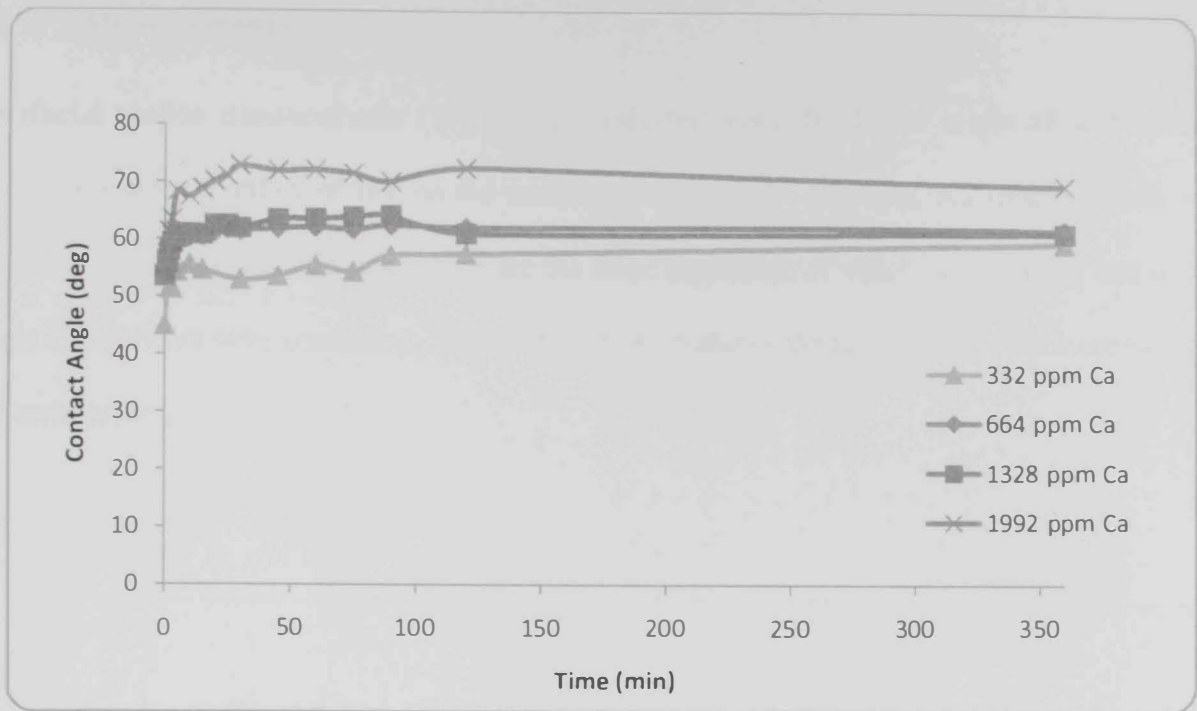


Figure 4.10 Contact angle measurements for different Ca^{2+} concentration.

Figure 4.9 shows that highest angle was observed at 47.66 ppm concentration of SO_4^{2-} . This observation can explain Figure 4.4 as the 47.66 ppm concentration of SO_4^{2-} yields the highest recovery. The result confirms the results of Chinedu Agbalaka et al. (2008) as they concluded that the best recovery appears to be achieved in the intermediate wet reservoirs. Zekri et al. (2011) investigated the effect of EOR techniques on wettability and oil recovery of carbonate and sandstone formation. They concluded that increasing the sulfate concentration in the injection brine changed the wettability the chalky and microcrystalline limestone used in their experiments to more water wet.

4.5 IFT Measurements:

Interfacial tension measurements (IFT) were conducted using Bu Hassa crude oil and different brines to assess the effect of IFT on the mechanism of LowSal flooding. All measurements were carried out at ambient conditions, which are the same conditions at which coreflooding and contact angle experiments were conducted. Figures 4.11 to 4.16 shows the results of IFT measurements for different brines.

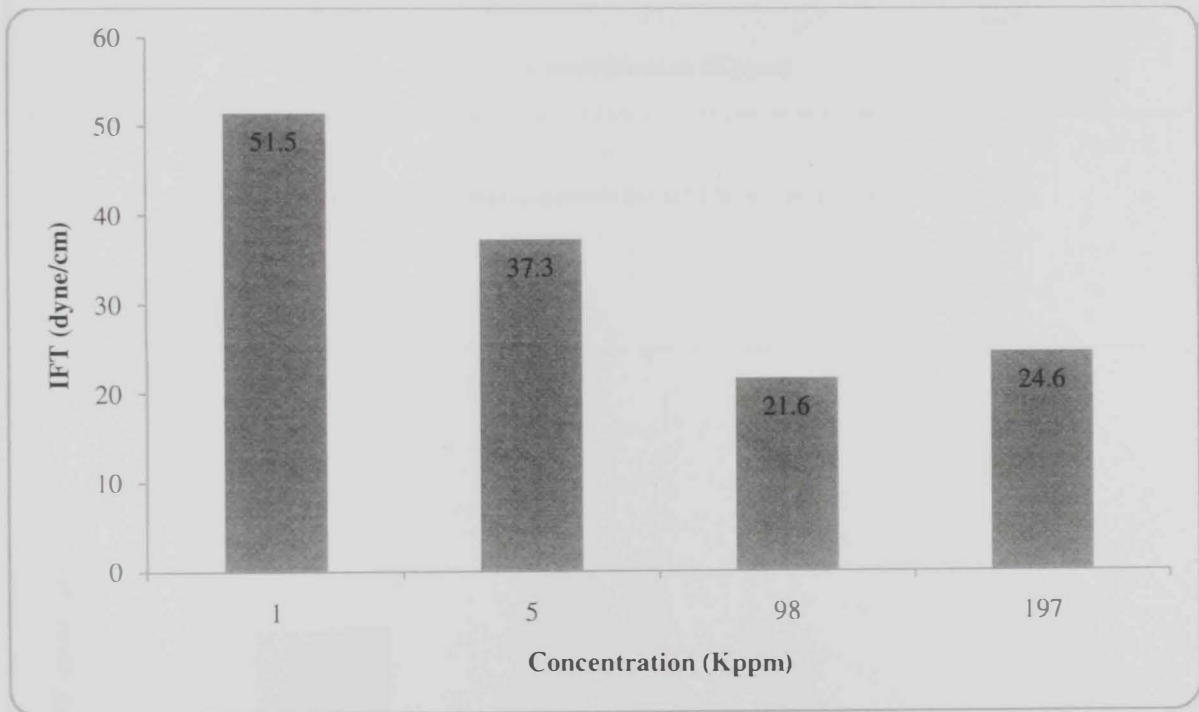


Figure 4.11 Results of IFT measurements for UER brines and its diluted samples.

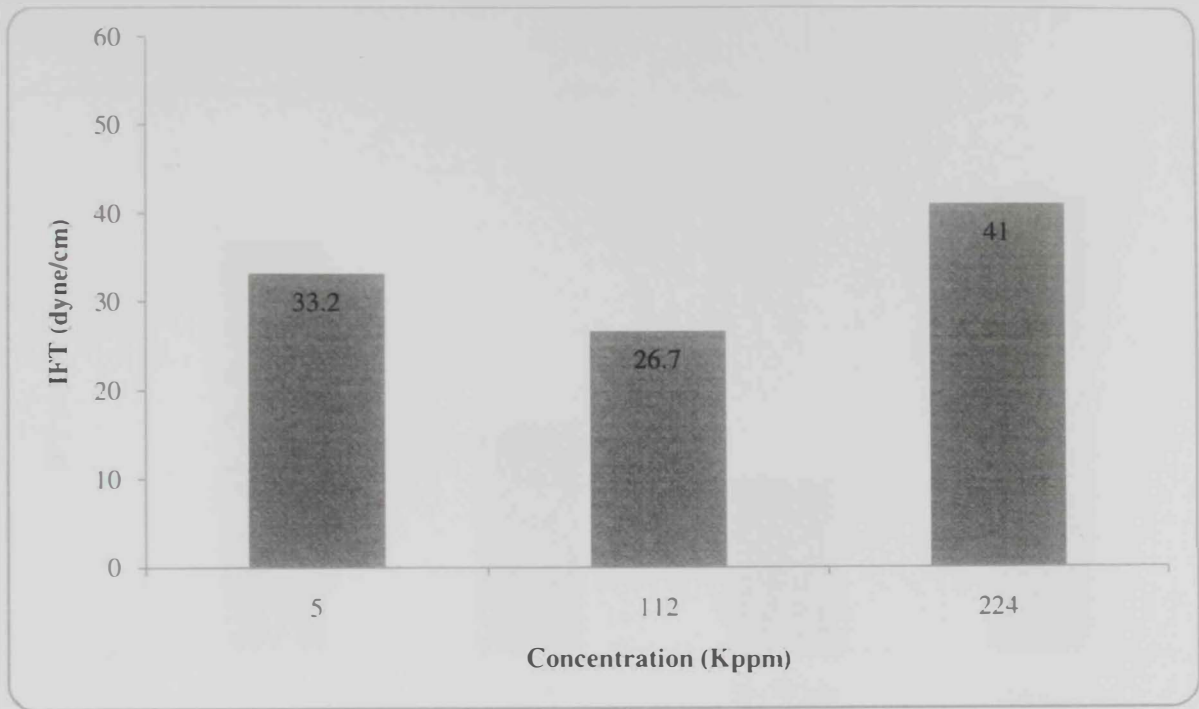


Figure 4.12 Results of IFT measurements for SIM brines and its diluted samples.

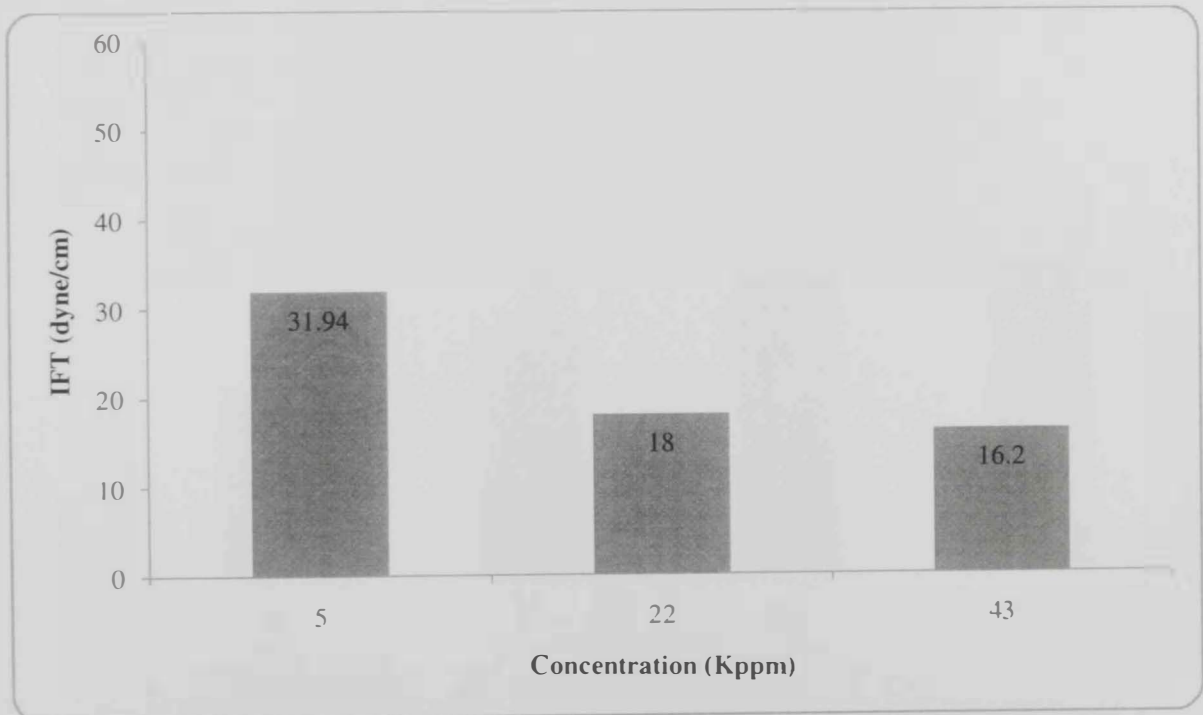


Figure 4.13 Results of IFT measurements for SW brines and its diluted samples.

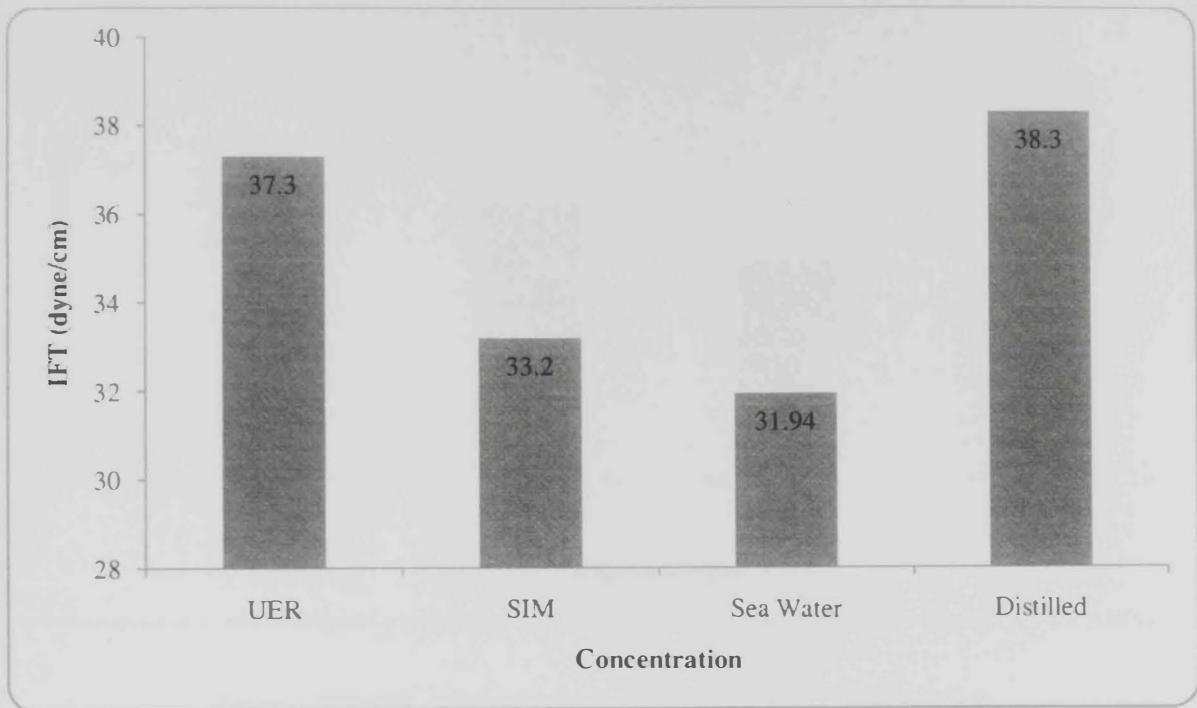


Figure 4.14 Results of IFT measurements for UER, SIM and SW brines at 5000 ppm dilution.

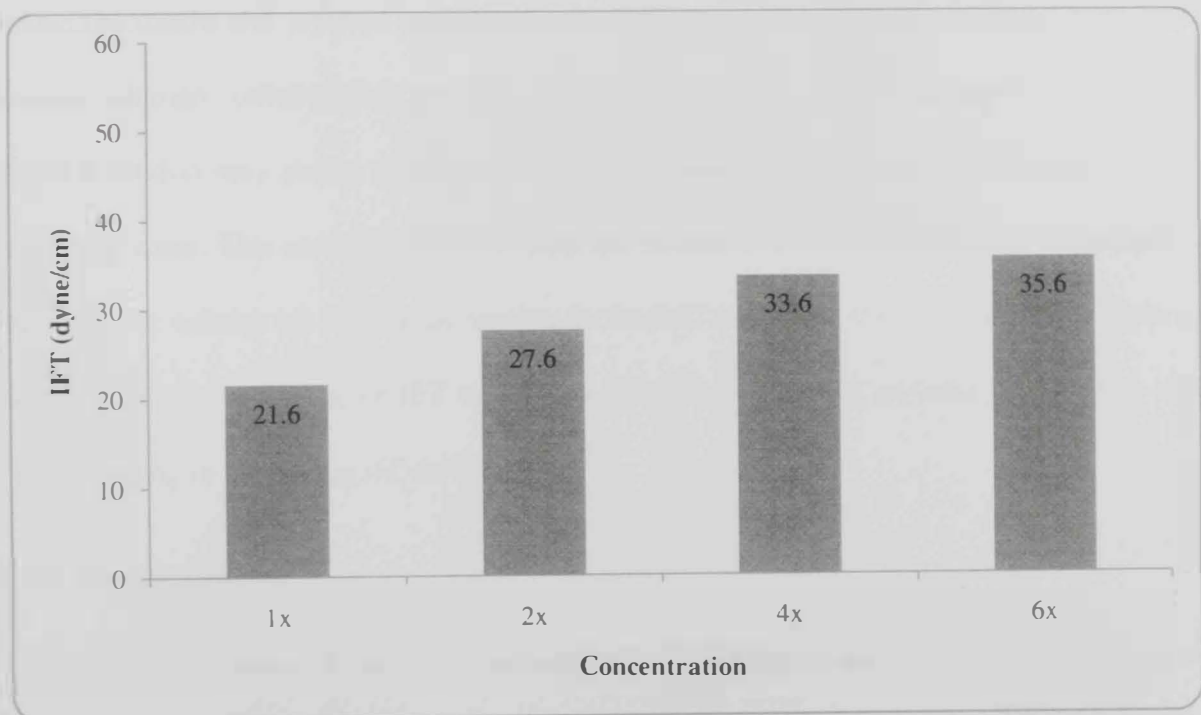


Figure 4.15 Results of IFT measurements for different SO_4^{2-} concentration.

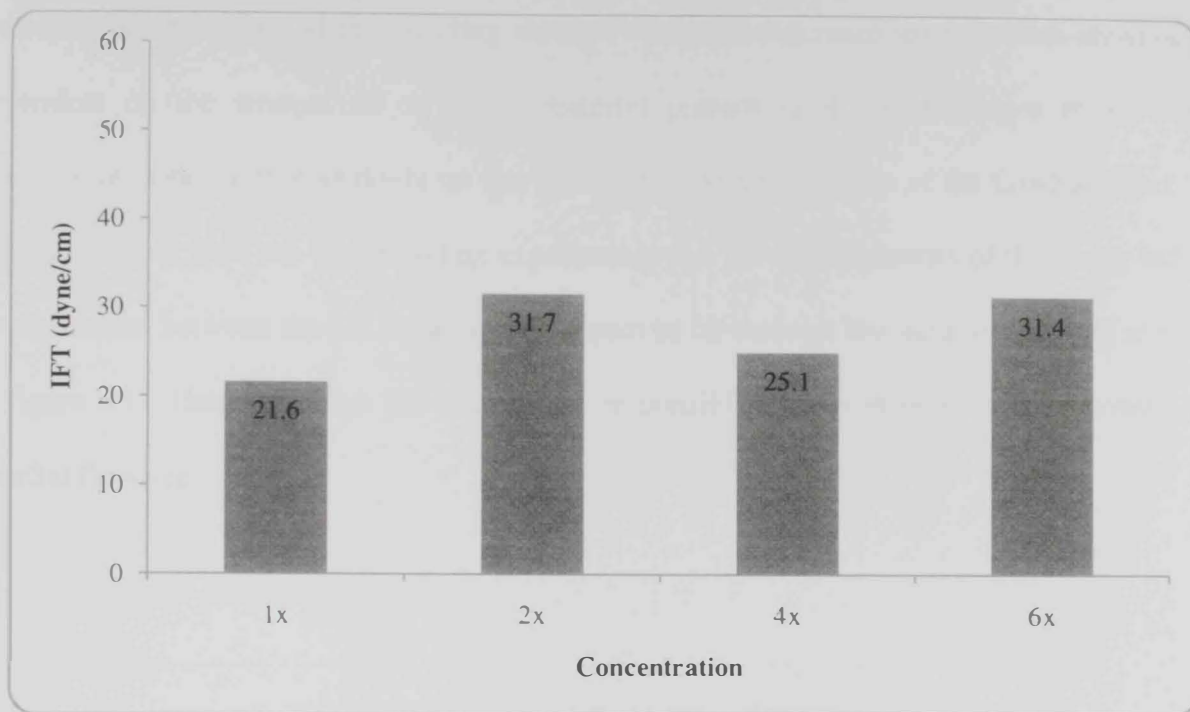


Figure 4.16 Results of IFT measurements for different Ca^{2+} concentration.

No clear trend was observed between the improved oil recovery and the measured interfacial tension. The results also indicate that there is an optimum salinity for different tested brines but the observed optimum salinity does not correlate the optimum oil recovery by LoSal. Therefore, interfacial tension may not be responsible for the increase in oil recovery due to the injection of low salinity water. This observation contradicts the results of Taha M. (2009) who investigated the effect of brine salinity on interfacial tension in Arab-D carbonate reservoir in Saudi Arabia. He concluded that the reduction of IFT with brine dilution reflects the potential implication of low salinity flooding in improving oil recovery.

4.6 PH Measurements:

Some studies have shown a rise in pH during LoSal™ laboratory experiments. This rise in pH is due to two concomitant reactions: carbonate dissolution and cation exchange. The dissolution of carbonate (i.e. calcite and/or dolomite) results in an excess of OH^- and cation exchange occurs

between clay minerals and the invading water. The dissolution reactions are relatively slow and dependent on the amount of carbonate material present in the rock (Lager et al., 2006). Conflicting evidence throws doubt on this mechanism being the cause of the LowSal effect. The results obtained from the core flooding experiments and pH measurements of this study indicate no correlation between the pH variation and improved oil through low salinity flooding as shown in figure 4.17 Therefore, high pH may not be responsible for the increase in oil recovery with LowSal flooding.

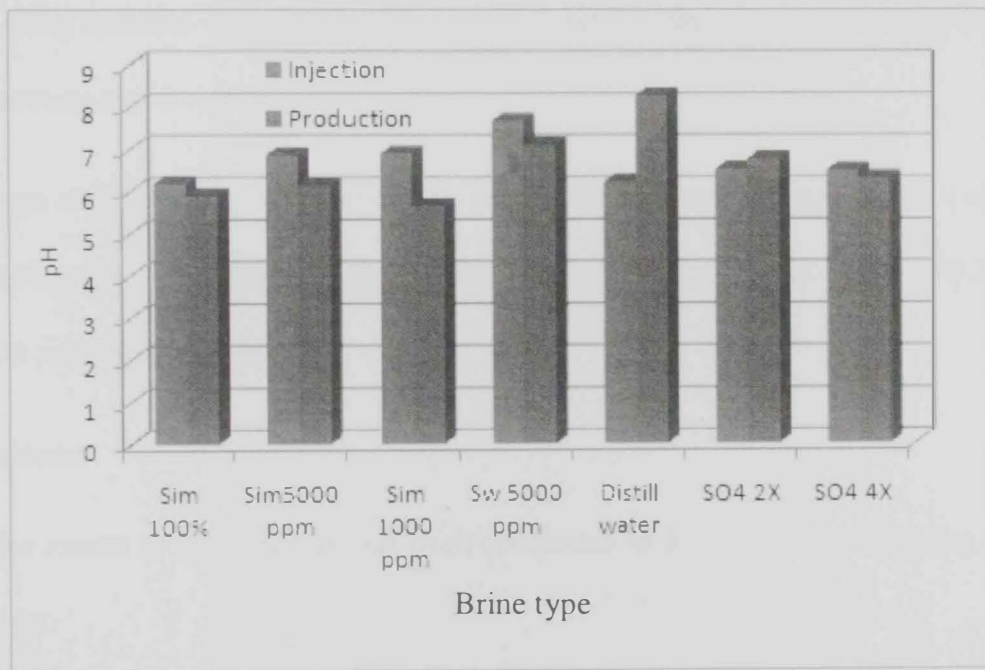


Figure 4.17 pH values for different brines.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary:

Core flooding experiments were conducted to investigate the effect of LowSal waterflooding on a selected carbonate reservoir (Bu Hasa field) in UAE and to investigate the effect of Ca^{2+} and SO_4^{2-} ion concentration on the recovery performance. A total of seventeen core floods were conducted using different types of brine and their dilutions. The experiments were conducted at room temperature and low pressure.

Contact angle and IFT measurements were performed to have a better understanding of the LowSal mechanism using different types of brine and their dilutions. The experiments were conducted at ambient conditions.

5.2 Conclusions:

Based on the results of the experimental work conducted in this study the following conclusions may be drawn:

1. Low salinity flooding seems to have good potentials in Bu Hasa field.
2. The results of the contact angle measurements indicate that lowering the solution salinity moves the wettability of the system toward intermediate wettability which could be the mechanism responsible for the improved oil recovery.
3. The results of the present core flooding experiments indicate that as the Ca^{2+} ion concentration is increased the ultimate oil recovery is decreased.

4. Increasing the sulfate tends to change the wettability to more intermediate wet.
5. There is an optimum SO_4^{2-} ion concentration of 47 ppm in the 5000 ppm UER which resulted in highest oil recovery. It is believed that this optimum concentration of SO_4^{2-} ion in the flooding tests is responsible for shifting the system's wettability to intermediate water-wet.
6. Based on the results of IFT measurements, it follows that it may not have a direct effect on LowSal flooding overall performance.

5.3 Recommendations:

Based on the results of this study it is recommended to conduct further work and as follows:

1. Investigate the effect of lowSal flooding under reservoir conditions of pressure and temperature.
2. Use of long cores, composite cores or whole cores, to better understand the flow mechanism.
3. Use x-ray scanner (LXRT) to have a picture of the in-situ saturation profiles.
4. Investigate the effect of other ions like Mg^{2+} and the effect of combining two ions on the oil recovery performance.

REFERENCES

- Ahmed, T., 2000. Reservoir engineering handbook. Gulf Publishing Company, Houston, Texas.
- Al-Maamari, R.S.H., Buckley, J. S., 2000. Asphaltene precipitation and alteration of wetting: Can wettability change during production? Paper SPE 59292 presented at SPE/DOE Improved Oil Recovery Symposium, Tulsa, OK, USA, April 3-5.
- Amott, E., 1959. Observations Relating to Wettability of Porous Rock, Trans., AIME 216, 156-162.
- Anderson, W., 1986a. Wettability Literature Survey- Part 2: Wettability Measurement. SPE Journal of Petroleum Technology, 38(11): 1246-1262.
- Anderson, W.G., 1986b. Wettability Literature Survey-Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. SPE Journal of Petroleum Technology, 38(10): 1125-1144.
- Anderson, W.G., 1987a. Wettability Literature Survey- Part 4: Effects of Wettability on Capillary Pressure. SPE Journal of Petroleum Technology, 39(10): 1283-1300.
- Anderson, W.G., 1987b. Wettability Literature Survey-Part 6: The Effects of Wettability on Waterflooding. SPE Journal of Petroleum Technology, 39(12): 1605-1622.
- Anderson, W.G., 1987c. Wettability Literature Survey Part 5: The Effects of Wettability on Relative Permeability. SPE Journal of Petroleum Technology, 39(11): 1453-1468.

Austad, T., 2010a. EOR by "Smart Water" Why? Personal communication.

Austad, T., RezaeiDoust, A., Puntervold, T., 2010b. Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs. Paper SPE 129767-PP presented at the 2010 SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 24-28 April. .

Bagci, S., Kok, M.V., and Turksoy, U. 2001. Effect of Brine Composition on Oil Recovery by Waterflooding. *Petroleum Science and Technology* 19(3-4): 359-372.

Bavière, M., 1991. Basic Concepts in Enhanced Oil Recovery Processes, *Critical Reports on Applied Chemistry*, 33, 6 pp.

Bernard, G.G., 1967. Effect of Floodwater Salinity on Recovery Of Oil from Cores Containing Clays, SPE California Regional Meeting. 1967 Copyright 1967, Los Angeles, California.

Boussour, S., Cissokho, M., Cordier, P., Bertin, H., Hamon, G., 2009. Oil Recovery by Low Salinity Brine Injection: Laboratory Results in Outcrop and Reservoir Cores. Paper SPE 124277 presented at the 2009 SPE Annual Technical Conference and Exhibition held in New Orleans, Louisiana, USA, 4-7 October.

Buckley, J.S., 1996. Mechanisms and consequences of wettability alteration by crude oils. Doctor of Philosophy Thesis. Department of Petroleum Engineering, Heriot-Watt University, Edinburgh, UK.

Buckley, J.S., Liu, Y. and Monsterleet, S., 1998. Mechanisms of Wetting Alteration by Crude Oils. *SPE Journal*, 3(1): 54-61.

Buckley, J.S., Liu, Y., 1998. Some mechanisms of crude oil/brine/solid interactions. *Journal of Petroleum Science and Engineering* 20: 155-160.

Buckley, J.S., Takamura, K., Morrow, N. R. , 1989. Influence of Electrical Surface Charge on the Wetting Properties of Crude Oils. . *SPE Reservoir Engineering*, 4(3): 332-340.

Burgos, W.D., Pisutpaisal, N., Mazzaresse, M.C., Chorover, J., 2002. Adsorption of quinoline to kaolinite and montmorillonite. *Environmental engineering science*, 19(2): 59-68.

Chen, J., Hirasaki, G. and Flaum, M, 2004. Study of Wettability Alteration From NMR: Effect of OBM on Wettability and NMR Responses, 8th International Symposium on Reservoir Wettability.

Chinedu Agbalaka, Abhijit Y. Dandekar, Shirish L. Patil, Santanu Khataniar, James R. Hemsath, 2008. The Effect of Wettability on Oil Recovery: A Review, Paper SPE 114496 presented at SPE Asia Pacific Oil and Gas Conference and Exhibition, 20-22 October 2008, Perth, Australia.

Cissokho, M., Boussour, S., Cordier, Ph., Bertin, H., Hamon, G., 2009. Low Salinity Oil Recovery on Clayey Sandstone: Experimental Study. . Paper SCA2009-05 presented at the International Symposium of the Society of Core Analysts held in Noordwijk, The Netherlands, 27-30 September. .

Fan, T., Buckley, Jill S., 2007. Acid Number Measurements Revisited. Paper SPE 99884 presented at the 2006 SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, 22-26 April.: 496-500.

Fjelde, I. 2008. Low Salinity Water flooding Experimental Experience and Challenges. Force RP Work Shop: Low Salinity Water Flooding, the Importance of Salt Content in Injection Water, Stavanger, Norway, 15 May.

Green, D.W., Willhite, G. P 1998. Enhanced Oil Recovery. SPE textbook series, 6. Henry L. Doherty Memorial Fund of AIME Society of Petroleum Engineers, Richardson, TX USA.

Hirasaki, G.J., 1991. Wettability: Fundamentals and Surface Forces. SPE Formation Evaluation, 6(2): 217-226.

Høgenesen, E.J., Strand, S., and Austad, T. 2005. Waterflooding of Preferential Oil-Wet Carbonates: Oil Recovery Related to Reservoir Temperature and Brine Composition. Paper SPE 94166 presented at the SPE Europec/EAGE Annual Conference, Madrid, Spain, 13-16 June.

Jadhunandan, P.P., Morrow, N. R., 1995. Effect of wettability on Waterflooding recovery for Crude-oil/Brine/Rock systems. . SPE Reservoir Engineering, February.: 40-46.

Jarrell, P.M., Fox, C.E., Stein, M.H., Webb, S.L, 2002. Practical Aspects of CO₂ Flooding, Johns, R.T. (editor), Monograph Series, SPE 22.

Jerauld, G.R., Lin, C.Y., Webb, K.J., Secombe, J.C., 2006. Modelling Low-Salinity Waterflooding. Paper SPE 102239 presented at the 2006 SPE Annual Technical Conference and Exhibition held in San Antonio, Texas, USA, 24-27 September.

Lager A., W.K.J., Black C. J. J., 2007. Impact of Brine Chemistry on Oil Recovery. Paper A24 presented at the 14th European Symposium on Improved Oil Recovery, Cairo, Egypt, 22-24 April.

Lager A., W.K.J., Black C. J. J., Singleton M., Sorbie K. S., 2006. Low Salinity Oil Recovery - An experimental investigation. Paper SCA2006-36 presented at the International Symposium of the Society of Core Analysts held in Trondheim, Norway 12-16 September.

Lager A., W.K.J., Collins, I.R., Richmond, D.M., 2008. LoSal™ Enhanced Oil Recovery: Evidence of Enhanced Oil Recovery at the Reservoir Scale. Paper SPE 113976 presented at the 2008 SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 19-23 April.

Leverett, M. C., 1942. Capillary Behavior in Porous Solids, Trans., AIME 142, 152-169.

Li, C.-J., Chan, Tak-Hang., 1997. Organic Reactions in Aqueous Media. John Wiley & Sons, Inc. , USA.

Ligthelm, D.J. et al., 2009. Novel Waterflooding Strategy By Manipulation Of Injection Brine Composition, EUROPEC/EAGE Conference and Exhibition. Society of Petroleum Engineers, Amsterdam, The Netherlands.

Maas, J.G., Wit, Krijn, Morrow, Norman R. , 2001. Enhanced Oil Recovery by Dilution of Injection Brine: Further Interpretations of Experimental Results. . Paper SCA2001-13.

Martin, J.C., 1959. The Effects of Clay on the Displacement of Heavy Oil by Water, Venezuelan Annual Meeting. Society of Petroleum Engineers of AIME, Caracas, Venezuela.

Mc Guire, P.L., Chatham, J. R., Paskvan, F. K., Sommer, D.M., Carini, F. H., , 2005. Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska's North Slope. Paper SPE 93903 presented at the 2005 Western Regional Meeting held in Irvine, CA, USA, 30. March - 1 April.

Morrow, N.R., 1976. Capillary Pressure Correlations for Uniformly Wetted Porous Media, J.Cdn. Pet. Tech. , 15, No. 4, 49 - 69.

Morrow, N.R., 1979. Interplay of Capillary, Viscous And Buoyancy Forces In the Mobilization of Residual Oil. 18(3).

Paul Vledder, Julio Carrera Fonseca, Ivan Gonzalez, Dick Ligthelm, 2010. Low Salinity Water Flooding: Proof Of Wettability Alteration On A Field Wide Scale, Paper SPE 129564 presented at SPE Improved Oil Recovery Symposium, 24-28 April 2010, Tulsa, Oklahoma, USA.

Pu, H., Xie, X., Yin, P. and Morrow, N.R., 2008. Application of Coalbed Methane Water to Oil Recovery from Tensleep Sandstone by Low Salinity Waterflooding, SPE/DOE Symposium on Improved Oil Recovery. Society of Petroleum Engineers, Tulsa, Oklahoma, USA.

Punternvold, T., 2008. Waterflooding of carbonate reservoirs, EOR by wetting alteration. PhD thesis, University of Stavanger.

Punternvold, T., 2010. Adsorption of polar organic material onto kaolinite in relation to oil recovery by low saline water flooding. Personal communication.

RezaeiDoust, A., Austad, T., Punternvold, T., 2009a. EOR by Low Salinity flooding of core material from Varg, Yme and Gyda: A technical report., University of Stavanger, Talisman Energy Norge AS.

RezaeiDoust, A., Puntervold T., Strand S., Austad T., 2009b. Smart Water as Wettability Modifier in Carbonate and Sandstone: A Discussion of Similarities/Differences in the Chemical Mechanisms. *Energy & Fuels*, 23(9): 4479-4485.

Robertson, E.P., 2007. Low-Salinity Waterflooding to improve Oil Recovery - Historical Field Evidence. Paper SPE 109965 presented at the 2007 SPE Technical Conference and Exhibition held in Anaheim, California, USA, 11-14 November.

Seccombe, J.C., Lager, A., Webb, K., Jerauld, G., Fueg, E., 2008. Improving Waterflood Recovery: LoSal™ EOR Field Evaluation. Paper SPE 113480 presented at the 2008 SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 19-23 April.

Sharma, M.M. & Filoco, P.R., 2005. Effect of Brine Salinity and Crude-Oil Properties on Oil Recovery and Residual Saturations. SPE 65402: Sept. 2000, 5 (3) 293-300.

Skjæveland, S.M., Kleppe, J., 1992. Recent Advances in Improved Oil Recovery Methods for North Sea Sandstone Reservoirs. Norwegian Petroleum Directorate, Stavanger.

Smith, K.W., 1942. Brines as Flooding Liquids. Paper presented at the Seventh Annual Tech. meeting, Min. Ind. Expt. Sta., Penn. State College, Nov.

Strand, S., 2005. Wettability alteration in chalk, a study of surface chemistry. PhD thesis, University of Stavanger.

Strand, S., and Austad, T. 2008. Effect of Temperature on Enhanced Oil Recovery from Mixed-wet Chalk Cores by Spontaneous Imbibition and Forced Displacement using Seawater. *Energy & Fuels* 22(5): 3222-3225.

Strandnes, D.C., 2001. Enhanced Oil Recovery from Oil-wet Carbonate Rock by Spontaneous Imbibition of Aqueous Surfactant Solutions. PhD thesis Stavanger.

Taha M. Okasha, Abdul-Jalil A. Al-Shiwaish, 2008. Effect of Brine Salinity on Interfacial Tension in Arab-D Carbonate Reservoir, Saudi Arabia, paper SPE presented at SPE Middle East Oil and Gas Show and Conference, 15-18 March 2009, Bahrain, Bahrain.

Talisman, 2007. Varg Field, Well History Book, Internal Report.

Tang, G., Morrow, N. R., 1999. Oil Recovery by Waterflooding and Imbibition - Invading Brine Cation Valency and Salinity. Paper SCA9911.

Tang, G.Q. & Morrow N.R., 1999. Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery, Journal of Petroleum Science and Engineering 24, 99-111.

Tang, G.Q. & Morrow, N.R., 1997. Salinity, Temperature, Oil Composition and Oil Recovery by Waterflooding SPE 36680: 12 (4) 269-276.

Tie, H. and Morrow, N.R., 2005. Low Flood Rate Residual Saturations in Carbonate Rocks, International Petroleum Technology Company, IPCT 10470.

Ursin, J.-R., Zolotukhin, A. B. , 1997. Introduction to Petroleum Reservoir Engineering. Høyskoleforlaget AS.

Webb, K.J., Black, C.J.J. & Al-Ajell, H., 2003. Low Salinity Oil Recovery -Log-Inject-Log, SPE 81460 presented at Middle East Oil Show, 9-12 June 2003, Bahrain.

Webb, K.J., Black, C.J.J., and Tjetland, G. 2005. A Laboratory Study Investigating Methods for Improving Oil Recovery in Carbonates. Paper IPTC 10506 presented at the International Petroleum Technology Conference, Doha, Qatar, 21-23 November.

Yildiz, H.O. & Morrow, N.R., 1996, Effect of Brine Composition on Recovery of Moutray Crude Oil by Waterflooding, *Journal of Petroleum Science and Engineering* 14, 159-168.

Zhang, Y. & Morrow N.R., 2006. Comparison of Secondary and Tertiary Recovery With Change in Injection Brine Composition for Crude Oil/Sandstone Combinations, SPE 99757.

Zhang, Y., Xie, X., Morrow, N.R., 2007. Waterflood performance by injection of brine with different salinity for reservoir cores. Paper SPE 109849 presented at the 2007 SPE Annual Technical Conference and Exhibition in Anaheim, California, USA, 11-14 November.

APPENDIX A

RESULTS OF CORE FLOODING

EXPERIMENTS

Table A- 1 Flooding results of original UER water.

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.1	0.1	100	1.0	1.1	0.1	1.0	8.5
2	1.2	0.1	200	1.1	2.3	0.1	2.1	17.8
3	1.2	0.15	300	1.1	3.5	0.2	3.2	26.7
4	1.1	0.3	400	0.8	4.6	0.3	4.0	33.5
5	0.4	0.2	500	0.2	5.0	0.3	4.2	35.2
6	1	0.5	600	0.5	6.0	0.3	4.7	39.4
7	1.1	0.8	700	0.3	7.1	0.4	5.0	41.9
8	1	0.8	800	0.2	8.1	0.5	5.2	43.6
9	2	1.8	1000	0.2	10.1	0.6	5.4	45.3
10	2.1	1.9	1200	0.2	12.2	0.7	5.6	47.0
11	2.2	2	1400	0.2	14.4	0.8	5.8	48.7
12	2.25	2.15	1600	0.1	16.7	0.9	5.9	49.6
13	4.65	4.45	2000	0.2	21.3	1.2	6.1	51.3
14	5	4.8	2400	0.2	26.3	1.5	6.3	53.0
15	5.55	5.3	2800	0.3	31.9	1.8	6.5	55.1
16	10.2	10	3500	0.2	42.1	2.4	6.7	56.8
17	11.2	10.9	4200	0.3	53.3	3.0	7.0	59.3
18	12.9	12.8	5000	0.1	66.2	3.8	7.1	60.2
19	16.1	16	5950	0.1	82.3	4.7	7.2	61.0
20	51.8	51.6	8900	0.2	134.1	7.6	7.4	62.7
21	100	99.95	11850	0.0	234.1	13.3	7.4	63.1

Table A- 2 Flooding results of 50% dilution of original UER water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.1	0	60	1.1	1.1	0.1	1.1	10.0
2	1.1	0	130	1.1	2.2	0.1	2.2	20.0
3	1	0	200	1.0	3.2	0.2	3.2	29.1
4	1.2	0.1	300	1.1	4.4	0.2	4.3	39.1
5	1.1	0.5	400	0.6	5.5	0.3	4.9	44.5
6	1.2	1	500	0.2	6.7	0.4	5.1	46.4
7	1.3	1.1	600	0.2	8.0	0.4	5.3	48.2
8	1.4	1.2	700	0.2	9.4	0.5	5.5	50.0
9	1.5	1.4	800	0.1	10.9	0.6	5.6	50.9
10	1.5	1.4	900	0.1	12.4	0.7	5.7	51.8
11	1.5	1.4	1000	0.1	13.9	0.8	5.8	52.7
12	3.2	3	1200	0.2	17.1	0.9	6.0	54.5
13	3.3	3.1	1400	0.2	20.4	1.1	6.2	56.4
14	3.6	3.5	1600	0.1	24.0	1.3	6.3	57.3
15	5.2	5	1900	0.2	29.2	1.6	6.5	59.1
16	12.6	12.2	2600	0.4	41.8	2.3	6.9	62.7
17	26	25.7	4000	0.3	67.8	3.7	7.2	65.5
18	50.8	50.5	6666	0.3	118.6	6.5	7.5	68.2
19	100.05	100.04	12064	0.0	218.7	12.1	7.5	68.3

Table A- 3 Flooding results of 5000 ppm dilution of original UER water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.4	0	60	1.4	1.4	0.1	1.4	19.7
2	1.4	0.3	120	1.1	2.8	0.2	2.5	35.2
3	1.5	0.7	180	0.8	4.3	0.3	3.3	46.5
4	1.5	1	240	0.5	5.8	0.5	3.8	53.5
5	1.6	1.3	300	0.3	7.4	0.6	4.1	57.7
6	1.5	1.3	360	0.2	8.9	0.7	4.3	60.6
7	3.3	3.1	480	0.2	12.2	0.9	4.5	63.4
8	5.2	4.9	660	0.3	17.4	1.4	4.8	67.6
9	14.5	14	1160	0.5	31.9	2.5	5.3	74.6
10	26	25.6	2000	0.4	57.9	4.5	5.7	80.3
11	27.7	27.5	3880	0.2	85.6	6.6	5.9	83.1
12	100.5	100.4	7700	0.1	186.1	14.4	6.0	84.5

Table A- 4 Flooding results of 1000 ppm dilution of original UER water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.25	0	60	1.3	1.4	0.1	1.3	12.5
2	1.2	0	120	1.2	2.6	0.2	2.5	24.5
3	1.3	0.01	190	1.3	3.9	0.3	3.7	37.4
4	0.8	0.1	240	0.7	4.7	0.4	4.4	44.4
5	1	0.6	300	0.4	5.7	0.5	4.8	48.4
6	1.1	0.8	360	0.3	6.8	0.5	5.1	51.4
7	1.2	0.9	420	0.3	8.0	0.6	5.4	54.4
8	2.3	2.3	530	0.0	10.3	0.8	5.4	54.4
9	3.9	3.5	700	0.4	14.2	1.1	5.8	58.4
10	5.1	4.9	900	0.2	19.3	1.6	6.0	60.4
11	5.8	5.6	1111	0.2	25.1	2.0	6.2	62.4
12	9.7	9.5	1450	0.2	34.8	2.8	6.4	64.4
13	12.3	12	1860	0.3	47.1	3.8	6.7	67.4
14	14.7	14.5	2350	0.2	61.8	5.0	6.9	69.4
15	27.1	26.8	3200	0.3	88.9	7.2	7.2	72.4
16	51	50.7	4700	0.3	139.9	11.3	7.5	75.4
17	100.8	100.6	7430	0.2	240.7	19.4	7.7	77.4

Table A- 5 Flooding results of original SIM water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1	0	80	1.0	1.0	0.0	1.0	5.6
2	1.1	0	180	1.1	2.1	0.1	2.1	11.7
3	1.1	0	300	1.1	3.2	0.2	3.2	17.8
4	1.7	0	500	1.7	4.9	0.2	4.9	27.2
5	1.5	0.1	700	1.4	6.4	0.3	6.3	35.0
6	0.7	0.5	800	0.2	7.1	0.3	6.5	36.1
7	0.8	0.6	900	0.2	7.9	0.4	6.7	37.2
8	0.8	0.6	1000	0.2	8.7	0.4	6.9	38.3
9	1.7	1.5	1200	0.2	10.4	0.5	7.1	39.4
10	2.7	2.5	1500	0.2	13.1	0.6	7.3	40.6
11	4.5	4.2	2000	0.3	17.6	0.9	7.6	42.2
12	4.8	4.6	2500	0.2	22.4	1.1	7.8	43.3
13	10	9.9	3500	0.1	32.4	1.6	7.9	43.9
14	12.6	12.3	4700	0.3	45.0	2.2	8.2	45.6
15	51.6	51.2	9100	0.4	96.6	4.7	8.6	47.8
16	100	99.8		0.2	196.6	9.6	8.8	48.9

Table A- 6 Flooding results of 50% dilution of original SIM water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1	0	100	1.0	1.0	0.0	1.0	7.9
2	1	0	200	1.0	2.0	0.1	2.0	15.9
3	0.9	0	300	0.9	2.9	0.1	2.9	23.0
4	0.7	0.05	400	0.7	3.6	0.2	3.6	28.2
5	0.7	0.1	500	0.6	4.3	0.2	4.2	32.9
6	0.7	0.2	600	0.5	5.0	0.2	4.7	36.9
7	0.7	0.3	700	0.4	5.7	0.3	5.1	40.1
8	0.7	0.5	800	0.2	6.4	0.3	5.3	41.7
9	0.7	0.5	900	0.2	7.1	0.4	5.5	43.3
10	0.9	0.5	1000	0.4	8.0	0.4	5.9	46.4
11	1.4	1.2	1200	0.2	9.4	0.5	6.1	48.0
12	2.3	2.1	1500	0.2	11.7	0.6	6.3	49.6
13	3.9	3.7	2000	0.2	15.6	0.8	6.5	51.2
14	5.2	5	2660	0.2	20.8	1.0	6.7	52.8
15	14.1	13.8	4400	0.3	34.9	1.7	7.0	55.2
16	14.5	14.2	6300	0.3	49.4	2.5	7.3	57.5
17	50.03	50.01	14017	0.0	99.4	5.0	7.3	57.7
18	100.04	100.03	21000	0.0	199.5	10.0	7.3	57.8

Table A- 7 Flooding results of 5000 ppm dilution of original SIM water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1	0	60	1.0	1.0	0.1	1.0	7.1
2	0.8	0	120	0.8	1.8	0.1	1.8	12.9
3	0.7	0	180	0.7	2.5	0.2	2.5	17.9
4	0.7	0	240	0.7	3.2	0.2	3.2	22.9
5	0.7	0	300	0.7	3.9	0.3	3.9	27.9
6	1.1	0	400	1.1	5.0	0.4	5.0	35.7
7	1.1	0	500	1.1	6.1	0.4	6.1	43.6
8	1	0.1	600	0.9	7.1	0.5	7.0	50.0
9	1	0.5	700	0.5	8.1	0.6	7.5	53.6
10	1	0.8	800	0.2	9.1	0.7	7.7	55.0
11	1	0.9	900	0.1	10.1	0.7	7.8	55.7
12	2	1.8	1080	0.2	12.1	0.9	8.0	57.1
13	4.8	4.5	1500	0.3	16.9	1.2	8.3	59.3
14	10.6	10.1	2380	0.5	27.5	2.0	8.8	62.9
15	12	11.6	3300	0.4	39.5	2.8	9.2	65.7
16	25.9	25.6	5150	0.3	65.4	4.7	9.5	67.9
17	52.7	52.5	9807	0.2	118.1	8.4	9.7	69.3
18	100.4	100.3	15920	0.1	218.5	15.6	9.8	70.0

Table A- 8 Flooding results of 1000 ppm dilution of original SIM water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.5	0	60	1.5	1.5	0.1	1.5	16.7
2	1.6	0	120	1.6	3.1	0.3	3.1	34.4
3	1.2	0.3	190	0.9	4.3	0.4	4.0	44.4
4	1.4	0.8	240	0.6	5.7	0.5	4.6	51.1
5	1.5	1.2	300	0.3	7.2	0.7	4.9	54.4
6	2.5	2.2	360	0.3	9.7	0.9	5.2	57.8
7	3.3	3.1	420	0.2	13.0	1.3	5.4	60.0
8	4.3	4.1	530	0.2	17.3	1.7	5.6	62.2
9	5.9	5.7	700	0.2	23.2	2.2	5.8	64.4
10	10.4	10.2	900	0.2	33.6	3.2	6.0	66.7
11	14.8	14.6	1111	0.2	48.4	4.7	6.2	68.9
12	27.1	26.9	1450	0.2	75.5	7.3	6.4	71.1
13	51.2	51	1860	0.2	126.7	12.2	6.6	73.3
14	100.1	100	2350	0.1	226.8	21.8	6.7	74.4

Table A- 9 Flooding results of original Sea water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1	0	120	1.0	1.0	0.1	1.0	9.7
2	0.9	0	240	0.9	1.9	0.1	1.9	18.4
3	0.7	0.2	360	0.5	2.6	0.2	2.4	23.3
4	1	0.7	500	0.3	3.6	0.2	2.7	26.2
5	1.6	1.2	700	0.4	5.2	0.3	3.1	30.1
6	2.6	2.2	1000	0.4	7.8	0.5	3.5	34.0
7	2.9	2.7	1300	0.2	10.7	0.7	3.7	35.9
8	3.1	2.9	1600	0.2	13.8	0.9	3.9	37.9
9	3.4	3.2	1900	0.2	17.2	1.1	4.1	39.8
10	12.1	11.7	2500	0.4	29.3	1.9	4.5	43.7
11	15.7	15.2	4100	0.5	45.0	2.9	5.0	48.5
12	26.2	25.9	6090	0.3	71.2	4.5	5.3	51.5
13	51.9	51.6	9860	0.3	123.1	7.8	5.6	54.4
14	101.3	100.9	16800	0.4	224.4	14.2	6.0	58.3
15	100.7	100.5	24850	0.2	325.1	20.6	6.2	60.2

Table A- 10 Flooding results of 5000 ppm dilution of original Sea water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.1	0	60	1.1	1.1	0.1	1.1	7.3
2	1	0	120	1.0	2.1	0.2	2.1	14.0
3	1	0	180	1.0	3.1	0.2	3.1	20.7
4	0.9	0	240	0.9	4.0	0.3	4.0	26.7
5	0.9	0.01	300	0.9	4.9	0.4	4.9	32.6
6	0.8	0.1	360	0.7	5.7	0.4	5.6	37.3
7	0.9	0.3	420	0.6	6.6	0.5	6.2	41.3
8	0.9	0.5	480	0.4	7.5	0.6	6.6	43.9
9	1.8	1.3	600	0.5	9.3	0.7	7.1	47.3
10	1.9	1.6	720	0.3	11.2	0.9	7.4	49.3
11	2.1	1.8	840	0.3	13.3	1.0	7.7	51.3
12	2.8	2.6	1000	0.2	16.1	1.2	7.9	52.6
13	3.65	3.5	1200	0.2	19.8	1.5	8.0	53.6
14	8.8	8.5	1660	0.3	28.6	2.2	8.3	55.6
15	18.8	18.5	2600	0.3	47.4	3.7	8.6	57.6
16	27	26.7	3900	0.3	74.4	5.8	8.9	59.6
17	50.6	50.4	6290	0.2	125.0	9.7	9.1	60.9
18	100.4	100.2	11400	0.2	225.4	17.5	9.3	62.3

Table A- 11 Flooding results of Distilled water

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.25	0	60	1.3	1.3	0.1	1.3	10.1
2	1.2	0	120	1.2	2.5	0.2	2.5	19.1
3	1.3	0.01	190	1.3	3.8	0.3	3.7	29.2
4	0.8	0.1	240	0.7	4.6	0.4	4.4	34.7
5	1	0.6	300	0.4	5.6	0.4	4.8	37.8
6	1.1	0.8	360	0.3	6.7	0.5	5.1	40.2
7	1.2	0.9	420	0.3	7.9	0.6	5.4	42.5
8	2.3	2.3	530	0.0	10.2	0.8	5.4	42.5
9	3.9	3.5	700	0.4	14.1	1.1	5.8	45.6
10	5.1	4.9	900	0.2	19.2	1.5	6.0	47.2
11	5.8	5.6	1111	0.2	25.0	1.9	6.2	48.8
12	9.7	9.5	1450	0.2	34.7	2.7	6.4	50.3
13	12.3	12	1860	0.3	47.0	3.7	6.7	52.7
14	14.7	14.5	2350	0.2	61.7	4.8	6.9	54.2
15	27.1	26.8	3200	0.3	88.8	6.9	7.2	56.6
16	51	50.7	4700	0.3	139.8	10.9	7.5	58.9
17	100.8	100.6	7430	0.2	240.6	18.8	7.7	60.5

Table A- 12 Flooding results of 5000 ppm UER with added two times SO_4^{2-} concentration

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1	0	40	1.0	1.0	0.1	1.0	11.1
2	1	0	80	1.0	2.0	0.2	2.0	22.2
3	1.4	0	150	1.4	3.4	0.3	3.4	37.8
4	1.5	0.4	230	1.1	4.9	0.4	4.5	50.0
5	2	1.5	325	0.5	6.9	0.6	5.0	55.6
6	2.6	2.3	435	0.3	9.5	0.8	5.3	58.9
7	2.9	2.7	550	0.2	12.4	1.0	5.5	61.1
8	3.6	3.3	690	0.3	16.0	1.3	5.8	64.4
9	4.3	4.1	850	0.2	20.3	1.7	6.0	66.7
10	5.8	5.6	1050	0.2	26.1	2.2	6.2	68.9
11	10.2	10	1400	0.2	36.3	3.0	6.4	71.1
12	14.9	14.7	1860	0.2	51.2	4.2	6.6	73.3
13	29.8	29.5	2700	0.3	81.0	6.7	6.9	76.7
14	51.7	51.4	4000	0.3	132.7	11.0	7.2	80.0
15	103.3	103.2	6400	0.1	236.0	19.5	7.3	81.1

Table A- 13 Flooding results of 5000 ppm UER with added four times SO_4^{2-} concentration

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.1	0	10	1.1	1.1	0.1	1.1	10.0
2	1	0	120	1.0	2.1	0.2	2.1	19.1
3	0.8	0	180	0.8	2.9	0.2	2.9	26.4
4	0.7	0	240	0.7	3.6	0.3	3.6	32.7
5	0.8	0	300	0.8	4.4	0.3	4.4	40.0
6	0.6	0	360	0.6	5.0	0.4	5.0	45.5
7	0.7	0.1	420	0.6	5.7	0.4	5.6	50.9
8	0.6	0.2	480	0.4	6.3	0.5	6.0	54.5
9	0.6	0.2	540	0.4	6.9	0.5	6.4	58.2
10	0.6	0.25	600	0.4	7.5	0.5	6.8	61.4
11	0.6	0.3	660	0.3	8.1	0.6	7.1	64.1
12	0.6	0.35	720	0.3	8.7	0.6	7.3	66.4
13	0.6	0.4	780	0.2	9.3	0.7	7.5	68.2
14	1.1	0.8	900	0.3	10.4	0.7	7.8	70.9
15	1.5	1.4	1060	0.1	11.9	0.9	7.9	71.8
16	3.6	3.4	1410	0.2	15.5	1.1	8.1	73.6
17	14.6	14	2790	0.6	30.1	2.2	8.7	79.1
18	26.1	25.6	5070	0.5	56.2	4.0	9.2	83.6
19	61.3	61	10138	0.3	117.5	8.5	9.5	86.4
20	101.1	101	18497	0.1	218.6	15.7	9.6	87.3

Table A- 14 Flooding results of 5000 ppm UER with added six times SO_4^{2-} concentration

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1	0	60	1.0	1.0	0.1	1.0	7.7
2	1	0	120	1.0	2.0	0.1	2.0	15.4
3	0.9	0	180	0.9	2.9	0.2	2.9	22.3
4	0.9	0	240	0.9	3.8	0.3	3.8	29.2
5	0.9	0.2	300	0.7	4.7	0.3	4.5	34.6
6	0.9	0.3	360	0.6	5.6	0.4	5.1	39.2
7	1.5	1.1	470	0.4	7.1	0.5	5.5	42.3
8	1.8	1.5	590	0.3	8.9	0.6	5.8	44.6
9	2.2	2	730	0.2	11.1	0.8	6.0	46.2
10	3.2	3	920	0.2	14.3	1.0	6.2	47.7
11	4.2	4	1160	0.2	18.5	1.3	6.4	49.2
12	5.2	5	1445	0.2	23.7	1.7	6.6	50.8
13	6	5.8	1785	0.2	29.7	2.1	6.8	52.3
14	10.7	10.5	2360	0.2	40.4	2.9	7.0	53.8
15	15	14.8	3160	0.2	55.4	4.0	7.2	55.4
16	26.1	25.8	4600	0.3	81.5	5.9	7.5	57.7
17	50.8	50.5	7380	0.3	132.3	9.5	7.8	60.0
18	100.4	100.2	10333	0.2	232.7	16.7	8.0	61.5

Table A- 15 Flooding results of 5000 ppm UER with added two times Ca²⁺ concentration

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	0.9	0	60	0.9	0.9	0.1	0.9	9.0
2	0.9	0	120	0.9	1.8	0.2	1.8	18.0
3	0.85	0	180	0.9	2.7	0.3	2.7	26.5
4	0.8	0	240	0.8	3.5	0.3	3.5	34.5
5	0.8	0	300	0.8	4.3	0.4	4.3	42.5
6	0.7	0.2	360	0.5	5.0	0.5	4.8	47.5
7	0.7	0.4	420	0.3	5.7	0.6	5.1	50.5
8	0.7	0.5	480	0.2	6.4	0.6	5.3	52.5
9	0.8	0.55	540	0.3	7.2	0.7	5.5	55.0
10	0.8	0.7	600	0.1	8.0	0.8	5.6	56.0
11	1.4	1.2	700	0.2	9.4	0.9	5.8	58.0
12	1.5	1.3	800	0.2	10.9	1.1	6.0	60.0
13	1.6	1.5	900	0.1	12.5	1.2	6.1	61.0
14	1.85	1.6	1000	0.3	14.3	1.4	6.4	63.5
15	3	2.8	1200	0.2	17.3	1.7	6.6	65.5
16	3	2.85	1400	0.2	20.3	2.0	6.7	67.0
17	4.7	4.6	1700	0.1	25.0	2.5	6.8	68.0
18	4.95	4.8	2000	0.2	30.0	3.0	7.0	69.5
19	8.1	7.9	1500	0.2	38.1	3.8	7.2	71.5
20	10	9.9	3600	0.1	48.1	4.8	7.3	72.5
21	14	13.8	4343	0.2	62.1	6.2	7.5	74.5
22	27.5	27.2	5800	0.3	89.6	9.0	7.8	77.5

Table A- 16 Flooding data of 5000 ppm UER with added four times Ca^{2+} concentration

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	1.4	0	60	1.4	1.4	0.1	1.4	10.9
2	1.5	0	120	1.5	2.9	0.2	2.9	22.7
3	2.3	0	220	2.3	5.2	0.4	5.2	40.6
4	2.3	1.1	320	1.2	7.5	0.6	6.4	50.0
5	2.5	2	420	0.5	10.0	0.8	6.9	53.9
6	4.7	4.2	600	0.5	14.7	1.1	7.4	57.8
7	5.7	5.4	800	0.3	20.4	1.6	7.7	60.2
8	6	5.8	1000	0.2	26.4	2.1	7.9	61.7
9	13.4	13	1400	0.4	39.8	3.1	8.3	64.8
10	22.5	22	2000	0.5	62.3	4.9	8.8	68.8
11	100.3	100	4410	0.3	162.6	12.7	9.1	71.1

Table A- 17 Flooding results of 5000 ppm UER with added Six times Ca^{2+} concentration

Tube No.	Total Vol. cc	Water vol. cc	time sec	oil Vol cc	Cum Vol. cc	Vpi	Cum oil cc	Recovery %
1	0.8	0	60	0.8	0.8	0.1	0.8	5.7
2	1	0	120	1.0	1.8	0.1	1.8	12.9
3	1	0	180	1.0	2.8	0.2	2.8	20.0
4	1	0	240	1.0	3.8	0.3	3.8	27.1
5	0.8	0	300	0.8	4.6	0.3	4.6	32.9
6	0.8	0.1	360	0.7	5.4	0.4	5.3	37.9
7	1.2	0.4	450	0.8	6.6	0.5	6.1	43.6
8	2	1.1	600	0.9	8.6	0.6	7.0	50.0
9	2.8	2.1	800	0.7	11.4	0.8	7.7	55.0
10	3.1	2.6	1000	0.5	14.5	1.0	8.2	58.6
11	6.6	6.2	1400	0.4	21.1	1.5	8.6	61.4
12	10.8	10.4	2000	0.4	31.9	2.3	9.0	64.3
13	20.2	20	3010	0.2	52.1	3.7	9.2	65.7
14	101.9	101.2	7380	0.7	154.0	11.0	9.9	70.7

APPENDIX B

CONTACT ANGLE MEASUREMENTS

Table B- 1 Contact angle results for original UER water.

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	136.4	2.4	2.7	2.0	43.6
1	136.3	2.5	2.8	1.7	43.7
2	135.3	2.7	2.9	1.7	44.7
3	135.0	2.7	2.9	1.6	45.0
5	136.1	2.7	2.9	1.6	43.9
10	137.0	2.7	3.0	1.6	43.0
15	136.0	2.7	2.9	1.6	44.0
20	134.6	2.7	2.9	1.6	45.4
25	133.3	2.7	3.0	1.6	46.7
30	132.8	2.8	3.0	1.6	47.2
45	135.3	2.7	2.9	1.6	44.7
60	133.5	2.7	2.9	1.6	46.5
90	133.7	2.7	3.0	1.6	46.3
120	132.8	2.7	2.9	1.6	47.2
360	132.2	2.7	2.9	1.7	47.8
720	131.6	2.7	2.9	1.7	48.4
1440	132.4	2.7	3.0	1.8	47.6

Table B- 2 Contact angle data for 50% dilution of UER water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	120.04	2.35	2.73	1.99	59.96
1	117.76	2.52	2.80	1.74	62.24
2	117.52	2.68	2.94	1.68	62.48
3	115.65	2.69	2.90	1.63	64.35
5	112.06	2.72	2.93	1.58	67.94
10	111.47	2.74	2.95	1.59	68.53
15	109.24	2.73	2.93	1.60	70.76
20	107.82	2.72	2.94	1.59	72.18
25	107.59	2.75	3.00	1.61	72.41
30	106.06	2.77	2.96	1.60	73.94
45	106.20	2.74	2.93	1.57	73.80
60	105.89	2.72	2.90	1.60	74.11
90	105.22	2.72	2.96	1.62	74.78
120	104.94	2.69	2.89	1.61	75.06
360	104.75	2.72	2.94	1.75	75.25
720	105.82	2.72	2.95	1.74	74.18
1440	104.18	2.74	2.97	1.75	75.82

Table B-3 Contact angle results for 5000 ppm of UER water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	135.0	2.0	2.9	2.4	45.0
1	125.7	2.1	2.9	2.4	54.3
2	128.5	2.1	2.9	2.4	51.5
3	128.7	2.2	3.0	2.4	51.3
5	125.7	2.1	3.0	2.3	54.3
10	124.4	2.2	3.0	2.3	55.6
15	125.3	2.2	3.0	2.3	54.7
30	127.0	2.3	3.0	2.3	53.0
45	126.3	2.3	3.0	2.2	53.7
60	124.5	2.4	3.0	2.3	55.5
75	125.5	2.3	3.1	2.3	54.5
90	122.7	2.3	3.0	2.3	57.3
120	122.3	2.3	3.0	2.3	57.7
360	120.4	2.4	3.0	2.2	59.6
720	117.1	2.7	3.2	2.0	62.9
1440	110.6	3.3	3.6	1.9	62.9

Table B- 4 Contact angle results for 1000 ppm of UER water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	121.47	1.99	2.55	1.96	58.53
1	119.89	1.99	2.55	1.96	60.11
2	115.47	2.09	2.61	1.99	64.53
3	113.70	2.13	2.64	1.99	66.30
5	113.06	2.14	2.58	1.96	66.94
10	112.56	2.18	2.63	1.98	67.44
15	110.69	2.18	2.63	1.92	69.31
20	111.24	2.18	2.65	1.95	68.76
25	112.65	2.15	2.63	1.95	67.35
30	111.47	2.22	2.64	1.95	68.53
45	110.82	2.21	2.63	1.95	69.18
60	111.49	2.28	2.67	1.98	68.51
75	109.62	2.24	2.67	2.02	70.38
90	108.31	2.21	2.66	1.95	71.69
105	108.39	2.22	2.67	1.99	71.61
120	106.53	2.24	2.66	1.98	73.47
360	108.96	2.28	2.80	2.02	71.04
720	108.50	2.48	3.03	2.12	71.50
1440	103.01	3.11	3.53	2.10	76.99

Table B- 5 Contact angle results for original SIM water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
1	142.2	2.3	3.1	2.2	37.8
2	139.9	2.4	3.1	2.1	40.1
3	139.8	2.4	3.1	2.1	40.2
5	138.4	2.4	3.1	2.0	41.6
10	139.0	2.5	3.2	2.0	41.0
15	137.1	2.5	3.2	2.0	42.9
20	138.1	2.5	3.1	2.0	41.9
25	136.7	2.5	3.2	2.0	43.3
30	134.9	2.5	3.2	2.0	45.1
45	134.4	2.5	3.2	2.0	45.6
60	133.4	2.4	3.1	2.0	46.6
75	133.3	2.5	3.1	1.9	46.7
90	132.6	2.4	3.1	2.0	47.4
120	133.0	2.4	3.0	2.1	47.0
360	132.5	2.3	3.1	2.2	47.5
720	131.2	2.3	3.1	2.1	48.8
1440	131.2	2.4	3.1	2.1	48.8

Table B- 6 Contact angle results for 50% dilution of SIM water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	134.73	2.12	2.95	2.32	45.27
1	134.47	2.32	3.11	2.15	45.53
2	134.47	2.40	3.06	2.11	45.53
3	132.18	2.36	3.06	2.07	47.82
5	132.08	2.40	3.10	2.02	47.92
10	133.12	2.48	3.19	1.99	46.88
15	133.41	2.52	3.18	1.98	46.59
20	133.96	2.48	3.14	1.98	46.04
25	133.62	2.48	3.19	2.03	46.38
30	132.73	2.48	3.18	1.98	47.27
45	133.88	2.53	3.19	1.99	46.12
60	134.32	2.44	3.11	1.99	45.68
75	134.35	2.52	3.14	1.94	45.65
90	133.54	2.45	3.11	2.03	46.46
120	133.20	2.36	3.02	2.07	46.80
360	133.34	2.32	3.06	2.15	46.66
720	133.80	2.27	3.05	2.14	46.20
1440	132.33	2.36	3.10	2.11	47.67

Table B- 7 Contact angle results for 5000 ppm of SIM water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	135.00	1.60	2.70	2.38	45.00
1	135.14	1.60	2.66	2.34	44.86
2	135.38	1.67	2.70	2.31	44.62
3	135.78	1.64	2.70	2.35	44.22
5	135.00	1.69	2.66	2.34	45.00
10	133.07	1.64	2.73	2.32	46.93
15	134.54	1.67	2.77	2.27	45.46
20	133.95	1.67	2.70	2.28	46.05
25	133.59	1.71	2.75	2.27	46.41
30	133.89	1.71	2.74	2.27	46.11
45	134.78	1.71	2.77	2.27	45.22
60	135.33	1.74	2.73	2.30	44.67
75	135.04	1.74	2.80	2.30	44.96
90	135.74	1.74	2.81	2.31	44.26
120	134.20	1.85	2.91	2.34	45.80

Table B- 8 Contact angle results for 1000 ppm of SIM water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	133.96	1.66	2.68	2.29	46.04
1	132.32	1.78	2.69	2.29	47.68
2	130.42	1.83	2.70	2.23	49.58
3	129.39	1.81	2.72	2.17	50.61
5	130.95	1.82	2.73	2.22	49.05
10	129.67	1.86	2.71	2.21	50.33
15	129.74	1.78	2.77	2.21	50.26
25	128.89	1.82	2.69	2.22	51.11
30	128.16	1.86	2.69	2.25	51.84
45	129.39	1.82	2.76	2.25	50.61
60	130.14	1.82	2.73	2.26	49.86
75	131.21	1.78	2.69	2.22	48.79
90	132.38	1.83	2.74	2.22	47.62
120	129.67	1.82	2.73	2.21	50.33
360	129.93	1.82	2.76	2.21	50.07
720	129.43	2.32	3.19	2.20	50.57
1440	126.96	3.23	3.86	2.28	53.04

Table B- 9 Contact angle results for original sea water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	139.41	1.60	2.68	2.27	40.59
1	139.87	1.81	2.71	2.08	40.13
2	137.31	2.01	2.83	1.93	42.69
3	138.43	2.08	2.86	1.86	41.57
5	135.00	2.32	2.93	1.81	45.00
10	133.36	2.44	2.95	1.77	46.64
15	133.62	2.40	2.99	1.63	46.38
20	131.33	2.41	3.04	1.63	48.67
25	131.38	2.44	2.99	1.59	48.62
30	130.87	2.44	2.96	1.63	49.13
45	129.13	2.49	3.01	1.60	50.87
60	130.70	2.51	3.03	1.66	49.30
75	128.47	2.40	2.91	1.66	51.53
90	128.31	2.35	2.94	1.65	51.69
120	126.05	2.40	2.95	1.70	53.95
360	124.66	2.31	2.79	1.84	55.34
720	123.97	2.26	2.76	1.87	56.03
1440	123.20	2.23	2.77	1.83	56.80

Table B- 10 Contact angle results for 5000 ppm of sea water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	128.30	1.71	2.58	2.13	51.70
1	126.78	1.72	2.61	2.13	53.22
2	127.60	1.74	2.62	2.09	52.40
3	126.91	1.87	2.65	2.03	53.09
5	127.00	1.90	2.67	2.03	53.00
10	126.71	1.98	2.71	1.97	53.29
15	125.80	1.98	2.69	1.94	54.20
20	126.55	2.06	2.71	1.95	53.45
25	126.71	2.00	2.71	1.96	53.29
30	125.79	2.03	2.70	1.99	54.21
45	125.83	2.06	2.74	2.00	54.17
60	125.60	2.10	2.74	1.97	54.40
75	126.77	2.10	2.77	2.03	53.23
90	125.50	2.09	2.77	2.03	54.50
120	125.26	2.03	2.81	2.10	54.74
360	125.28	2.23	3.06	2.23	54.72
720	126.15	2.75	3.59	2.52	53.86
1440	124.12	3.68	4.31	2.60	55.88

Table B- 11 Contact angle results for distilled water

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	121.68	1.64	2.54	2.07	58.32
1	116.13	1.90	2.60	1.99	63.87
2	119.44	1.90	2.58	1.90	60.56
3	117.09	1.94	2.57	1.94	62.91
5	117.04	1.98	2.57	1.89	62.96
10	115.46	1.96	2.53	1.94	64.54
15	115.04	1.98	2.57	1.89	64.96
20	116.37	1.99	2.57	1.90	63.63
25	114.54	1.95	2.62	1.90	65.46
30	115.30	1.98	2.61	1.89	64.70
45	115.68	1.99	2.58	1.90	64.32
60	114.74	1.94	2.61	1.94	65.26
75	113.51	1.95	2.62	1.99	66.49
90	114.81	1.99	2.58	1.95	65.19
120	114.24	2.04	2.67	1.95	65.76
360	114.85	1.94	2.75	2.03	65.15

Table B- 12 Contact angle results of 5000 ppm UER with added two times SO_4^{2-} concentration

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	127.93	1.55	2.48	2.18	52.07
1	125.54	1.67	2.59	2.09	54.46
2	125.65	1.69	2.55	2.05	54.35
3	125.02	1.71	2.59	2.05	54.98
5	124.36	1.79	2.60	2.02	55.64
10	123.35	1.83	2.59	1.98	56.65
15	123.35	1.79	2.62	1.98	56.65
20	122.87	1.86	2.62	1.90	57.13
25	121.92	1.86	2.55	1.94	58.08
30	121.21	1.86	2.59	1.94	58.79
45	120.81	1.90	2.62	1.98	59.19
60	120.73	1.92	2.64	1.95	59.27
75	121.01	1.88	2.64	1.99	58.99
90	120.77	1.84	2.61	1.99	59.23
120	119.76	1.91	2.67	2.02	60.24
360	119.28	2.12	2.96	2.19	60.72
720	120.11	2.49	3.30	2.34	59.89
1440	120.01	2.80	3.72	2.45	59.99

Table B- 13 Contact angle results of 5000 ppm UER with added four times SO_4^{2-} concentration

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	126.75	1.75	2.83	2.27	73.25
1	122.52	2.04	2.92	2.20	77.48
2	120.17	2.11	2.87	2.23	79.83
3	120.85	2.12	2.96	2.20	79.15
5	120.53	2.11	2.91	2.19	79.47
10	119.27	2.15	2.91	2.15	80.73
15	118.55	2.15	2.95	2.19	81.45
20	118.29	2.17	2.99	2.15	81.71
25	118.09	2.19	2.99	2.15	81.91
30	118.53	2.17	2.99	2.19	81.47
45	119.04	2.15	2.99	2.11	80.96
60	117.97	2.16	3.00	2.16	82.03
75	117.66	2.11	2.99	2.19	82.34
90	117.13	2.08	3.04	2.20	82.87
120	116.34	2.19	3.07	2.15	83.66
360	118.43	2.23	3.19	2.31	81.57
720	119.50	2.39	3.39	2.51	80.50
1440	119.50	2.39	3.39	2.51	80.50

Table B- 14 Contact angle results of 5000 ppm UER with added six times SO_4^{2-} concentration

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	108.58	2.16	2.73	2.03	61.42
1	106.94	2.26	2.83	2.00	63.06
2	105.97	2.34	2.77	1.95	64.03
3	103.96	2.38	2.77	1.90	66.04
5	102.59	2.42	2.81	1.95	67.41
10	101.86	2.38	2.77	1.86	68.14
15	101.88	2.44	2.83	1.91	68.12
20	100.43	2.48	2.87	1.83	69.57
25	101.06	2.52	2.91	1.87	68.94
30	100.37	2.52	2.83	1.83	69.63
45	100.19	2.48	2.83	1.83	69.81
60	100.68	2.47	2.86	1.86	69.32
75	102.77	2.52	2.87	1.91	67.23
90	102.46	2.48	2.91	1.91	67.54
120	102.20	2.52	2.91	1.87	67.80
360	101.95	2.57	3.00	2.00	68.05
720	102.59	2.71	3.19	2.14	67.41
1440	102.59	2.71	3.19	2.14	67.41

Table B- 15 Contact angle results of 5000 ppm UER with added two times Ca²⁺ concentration

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	124.96	1.81	2.77	2.37	55.04
1	122.14	1.89	2.85	2.25	57.86
2	121.16	1.93	2.89	2.25	58.84
3	120.05	2.01	2.89	2.21	59.95
5	119.14	2.01	2.89	2.21	60.86
10	119.62	2.05	2.93	2.17	60.38
15	119.47	2.13	2.89	2.17	60.53
20	118.71	2.13	2.97	2.13	61.29
25	118.15	2.09	2.93	2.17	61.85
30	118.45	2.13	2.93	2.09	61.55
45	118.03	2.17	2.97	2.13	61.97
60	117.81	2.16	2.96	2.12	62.19
75	118.14	2.17	3.01	2.17	61.86
90	117.38	2.17	3.01	2.17	62.62
120	117.76	2.17	2.97	2.17	62.24
360	118.09	2.16	3.12	2.24	61.91
720	122.31	2.53	3.54	2.49	57.69
1440	129.33	2.72	3.96	2.84	50.67

Table B- 16 Contact angle results of 5000 ppm UER with added four times Ca²⁺ concentration

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	126.52	1.62	2.82	2.41	53.48
1	124.11	1.90	2.92	2.22	55.89
2	122.03	2.05	3.02	2.19	57.97
3	120.65	2.09	3.01	2.18	59.35
5	119.79	2.13	3.06	2.18	60.21
10	119.07	2.08	3.01	2.08	60.93
15	119.14	2.19	3.02	2.14	60.86
20	117.48	2.19	3.02	2.09	62.52
25	117.44	2.22	3.01	2.13	62.56
30	118.03	2.19	3.07	2.14	61.97
45	116.45	2.13	3.01	2.08	63.55
60	116.32	2.18	3.01	2.08	63.68
75	116.01	2.07	3.00	2.12	63.99
90	115.70	2.08	2.96	2.18	64.30
120	118.79	2.08	2.96	2.13	61.21
360	118.63	2.09	2.96	2.13	61.37
720	118.31	2.09	2.92	2.18	61.69
1440	117.80	2.13	2.96	2.22	62.20

Table B- 17 Contact angle results of 5000 ppm UER with added six times Ca²⁺ concentration

Time Min.	A CA Degree	Rest Droplet Dist mm	Large Diam mm	Depth mm	Real contact angle Degree
0	116.19	2.19	2.67	2.03	53.81
1	112.62	2.31	2.75	1.95	57.38
2	108.69	2.35	2.71	1.87	61.31
3	106.55	2.39	2.79	1.79	63.45
5	101.69	2.47	2.79	1.75	68.31
10	102.56	2.51	2.79	1.71	67.44
15	101.17	2.52	2.84	1.72	68.83
20	99.85	2.50	2.88	1.76	70.15
25	98.95	2.51	2.83	1.75	71.05
30	97.16	2.47	2.79	1.71	72.84
45	97.99	2.56	2.88	1.72	72.01
60	97.82	2.56	2.84	1.76	72.18
75	98.39	2.51	2.87	1.75	71.61
90	99.85	2.47	2.83	1.75	70.15
120	97.39	2.47	2.87	1.75	72.61
360	100.28	2.56	2.96	1.80	69.72
720	100.60	2.67	3.11	1.87	69.40
1440	101.06	3.16	3.52	1.92	68.94

المخلص

استخدم الحقن بالمياه قليلة الملوحة لتحسين استخراج النفط لعقود عديدة. تاريخياً، الآليات وراء هذا التحسن في معدلات استخراج النفط نسبت إلى المحافظة على الضغط وإزاحة النفط عن طريق امياه المحقونة بالحركة الآلية. في الآونة الأخيرة أشارت الأدلة من المختبرات المعملية والميدانية أن الحقن بالماء ينطوي أيضاً على عمليات كيميائية، وأن تعديل تركيز الماء المحقون وتكوينها الأيوني يمكن أن تؤثر بشكل كبير على استخراج النفط. وقد تمت مناقشة العديد من النظريات حول آلية الحقن بالماء قليل الملوحة في البحوث. وتشمل الحد من التوتر البيني، وتغيير قدرتها على الابتلال (تبادل الأيونات الموجبة)، وتغير في الرقم الهيدروجيني (الزيادة)، وتشكيل مستحلب، وحركة الطين. فمن الواضح من البحوث أنه لا يوجد اتفاق بين الباحثين حول آلية الحقن بالماء قليل الملوحة وهناك أيضاً بحوث محدودة أجريت على الصخور الكربونية، وبعض الدراسات قد خلصت إلى أن الحقن بالماء قليل الملوحة لا يكون له تأثير على استخراج النفط.

هذا العمل يقدم نتائج الاختبارات الأساسية على تجارب الحقن بواسطة مياه البحر، ومياه أم الردومة ذات الملوحة (197584 جزء في المليون)، ومياه سمسمة ذات الملوحة (224987 جزء في المليون) في الصخور الكربونية لتقييم آثار ملوحة المياه المالحة والتكوين الأيوني على التفاعلات الممكنة من الصخور الكلسية / الماء المالح / والنفط، وتحديد آلية الاستخراج. وقد تم تخفيف ملوحة المياه في الأنواع الثلاثة السابق ذكرها لتصل إلى الملوحة إلى 5000 و 1000 جزء في المليون واخترنا الأمثل، ثم تم تغيير تركيز أيون الكالسيوم والكربونات، وتم تحديد التغير في القابلية للابتلال بواسطة قياسات زاوية الاتصال. وأجريت قياسات للتوتر البيني في محاولة لتقييم آلية الحقن بواسطة المياه قليلة الملوحة.

أظهرت النتائج التجريبية أنه يمكن أن يتحقق تحسن كبير في استخراج النفط من خلال تغيير ملوحة مياه الحقن. عندما تم تخفيف ملوحة مياه أم الرادومه من 197362 جزء من المليون إلى 5000 جزء في المليون أدى إلى تحسين معدلات استخراج النفط من 63% إلى 84.5% من كمية النفط الموجودة في المكمن على التوالي. ولذلك، فقد اعتبرت مياه أم الرادومة عند تركيز 5000 جزء في المليون الملوحة المثلى لتقييم تأثير الكبريتات وتركيز أيون الكالسيوم. أوضحت النتائج أيضاً أن تركيز الكبريتات له تأثير كبير على هذه العملية، وزيادة تركيز الكبريتات عن (47 جزء في المليون) أدى إلى تأثير سلبي. وأشارت قياسات زاوية الاتصال أن تخفيض نسبة الملوحة يحول القدرة على الابتلال للنظام المتوسط البليل، وأن ماء أم الردومة الأكثر تأثيراً في عملية تحويل القدرة على الابتلال للنظام المتوسط بالمقارنة مع المياه الأخرى. أوضحت النتائج أيضاً أنه ليست هناك علاقة واضحة بين التحسينات في استخراج النفط والتوتر البيني والرقم الهيدروجيني للأنظمة التي تمت دراستها.

برنامج ماجستير الهندسة البترولية

قسم الهندسة الكيميائية و البترول

كلية الهندسة

جامعة الإمارات العربية المتحدة

عنوان الرسالة:

الازاحة بالماء القليل الملوحة في احد المكامن الكلسية: اسلوب تجريبي

محمد يحيى محمد محمود

اسم الباحث:

أسماء المشرفين:

د. حازم العطار

الأستاذ المشارك في الهندسة البترولية

قسم الهندسة الكيميائية و البترول بكلية الهندسة

جامعة الإمارات العربية المتحدة

الإمارات العربية المتحدة

أ.د. عبد الرزاق بن ذكرى

الأستاذ في الهندسة البترولية

قسم الهندسة الكيميائية و البترول بكلية الهندسة

جامعة الإمارات العربية المتحدة

الإمارات العربية المتحدة

الازاحة بالماء القليل الملوحة في احد المكامن الكلسية: اسلوب تجريبي

إعداد

محمد يحيى محمد محمود

قسم الهندسة الكيميائية و البترول
كلية الهندسة
جامعة الإمارات العربية المتحدة

رسالة مقدمة لاستكمال متطلبات الحصول على درجة
ماجستير العلوم في الهندسة البترولية

برنامج ماجستير الهندسة البترولية
قسم الهندسة الكيميائية و البترول
كلية الهندسة
جامعة الإمارات العربية المتحدة

يونيو 2012