
Smart Waterflooding in Carbonate Reservoirs

Adeel Zahid

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Center for Energy Resources Engineering

Department of Chemical and Biochemical Engineering

Technical University of Denmark

DK-2800 Lyngby, Denmark

Preface

This thesis is submitted as partial fulfillment of the requirement for the PhD degree at Technical University of Denmark (DTU). The work has been carried out at the Department of Chemical and Biochemical Engineering and Center for Energy Resources Engineering (CERE) from January 2009 to February 2012 under the supervision of Alexander Shapiro, Erling H. Stenby and Wei Yan. The project was funded by DONG Energy and The Danish Council for Independent Research | Technology and Production Sciences (FTP) as a part of the ADORE project (09-062077/FTP).

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Adeel Zahid
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2800 Kgs. Lyngby Denmark

This dissertation is dedicated to my sweet mom your love is the most precious thing for me !

Summary

During the last decade, smart waterflooding has been developed into an emerging EOR technology both for carbonate and sandstone reservoirs that does not require toxic or expensive chemicals. Although it is widely accepted that different salinity brines may increase the oil recovery for carbonate reservoirs, understanding of the mechanism of this increase is still developing. To understand this smart waterflooding process, an extensive research has been carried out covering a broad range of disciplines within surface chemistry, thermodynamics of crude oil and brine, as well as their behavior in porous media.

The main conclusion of most previous studies was that it is the rock wettability alteration towards more water wetting condition that helps improving the oil recovery. In the first step of this project, we focused on verifying this conclusion. Coreflooding experiments were carried out using Stevens Klint outcrop chalk core plugs with brines without sulfate, as well as brines containing sulfate in different concentrations. The effects of temperature, injection rate, crude oil composition and different sulfate concentrations on the total oil recovery and the recovery rate were investigated. Experimental results clearly indicate improvement of the oil recovery without wettability alteration.

At the second step of this project, we studied crude oil/brine interactions under different temperatures, pressures and salinity conditions in order to understand mechanisms behind the high salinity waterflooding. Our results show, in particular that sulfate ions may help decreasing the crude oil viscosity or formation of, seemingly, an emulsion phase between sulfate-enriched brine and oil at high temperature and pressure.

Experimental results indicate that crude oils interact differently with the same brine solutions regarding phase behavior and viscosity measurements. This difference is attributed to the difference in composition of the different crude oils. More experiments are carried out in order to understand mechanisms of the crude oil viscosity reduction and emulsion formation. We observed that a heavy oil (that with a large fraction of heavy components) exhibited viscosity reduction in contact with brine, while a light crude oil exhibited emulsion formation.

Most of reported high salinity waterflooding studies were carried out with outcrop chalk core plugs, and by performing spontaneous imbibition rather than forced flooding. The objective of the third step of this project was to investigate the potential of high salinity waterflooding process by carrying out experiments with reservoir chalk samples. We carried out waterflooding instead of spontaneous

imbibition using core plugs with and without aging. The total oil recovery, recovery rate and interaction mechanisms of ions with rock were studied for different injected fluids under different temperatures and wettability conditions. Experimental results demonstrate that the oil recovery mechanism under high salinity seawater flooding at high temperatures is different for the different chalk rocks (outcrop and reservoir), although they have similar surface area and reactivity of the potential determining ions.

In the last decade, laboratory waterflooding experiments and field tests have proven increase in oil recovery from sandstone reservoirs by injecting brine of low salinity. However, this effect has not been thoroughly investigated for carbonates. At the final stage of this project, we have experimentally investigated the oil recovery potential of low salinity water flooding in the carbonate rocks. We used both reservoir carbonate and outcrop chalk core plugs. The flooding experiments were carried out initially with the seawater. Afterwards the contribution to oil recovery was evaluated by sequential injection of various diluted versions of the seawater.

The significance of this work may be summarized in five main findings:

- Injection of sulfate rich brine may lead to additional recovery from Stevens Klint chalk even under completely water wet conditions. Therefore, increment in oil recovery with sulfate ions cannot be explained just by the rock wettability alteration.
- Experimental results show that sulfate ions may help decreasing the crude oil viscosity when brine is contacted with oil under high temperature and pressure. We have also observed formation of an emulsion-like phase between oil and brine with increased sulfate ion concentration under high temperature and pressure. The viscosity decrease and formation of an emulsion phase could be the possible reasons for the observed increase in oil recovery with sulfate ions at high temperature in chalk reservoirs, besides the mechanism of the rock wettability alteration.
- Crude oil/brine interaction study suggests that viscosity reduction for crude oil in contact with brine is connected to the presence of heavy components in the crude oil, while formation of emulsions with brine is a phenomenon related to the presence of lighter components in the crude oil.
- The reservoir chalk rocks showed relatively less effect of temperature and sulfate ions concentration on oil recovery as compared to Stevens Klint outcrop chalk. This indicates that the rock may also determine whether the effect of temperature and high salinity brine on the recovery is observed.

- Migration of fines and dissolution of rock particles are possible mechanisms of oil recovery increment with low salinity brines from carbonate core plugs at 90 °C.

Resumé på dansk

'Smart waterflooding', har det sidste årti gennemgået en enorm udvikling og haft gennembrud indenfor forbedret indvinding af olie. Dette gælder både for karbonat og sandstens reservoirs, hvor denne metode ikke kræver giftige eller bekostelige kemikalier. På trods af, at det generelt er accepteret, at forskellige saltopløsninger i forhold til saltindhold er medvirkende til forbedret olieindvindingen for karbonate reservoirs, er der stadig behov for bedre forståelse af de mekanismer som resultere i disse observationer og derfor er der stor interesse for og udvikling på dette område. For at opnå en mere optimal forståelse for 'smart waterflooding'-processen er der gennemført et omfattende studie, som dækker en bred vifte af discipliner indenfor grænsefladekemi, termodynamik for råolier og saltopløsninger, samt hvilken adfærd der dominerer i porøse medier.

I de fleste tidligere undersøgelser er den overordnede konklusion at den afgørende faktor i forhold til at forbedre olieudvindingen er ændringer i stenlagets evne til at blive våd, den såkaldte befugtningsevne i jordlaget, som ændrer sig mod at stenlaget i højere grad gøres befugtes af vand frem for råolie. Første del af dette projekt er fokuseret på at bekræfte denne konklusion. Gennemstrømning af olie og saltvandsopløsninger gennem kernemateriale (coreflooding) er udført med Stevens Klint kalkkerner, tilstoppet med saltopløsninger uden sulfat og med sulfat tilsat i forskellige koncentrationer. Indflydelsen fra temperatur, injektions hastighed, råolie sammensætning og forskellige sulfat koncentrationer på den totale olieindvinding, samt indvindingsgraden er undersøgt. Eksperimentelle resultater indikerer tydeligt at forbedret olieindvinding er mulig uden ændringer i stenlagets befugtningsevne.

Anden del af dette projekt dækker et studie i interaktionerne imellem råolie og saltvandsopløsninger ved forskellige temperature, tryk og saltindhold. Formålet er at opnå en bedre og mere præcis forståelse for de mekanismer der er forbundet med højt saltindhold i waterflooding. Resultaterne viser at sulfat ioner muligvis bidrager til reduktion i viskositeten af råolie eller, tilsyneladende, dannelsen af en emulsions fase mellem den sulfat rige saltopløsning og råolien ved høje temperature og tryk.

Det eksperimentelle arbejde har vist at forskellige råolier interagerer forskelligt med den samme saltvandsopløsning når man betragter hvorledes faserne optræder sammen og kigger på viskositeten af råolierne. Denne forskel kan blive forklaret ud fra forskellige komponent sammensætninger i de forskellige råolier. Flere forsøg er udført i denne forbindelse for at fastlægge og forstå mekanismerne bag den observerede reduktion i viskositeten og i dannelsen af emulsioner.

Resultaterne fra det eksperimentelle arbejde viste, at viskositeten for en tungere råolie, (indeholdende en meget stor mængde tunge komponenter), reduceres efter at have været i kontakt med saltvandsopløsninger. En lettere råolie ændrede ikke viskositet, men derimod resulterede dette i dannelsen af emulsioner.

Hovedparten af waterflooding studier med høj concentration af saltindhold er udført med kalkkerner, hvor spontan absorption snarere end tvunget waterflooding udføres. Formålet med denne tredje del af projektet har været at undersøge potentialet for waterflooding med saltvandsopløsninger med høje saltkoncentrationer ved at udføre eksperimenter på kalkkerner fra reservoirs. Der er udført waterflooding fremfor spontan absorption, hvor der er anvendt friske kerne, samt aldringskerner. Den samlede forbedrede olieindvinding, indvingsgraden, samt interaktionsmekanismerne for ionerne med stenlaget er studeret for forskellige injektionsvæsker ved forskellige temperature and forskellige absorptionsbetingelser. Resultaterne viser, at olieindvindingen ved 'seawaterflooding' med høj saltkoncentration og endvidere høje temperature er forskellig for forskellige kalkstenlag (kerner fra klippefremspring og kerner fra reservoirs). Dette er på tråds af, at de har lignende grænseflader og lignende reaktionsevne af de potentielle afgørende ioner.

Gennem det sidste årti har waterflooding, både i laboratorieskala og i 'field-test'-skala, vist en forøgelse i olieindvinding from sandstens reservoirs, ved injektion af saltvand med lavt saltindhold. Denne effekt, er dog imidlertid ikke grundigt udforsket for karbonat reservoirs. Den sidste del af dette projekt omhandler eksperimentelle studier, hvor olieindvindingspotentialet for waterflooding med lave saltkoncentrationer i karbonat stenlag udforskes. Der er anvendt reservoir karbonatkerner, samt kalkkerner fra klippefremspring. Eksperimenterne startede med at være 'seawater flooding'-eksperimenter. Derefter blev bidraget til olieindvinding vurderet ved sekvensiel injektion af varierende fortyndede versioner af havvandet.

Betydningen af dette arbejde kan overordnet summeres i form af fem hovedkonklusioner:

- Injektion af sulfat-rige saltvandsopløsninger føre formentligt til yderligere indvinding fra Stevens Klint kalkkerner, selv ved betingelser hvor der udelukkende sker befugtning med vand. Dette betyder at den øgede olieindvinding ved anvendelse af sulfat ioner ikke kun kan skyldes ændringen i stenlagets befugtningsevne.
- Eksperimentelle resultater viser at sulfationer tilsyneladende bidrager til reduktion i viskositeten af råolie, ved kontakt med råolie under høj temperatur og højt tryk. Endvidere viser resultaterne også dannelse af en emusionslignende fase mellem olie og saltvand, som

viser sig ved øgede sulfatkoncentrationer og samtidigt høj temperatur og højt tryk. Reduktionen i viskositeten og dannelsen af emulsioner kan være medvirkende årsager til den forbedrede olieindvinding, som der er observeret ved anvendelsen af sulfationer ved høje temperature i kalkreservoirs sammen med mekanismerne for ændringer af befugtningsevnen for stenlaget.

- Undersøgelser af råolie/ saltvand interaktioner viser at reduktion i viskositeten for råolie, efter at have været i kontakt med saltvand formentligt er relateret til indholdet af tunge komponenter i råolien. Dannelsen af emulsioner med saltvand, kan derimod formentligt relateres til indholdet af lettere komponenter i råolien.
- Reservoir kalkkerner udviste relativ lille effekt af temperatur og koncentration af sulfationer i forhold til olieindvinding i sammenligning med Steven Klint kalkkerner. Dette indikere at stenlaget formentligt er medvirkende til at bestemme om effekt fra temperatur og høj saltindhold i saltvandet kan observeres.
- Det er muligt at små stenlagspartikler der flyttes og opløsning af stenlagspartikler er mekanismer der er medvirkende til forbedret olieindvinding fra karbonatkerner ved anvendelse af saltvand med lav saltkoncentration ved 90 °C.

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Introduction

1.1 Background and Motivation

The economic significance of carbonate (chalk and limestone) reservoirs is enormous. More than half of the world's remaining oil exists in carbonate reservoirs [2]. These reservoirs are among the most complex reservoirs to characterize, model and manage. They are characterized by rather low primary oil recovery; therefore, the enhanced oil recovery potential of these reservoirs is high. Many carbonate reservoirs are believed to be intermediate oil wet and are very low permeable, so the enhanced oil recovery from such reservoirs is regarded as a great challenge.

A range of techniques have been developed and applied to improve oil recovery to meet the increasing demands in energy resources. Reservoir lithology is one of the important screening variable for the application of an EOR method [3]. According to an international EOR project database containing 1507 projects during the last decade [4], gas injection (continuous or in a WAG mode) is still the most common EOR method in carbonate formations. (see Figure 1.1)

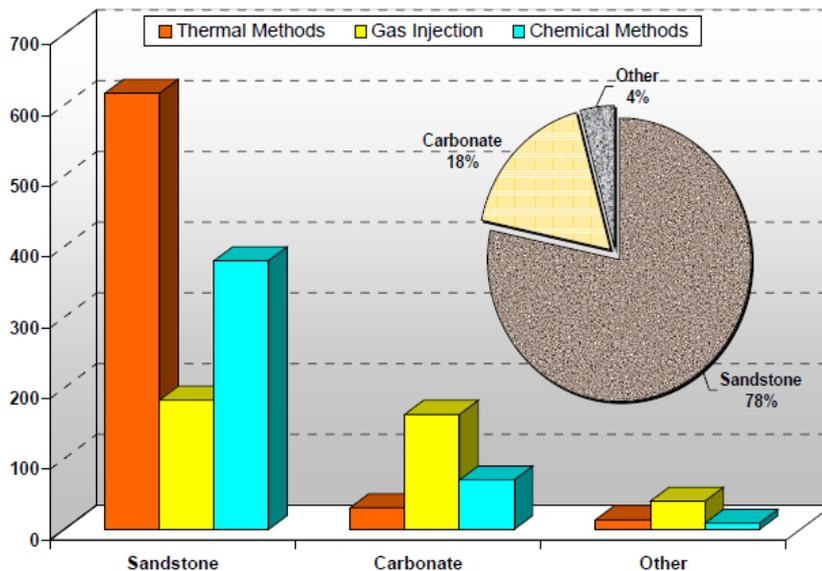


Figure 1.1: EOR field projects by lithology [4]

Thermal methods have made a relatively small contribution to improve the oil recovery from carbonate formations. In chemical methods, polymer flooding is the only proven EOR

technology that has been conducted mostly in early stages of waterflooding [4]. Surfactant flooding is also used to improve oil recovery by wettability modification of carbonate formations and interfacial tension (IFT) reduction [5, 6].

According to a survey of the EOR projects, a total of 19 reported EOR technologies were tested in the North Sea. WAG injection is considered to be the most successful EOR technology applied in the North Sea [7]. Chemical injection methods (surfactant and polymer flooding) are costly and their application up till now has been considered too expensive.

Waterflooding is a cheap oil recovery process and is by far the most widely applied method for improving the oil recovery. Traditionally, it was practiced for pressure maintenance after primary depletion. Composition of water was not considered as an important factor influencing the amount of oil recovered. However, over the last decade extensive studies have shown that composition of injected water can affect crude oil/brine/rock interactions in a favorable way to improve oil recovery [8-15]. High salinity seawater flooding in high temperature chalk reservoirs and low salinity waterflooding in sandstone reservoirs are two examples of smart waterflooding.

Kokal and Al-Kaabi [16] reported that smart waterflooding has several advantages compared to other EOR methods: (1) It can achieve higher ultimate oil recovery with minimal investment in current operations; (2) It can be applied during the early life cycle of the reservoir. ; (3) The payback is faster, even with small increment of oil recovery.

Several laboratory experimental studies of high salinity water injection were carried out by T.Austad and co-workers, who studied recovery as a function of brine composition and temperature [1, 17-20]. It was observed that SO_4^{2-} , Ca^{2+} and Mg^{2+} are the potential determining ions for improving the oil recovery in chalk reservoirs at high temperatures (above 90 °C). It was also reported that these ions must act together, because neither of them alone had an effect on spontaneous imbibition. Based on these experimental results, wettability alteration was proposed to be a key reason for the improvement of oil recovery.

In the last decade, laboratory waterflood and successful field tests have showed that low salinity waterflooding can improve the oil recovery in sandstone reservoirs [14, 21-27]. However, potential of low salinity waterflooding has not been investigated for carbonates. The reason is that the low salinity effect was mainly attributed to interaction with the clay minerals, which are lacking in carbonates [13]. Doust et al. [28] reported that another chemical mechanism may also be responsible for the effect: it is the crude oil adsorption onto positively

charged calcite surface and negatively charged quartz surface. Fathi et al. [9] carried out spontaneous imbibition and flooding tests with low salinity brine solutions using Stevens Klint outcrop chalk core plugs at 110 and 120 °C. A negative impact of diluting the seawater to low salinity was reported which significantly decreased oil recovery in spontaneous imbibition. Tertiary diluted seawater flooding also did not help in producing any extra oil. Decrease in the concentration of the active ions (SO_4^{2-} , Ca^{2+} and Mg^{2+}) was reported as a reason for drastic decrease in oil recovery.

Contrary to these results, Saudi Aramco reported 16-18 % OOIP increase in oil recovery by low salinity waterflooding in composite rock samples from Saudi Arabian carbonate reservoirs [29]. Experiments were carried out using live oil and at a reservoir temperature of 212 °F. Wettability alteration (determined by NMR T2 distribution and contact angle measurement) was reported as a key mechanism for increment in oil recovery.

Although it is widely accepted that high salinity waterflooding may increase the oil recovery for chalk reservoirs [1, 30, 31], understanding of the mechanisms behind this increase is still developing. Most of the reported studies have been made on the basis of spontaneous imbibition using outcrop chalk core plugs. Very few studies have been carried out on the basis of forced injection using reservoir chalk core plugs. Further, reported evidence of wettability alteration is indirect and that is based on increased spontaneous imbibition. In addition to these, crude oil/brine interactions have generally been ignored in most reported studies, which might also be contributing to recovery increase. On the other hand, the experimental data of low salinity waterflooding in carbonates is very limited, so more data plus mechanistic studies is needed.

1.2 Scope and Objectives

The objectives of PhD study are to attempt answering the following questions:

- Is the observed increment in oil recovery using high salinity waterflooding caused only by the wettability alteration or there are some other reasons also? (Chapter 3)
- If some other reasons are also involved then what could they be? (crude oil/brine interactions study) (Chapter 4 and 5)
- Will smart waterflooding improve oil recovery in all chalk reservoirs?
 - Identification of the sufficient conditions and understanding the circumstances under which little or no recovery (Chapter 6)

- To investigate experimentally the recovery mechanism of low salinity waterflooding in carbonate reservoirs (Chapter 7)

1.3 Thesis Outline

The work presented in this thesis is organized into two main parts. The first part (Chapter 1-2) serves as a general introduction and overview of the research. The second part of the thesis (Chapter 3-8) is written on the basis of the five research papers published or submitted previously, with some important modifications. The detail of chapters is given as follows:

- ❖ **Chapter 1** provides an introduction to the project, describes its industrial importance and objectives.
- ❖ **Chapter 2** presents a literature study on smart waterflooding in carbonate reservoirs. In this chapter, we review first the extensive work of seawater flooding in chalk reservoirs and then low salinity waterflooding in sandstone and carbonate reservoirs.
- ❖ **Chapter 3** describes the experimental work to investigate the reasons behind observed improvement in oil recovery with sulfate ions. Is it really wettability alteration or something else also? The work is based on flooding and utilizes completely water wet Stevens Klint core plugs without being aged in crude oil, just saturated with crude oil under vacuum. This excludes alteration of wettability as a factor, which is supposed to act positively on recovery. Waterflooding experiments were carried out with brines without sulfate, as well as brines having different concentrations of sulfate. We observed that injection of sulfate rich brine may lead to additional recovery even under completely water wet conditions.
- ❖ **Chapter 4** presents a crude oil/brine interaction study at different temperatures, pressures and sulfate ion concentrations. We studied crude oil/ brine interactions in normal glassware and in a DBR JEFRI PVT cell. Three different crude oils have been used for the study. Detailed measurements of density, viscosity and water content before and after the experiment are presented. We also carried out IFT measurements at room temperature. We demonstrate that crude oil/brine interactions may also be partly responsible for the increase in oil recovery.
- ❖ **Chapter 5** presents the further development of the crude oil/brine interaction study. We investigated the effects of compositional differences of crude oils and also studied heptane/seawater interactions under different temperatures, pressures and sulfate ion

concentrations. Gas chromatography (GC) and SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis of the crude oils were carried out in order to investigate compositional differences of crude oils. For comparison, we also carried out heptanes/brine interaction study. Finally, the mechanisms of viscosity reduction and emulsion formation are discussed.

- ❖ **Chapter 6** describes high salinity waterflooding experiments with reservoir chalk samples. Two different flooding schemes (with and without aging) were used for flooding North Sea reservoir chalk samples. For comparison, two tests were also carried out with Stevns Klint core plugs. The total oil recovery, recovery rate and interaction mechanisms of ions with rock were studied for different injected fluids at different temperatures and wettability conditions. Experimental results demonstrate that the oil recovery mechanism at high temperatures is different for the different rocks.
- ❖ **Chapter 7** describes the experimental work on low salinity waterflooding in carbonate reservoirs. Initially the flooding experiments were carried out with the seawater. Afterwards oil recovery was monitored under sequential injection of various diluted versions of the seawater. Total oil recovery, ion interaction and wettability changes were studied for the different rocks. In the light of experimental results, discussions are made about possible mechanisms for improving oil recovery in carbonate reservoirs.
- ❖ Finally **Chapter 8** provides the overall conclusions and recommendations for future work.

1.4 List of Research Papers

The following is a list of papers of relevance to the subject of the thesis, authored or co-authored by the author of this thesis, which have been published or submitted for publication.

Journal Articles

- Zahid, A.; Sandersen, S.B; Stenby, E. H.; Solms, N.V. and Shapiro, A. A., Advanced Waterflooding in Chalk Reservoirs: Understanding of Underlying Mechanisms, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 389 (2011) 281– 290.
- Zahid, A.; Shapiro, A. A; Shapiro and Stenby, E. H., Managing Injected Water Composition to Improve Oil Recovery: A Case Study of North Sea Chalk Reservoir, Energy & Fuels (2011), Submitted.

- Sandersen, S.B; Zahid, A.; Stenby, E. H.; Solms, N.V. and Shapiro, A. A., Mechanisms of Advanced Waterflooding in Chalk Reservoirs: Role of Seawater-Crude Oil Interactions, Colloids and Surfaces A: Physicochemical and Engineering Aspects (2012), submitted.
- Zahid, A.; Shapiro, A. A; Shapiro and Skauge, A., Experimental Studies of Low Salinity Waterflooding in Carbonate Reservoirs, Energy & Fuels (2012), Submitted.

Conference Papers

- Zahid, A.; Stenby, E. H. and Shapiro, A. A., Improved Oil Recovery in Chalk: Wettability Alteration or Something Else? SPE 131300, presented at SPE EUROPEC/EAGE Annual Conference and Exhibition, Barcelona, Spain, 14-17 June, 2010.
- Zahid, A.; Stenby, E. H. and Shapiro, A. A., Advanced Waterflooding in Carbonate Reservoirs, Poster presented at 11th International Symposium on Evaluation of Wettability and Its Effect on Oil Recovery, University of Calgary, Alberta, Canada, 6-8 September, 2010.
- Zahid, A.; Stenby, E. H. and Shapiro, A. A., Advanced Waterflooding in Chalk Reservoirs: Crude Oil/Brine Interaction Study, presented at the 2nd Annual World Congress of Well Stimulation & Enhanced Oil Recovery, Chongqing, China, 17-19 May, 2011.
- Zahid, A.; Stenby, E. H. and Shapiro, A. A., Smart Waterflooding (High Sal/Low Sal) in Carbonate Reservoirs, SPE 154508, will be presented at SPE EUROPEC/EAGE Annual Conference and Exhibition, Copenhagen, Denmark, 4-7 June, 2012.
- Zahid, A.; Skauge, A. and Shapiro, A. A., Experimental Studies of Low Salinity Waterflooding in Carbonate Reservoirs: A New Promising Approach, SPE 155625, will be presented at SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 16-18 April, 2012.

Smart Waterflooding in Carbonates: An Update Review

2.1 Introduction

Waterflooding was first practiced for pressure maintenance after primary depletion and has since become the most widely applied improved oil recovery technique. The key features which make waterflooding an essential process for most of the mature fields are: (1) water is easily available, and most important, inexpensive; (2) it is relatively easy to inject and efficient for displacing oil; (3) is associated with a much lower capital investment and operating cost. A number of technologies and practices have been used previously to improve the oil recovery by waterflooding, such as multilateral wells, infill drilling, improved reservoir characterization and modern monitoring and surveillance, and other. Traditionally, a little attention has been given in reservoir engineering practice to the role of chemistry of injection water on displacement efficiency or its impact on oil recovery. However, over the last decade extensive studies have shown that composition of injected water can affect crude oil/brine/rock interactions in a favorable way to improve oil recovery. Seawater flooding in high temperature chalk reservoirs and low salinity waterflooding in sandstone reservoirs are two examples of smart waterflooding. But most recently, low salinity waterflooding has also been applied to carbonates.

In this chapter, we will first review the extensive research regarding seawater flooding in chalk reservoirs. Then low salinity waterflooding in sandstone and carbonate reservoirs will also be discussed.

2.1 High Salinity Water (HSW)/Seawater Flooding in Chalk Reservoirs

The exceptional success of seawater injection in the Ekofisk chalk reservoir [32] has been the motivation for a number of experimental studies to understand complex crude oil/water/rock chemical interactions for carbonate reservoirs.

Improved oil recovery in chalk reservoirs by seawater flooding was first reported by Austad et al. [8]. Since then several laboratory experimental studies of water injection were carried out

using different core plugs, crude oils and aqueous phase compositions at various wettability and temperature conditions [1, 17-20]. The high salinity flooding is relatively new and still in research and development phase. The laboratory studies, but not the pilot tests or field trials have been reported. Some recovery mechanisms were discussed, but still many questions and uncertainties remained. Without understanding why and how the recovery method works, its application on the industrial scale is doubtful, since it is not clear under what conditions it will lead to additional recovery.

To understand this high salinity waterflooding (HSW) process in chalk reservoirs, an extensive research has been carried out covering a broad range of disciplines. Most of these works will be discussed, categorized by a studied parameter influencing the recovery.

2.1.1 Injected Fluids

Seawater injection studies for chalk reservoirs initially started with spontaneous imbibition studies of surfactant solutions in brines. Standnes et al. [33] reported improved spontaneous imbibition of water into neutral to preferential oil-wet chalk with application of cationic surfactants. Later Strand et al. [34] carried out a spontaneous imbibition study using cationic surfactants with chalk and dolomite cores, concentrating on the effect of brine salinity and composition. It was observed that spontaneous imbibition can be improved for chalk core plugs by sulfate addition to the imbibed fluid. Sulfate concentration had a much lesser effect on dolomite as compared to chalk, suggesting that sulfate somewhat reacted with chalk. It was also experimentally documented that sulfate ions can improve the oil recovery alone, without expensive surfactants [8, 35]. A significant additional increase in oil recovery was observed as the concentration of sulfate increased. Zhang et al. [36] studied symbiotic effects between sulfate and calcium ions, aiming at improvement of the oil recovery from chalk reservoirs. Increase of the oil recovery with the increase in calcium concentration in the imbibing brine was reported.

Among the divalent ions present in seawater, Mg^{2+} has a concentration twice higher than SO_4^{2-} ion concentration and four times higher than Ca^{2+} concentration. Hence, Zhang et al. [1] carried out spontaneous imbibition experiments to investigate the impact of Mg^{2+} ions on oil recovery. It was observed that Mg^{2+} without SO_4^{2-} resulted only in marginal extra oil recovery, but Mg^{2+} along with SO_4^{2-} resulted in a significant increase in oil recovery. Neither SO_4^{2-} nor Ca^{2+} alone was able to increase recovery under spontaneous imbibition. Thus, SO_4^{2-} must act together with either Ca^{2+} or Mg^{2+} to improve the oil recovery.

Karoussi et al. [31] investigated extreme cases of waterflooding of Stevns Klint core plugs with the ion-free water and water containing just Mg^{2+} or SO_4^{2-} ions. Water saturated with Mg^{2+} ions (without SO_4^{2-} and Ca^{2+} ions) showed the highest oil recovery in the spontaneous imbibition experiments.

Webb et al. [37] presented a comparative study of the oil recovery from a North Sea (Valhall) carbonate core sample with simulated SO_4^{2-} free brine (formation water) and with seawater containing SO_4^{2-} under reservoir conditions. The imbibition tests were performed with a core saturated by live oil. A clear improvement in oil recovery was observed with seawater in comparison to the formation water. Fjelde et al. [12] carried out spontaneous imbibition experiments using seawater and formation brine with core plugs from two fractured chalk fields at reservoir temperature. Only a small increase in oil recovery was observed with the seawater as compared to the formation brine (containing no SO_4^{2-}) for reservoir core plugs as compared to Stevns Klint outcrop chalk core plugs.

Fernø et al. [11] studied the effect of sulfate concentration on oil recovery during spontaneous imbibition in different outcrop chalks (Stevens Klint, Rørdal and Niobrara). Spontaneous imbibition tests showed increasing oil recovery with increased concentration of sulfate ions in Stevens Klint chalk core plugs, while this effect was not observed in Rørdal and Niobrara plugs. The effect of sulfate ions on oil recovery in Stevens Klint plugs was smaller in comparison to previously reported. This shows that effect from sulfates on spontaneous imbibition in chalk is dependent on chalk type (i.e rock mineral composition).

It is well known that produced water contains some low molecular weight aromatic hydrocarbons. The easiest way to prevent from polluting the seawater is to re-inject the produced water into the reservoir. Puntervold et al. [18] investigated the oil recovery potential using different mixtures of produced water and seawater by spontaneous imbibition. The oil recovery with different mixtures of produced water and seawater was significantly higher than under injection of the pure produced water.

Fathi et al. [9] observed that not only the concentrations of active ions (SO_4^{2-} , Ca^{2+} and Mg^{2+}) are important for improving the oil recovery, but the amount of NaCl could also have some impact on this process. Spontaneous imbibition experiments were carried out on the Stevens Klint chalk core plugs with seawater and seawater depleted in NaCl. Both the imbibition rate and oil recovery increased with seawater depleted in NaCl in comparison to seawater. A decrease in oil recovery was observed with the increase of the amount of NaCl in seawater.

Most recently, Fathi et al. [38] carried out spontaneous imbibition study using Stevens Klint core plugs to optimize the concentration of the active ions, especially SO_4^{2-} and Ca^{2+} . in the seawater depleted in NaCl. The ultimate oil recovery increased by 5-18 % of OOIP when the concentration of SO_4^{2-} increased four times in the seawater depleted in NaCl. The concentration of Ca^{2+} did not have a significant effect on oil recovery at 100 °C, but showed some improvements at 120 °C.

2.1.2 Temperature

Temperature is a critical parameter in most of the water based EOR studies in chalk reservoirs. Høgnesen et al. [39] carried out spontaneous imbibition experiments using Stevens Klint outcrop chalk core plugs at different temperatures (70, 90, 110 and 130 °C). The oil recovery increased with both the concentration of sulfate and temperature. The average oil recovery increased from 22 to 45%, when increasing the temperature from 90 to 130 °C.

Strand et al. [19] studied enhanced oil recovery from Stevens klint chalk core plugs using seawater, by both spontaneous imbibition and viscous flooding at 90, 110 and 120 °C. At the first temperature, no difference in oil recovery was observed in the spontaneous imbibition process with application of seawater and formation water (without any sulfate). However, during the forced flooding process, seawater increased oil recovery by 14% compared to formation water. At 110 and 120 °C, impact of seawater became even more significant.

Punternold et al. [18] performed both spontaneous imbibition and forced flooding experiments with chalk core plugs injecting various mixtures of seawater and produced water. At 50 and 70 °C, no discrimination in oil recovery was observed for different mixtures of seawater and produced water. At 90 °C, a small difference in the oil displacement potential for the different mixtures could be detected. The fluids containing sulfate ions appeared to give 5-10 % higher oil recovery compared to the produced water containing no sulfate. Seawater appeared to be much more efficient than produced water above 100 °C.

Fathi et al. [38] also observed great difference in oil recovery between different imbibing fluids (seawater, seawater depleted in NaCl, seawater depleted in NaCl spiked by sulfate) above 100 °C.

2.1.3 Recovery Mechanisms

Although a large body of experimental data exists on the effect of potential determining ions on oil recovery, there is still no general consensus regarding the mechanisms behind the observed effect.

Several experimental studies have been carried out on seawater flooding in chalk reservoirs by Austad and co-workers [1, 17, 20, 36, 39, 40]. Based on these experimental results, wettability alteration was proposed to be a key reason for the improvement of the oil recovery. A schematic model of the chemical mechanism for wettability modification was suggested. Figure 2.1 shows this schematic model.

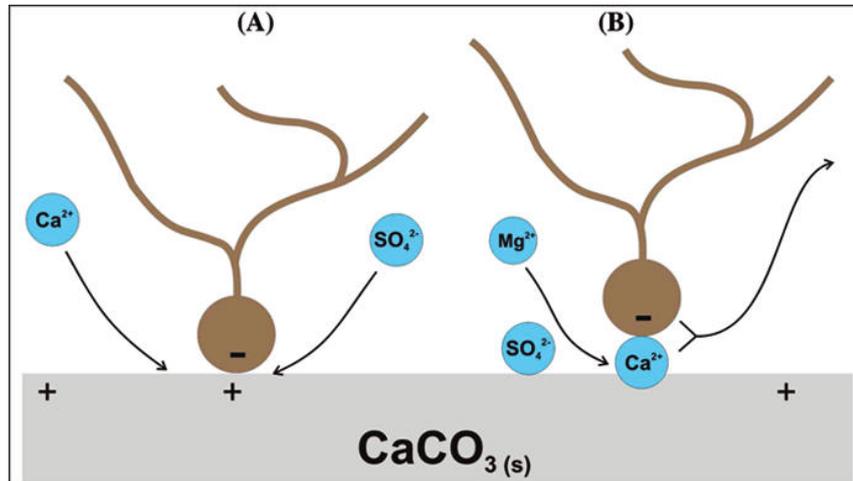


Figure 2.1: Schematic model of the wettability alteration induced by sea water. (A) Proposed mechanism when Ca^{2+} and SO_4^{2-} are active. (B) Proposed mechanism when Mg^{2+} and SO_4^{2-} are active [1].

According to this model, negatively charged carboxylic acid components of crude oil are adsorbed on positively charged chalk surface. When seawater is injected into the system, sulfate ions adsorb to the rock surface, which changes the surface charge, so that some of the adsorbed crude oil may be removed from the rock. Due to less electrostatic repulsion, calcium ions also approach the chalk surface and displace a little more crude oil by ion-binding. At high temperature ($> 90\text{-}100\text{ }^\circ\text{C}$), magnesium is also involved in the wettability alteration process. Experimental results have shown that magnesium substitutes calcium on the chalk surface when seawater is slowly flooded through an outcrop chalk core. Thus, magnesium may displace the calcium-carboxylate complex (Figure 2.1B).

Hiroth et al. [41] investigated how water chemistry affects surface charge and rock dissolution in a pure calcium carbonate rock. A chemical model is constructed that couples both bulk aqueous and surface chemistry to predict the surface potential of calcite and adsorption of sulfate ions from the pore water. It was shown that predicted temperature dependence of the surface charge does not follow the temperature dependence of oil recovery. It was concluded that surface potential changes (caused by injection water chemistry) are not able to explain the

observed changes in the oil recovery. Chalk dissolution appeared to be the controlling factor which can explain compaction and increase in oil recovery.

According to the above described schematic model of wettability modification, no potential determining ions (Ca^{2+} , Mg^{2+} and SO_4^{2-}) alone could increase the oil recovery. Karoussi et al. [31] reported that water saturated with Mg^{2+} ions (without SO_4^{2-} and Ca^{2+} ions) could also increase the oil recovery in the spontaneous imbibition experiments from chalk core plugs. Madland et al. [42] studied the effect of aqueous chemistry on the mechanical strength of chalk. Hydrostatic creep tests were carried out with continuous flooding of seawater, distilled water, NaCl and MgCl_2 . It was shown that the presence of only Mg^{2+} in the injected brine can deform the rock. Both these studies indicate that oil recovery increase could be governed by some other recovery mechanisms than wettability alteration.

2.1.1 Rock Material

Austad and co-workers performed several displacement experiments of oil by seawater from chalk rock samples [9, 36, 38]. Most of these studies were carried out with Stevens Klint outcrop chalk core plugs. A significant increase in oil recovery was observed with sulfate enriched brine flooded core plugs as compared to core flooded with brine without sulfate ions.

Fernø et al. [11] tested core plugs from three different quarries (Niobrara, Rørdal and Stevens Klint) and observed that effect of sulfate is dependent on the chalk type (i.e., rock mineral composition). Niobrara and Rørdal outcrop chalk core plugs, unlike Stevens Klint, showed no added effect from sulfate on oil recovery during spontaneous imbibition.

Fjelde et al. [12] carried out spontaneous imbibition experiments using seawater and formation brine with core plugs from two fractured chalk fields at reservoir temperature. Only a small increase in oil recovery was observed with the seawater as compared to the formation brine (containing no SO_4^{2-}) for reservoir core plugs as compared to Stevens Klint outcrop chalk core plugs.

Strand et al. [43] experimentally investigated the oil recovery potential of seawater flooding process for limestone core plugs. Previous spontaneous imbibition studies on chalk have revealed that the oil recovery improved when the concentration of SO_4^{2-} increased [8, 35]. But no additional increase in oil recovery from the limestone core was detected, when the concentration of SO_4^{2-} was increased 3 times the concentration in seawater.

2.1.2 Interfacial Tension

It has been established in the literature that surface forces play an active part in oil production. The magnitude of these forces is partly determined by the interfacial tension [44]. Zhang et al. [35] carried out IFT measurements between oil and brine (with different concentrations of SO_4^{2-}) at room temperature. It was observed that sulfate ions did not contribute to variation of the IFT. The effect of temperature on the IFT is not fully studied, but in most cases, the IFT between water/oil decreases with the increase in temperature [45].

2.2 Low Salinity Waterflooding (LSW) in Sandstone Reservoirs

The idea of LSW has been addressed since 1960s. Work [46] demonstrated that injection of fresh water can increase oil recovery from sandstone cores containing clay. Permeability reduction and the development of a relatively high pressure drop was also observed. This work could not get the attention of the oil industry. The pioneering work by Morrow and co-workers reported improved recovery of crude oil by LSW [23, 47]. Since then many laboratories and organizations have addressed the problems associated with identifying, reproducing and explaining the low-salinity effect (LSE). Successful field tests and field wide analysis also documented increase in oil recovery by injecting brine of low salinity [14, 25-27]. Many recent examples of increased in oil recovery by LSW also confirmed this emerging trend [15, 48]. In most of these studies, 15-20 % extra oil recovery from low salinity waterflooding is reported.

During the last ten years, there have been several papers and presentation at various conferences around the globe on LSW. Figure 2.2 shows number of published papers in the 15 years before 2010.

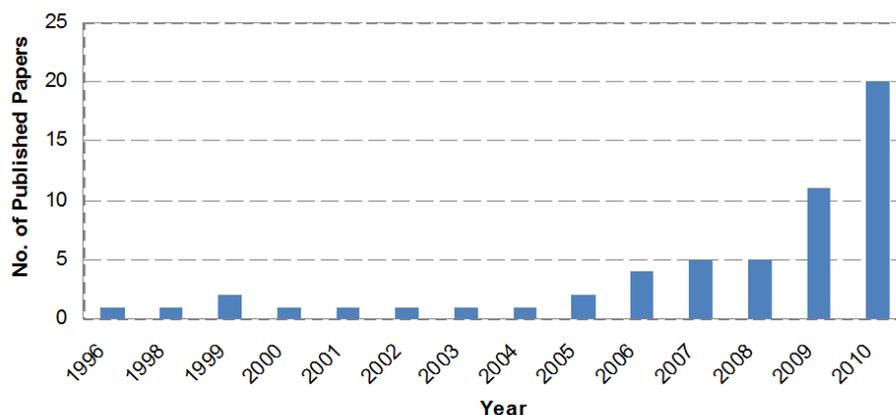


Figure 2.2: Number of paper published on LSW in last 15 years. Interest in LSW has increased as indicated by the number of publications and presentations focused on LSE. [49]

Various mechanisms responsible for improved oil recovery by LSW have been proposed. The purpose of this review is not to go into detail concerning the argumentation behind the suggested mechanisms, but rather give an overview of various proposed mechanisms and conditions for LSE.

2.2.1 Conditions for LSE

- Porous Medium
 - Significant clay fraction. A type of clay may also play a role [47].
- Oil
 - Oil must contain polar components. No effect was observed in experiments with refined oil [47].
- Water
 - Presence of formation water containing divalent cations (Ca^{2+} and Mg^{2+}) [13].
 - Injection low salinity fluid usually between 1000 and 2000 ppm (but some effect have been observed under salinity up to 5000 ppm) [47].
- Production/migration of fines
 - In some cases production of fines has been reported, although low salinity effects have also been reported without visible production of fines [13]. A commonly used technology tries avoiding fine production, in order to avoid formation damage.
- Permeability decrease
 - Usually an increase in pressure drop is observed but there is a lack of experimental evidence to say that LSE is always associated with permeability reduction [47].
- Temperature
 - There appears to be no temperature limitations [47].

2.2.2 LSE Mechanisms

Despite growing interest in LSE, still no consistent explanation has been emerged. This may be because of wide variation of rocks, crude oils and experimental conditions in the applied test procedures. Probably, LSE is a result of different mechanisms acting together. The different mechanisms found in the literature will be briefly described below.

Tang et al. [47] suggested that LSW could release clay particles that could improve the wettability of the clay minerals. These particles could also block pore throats and divert flow of water to non-swept zones to improve microscopic sweep efficiency. McGuire et al. [14] suggested that mechanism of action for LSW appears to be similar to that of alkaline flooding: in-situ generation of surfactants, changes in wettability and reduction in IFT. Lager et al. [13] proposed a multi ion exchange, (MIE) as a possible mechanism of LSW. It was speculated that

the presence of divalent cations (Ca^{2+} and Mg^{2+}) in formation water plays an important role in the interaction between clay minerals and surface active components of the crude oil. An adsorption model is suggested where Ca^{2+} ion acts a bridge between clay surface and carboxylic materials present in the crude oil. Cationic ion exchange at the clay surface may remove adsorbed crude oil. Doust et al. [28] introduced the two effects: salting-out (addition of salt into the solution drastically decreases solubility of organic materials in water) and salting-in (removal of salt increases solubility of organic materials in water). It was suggested that decrease in salinity below a critical ionic strength could desorb crude oil from the clay surface because of its increased solubility in water.

2.3 Low-salinity Waterflooding in Carbonate Reservoirs

LSW is well studied for sandstone reservoirs, both in the laboratory and field tests. Up to very recently, the LSE effect has not been detected for carbonates. Lager et al. [13] concluded that, unlike for sandstones with high clay content, LSW does not work for carbonate reservoirs, since they have a minimal amount of clay. Doust et al. [28] reported, however, that a different chemical mechanism may also be responsible for the effect: it is the crude oil adsorption onto the positively charged calcite surface and the negatively charged quartz surface.

Saudi Aramco showed, however, that substantial additional oil recovery can be achieved when successively flooding composite carbonate core plugs with various diluted versions of seawater [29]. The authors of this work pointed out that a mechanism for improved oil recovery was probably different from the reported in the previously published works.

Austad et al. [50] also reported a laboratory study showing LSE from core material sampled from the aqueous zone of a limestone reservoir. They observed 2-5 % increment in oil recovery by flooding the cores with diluted formation water or diluted seawater. The chemical mechanisms for LSE was reported to be similar to the wettability alteration taking place by HSW in carbonates.

The experimental data on carbonates is very limited, so more data plus mechanistic studies is needed to understand and utilize the low salinity flooding for carbonate reservoirs.

Paper I

Adeel Zahid, Erling H. Stenby and Alexander Shapiro:

Improved Oil Recovery in Chalk: Wettability Alteration or Something Else?

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Barcelona, Spain, 14-17 June, 2010.

Seawater Flooding in Chalk: Wettability Alteration or Something Else?

Abstract

Improved oil recovery from low permeable chalk reservoirs is regarded as a great challenge because of their complexity and heterogeneity. Historically seawater salinity has not been considered as an important factor in determining the amount of oil recovered. Over the last decade, a number of studies have shown that waterflooding performance is dependent on the composition of injecting brine solution. Extensive laboratory research has been carried out in order to understand improved oil recovery from chalk using surfactant solutions and later on using the modified sea water. The researchers suggested wettability alteration towards more water wetting conditions to be the reason for improvement in oil recovery.

In this paper, we are further investigating the reasons of observed improvement in oil recovery with sulfate ions. Is it really wettability alteration or something else also? Most of the previous work has been made on the basis of spontaneous imbibition using core plugs aged in crude oil. Our study is based on flooding and utilizes completely water wet cores without being aged in crude oil, just saturated with crude oil under vacuum. This would exclude alteration of wettability as a positive factor. Brine without sulfate is considered as the base injected fluid. Waterflooding experiments were carried out with brines without sulfate, as well as brines having different concentrations of sulfate. The effect of temperature, injection rate, crude oils and different sulfate concentration on the total oil recovery and the recovery rate was investigated.

In Stevens Klint outcrop chalk samples, 10% increase in oil recovery was observed with sulfate enriched brine flooded core as compared to core flooded with brine without sulfate ions. We observed also 4-6 % increment of OOIP using brine with sulfate for water wet chalk at high temperatures. This clearly indicates improvement in oil recovery without wettability alteration, because chalk is already water wet. No increment in oil recovery was observed at 40 °C and,

neither, in experiments with North Sea crude oil. This clearly explained that crude oil type also plays a significant role in the effect that brine composition has on waterflood oil recovery.

This study will help in getting more in depth understanding of seawater improved oil recovery process for chalk reservoirs.

3.1 Introduction

More than half of the world's remaining oil exists in carbonate (chalk and limestone) reservoirs [51]. They are characterized by rather low primary oil recovery; therefore, the improved oil recovery potential of these reservoirs is high. Many carbonate reservoirs are intermediate oil wet and very low permeable, so the improved oil recovery from such reservoirs is regarded as a great challenge.

Due to high EOR potential, many studies have been carried out to increase the oil recovery from such challenging reservoirs. Mohanty et al. [52] reported the lab imbibition studies with different anionic surfactants using aged outcrop limestone core plugs. They observed more than 50 % OOIP recovery. Wettability alteration was considered as an important contribution.

Hirasaki et al. [53] used an anionic surfactant in combination with sodium carbonate for enhancing oil recovery by spontaneous imbibition from oil wet carbonate rocks. They found the carbonate ion to be a potential determining ion at high pH. This reversed the charge of the rock surface and mitigated the problem of adsorption. The wettability alteration with alkaline surfactants from preferentially water-wet to intermediate water-wet range was claimed to be responsible for the observed improvement in oil recovery.

Xie et al. [54] observed that injection of the surfactant solutions can produce additional 5-10 % OOIP after the imbibition with brine solution has stopped. They described this additional oil recovery to the increased water wetness of the core plug. Although the surfactants have proven to increase the recovery, their application on reservoir scale is hampered by their high prices. Each reservoir requires a particular surfactant, for which specific production may not be advantageous for the chemical industry. On the contrary, waterflooding is a cheap secondary oil recovery process and is by far the most widely applied method for improving the oil recovery. Over the last decade, a number of studies have shown that waterflooding performance is dependent on the composition of the injected brine. Optimizing this composition has been developed into an emerging IOR technology for both sandstone and carbonate reservoirs.

Effect of brine composition on oil recovery by waterflooding was studied by Bagci et al. [55]. They tested NaCl, KCl and CaCl₂ brines. The highest oil recovery was observed for the 2wt% KCl brine. Without any further explanation, wettability alteration was mentioned as a reason for recovering more oil in this case.

Extensive laboratory research has been carried out by Austad and co-workers in order to understand improved oil recovery from chalk using surfactant solutions and later on using modified sea water [1, 8, 18, 20, 33]. They have observed SO₄²⁻ as a potential determining ion for improving the oil recovery in chalk reservoirs. This ion must act together with Ca²⁺ and Mg²⁺ because sulfate alone is not able to increase spontaneous imbibition. They proposed wettability alteration towards more water wetting conditions to be the only reason for improvement in oil recovery with these seawater ions. A chemical mechanism for wettability alteration was also studied.

Webb et al. [37] presented a comparative study of the oil recovery from a North Sea carbonate core sample with simulated SO₄²⁻ free brine and with seawater which contains SO₄²⁻ at reservoir conditions. The imbibition tests were performed with live oil. It was concluded that the wettability alteration of the carbonate rock with SO₄²⁻ ion is responsible for the saturation changes.

In spite of a large body of experimental work, many questions still remain unclear. In all the above discussed studies the core plugs were aged in crude oil, in order to make them oil wet. A conclusion about wettability alteration as a main mechanism for improving the oil recovery was achieved by exclusion of other reasons: miscibility, mobility control or significant reduction of the interfacial tension. This is by no means the proof. Without understanding why and how the recovery method works, its application on the industrial scale is doubtful, since it is not clear under what conditions it will lead to additional recovery.

In order to check the wettability alteration, the core plugs were aged in the crude oils with the different acid numbers or, alternatively, in the same crude oil, but for the different time periods. Such an approach has several shortcomings. It is very difficult to get a uniform wettability alteration along a core. Moreover, there is no established way to check its uniformity. The strength of the wettability alteration cannot be controlled. Especially in high temperature experiments, organic molecules of crude oil might be detached from the rock surface, resulting in returning to the original water-wet state.

In this study we try to obtain more precise answers on the following questions: Is the observed increment in oil recovery with sulfate ions caused only by the wettability alteration or there are other reasons? If some other factors are also involved then what could they be? Is the recovery increase caused by only sulfate-rock interactions and the corresponding wettability changes, or also by the sulfate-oil interactions?

In order to obtain these answers, we modified an experimental procedure. We used outcrop chalk core plugs, which, according to the literature, may be considered as completely water wet. No aging was carried out for a long time at high temperature. To the authors' knowledge, no one claimed the wettability alteration with the crude oil in just two hour at room temperature. Babadagli [56] saturated the cores for 24 hours with crude oils in vacuum and considered them as water wet cores. Thus, we performed the waterflooding experiments under the initially water-wet conditions. This would exclude alteration of wettability as a positive factor. We carried waterflooding instead of spontaneous imbibition, which was applied in the previous studies.

Our results show that the mechanisms of enhancing the oil recovery with the SO_4^{2-} containing brine are different from just a wettability alteration. The details are given below.

3.2 Experimental

3.2.1 Core Plugs

Most of the core plugs used for this study are from Stevns Klint outcrop chalk. The reason for selecting the outcrop chalk samples is that they are easily available allowing multiple displacement experiments under similar conditions. This outcrop chalk is of Maastrichtian age and has a large specific surface area of around $2\text{m}^2/\text{g}$, as determined by the nitrogen adsorption [57]. The chalk structure is open. The porosity is about 47-50% and permeability about 3-4 mD. Single pores may be larger than single grains but still have low permeability due to narrow pore throats. The core plugs are very homogenous regarding permeability and porosity, which makes them suitable for parametric studies.

The Stevns Klint core plugs were cut from the two blocks. Thirteen core plug samples from the first block were of 1 inch in diameter and of the length of around 7-8 cm. Two core plug samples from the second block were of 1.5 inch in diameter; the plugs were also of the lengths of 7-8 cm. Both batches of core plugs were provided by the Danish Geotechnical Institute (GEO). Most of the core plugs looked homogeneous. In order to confirm homogeneity, the X-

ray computer tomography (CT) scan analysis was performed on each core plug to evaluate the heterogeneity at the core scale and the absence of fissures.

3.2.2 Crude Oils

We used three natural crude oils from the three different parts of the world: North Sea crude oil; Latin American crude oil; and the crude oil from a Middle East field. No model oil was used in this study, since the goal was to provide more realistic fluid/fluid and fluid/rock interactions. Puntervold et al.[18] observed that natural and model oils behave differently under displacement.

Acid and base numbers of the crude oils were measured using Metrohm 702 SM Titrino by the methods developed by Fan and Buckley [58] (the modified versions of ASTM D2896 for the base titration and of ASTM D664 for acid number titration). Density, acid number, base number and viscosity of all the three crude oils are given in Table 3.1.

Table 3.1: Crude oil properties.

Crude Oils	Density @ 20 °C (g/cm ³)	Acid Number (mg KOH/g oil)	Base Number (mg KOH/g oil)	Asphaltene (%)	Viscosity (cp)
Latin America	0.85	0.16	0.56	3.43	24.41
North Sea	0.85	0.09	2.44	0.30	8.83
Middle East	0.84	0.09	0.64	1.09	10.53

3.2.3 Brine Solutions

The synthetic brine solutions were prepared by adding the different amounts of NaCl, NaHCO₃, KCl, MgCl₂·6H₂O, CaCl₂·2H₂O and Na₂SO₄ to the distilled water. The three different brine solutions were prepared: the first synthetic seawater without sulfate ions; the second one synthetic seawater; and the third with the sulfate concentration three times larger than the synthetic seawater. They will be denoted as SW0S, SW, and SW3S, correspondingly. The total dissolved solid for all the three brine solutions was made the same by adjusting the quantity of NaCl. The detailed composition for all three brine solutions is given in Table 3.2.

Table 3.2: Injected Brine Compositions.

Components	SW0S (mol/l)	SW (mol/l)	SW3S (mol/l)
Na ⁺	0.368	0.358	0.337
K ⁺	0.010	0.010	0.010
Mg ²⁺	0.045	0.045	0.045
Ca ²⁺	0.013	0.013	0.013
Cl ⁻	0.492	0.434	0.317
HCO ₃ ⁻	0.002	0.002	0.002
SO ₄ ²⁻	0.000	0.024	0.072
TDS (g/l)	33.39	33.39	33.39

3.2.4 Core Preparation

The drilled core plugs from both blocks were dried in the oven at 80 °C overnight. Then they were saturated, each with a different crude oil, for two hours in vacuum. The pore volume was calculated for each core by comparison of the weights of a dry and saturated core.

3.2.5 Flooding Experiment

The initially saturated core plugs without any further aging at high temperature were put into the Hassler core holder with a sleeve pressure of 30 bars. Flooding experiments were carried out using combinations of the different temperatures, injection rates, crude oils, core plugs and compositions of the injected brine. The concentration of calcium and magnesium was kept constant in all of these flooding tests to avoid uncontrolled concentration effect from these ions and, just, to study the effect of sulfate ions on the IOR process.

Experiments at 40 °C were carried out without any back pressure. The flooding tests at 90, 110 and 130 °C were carried out using a back pressure of 15 bars to avoid boiling of the liquids. The volume of produced oil was measured as a function of pore volumes injected. Core data with the flooding schemes and conditions for the different experiments are given in Table 3.3.

Table 3.3: Experimental Information of Core Flooding Tests.

Core Tests	PV (cm ³)	Saturating Oil	Injection Rate (PV/day)	Temperature (°C)	Remarks
1	17.19	Latin American	5	40	Injected Fluid: SW0S, SW
2	17.41	Latin American	5	40	Injected Fluid: SW0S, SW3S
3	17.75	Latin American	5	90	Injected Fluid: SW0S, SW
4	17.60	Latin American	5	90	Injected Fluid: SW0S, SW
5	17.62	Latin American	5	110	Injected Fluid: SW0S, SW
5	17.79	Latin American	5	110	Injected Fluid: SW
6	17.95	Latin American	5	110	Injected Fluid: SW3S
7	17.79	Latin American	1	130	Injected Fluid: SW0S, SW3S
8	17.62	Latin America	1	130	Injected Fluid: SW3S
9	16.15	North Sea	5	110	Injected Fluid: SW0S, SW
10	17.55	North Sea	5	110	Injected Fluid: SW3S
11	17.62	Middle East	5	110	Injected Fluid: SW0S, SW
12	18.19	Middle East	5	110	Injected Fluid: SW3S
13	36.99	Latin American	5	110	Injected Fluid: SW0S
14	39.86	Latin American	5	110	Injected Fluid: SW3S
15	17.19	Latin American	5	40	Injected Fluid: SW0S, SW

3.3 Results and Discussion

A preliminary flooding test was carried out at 40 °C using the plug fully saturated with the Latin American crude oil without any initial water presence, at water wetting condition. At first, brine without sulfate (denoted as SW0S) was injected with a rate of 5pv/day. After that, a brine solution (SW) with the sulfate concentration equal to that in seawater was injected at the same flowrate and for approximately the same time. As shown in Figure 3.1a, 63.98 % OOIP was recovered with SW0S injection and no significant increment in oil recovery was observed with SW injection. This is in accordance to our expectations, since previous studies have also observed that sulfate ions do not play a significant role in the oil displacement process at such a relatively low temperature.

The second test was carried out with the same settings except that brine SW3S which has three times higher sulfate concentration than seawater was injected after brine SW0S. Even for this case no significant increment in oil recovery was observed, as shown in Figure 3.1b. This made it clear that at low temperature under strongly water wet conditions the sulfate concentration does not influence the final recovery. Similar experimental observations were made previously in experiments under oil-wet conditions by Austad and coworkers.

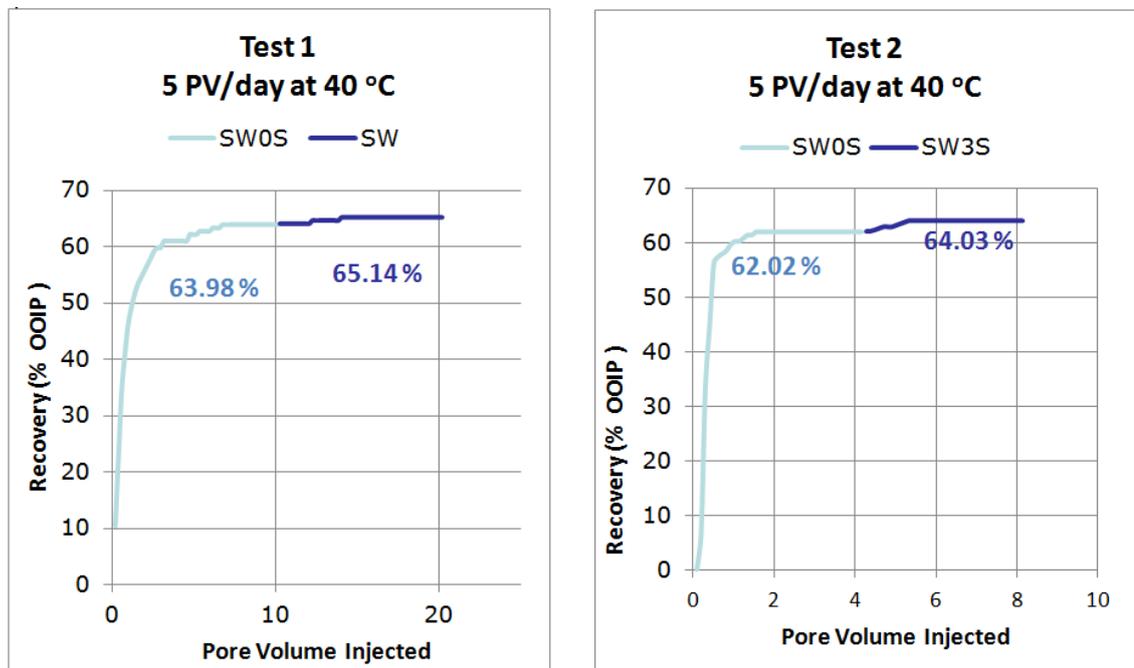


Figure 3.1: (a), (b) Oil recovery (% OOIP) as a function of pore volume injected (PV) for water wet core plugs saturated with Latin American crude oil @ 40 °C.

It has been documented that temperature plays a very important role for the different chemical reactions taking place at the chalk surface and also for the diffusion of potential

determining ions (SO_4^{2-} , Ca^{2+} and Mg^{2+}) into the chalk matrix [19]. To verify this effect on the recovery, a chalk core plug was flooded at 90 °C by injection of brines SWOS and SW. The injection flowrate was kept the same as in the previous experiment. The final oil recovery under injection of SWOS amounted to 60.28 %, as shown in Figure 3.2a.

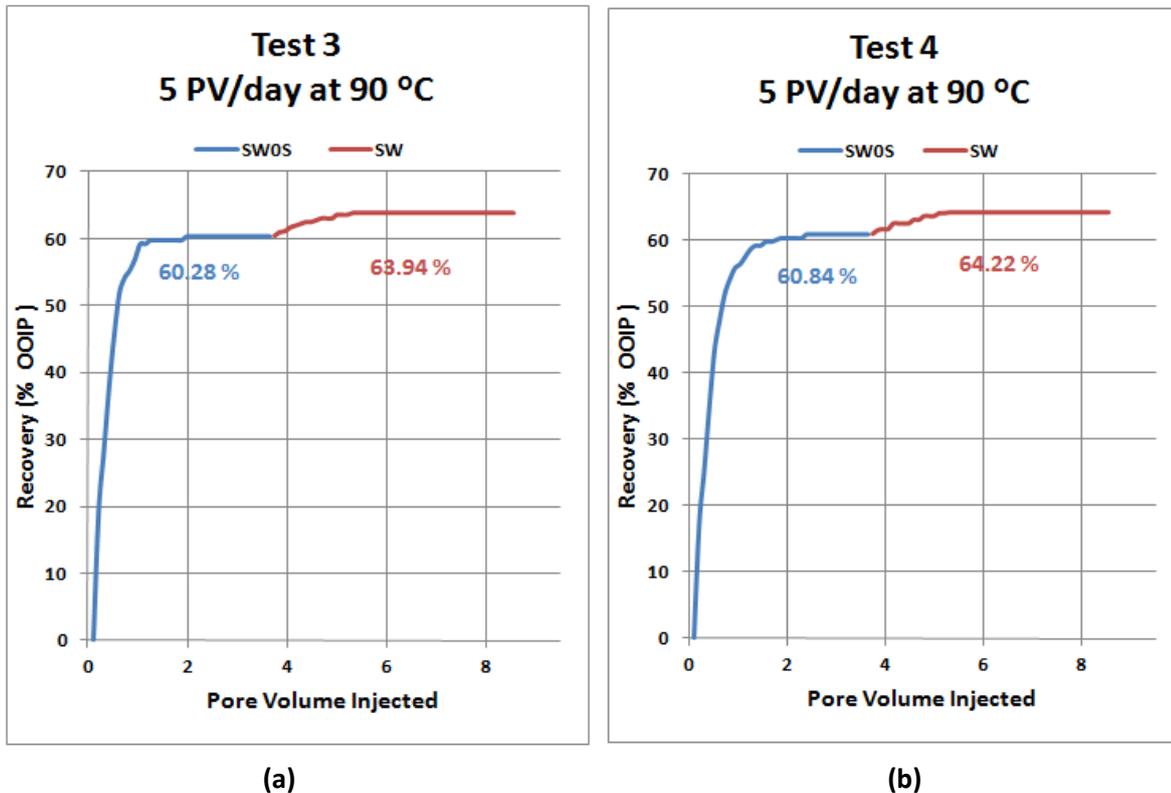


Figure 3.2: Figure 3.2 (a), (b) Oil recovery (% OOIP) as a function of pore volume injected (PV) for water wet core plugs saturated with Latin American crude oil @ 90 °C.

Exchanging the injected fluid from SWOS to SW increased the recovery by about 3.7 %. This noticeable additional increase in oil recovery at strongly water wet conditions gives an indication that there are other factors, apart from wettability, that contribute to recovery. In order to verify this conclusion, the test was repeated twice. Figure 3.2b shows that the results were very close, and the same increase of recovery was observed.

The affinity of SO_4^{2-} towards the chalk surface increases drastically with the temperature. The highest affinity is observed at temperatures over 100°C [40]. Another study also reported that success of seawater injection is greater above 100 °C [18]. Successful injection of seawater in Ekofisk formation also confirms this conclusion [8]. In order to verify it, flooding tests were conducted at high temperature, 110 °C. The three different core plugs from the same block were saturated with the Latin American crude oil. The first plug was flooded with the brine SWOS, the second with SW, and the last with SW3S, correspondingly. The total oil recovery and the recovery rates for the three tests are shown in Figure 3.3b.

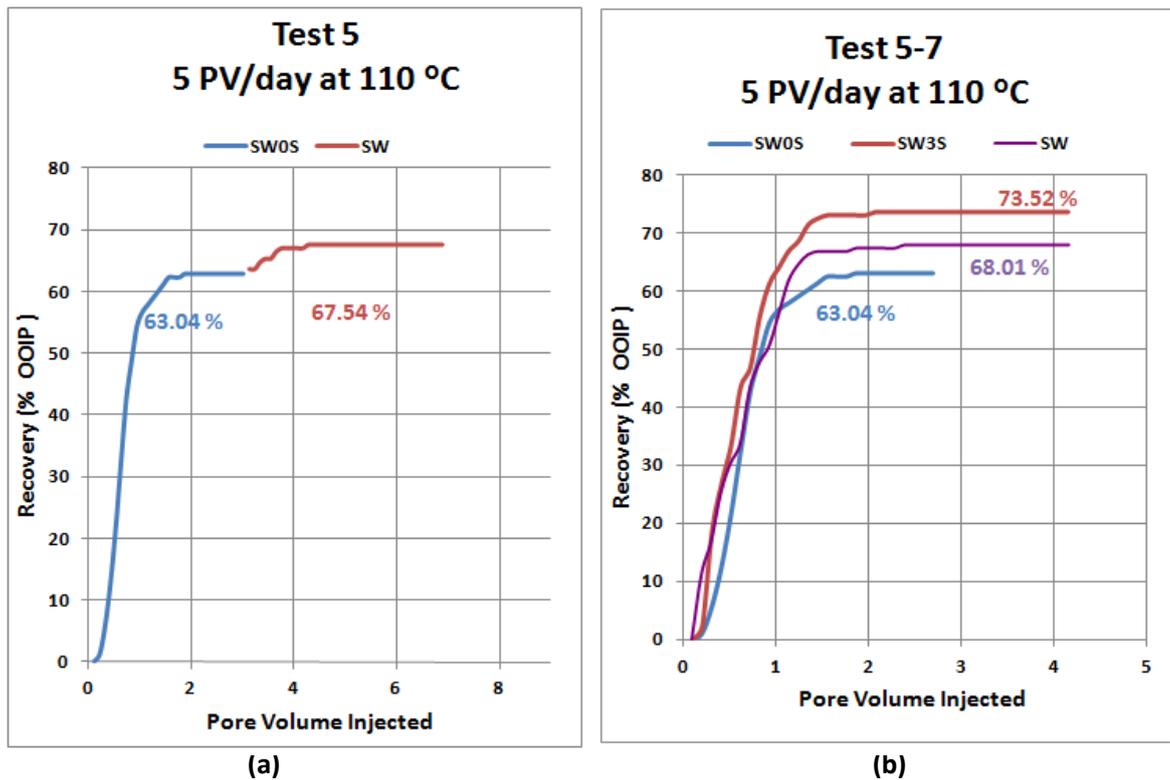


Figure 3.3: (a), (b) Oil recovery (% OOIP) as a function of pore volume injected (PV) for water wet core plugs saturated with Latin American crude oil @ 110 °C.

There is a clear difference in the total oil recovery and also in the recovery rates for the different sulfate concentrations. For brine SW3S injection, the highest oil recovery is 73.52%, while for SW and SW0S it is 68.01% and 63.04%, respectively. Thus, at such water wetting conditions there is a 10% higher oil recovery for the sulfate rich brine as compared to the brine solution with no sulfate. These results indicate presence of other physical mechanisms in increasing the oil recovery than just wettability alteration. The first core was also flooded with SW also after SW0S (Figure 3.3a). We can see 4.5 % increment in oil recovery in this case. This number is similar to the incremental recovery for the SW flooding from very beginning (5%); the minor difference is probably explained by the fact that the different core plugs were taken for the two experiments.

In order to make sure that enough time had been allowed for different potential determining ions to interact with chalk matrix, the two core flooding tests were carried out at relatively slow injection rates of about 1 pv/day. The tests were performed with the Latin American saturated crude oil cores at 130°C. The first core plug was flooded with the brine SW0S and SW3S in sequence, and second one was flooded with SW3S from the start. Total oil recovery and recovery rates for both of these cases are shown in Figures 3.4a and 3.4b.

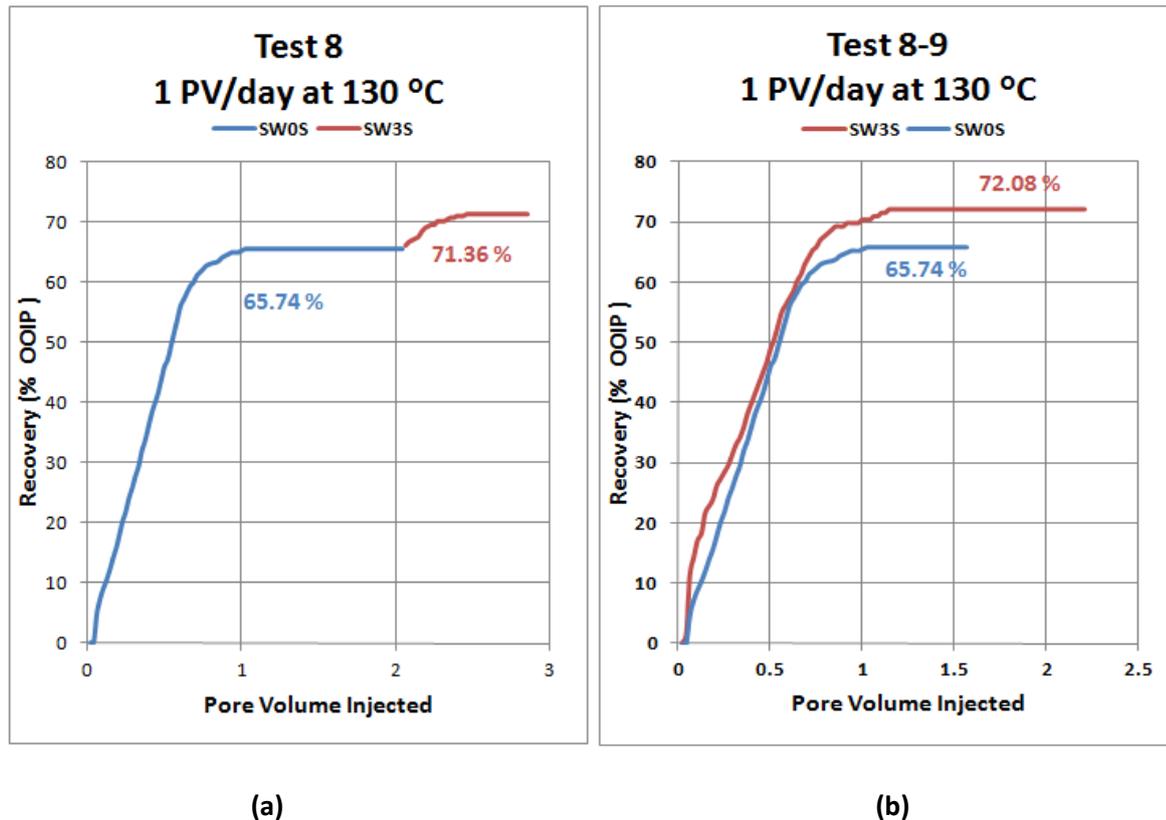


Figure 3.4: (a), (b) Oil recovery (% OOIP) as a function of pore volume injected (PV) for water wet core plugs saturated with Latin American crude oil @ 130 °C.

Around 6 % incremental recovery was obtained in both cases for SW3S compared to SW0S. A slower injection rate produced 4 % less amount of oil comparing to the oil produced with 5 pv/day. Results indicate that 5 pv/day is more optimized injection rate in terms of total oil recovery. During one day of the experiment one could expect partial alteration of wettability in the core. If so, the present experiment shows that this wettability alteration is a factor hindering the recovery (6 % instead of 10 % in the previous experiment). Moreover, such a wettability alteration probably cannot be successfully overcome by brine enrichment by sulfate. However, these conclusions need further experimental verification.

Most of the previous studies focused on brine/rock, rather than brine/oil interactions. In order to verify the effect of the oil composition, four parallel tests were carried out with the two crude oils at 110°C. In first two tests, cores were saturated with the North Sea crude oil. The first core was flooded with the brines SW0S and SW3S in sequence, while the second core by SW3S from the start. For the first flood, only 1 % incremental recovery was observed, but for second case the recovery was 8 % higher (see Figures 3.5a and 3.5b).

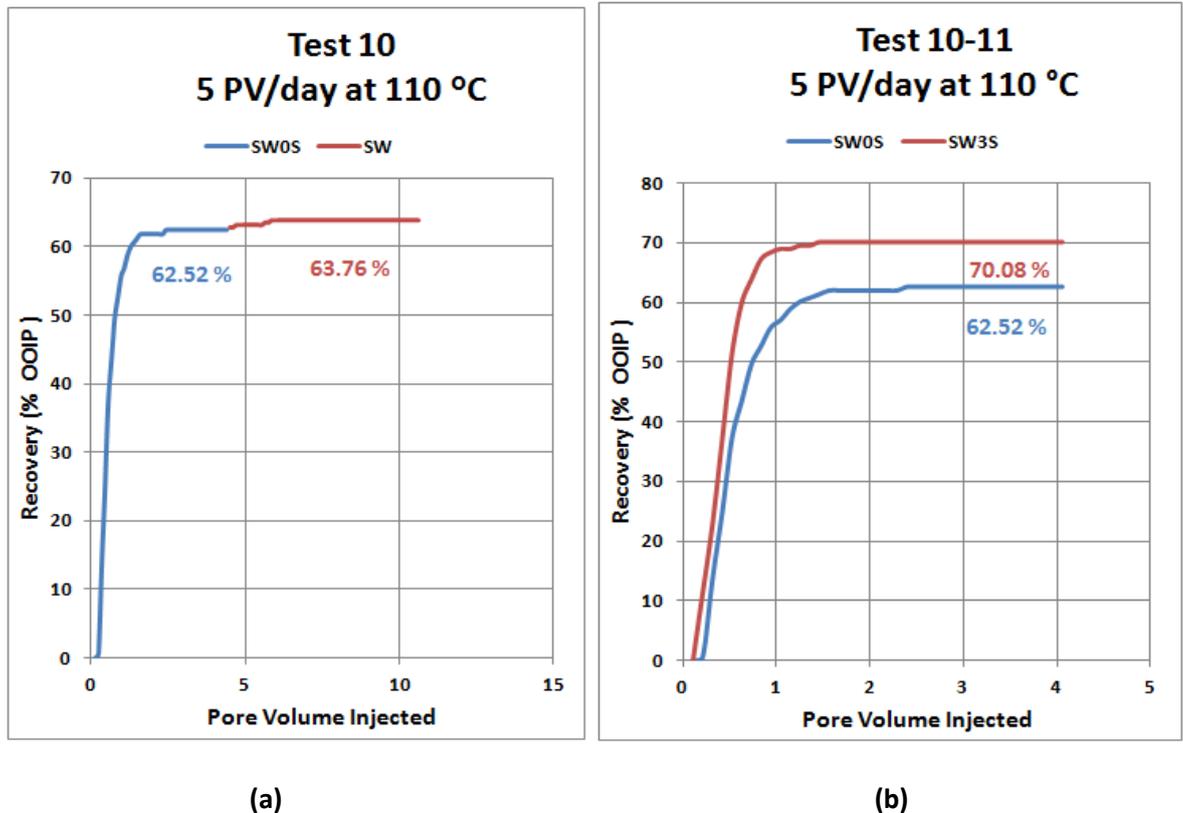


Figure 3.5: (a), (b) Oil recovery (% OOIP) as a function of pore volume injected (PV) for water wet core plugs saturated with North Sea crude oil @ 110 °C.

In the next two tests, cores were saturated with Middle East crude oil and the same experimental sequence was repeated. For the two cores which were saturated in Middle East, around 3 % oil recovery increment was observed with SW3S after the SW0S injection, and approximately 7 % higher oil recovery was observed when SW3S was injected from the start (Figures 3.6a and 3.6b). The results indicate that a more successful recovery strategy is flooding by the high-concentrated solution from the start. The second important conclusion is that the oil composition significantly affects the recovery.

All the above tests were carried out with 1 inch core plugs. Two more tests were carried out with the Stevns Klint core plugs of 1.5 inch in diameter at 110°C. The cores were saturated with the Latin American crude oil. In the first test the core was flooded with SW0S, and in second test with SW3S. The oil recovery curves are shown in Figure 3.7. For these larger cores, injection of SW3S results in approximately 6 % higher oil recovery, compared to SW0S flood.

This experimental study has indicated that even under complete water wettability conditions presence of the sulfate ions in the injected brine may increase oil recovery. The factors

contributing to the recovery are also oil composition and temperature. Further experimental studies are required in order to find out, what physical mechanisms (emulsification of oil, dissolution of rock, adsorption of salt etc.) determine the recovery increment.

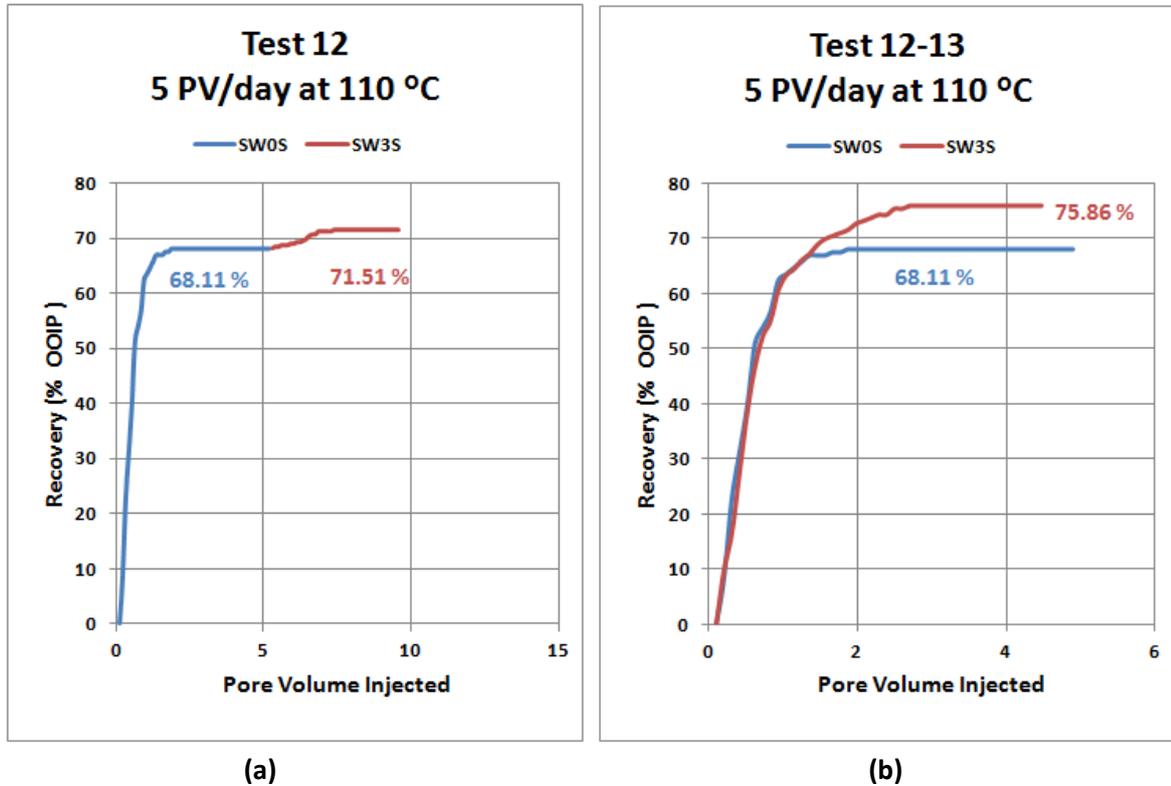


Figure 3.6: (a), (b) Oil recovery (% OOIP) as a function of pore volume injected (PV) for water wet core plugs saturated with Middle East crude oil @ 110 °C.

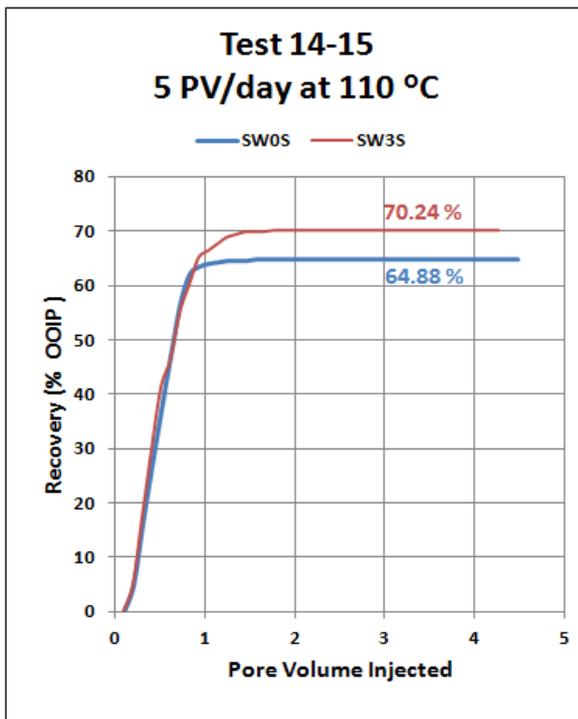


Figure 3.7: Oil recovery (% OOIP) as a function of pore volume injected (PV) for water wet core plugs (1.5 inch diameter) saturated with Latin American crude oil @ 110 °C.

3.4 Conclusions

The main conclusions of this work are

1. Increment in oil recovery with sulfate ions cannot be explained just by the rock wettability alteration. Injection of sulfate rich brine may lead to additional recovery even under completely water wet conditions.
2. The oil recovery depends upon the sulfate concentration and increases as the sulfate concentration increases.
3. Effectiveness of sulfates increases with increase of the temperature.
4. Crude oil composition type plays a dominant role in the effect that brine composition has on recovery.
5. Order of injecting fluids also affects the recovery.

3.5 Acknowledgement

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Paper II

Zahid, A.; Sandersen, S.B; Stenby, E. H.; Solms, N.V. and Shapiro, A. A.

Advanced Waterflooding in Chalk Reservoirs: Understanding of Underlying Mechanisms

Colloids and Surfaces A: Physicochemical and Engineering Aspects, 389 (2011) 281– 290.

Seawater Flooding in Chalk Reservoirs: Crude Oil/Brine Interactions

Abstract

Over the last decade, a number of studies have shown SO_4^{2-} , Ca^{2+} and Mg^{2+} to be potential determining ions, which may be added to the injected brine for improving oil recovery during waterflooding in chalk reservoirs. However the understanding of the mechanism leading to an increase in oil recovery is still not clear. In this work the crude oil/seawater ions interaction at different temperatures, pressures and sulfate ion concentrations is investigated. Our results show that sulfate ions may help decrease the crude oil viscosity when brine is contacted with oil under high temperature and pressure. We have also observed formation of an emulsion phase between brine and oil with the increase in sulfate ion concentration at high temperature and pressure. In addition, sulfate ions can reduce interfacial tension (IFT) between oil and water. We propose that the decrease in viscosity and formation of an emulsion phase could be the possible reasons for the observed increase in oil recovery with sulfate ions at high temperature in chalk reservoirs besides the mechanism of the rock wettability alteration, which has been reported in most previous studies.

4.1 Introduction

More than half of the world's oil is found in carbonate formations (chalk and limestone)[2]. Due to the potential for enhanced oil recovery (EOR), different techniques have been applied in order to improve oil recovery from carbonate formations. During the last decade, injection of brines with high salinity has been developed into an emerging EOR technology for chalk reservoirs that does not require toxic or expensive chemicals [1, 12, 30, 31, 59, 60]. Although it is widely accepted that high salinity brine may increase the oil recovery for chalk reservoirs [1, 30, 31], understanding of the mechanism of this increase is still developing. To understand this advanced waterflooding process, an extensive research program has been carried out covering a broad range of disciplines within colloid and surface chemistry, the thermodynamics of crude oil and brine, as well as their behavior in porous media.

The major focus of the research has been core flow and imbibition experiments. Bagci et al. [61] studied the effect of brine composition on oil recovery by waterflooding and tested injection of NaCl, KCl, CaCl₂ and mixed brines such as 2 wt% KCl + 2 wt% NaCl and 2 wt% KCl + 5 wt% CaCl₂. The highest oil recovery was observed for 2 wt% KCl brine. Extensive laboratory research was carried out by Austad and co-workers in order to understand improved oil recovery from chalk using modified sea water [1, 18, 20, 59, 62]. It was reported that SO₄²⁻ is a potential determining ion for improving oil recovery in chalk reservoirs. This ion must act together with Ca²⁺ and Mg²⁺ because sulfate alone is not able to increase the spontaneous imbibition. In all the presented cases, wettability alteration was proposed as a reason for improved oil recovery.

Zeta potential, contact angle and interfacial tension (IFT) measurements were also carried out with brine solutions of different Ca²⁺, SO₄²⁻ and Mg²⁺ ion concentrations. Strand et al. [59] carried out zeta potential measurements on mild Stevns Klint chalk suspended in brine solutions of different ionic ratios of Ca²⁺ and SO₄²⁻. It was reported that surface charge is dictated by the relative concentration of Ca²⁺ and SO₄²⁻. Gomari et al. [63] performed zeta potential measurements with calcite powder. Zeta potential is decreased from +15.03 to +1.23 mV for the sodium sulfate solution and is increased from +15.03 to 17.7 mV in case of magnesium chloride solution. This also documented the affinity of these ions towards the calcite surface. Tweheyo et al. [60] and Gomari et al. [63] carried out contact angle measurements on calcite surface modified with oil and then exposed to brines of different compositions at different temperatures. It was observed that Ca²⁺, SO₄²⁻ and Mg²⁺ are potential determining ions and these ions become more effective as temperature increases. It has been established in the literature that surface forces play an active part in oil production. The magnitude of these forces is partly determined by the interfacial tension value [44]. Zhang et al. [35] carried out IFT measurements between oil and brine (with different concentration of SO₄²⁻) at room temperature. It was observed that sulfate ions did not contribute to decreasing the IFT.

Most of above reported experimental work has been carried out using crude oil/brine/rock or brine/rock systems. The main conclusion from this extensive work was that it is the affinity of potential determining ions for the chalk surface which increases with temperature, and that this helps to improve oil recovery. However, this conclusion has not been confirmed by studies of the oil/brine interactions, which might also be contributing to recovery increase. In the study presented here we demonstrate that these interactions may also be partly responsible for the increase in oil recovery.

We have studied crude oil/ brine interactions at room temperature in normal glassware and also in a DBR JEFRI PVT cell at the different temperatures and pressures. Three crude oils have been used for the study. Detailed measurements of density, viscosity and water content before and after the experiment are presented. We also carried out IFT measurements at room temperature. The details are given below.

4.2 Experimental

4.2.1 Crude Oil

The same three crude oils, the Latin American crude oil, the middle east crude oil and the north sea crude oil, reported on previously in Table 3.1, were also used in this study.

4.2.2 Brine Solutions

The synthetic brine solutions were prepared by adding different amounts of NaCl, NaHCO₃, KCl, MgCl₂.6H₂O, CaCl₂.2H₂O and Na₂SO₄ to the distilled water. Seven brine solutions with different sulfate concentrations were prepared. The first brine solution is synthetic seawater without sulfate ions (SW0S); the second solution is synthetic seawater with normal sulfate ions (SW). The detailed composition and names of all seven brine solutions is given in Table 4.1.

Table 4.1 Different Brine Compositions.

Component	SW0S (mol/l)	SW0.5S (mol/l)	SW (mol/l)	SW1.5S (mol/l)	SW2S (mol/l)	SW2.5S (mol/l)	SW3S (mol/l)
Na ⁺	0.368	0.363	0.358	0.353	0.348	0.343	0.337
K ⁺	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Mg ²⁺	0.045	0.045	0.045	0.045	0.045	0.045	0.045
Ca ²⁺	0.013	0.013	0.013	0.013	0.013	0.013	0.013
Cl ⁻	0.492	0.463	0.434	0.405	0.376	0.347	0.317
HCO ₃ ⁻	0.002	0.002	0.002	0.002	0.002	0.002	0.002
SO ₄ ²⁻	0.000	0.012	0.024	0.036	0.048	0.060	0.072
TDS (g/l)	33.39	33.39	33.39	33.39	33.39	33.39	33.39

In this Table, various brines are termed as SWXS. The notation X represents relative concentration of sulfate ions related to SW (so for example SW2.5S was brine containing 2.5 times more sulfate than SW). The total dissolved solids for all the brine solutions was made the

same by adjusting the quantity of NaCl. All the brine chemicals were delivered by Fluka and have a purity of > 99.5%.

pH measurements of the brine solutions were carried out before and after the experiment in the PVT cell. The radiometer analytical 'Red Rod' combined pH electrode was used to measure pH.

4.2.3 Crude Oil/Brine Interaction Experiment at Room Temperature

The initial experiments were carried out at room temperature and atmospheric pressure. All three crude oils with five different synthetic brine solutions were used for this part of the study. The crude oils were mixed with the brine solutions such that each system consisted of 20 vol% (2 ml) of crude oil and 80 vol% (8 ml) of brine placed in a small sample bottle. The mixtures were thoroughly stirred at 1000 rpm for 15 minutes in a centrifuge. Afterwards the samples were left for two to three hours, until the crude oil and the brine solution separated. After equilibration, the system spontaneously divided into two phases; the oil phase on the top and the water phase on the bottom.

All five systems were photographed. The formation of emulsions was determined by visual observation of the interface between the crude oil and the brine. The mixtures after separation are shown in Figure 4.1. The viscosity and density of the crude oil were measured again after separation of the mixtures.

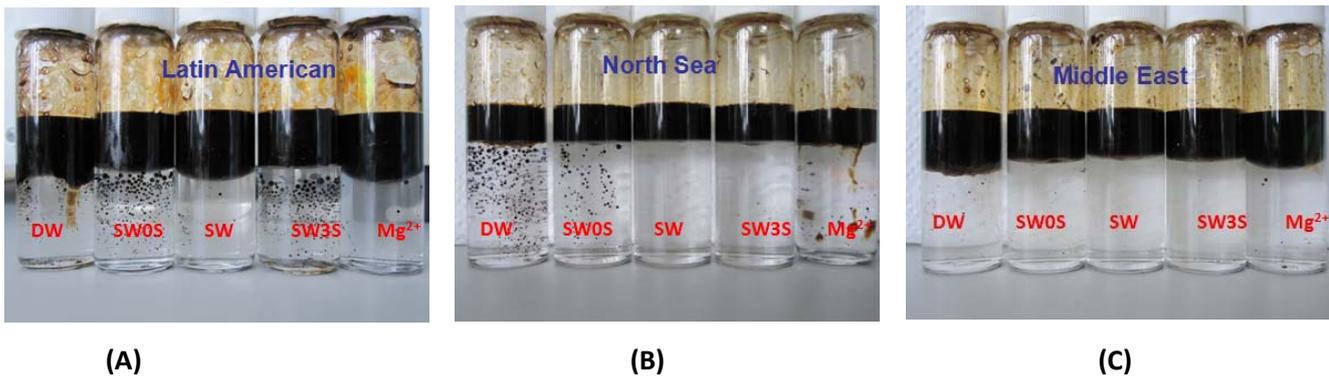


Figure 4.1: Different crude oils and brine samples after stirring them @ 1000 rpm for 15 minutes at room temperature. The sample bottles are filled with crude oil and brine solution and have been equilibrating for two to three hours. In each picture; A, B and C, the same crude oil is mixed with different brine solutions and after equilibration the sample bottles are compared to define if any phase behavior has changed simply due to the content of the brine solutions.

4.2.4 Crude Oil/Brine Interaction in DBR PVT JEFRI Cell

The high pressure experimental measurements were carried out in a DBR JEFRI PVT cell (model: JEFRI PVT 150-155 from D B Robinson), which is shown in detail in Figure 4.2. This is a high pressure cell allowing measurements for up to 700 bar and 180 °C. The DBR JEFRI PVT cell has been used in a variety of applications such as solubilities of supercritical fluids, VLE studies with gas condensates mixed with brine and other conventional PVT analysis of gas condensates and black oils[64, 65].

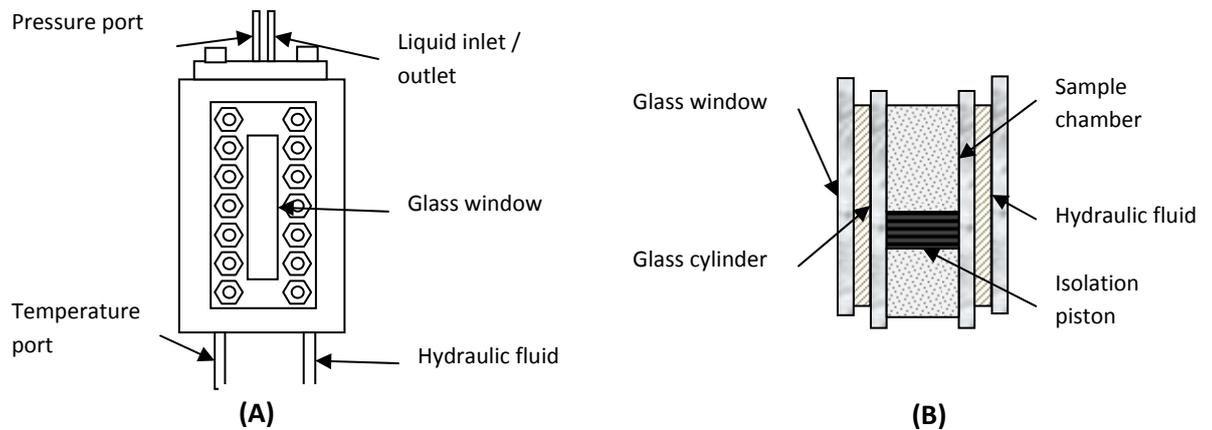


Figure 4.2: Experimental setup of the DBR JEFRI PVT cell. (A) is a sketch of the cell from the outside and (B) is a segment illustrating the construction of the cell from the inside.

The main body of the DBR JEFRI PVT cell consists of a glass cylinder appropriate for measurements at high pressures and temperatures. The glass cylinder is 20.3 cm long and has an internal diameter of 3.2 cm, which gives a total working volume of 163 cm³ inside the sample chamber. However, it is not recommended to use the full capacity of the working volume because there must be some room for expansion and compression of the sample. The cylinder is located inside a steel shell with vertical glass plates, which makes possible visual observations of the glass cylinder. An ISCO displacement pump is used to control the pressure inside the sample chamber via a floating isolation piston, which ensures that the pressure will remain constant. The entire PVT cell is installed on a rocking mechanism inside a temperature controlled forced air oven in the so-called air bath. The arrangement of the entire JEFRI cell in its rocking mechanism and inside the oven is shown in Figure 4.3. The rocking mechanism is used to ensure thorough mixing of the samples in the glass cylinder. The temperature is read from a digital display mounted on the PVT cell and is measured with a PC100 with an accuracy of ± 0.3 °C.



Figure 4.3: Picture of the DBR JEFRI PVT cell. This is high pressure equipment for phase behavior measurements at various temperatures and pressures. The surrounding steel is the inside of the temperature controlled forced air oven. The cell is monitored on a rocking mechanism suitable for mixing the systems inside the glass chamber. In the middle the glass window is seen which allows visual observations.

In each experiment the water-oil ratio (WOR) is kept constant. Each system consists of 30 vol% crude oil (15 ml) and 70 vol% brine solution (35 ml). During the operation, the system is exposed to the following temperature and pressure conditions: (a) 37 °C, 15 bar (b) 37 °C, 300 bar (c) 110 °C, 15 bar (d) 110 °C, 300 bar. When the PVT cell is loaded with the desired system, the rocking mechanism is activated for 30 minutes and thereafter the system is left to equilibrate for 30 minutes to 2 hours depending on the conditions. The equilibration period is recorded with video camera in order to evaluate the equilibration for different systems and to have pictures of the equilibrated system. Finally the heights of the phases inside the PVT cell were measured through the observation window using a micrometer from 'Precision Tools & Instrument C° LTD, Surrey, England'. Phase volumes were calculated from the measured heights of the phases and the known internal diameter of the cell. The interface between the oil phase and the brine phase was thoroughly studied for every test case to see if any emulsion phase is formed at the interface.

We used the Latin American and the Middle East crude oils for this part of the study where they were tested with the different brine solutions. The properties of the crude oils are presented in Table 1.

4.2.5 Viscosity Measurement

We measured the viscosity of the crude oil using an AMV-200 Automated Microviscometer. The viscometer operates on the rolling ball principle, according to which a ball is introduced into an inclined, sample-filled capillary. The time it takes for the ball to roll a fixed distance is measured and from this viscosity is calculated. After all the experiments were completed – both those in normal glassware at ambient conditions and those at higher temperature and pressure in the JEFRI cell - the oil samples were transferred from the cell into a sample bottle. The sample was left overnight to ensure complete separation of crude oil and water. Then approximately 3 ml of oil sample from the middle of the oil phase was used for viscosity measurements, as shown in Figure 4.4.

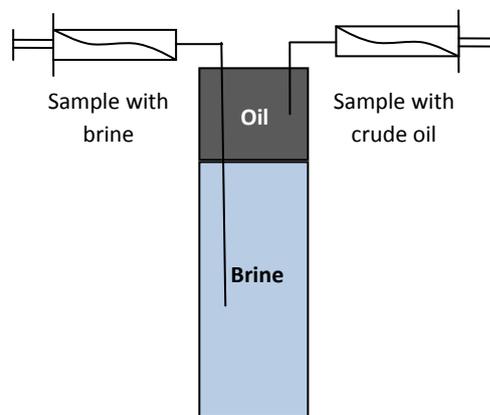


Figure 4.4: Illustration of how crude oil and brine samples are extracted for further viscosity examination.

4.2.6 Water Content Measurement in Crude Oil

We also measured the water content in the crude oil before and after the experiments in the JEFRI cell by the coulometric Karl Fisher (KF) titration method. A Metrohm 756 KF coulometer was used for this. Several reactions take place during titration of a sample. They can be summed up by the following overall reaction equation:



In the coulometric KF titration, the iodine needed is generated directly in the electrolyte by electrochemical means (electronic burette). The end point is indicated voltametrically by applying an alternating current of constant strength to a double platinum electrode. The reagent used for the titration is HYDRANAL-Coulmat AG from Fluka which is filled into the titration vessel. We also added 20 % toluene to the reagent to avoid contamination of the cell and electrode. This method is described in API Manual of Petroleum Measurement Standards (MPMS) chapter 10.9 and in ASTM D 4928.

The coulometer was calibrated by measuring the water content of a water standard Hydranal 34847 delivered by Riedel-de Haen after which the water content in the crude oil samples was measured. The measurements were repeated 2-3 times to confirm the repeatability of the results.

4.2.7 Interfacial Tension Measurement

Interfacial tension (IFT) was measured using a pendant drop method. This was conducted with a Data Physics OCA20 pendant drop apparatus, with a small drop of oil formed upwards at the tip of a stainless steel needle immersed in aqueous brine. IFT was calculated from the shape of the drop by fitting to the Young-Laplace equation. To get reliable results with the pendant drop method, a stable drop should be formed. For this, we used a needle of 0.63 mm diameter. IFT measurements were carried out only for the fresh Latin American crude oil and at ambient conditions.

4.3 Results

The effect of oil/brine interaction may be compared, to some extent, to the effects arising from surfactant/oil/brine systems characteristic of surfactant flooding. It is known that such systems are sensitive to salinity and temperature [66]. Our work indicates that similar effects are observed for selected crude oil/brine systems. Surfactants create emulsions, which reduce the interfacial tensions to ultra-low values. In this work it is examined whether emulsions are present in certain crude oil/brines systems. The effect of significant viscosity reduction of oil in contact with particular brine is also observed but this strongly depends on the thermodynamic conditions, as well as on the brine and oil compositions.

4.3.1 Room Temperature Crude Oil/Brine Study

A preliminary de-emulsification test was carried out initially with the Latin American crude oil and different brine solutions at room temperature. As shown in Figure 4.1a, in some of the sample bottles (SW0S and SW3S), dispersion of crude oil droplets in the brine solution is observed, while in other bottles formation of emulsions is observed and some crude oil is suspended in the brine solution. This emulsion formation is more noticeable in distilled water and in the brine saturated by Mg^{2+} ions. This indicates that salinity affects the emulsion formation, but no clear trend is observed at this stage. As some of the crude oil components may dissolve in the brine solution, the density and viscosity of the crude oil was measured before and after stirring in the sample bottle with different brine solutions. Table 4.3 provides the density and viscosity of the crude oils for the different tests. No significant change in viscosity and density of the crude oil was observed.

In the next stage, the two other crude oils were studied. Figure 4.1b shows the result of the mixing tests for the North Sea crude oil and Figure 4.1c for the Middle East crude oil. In the case of the North Sea crude oil, no formation of emulsion was observed, although there is some dispersion of crude oil in the distilled water (DW) and in the SW0S brine. In the case of the Middle East crude oil, dispersion of the crude oil in the brine was not observed in any of the experiments. However, more noticeable emulsion formation is observed for DW and for the brine saturated with Mg^{2+} ions. No significant change in viscosity and density was observed for either of the crude oils after contacting with brine solutions, as presented in Table 4.2.

Table 4.2: Density and Viscosity Data of Three Crude Oils after Interacting with Brine Solutions at Room Temperature.

Brine	Latin American		North Sea		Middle East	
	Viscosity (cp)	Density (g/cm^3)	Viscosity (cp)	Density (g/cm^3)	Viscosity (cp)	Density (g/cm^3)
Only Oil	24.4	0.877	13.5	0.845	12.7	0.865
DW	-	-	13.5	0.846	13.3	0.865
SW0S	24.4	0.897	13.9	0.847	12.6	0.866
SW	22.2	0.901	14.0	0.848	12.9	0.866
SW3S	24.2	0.894	14.1	0.848	13.2	0.884
0.1 M $MgCl_2$	24.7	0.890	13.1	0.849	13.9	0.866

With respect to emulsion formation, both the Middle East and the Latin American crude oil behave in the same way, i.e. both show more noticeable emulsion formation with the DW and with the brine solution saturated by Mg^{2+} ions. The potential determining ions, especially the sulfate ions, did not help to de-emulsify the crude oil at room temperature, for any of the three crudes.

4.3.2 DBR JEFRI Cell Crude Oil/Brine Study

A preliminary test was carried out with the Latin American crude oil and DW as a base case. After loading the samples in the cell, the liquid-liquid system was rocked and then left to equilibrate. After that phase volumes were measured and photographs were taken at every temperature and pressure condition. More experiments were carried out for the same crude oil with other brine solutions in a similar way. The photographs taken of the various crude oil and brine systems are shown in Figures 4.5, 4.6, 4.7 and 4.8.

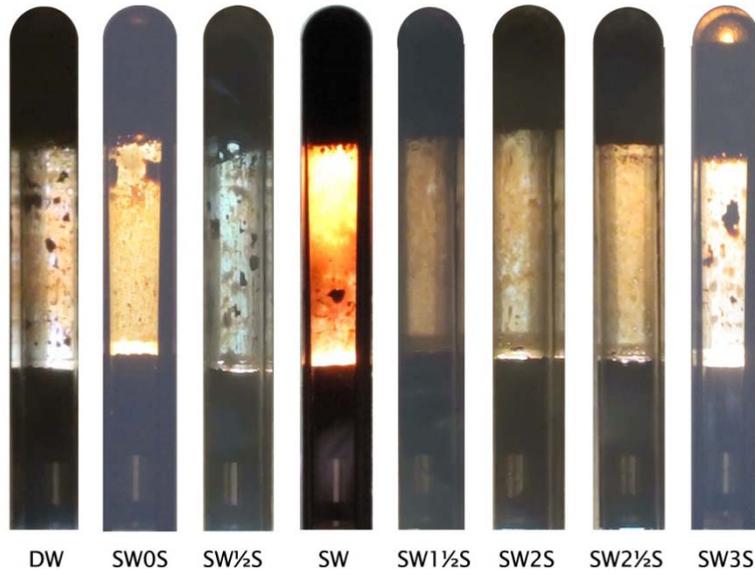


Figure 4.5: Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 °C and 15 bar.

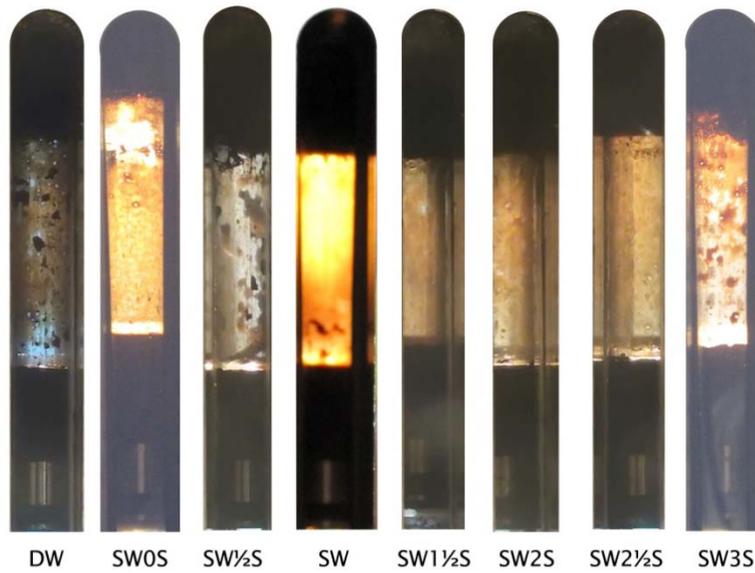


Figure 4.6: Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 °C and 300 bar.

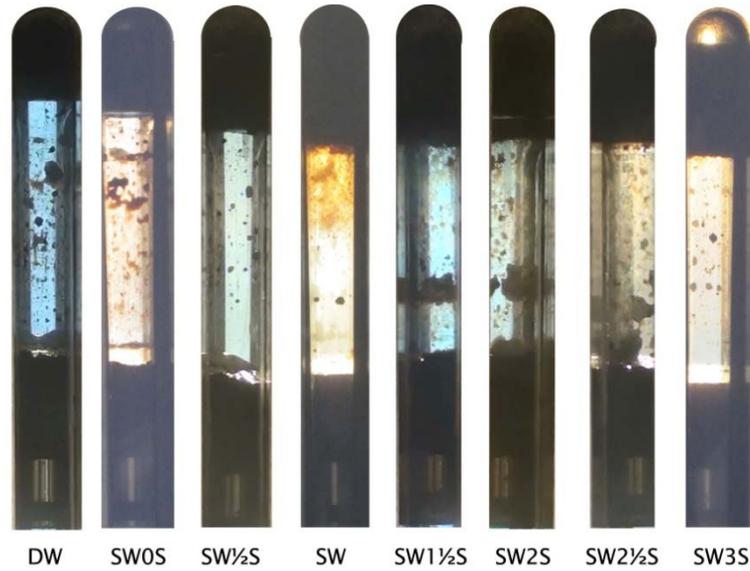


Figure 4.7: Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 °C and 15 bar.

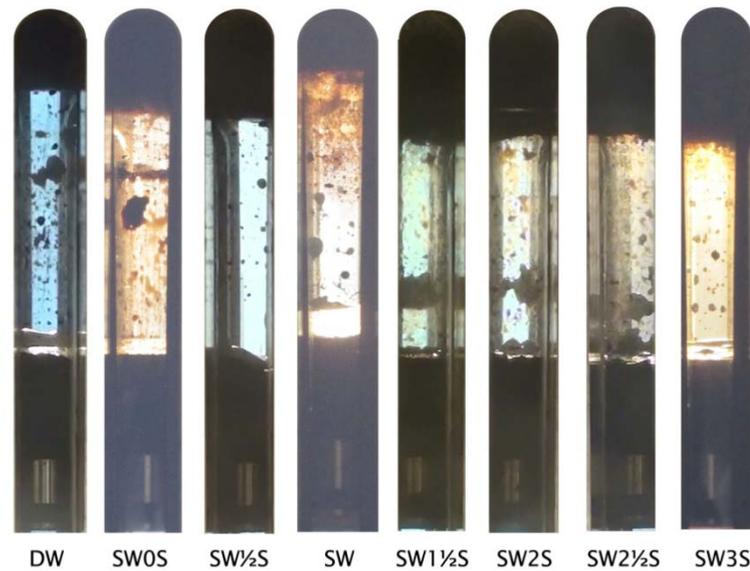


Figure 4.8: Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 °C and 300 bar.

Comparison of Figures 4.5 and 4.7, as well as Figures 4.6 and 4.8 clearly shows that increasing the temperature results in de-emulsification of the crude oil in almost all cases. Brine SW1.5S is an exception as this particular brine solution generates a less clear separation of the crude oil and brine. Interesting about this observation is that the same trend occurs very similar in at all conditions, which indicates that this sulfate concentration is responsible. At the lower temperature, $T = 37\text{ }^{\circ}\text{C}$, sulfate ions at certain concentrations (SW to SW2.5S) help to clarify the oil/brine interface, see Figures 4.5 and 4.6. At a higher temperature, $T = 110\text{ }^{\circ}\text{C}$, sulfate does

not de-emulsify the oil at all, see Figure 4.7 and 4.8. We measured the phase volumes at every test conditions, but no significant change was observed at any combination of the pressure and temperature conditions. The observed formation of emulsions has been of such a small volume, that it has not been possible to make useful measurements of their volumes. It was only possible to detect through the used microscope.

After finishing the experiment in the JEFRI cell, the samples were transferred from the cell into a sample bottle and left overnight. Then viscosity measurements of the crude oil phase were performed for every experiment. Results are shown in Table 4.3.

Table 4.3: Crude Oil Viscosity Data after Interacting with Brine Solutions in JEFRI Cell.

Latin American Crude Oil	
Samples	Viscosity (cp)
Only Oil	24.4
SW0S	21.5
SW	20.2
SW1.5S	18.7
SW2S	18.1
SW2.5S	18
SW3S	16.4

In the case of the Latin American crude oil it can be seen that the viscosity of the crude oil decreased with the increase in sulfate concentration when the system was exposed to high temperatures and pressures.

In order to check solubility of the crude oils in the brine phase, we measured the pH of the brine phases in all cases. Results for the pH of different brine solutions are shown in Table 4.4. A decrease in pH was experienced in all cases. In highly sulfated brine solutions, less change in pH was observed as compared to DW and SW0S. This suggests that some of the acidic components of the crude oil are being washed into the brine solution, causing the decrease in pH of the brine solutions. However, this change in pH is not sufficient to explain the decrease in viscosity of the Latin American crude oil.

Table 4.4: pH of Brine Solutions before and after experiments.

Brine Solutions from Latin American Crude Oil Samples		
Samples	pH (before)	pH (after)
DW	5.97	3.49
SW0S	6.29	4.30
SW0.5S	-	7.07
SW1.5S	8.02	7.50
SW2S	8.09	7.51

Furthermore, the measured water content in the crude oil phase (Table 4.5) makes it clear that the observed decrease of viscosity cannot be explained by water present in the oil phase. We did not observe a significant change in the viscosity of oil in contacted with SW0S, but on the other hand it has comparatively high water content with respect to other tests.

Table 4.5: Water Contents in Crude Oils after Interacting.

Latin American Crude Oil	
Samples	Water Content (%)
Only Oil	0.017
DW	0.024
SW0S	0.645
SW0.5S	0.029
SW1.5S	0.473
SW2S	0.045

To confirm that viscosity indeed decreases, further experiments were carried out with the Middle East crude oil and different brine solutions in the same way as for Latin American crude oil. The Middle East crude oil and different brine solutions at various temperature and pressure conditions (the same as reported for the experiments with the Latin American crude oil) are photographed, as shown in Figures 4.9, 4.10, 4.11 and 4.12. If we compare Figure 4.9 and 4.11, as well as Figure 4.10 and 4.12, we can see that the high operating temperature de-emulsifies the Middle East crude oil also. A more interesting feature is the formation of a new emulsion phase at the high temperature, $T = 110\text{ }^{\circ}\text{C}$, with the increase in sulfate concentration (see

Figures 4.11 and 4.12). The emulsion phase formed can be seen for SW3S in Figure 4.11 and for SW1.5S and SW3S case in Figure 4.12.

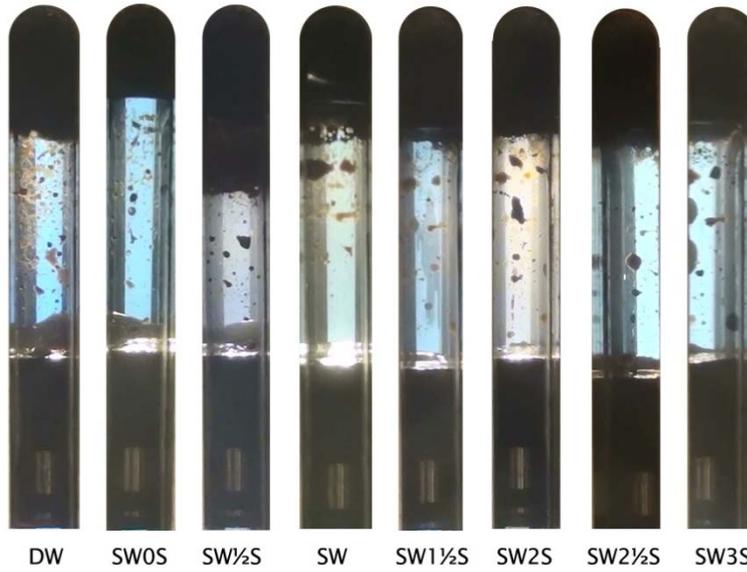


Figure 4.9: Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 °C and 15 bar.

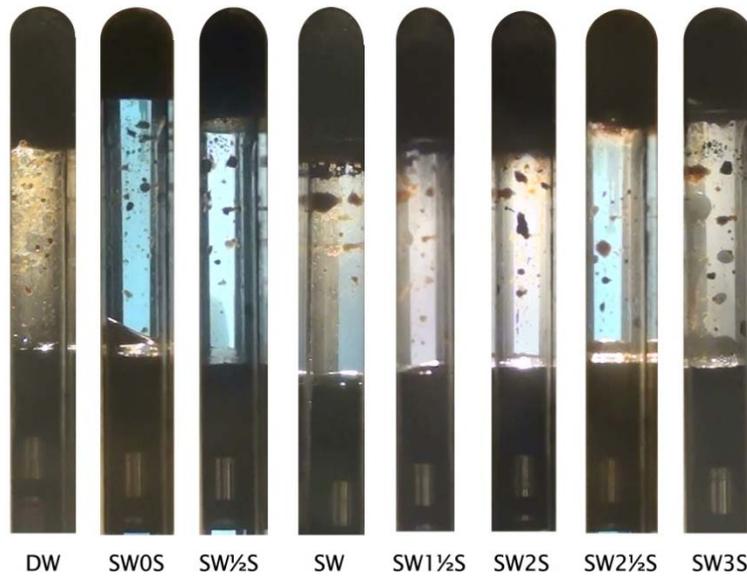


Figure 4.10: Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 °C and 300 bar.

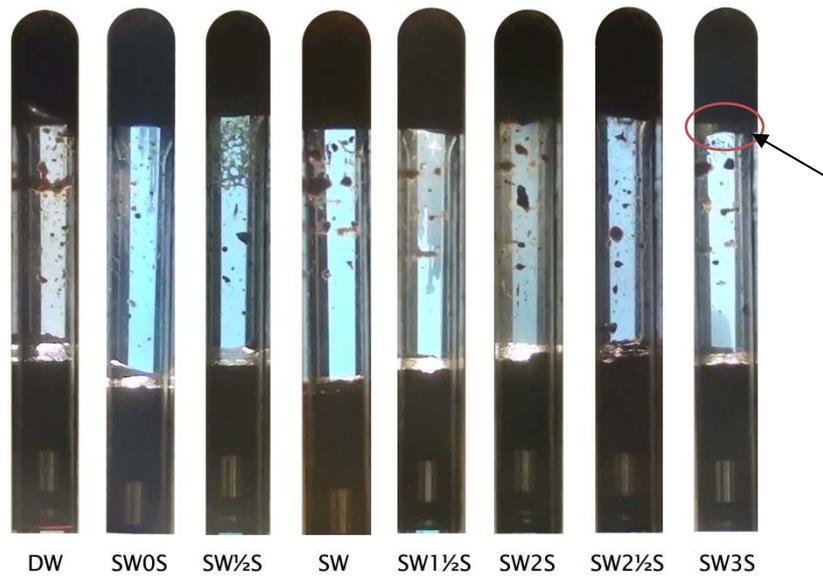


Figure 4.11: Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 °C and 15 bar. The formation of an emulsion phase can be observed in case of SW3S, present as a dark grey phase between the oil and the brine phases.

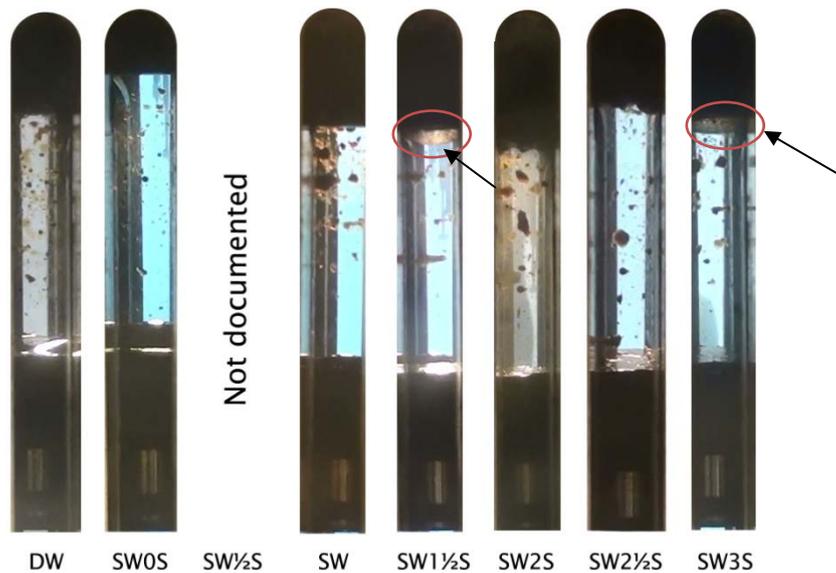


Figure 4.12: Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 °C and 300 bar. The formation of an emulsion phase can be observed in case of Sw1½ and SW3S, present as a dark grey phase between the oil and the brine phases.

After completing the experiment with the Middle East crude oil and brine solutions in the DBR JEFRI PVT cell, the samples were removed from the cell and left overnight in the same way as for the Latin American crude oil. Viscosity measurements of the crude oil samples were then carried out. Results are shown in Table 4.6. No significant change in the viscosity of the crude oil was observed in this case.

Table 4.6: Crude Oil Viscosity Data after Interacting with Brine Solutions in JEFRI Cell

Middle East Crude Oil	
Samples	Viscosity (cp)
Only Oil	10.54
DW	9.03
SW0S	8.02
SW0.5S	7.88
SW	7.92
SW3S	8.00

4.3.3 Interfacial Tension Measurements

IFT measurements were performed between the Latin American crude oil and brine at room temperature and atmospheric pressure in order to study the effect of brine salinity on interfacial tension. IFT values between oil and different brines are summarized in Table 4.7.

Table 4.7: Interfacial Tension of Latin American Oil/Brines @ 25 °C with Brine Solutions in JEFRI Cell.

Latin American Crude Oil	
Samples	IFT (mN/m)
SW0S	13.92
SW	7.19
SW1.5S	6.98
SW2S	6.83
SW3S	6.31

Results show that IFT decreases with the increase in sulfate concentration. IFT for SW0S/oil is 13.92 mN/m and this decreased to 6.31 mN/m for SW3S/oil. This demonstrates that sulfate helps to decrease the IFT. However, this decrease seems to be insufficient to account for the observed increment in oil recovery.

4.4 Discussion

We observed that viscosity of Latin American crude oil in contacted with brine solution decreased with the increase in sulfate concentration at high temperature and pressure condition. One possible reason for decrease in viscosity of crude oil may be the change of shape of heavy component (aromatics, asphaltenes and resins) molecules. This happens in polymer solutions. Many authors reported decrease in viscosity of polymer solution when salt is added to solution [67, 68]. If a polymer is poly-acid, it may dissociate in a solution. The molecules of non-dissociated polymer are normally coiled. Most of the interaction forces are hidden inside the coiled molecules. The effect on viscosity is relatively small. When acidity of the solution changes the molecules of the polymeric acid may dissociate. The segments of such molecules become negatively charged and repel from each other. As a result, the molecules stretch. In the flow, the negatively charged stretched molecules occupy a larger volume and interact stronger with each other. This is likely to increase the viscosity of the solution (although there may be other considerations). Addition of some salts or into the solution may result in the fact that the salt ions neutralize the negatively charged segments, and the polymer molecules become coiled again, which decreases the viscosity. In the same way, sulfate ions along with other potential determining ions could affect the shape of heavy components of crude oils at high temperature and pressure. This mechanism looks reasonable because we have observed decrease in viscosity only in the case of Latin American crude oil whose asphaltene content is three times higher than of the Middle East crude oil where we did not observe any decrease in viscosity. The exact mechanism of interaction of the sulfate ions with the crude oil which leads to viscosity decrease is still not clear and the role of the potential determining ions with respect to temperature and pressure needs further study. However, the effect is pronounced and repeatable, and may definitely affect the oil recovery under reservoir conditions.

Another important finding is the formation of a new emulsion phase with the Middle East crude oil at high temperature, pressure, and sulfate concentration. Although we could not analyze the new formed phase, we believe that it could be a microemulsion, since microemulsions may form upon simple mixing of the components, as in our experiments, and do not require the high shear conditions generally used in the formation of ordinary emulsions. The newly formed phase was stable under experimental conditions. Investigation of the new phase under high temperature and pressure conditions in JEFRI cell requires specialized equipment and is outside the scope of the present work. Even if it is not microemulsion, it may have an important influence on oil recovery mechanisms that was not studied previously.

It has been established that seawater is an excellent EOR fluid for chalk reservoirs at high temperature [69]. On the other hand both the decrease in viscosity of the Latin American crude oil and formation of an emulsion phase with the Middle East crude oil were also observed at high temperature. This clearly shows that these two factors could be possible explanations for the observed increase in oil recovery. On the other hand, recent studies in our laboratory [70] indicate that the rock may also determine whether the effect of the temperature on the recovery is observed. Thus, brine/crude oil interaction alone may be insufficient to explain all the mechanisms of the EOR based on enhanced water salinity.

Experimental results show that both crude oils interact differently with the same brine solutions regarding phase behavior and viscosity measurements. This difference is attributed to the difference in composition of the different crude oils. Thus, variation of the oil viscosity with brine salinity is oil-dependent. Unless an explanation is given, this viscosity variation needs to be checked in each particular case of application of the salinity-based EOR. Further experimental studies are in progress in our laboratory in order to understand the complex interaction of crude oil components with brine solutions.

4.5 Conclusions

1. Room temperature crude oil/brine studies indicate that the salinity of the brine affects the emulsion formation. No trend was observed with regard to amounts of the potential determining ions and especially with sulfate ions. Brine solutions did not affect the viscosity and density of crude oils at room temperature.
2. The DBR JEFRI PVT cell high-pressure studies show that an increase in temperature de-emulsifies crude oils in all cases.
3. The viscosity of the Latin American crude oil was significantly reduced after interacting with sulfate ions at high temperature and pressure conditions in the DBR JEFRI PVT cell. A trend of decrease in viscosity with the increase in sulfate concentration was observed.
4. Formation of an emulsion phase was observed with the Middle East crude oil with the increase in sulfate concentration especially at the high temperature and pressure conditions in the DBR JEFRI PVT Cell. No significant viscosity change was observed in this case.
5. At room temperature sulfate ions helped to reduce the IFT between the Latin American crude oil and brine. However decrease of the IFT with sulfate concentration seems to be insufficient to significantly affect the oil recovery.

6. The viscosity decrease for the Latin American crude oil and formation of an emulsion phase with the Middle East crude oil are possible reasons for the increment in oil recovery with sulfate ions. Increase in oil recovery in Stevns Klint chalk was reported at higher temperatures (over 90 °C)[69] and both these effects were also observed at the high temperature conditions. Further experimental studies are required in order to understand this complex interaction of crude oil components with brine solutions.

4.6 Acknowledgements

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Paper III

Sandersen, S.B; Zahid, A.; Stenby, E. H.; Solms, N.V. and Shapiro, A. A.

Mechanisms of Advanced Waterflooding in Chalk Reservoirs: Role of Seawater-Crude Oil Interactions

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Mechanism of Seawater Flooding in Chalk Reservoirs: Role of Crude Oil/Brine Interactions

Abstract

It is experimentally documented that seawater with increased amounts of the potential determining ions, SO_4^{2-} , Ca^{2+} and Mg^{2+} , can significantly improve the oil recovery in chalk reservoirs at high temperatures. Usually, wettability alteration is reported as the main mechanism for the improvement in oil recovery. Our recent study proposed that the decrease in viscosity and formation of an emulsion phase could also be a possible reason for the observed increase in oil recovery. It was found that two crude oils exhibited different phase behavior and viscosity variation in contact with the same brine solutions. In this work, we study crude oil/brine interactions further: We investigate the effects of compositional differences of crude oils and also study heptane/seawater interactions under different temperatures, pressures and sulfate ion concentrations. For the two crude oils studied, the heavier oil (that with a large fraction of heavy components) exhibited viscosity reduction in contact with brine, while the lighter crude oil exhibited emulsion formation. We have also observed formation of an emulsion phase in the heptane/brine systems under high pressures and temperatures. It is concluded that viscosity reduction for a crude oil in contact with brine is connected to the presence of heavy components in the crude oil, while formation of emulsions with brine is a phenomenon related to the presence of lighter components in the crude oil.

5.1 Introduction

Although waterflooding is an extensively practiced recovery method for mechanical displacement of oil and for pressure maintenance, the composition of the injection water has not generally been considered an important factor in waterflood design. In recent years, however, research on so-called “smart” waterflooding has shown that injection of suitably composed brine can substantially increase oil recovery from both sandstone and carbonate reservoirs. For example it has been documented experimentally that low salinity waterflooding in sandstones and high salinity seawater flooding in carbonates contribute to an increase in oil

recovery [1, 31, 37]. Understanding the underlying mechanisms behind these effects is, however, still in progress.

Several experimental studies have been carried out on seawater flooding in chalk reservoirs by Austad and co-workers [1, 20, 34-36, 40, 45]. Concentrations of the active ions Ca^{2+} , SO_4^{2-} and Mg^{2+} as well as temperature were documented as governing parameters in determining the amount of oil recovered both by spontaneous imbibition and by forced displacement. Recently, Fathi et al. [9] reported that not only are the concentrations of the active ions Ca^{2+} , SO_4^{2-} , and Mg^{2+} important, but also the amount of NaCl has an impact on oil recovery. Other experimental studies also reported positive effects from different seawater ions (SO_4^{2-} and Mg^{2+}) on oil recovery from carbonate rocks [31, 37, 71].

To understand the mechanism of improved oil recovery, surface chemistry was the major focus in most of the studies mentioned, and wettability alteration of the porous surface was reported as a key reason for recovery improvement. The main conclusion from this earlier work is that it is the affinity of the potential determining ions to the chalk surface, which increases with temperature, which helps to improve the oil recovery [1, 40].

Crude oil/brine interactions have generally been ignored in most reported studies. Our recent laboratory study [72] was one of the first to demonstrate that these interactions may also be responsible for an increase in oil recovery. We studied crude oil/brine interactions at room temperature and atmospheric pressure, as well as at high temperature and pressure in a DBR JEFRI cell. Two different crude oils (from Latin America and the Middle East) were studied. Our results showed that sulfate ions could help decrease the viscosity of one of the crude oils when brine is contacted with it at high temperature and pressure. For the other crude oil, sulfate ions in brine could also be responsible for creation of an emulsion phase at the interface between crude oil and brine. Decrease of viscosity of a crude oil and formation of emulsion phase were reported as possible reasons for improved oil recovery, aside from the wettability alteration reported in other works. Formation of emulsions between water and crude oil is a known effect during oil production. Appearance of emulsions may result in major processing problems and can affect the quality of the produced crude oil [73, 74]. However, most often formation of emulsions (especially, microemulsions) is considered to be a positive effect, as the interfacial tension (IFT) is lowered such that the mobility of the crude oil inside the reservoir is enhanced [66].

Both crude oils used in our previous study interacted in a different way with the same brine solutions in terms of phase behavior and viscosity. This difference is ascribed to the different compositions of the crude oils. The motivation of the present work is to understand the interactions of the crude oil components with the brine solutions. Specifically we address the following questions:

What is the mechanism for crude oil viscosity reduction?

Which components of the crude oil are responsible for the formation of emulsions?

Why do different crude oils interact in a significantly different way with the same brine solutions?

In this work, gas chromatography (GC) analysis of the crude oils (before and after contacting with brine solutions in a DBR JEFRI cell) is carried out in order to determine the effect of brine on the compositions of the crude oils. A SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis of both crude oils is also carried out. For comparison, we carried out a similar study with heptane instead of crude oil in order to determine whether formation of the emulsion phase and viscosity reduction could also occur in such a simple, single hydrocarbon/brine system. The procedure described previously was followed [17]. Attention was also given to any possible color change in the heptane after interacting with brine solutions, since it was recently reported that the amount of sulfate in the brine solution is correlated to discoloration of decane [11]. We also conducted light scattering analysis of the emulsions using a TurbiScan apparatus [24]. Moradi et al. [75] reported the measurement of droplet size and stability of emulsions using a transmitted-light microscope. Our target was to make a detailed analysis of the formation of emulsions in order to characterize the emulsion (which kind of emulsion the system forms size of droplets, the time range of separation between oil and water phase, and the stability of the emulsions)

5.2 Experiments

Experiments designed in this study are based on the results from our previous work [72]. The experimental work consists of two parts: The first part is a compositional analysis of the crude oils studied in previous work. In the second part, a new model oil/brine system (heptane/brine) is studied in order to clarify whether the lighter components in the oil are responsible for one of our previous observations, either that viscosity of the oil decreases after operation in high pressure and temperature equipment or that formation of oil and water emulsions are

experienced when the system is at high pressure and temperature. In addition, Turbiscan analysis of a crude oil/brine system is also carried out.

5.2.1 Crude Oils

The same two crude oils, the middle east crude oil and the Latin American crude oil, reported on previously, [72] were also used in this study for detailed compositional analysis. The properties of the crude oils, (density, viscosity, acid number and base number) are given in Table 3.1. In addition to the crude oils, n-heptane was also used as a model fluid to understand the complex crude oil/brine interactions.

5.2.2 Brine Solutions

The same seven brine solutions reported previously were also used in this study. The detailed compositions of brine solutions used are given in Table 4.1.

5.2.3 SARA Analysis

SARA analysis was first described by Jewell et al. [76], where it was based on adsorption chromatography by gravity. In the present work SARA analysis was applied to two crude oils. Component separation was carried out in five different steps: A column was prepared with heptane and silica was carefully added to avoid air bubbles. Heptane must be present at all times and the column cannot dry out. 100 g of silica and 5 g of oil was used. The separation was carried out in 5 steps:

1. 1.25 L heptane solution was added to the column and the separation begins.
2. Separation with 1.25 L heptane-toluene 1:1 solution was carried out. The fractions collected from step 1 and step 2 are the saturates fraction In a new collector the process was continued with heptane-toluene solution until the eluent was light yellow.
3. The separation was continued with 1.5 L toluene. The collected fraction is the first part of the aromatics. Toluene was added until the eluent was almost colorless.
4. 1.5 L toluene-methanol solution in a 4:1 relation was added to the column. From step 3 and 4 the first and the second part of the aromatics was collected. With another new collector the separation continues with the toluene-methanol solution until the eluent was almost colorless. In the final step 0.5 L dichloromethane-methanol solution in the ratio of 4:1 was added until the eluent became colorless. The resins were collected from the final separation part. The asphaltenes stay in the column, held there due to the silica powder.

5.2.4 GC Analysis

The two crude oils were analyzed with simulated distillation gas chromatography, both before and after they were contacted in the high pressure cell with different brine solutions. An Agilent 7890A gas chromatograph was used. In order to determine the carbon numbers of each of the fractions obtained in the simulated distillation, ASTM method D6352 was applied. This method covers hydrocarbons with boiling points up to 700 °C, which is the boiling point of C94. The method is not applicable to fractions with carbon numbers lower than C10-C11. To overcome this, the GC was also fitted with a sub-ambient column oven, where liquid carbon dioxide was used to extend the 7890A lower oven temperature down to -40 °C. Table 5.1 gives details of the setup.

Table 5.1 Instrument conditions for the cryogenic ASTM D6352 simulated distillation.

Auto injector	Agilent 7693 ALS Syringe size: 1µL Injection volume: 0.05 µL
Inlet	Split/splitless operated in split mode Temperature: 50 °C for 0 min then 200 °C/min to 430 °C for 6 min
Column	Dimensions: 5m x 530µm x 0.15µm Temperature: 450 °C
Oven	-20 °C for 1 min then 20 °C/min to 430 °C for 5 min.
Detector	Flame Ionization Detector (FID) Temperature 400 °C FID Hydrogen flow rate: 40mL/min FID Air flow rate: 450mL/min Make-up flow: 45mL/min nitrogen Data acquisition rate 5Hz
Data system	Agilent Chemstation

Calibration was done in two steps in order to identify the retention times of the fractions with the carbon numbers ranging from C5 to C90. Initially a known solution of C5-C18 (Agilent 5080-8768) was injected into the gas chromatograph, from which the corresponding retention time could be obtained. Second, a solution of 10 mg of polywax 655 (Agilent 5188-5317) was injected with 1.5 ml of toluene to identify the retention times of carbon numbers C20 to C94. To analyze the crude oils, the two samples were injected into the GC before and after the high pressure experiments. From the resulting chromatograms the amounts of the carbon fractions from C5 to C94 could then be calculated.

5.2.5 Heptane/Brine Interaction Study at Ambient Conditions

Initially the heptane/brine interactions were studied at room temperature and atmospheric pressure. Heptane and different synthetic brines were mixed in a volumetric ratio of 20/80 and stirred. The mixture was centrifuged at 1000 rpm for 15 minutes as in the previous study [72]. After equilibration, the systems were photographed and examined for any possible color change or emulsion formation.

5.2.6 2.6 Heptane/Brine Interaction Study in DBR JEFRI PVT Cell

The heptane/brine interactions at high pressures and temperatures were studied in the DBR JEFRI PVT cell. The equipment details and the experimental procedures are described in Zahid et al. [72]. The cell is shown in figures 4.2 and 4.3. The four sets of experimental conditions were: (a) 37 °C, 15 bar (b) 37 °C, 300 bar (c) 110 °C, 15 bar (d) 110 °C, 300 bar. The brine-heptane volumetric ratio (WOR) was 30/70 which corresponds to 15 ml heptane and 35 ml brine in each experiment.

After the heptane/brine systems were contacted in the DBR JEFRI PVT cell, the density and viscosity of the heptane were measured. The heptane was also examined for any possible color change.

5.2.7 Turbiscan Analysis of the Crude Oil/Brine Emulsions

The crude oil/brine systems were also analyzed in the Turbiscan [24]. This is a light scattering measurement tool for analysis of concentrated dispersions. Typically the Turbiscan is used to analyze formulations, documenting stability. In the present work the Turbiscan was used to monitor equilibrium in the mixed crude oil/brine systems. To determine if the observed emulsions could be quantified with regard to the droplet size and stability.

For this work a commercial apparatus Turbiscan MA 2000 was used. A cylindrical glass test-tube is placed vertically into the device. A reading head moves up and down in order to scan the entire sample length, as shown in figure 5.1. There are two detectors, one to detect the light transmitted through the sample from the light source, and another to receive the light backscattered by the sample. The Turbiscan operates at room temperature and atmospheric pressure. The details of the Turbiscan MA 2000 operation are reported by Mengual et al. [77].

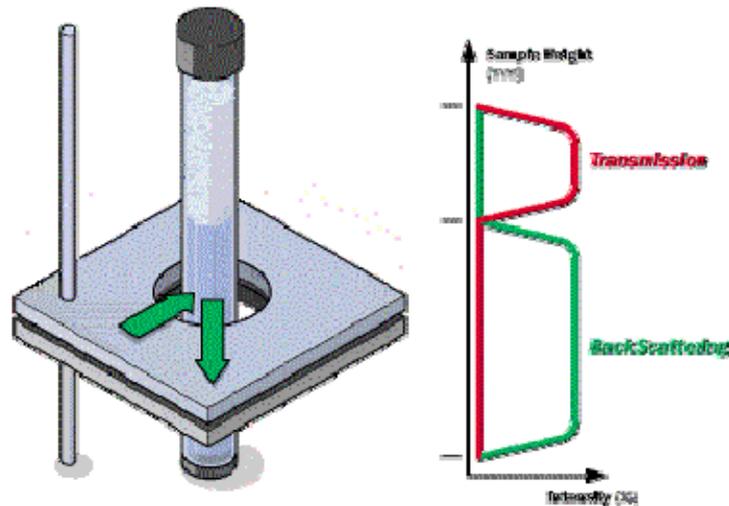


Figure 5.1 Drawing of the inside of the TurbiScan. The squared platform is the reading head, which is moving up and down along the cylindrical cell to scan the entire sample length [78].

In the Turbiscan experiments, the crude oil/brine ratio is kept similar to the crude oil/brine study in the DBR JEFRI PVT cell: 30 vol% crude oil (2.1 ml) and 70 vol% brine solution (4.9 ml). Two brine/water solutions were used: DW and SW3S. The crude oil/brine samples were loaded into the glass tubes and mixed by vigorous hand-shaking. Thereafter the tube was placed inside the Turbiscan and the sample was scanned for 12 hours with a measurement every hour. The results were stored in the enclosed software and the output graphs were analyzed.

Due to some unexpected phase behavior, where the two phase crude oil brine system changed into a relatively stable single gel-like phase, during the preparation of the samples in the glass tubes other water-oil ratios were also analyzed: 50 vol% crude oil and 50 vol% distilled water; 20 vol% crude oil and 80 vol% distilled water, and 10 vol% crude oil and 90 vol% distilled water. The Latin American Crude oil and the Middle East Crude oil were used for these analyses, in combinations with the two different brine/water solutions.

5.3 Results

5.3.1 SARA Analysis

Our previous experimental results [17] showed that both crude oils interact differently with the same brine solution at high temperatures and pressures. While the viscosity of the highly viscous Latin American oil is strongly reduced after contact with brines containing high amounts of sulfates, the Middle East oil forms emulsions with them. However, the Latin American oil does not form emulsions, nor is the viscosity of the Middle East oil reduced. This difference is attributed to compositional differences between the oils. SARA analysis of both crude oils was performed to study this difference and the results are summarized in Table 5.2.

Table 5.2 SARA Analysis of Crude Oils.

Crude Oil	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltene (%)	Viscosity (cP)
Latin America	43.26	9.19	7.49	3.43	24.4
Middle East	46.78	2.34	4.66	1.093	10.538

The Latin American crude oil has (as expected) a much higher percentage of aromatics, resins and asphaltenes compared to the Middle East crude oil. The conclusion is that the oil containing the highest amounts of heavy components was less inclined to form emulsions with brines, while at the same time demonstrating viscosity reduction after contact with them.

5.3.2 GC Analysis of Crude Oils

The graphical results from GC analysis are shown in figures 5.2 and 5.3. For the Latin American crude oil, there are no noticeable changes in the GC profiles when comparing the unprocessed crude oil with crude oil samples that have been contacted with brine in the DBR JEFRI PVT cell. On the other hand, there are changes in the chromatograms of the Middle East Crude Oil.

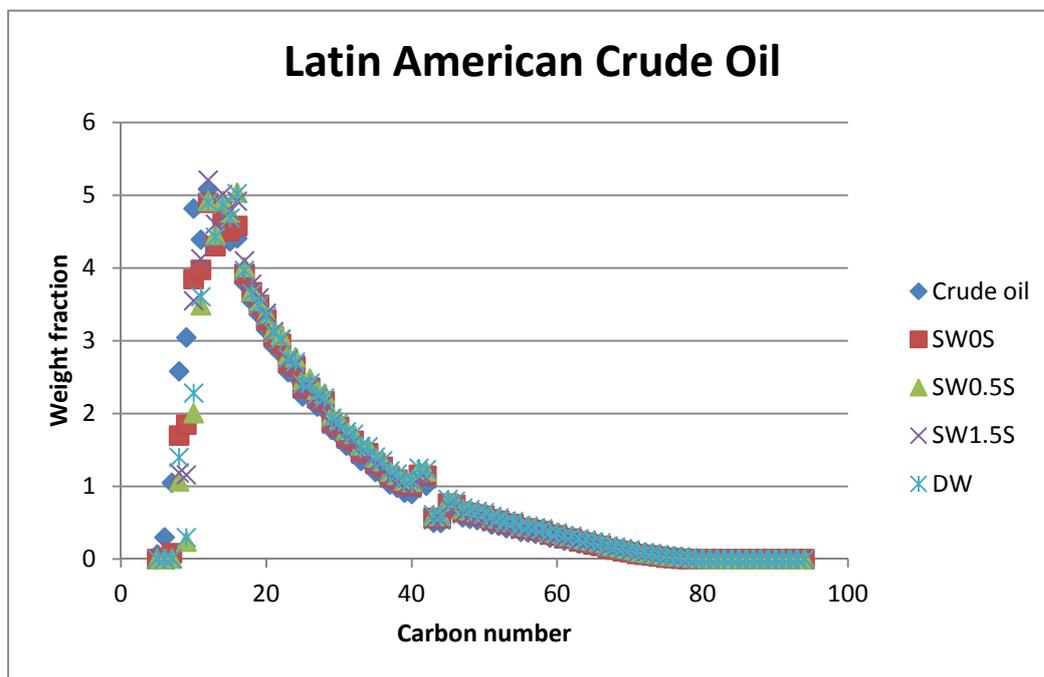


Figure 5.2 Graphical results from GC analysis of the Latin American Crude Oil before and after contact in the JEFRI cell with brines of varying sulfate concentration. For the GC analysis the required sample amount is removed from the full original oil/brine sample, which was operated in the high pressure cell.

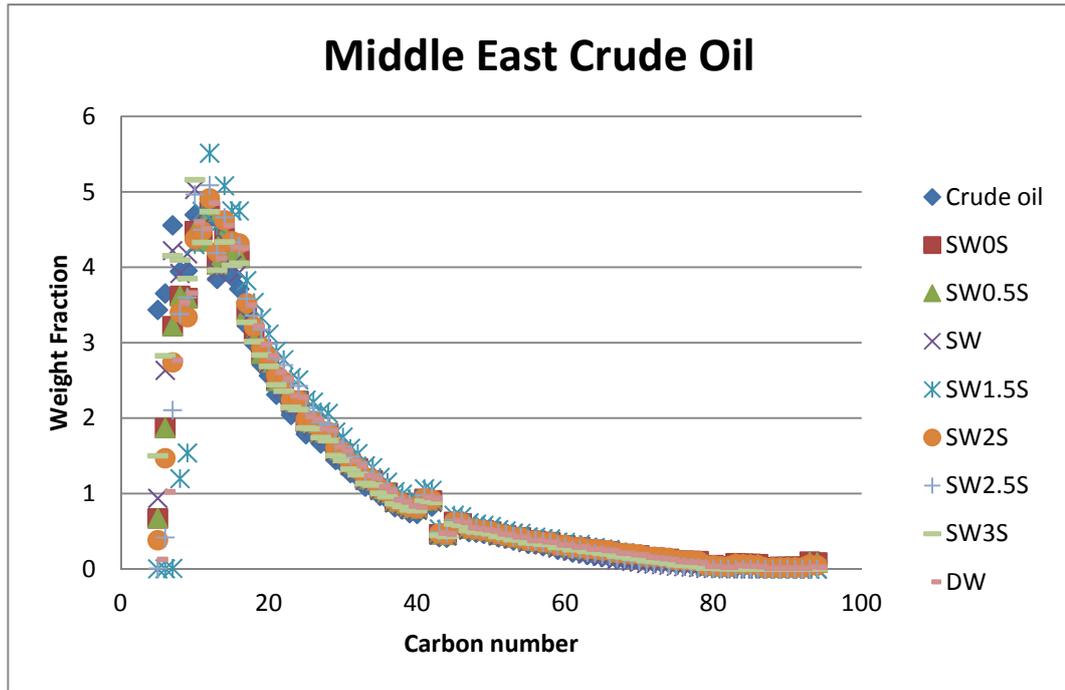


Figure 5.3 Graphical results from GC analysis of the Middle East Crude Oil before and after contact in the JEFRI cell with brines of varying sulfate concentration. For the GC analysis the required sample amount is removed from the full original oil/brine sample, which was operated in the high pressure cell.

From figure 5.3 it is seen that the unprocessed crude oil has a significantly higher content of light components than the crude oil after contact with brine. To verify this observation, measurements with the original crude oil were repeated 3 times, and the conclusion was the same in each case.

5.3.3 The Room Temperature Heptane/Brine Study

The purpose of the heptane-brine interaction study was to understand the effects observed in the seawater-crude oils interaction study by analyzing a simple model system. The experiments with crude oil indicated that the light oil components are most probably responsible for formation of emulsions, while heavy components may participate in viscosity reduction. In order to support this conclusion, we determined whether formation of emulsions and viscosity reduction could be obtained in heptane/brine systems.

The heptane-brine interactions were initially studied at room temperature. Unlike in the crude oil study [72], no dispersion of the heptane droplets in the brine solution was observed (figure 5.4). Density and viscosity of heptane was measured before and after stirring the sample bottle with different brine solutions (SW0S, SW, SW2S, SW2.5S and SW3S). No significant changes were observed.

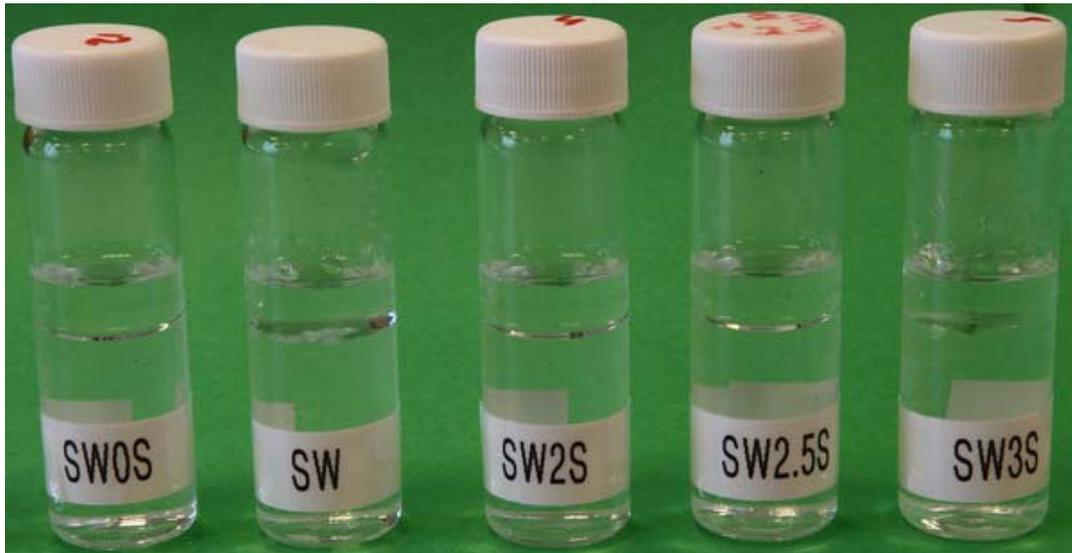


Figure 5.4 Heptane and different brine solutions after stirring them @ 1000 rpm for 15 mins at room temperature. The sample bottles are filled with heptane and brine solution and have been equilibrated for 1-2 hrs. These tests at ambient conditions were performed to see whether unusual phase behavior or discoloration of the heptane was solely due to the composition of the brine solutions.

5.3.4 Heptane/ Brine Interaction in the DBR JEFRI PVT Cell

Heptane/brine interactions were also investigated under different temperatures and pressures in the DBR JEFRI cell. The system was monitored continuously to detect any changes in the number of phases or in the color of the heptane phase.

After equilibration of the liquid-liquid systems the separation was monitored until the liquids were stabilized. Phase volumes were measured and the equilibrated systems were photographed. The photographs taken of different heptane/ brine systems (brine solutions having different sulfate concentration) at different temperatures and pressures are shown in figures 5.5 to 5.8. Besides the cases of DW at 37 °C and 15 bar and SW3S at 110 °C and 15 bar, the heptane/ brine systems formed a cloudy milky white emulsion phase at the interface between heptane and water. This emulsion phase is even more significant than the emulsion formed by the Middle East crude oil described previously. Formation of the emulsion phase is sensitive to both temperature and pressure. By observation of the volumes involved it may be concluded that this phase is formed from both the upper oil phase and the lower water phase.

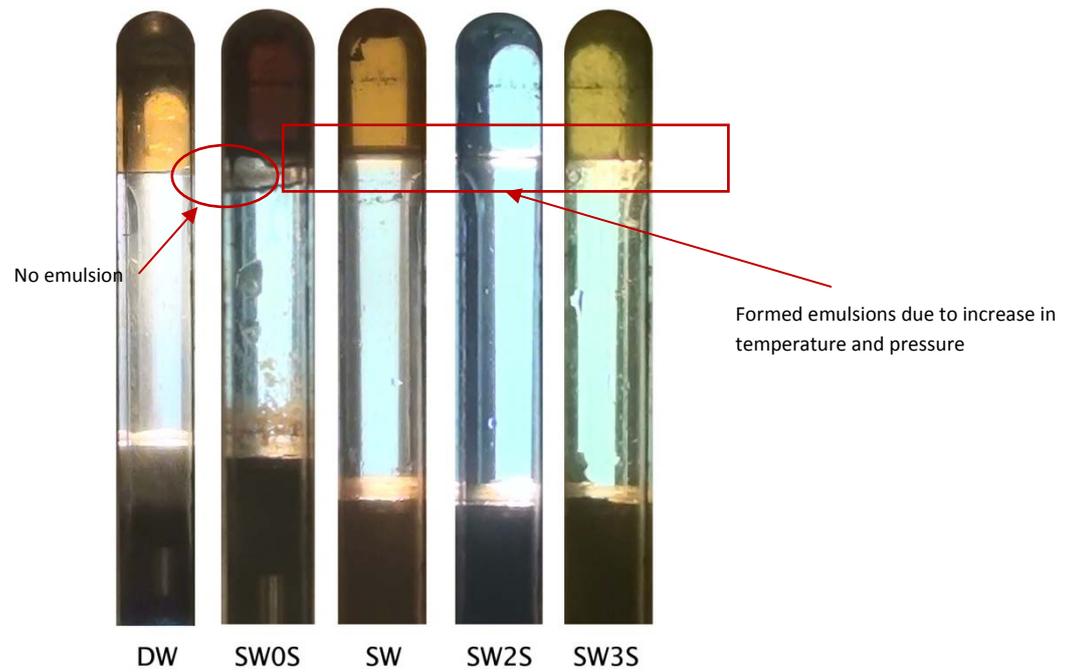


Figure 5.5 Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 37 °C and 15 bar. Sample with DW shows no emulsion at the interface between oil and brine. Sample SW0S, SW, SW2S and SW3S shows formed emulsions. The emulsions are formed as the temperature and pressure has been increased.

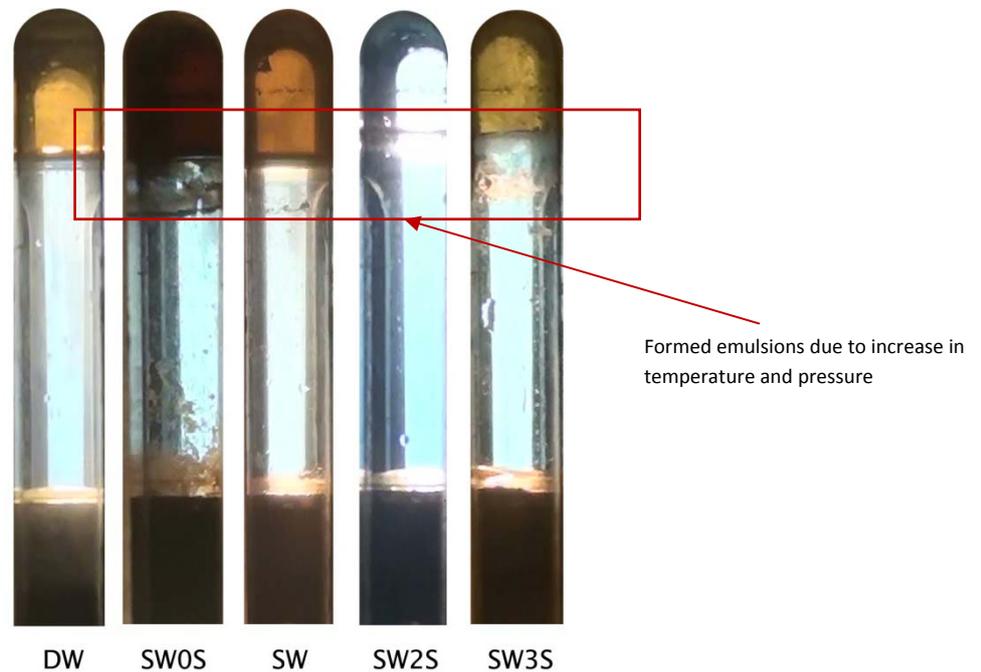


Figure 5.6 Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 37 °C and 300 bar. All samples shows formed emulsions. The emulsions are formed as the temperature and pressure has been increased.

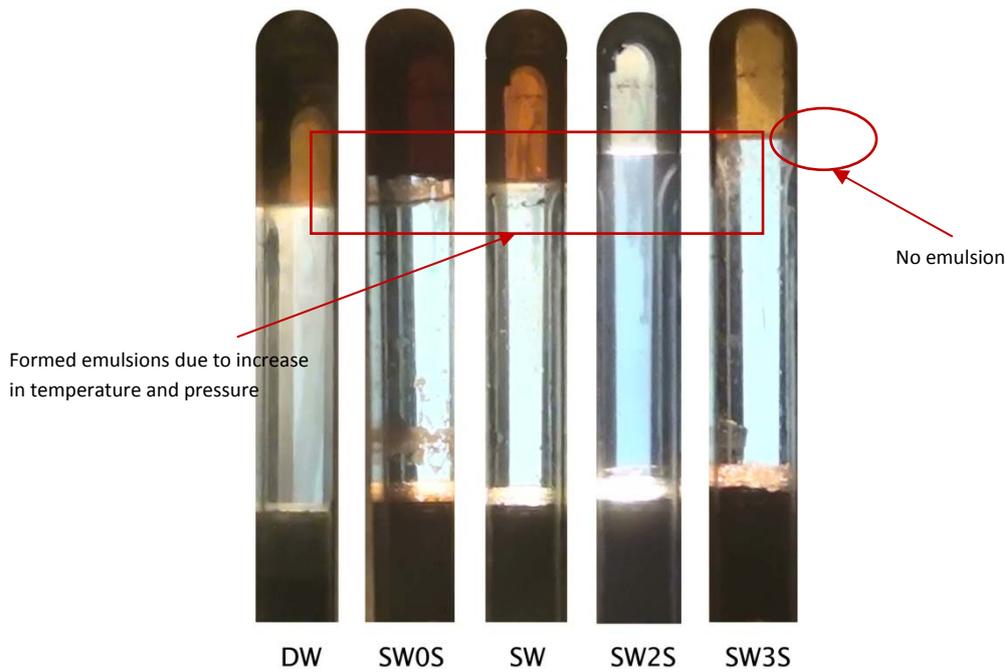


Figure 5.7 Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 110 °C and 15 bar. Sample with SW3S shows no emulsion at the interface between oil and brine. Sample DW, SW0S, SW and SW2S shows formed emulsions. The emulsions are formed as the temperature and pressure has been increased.

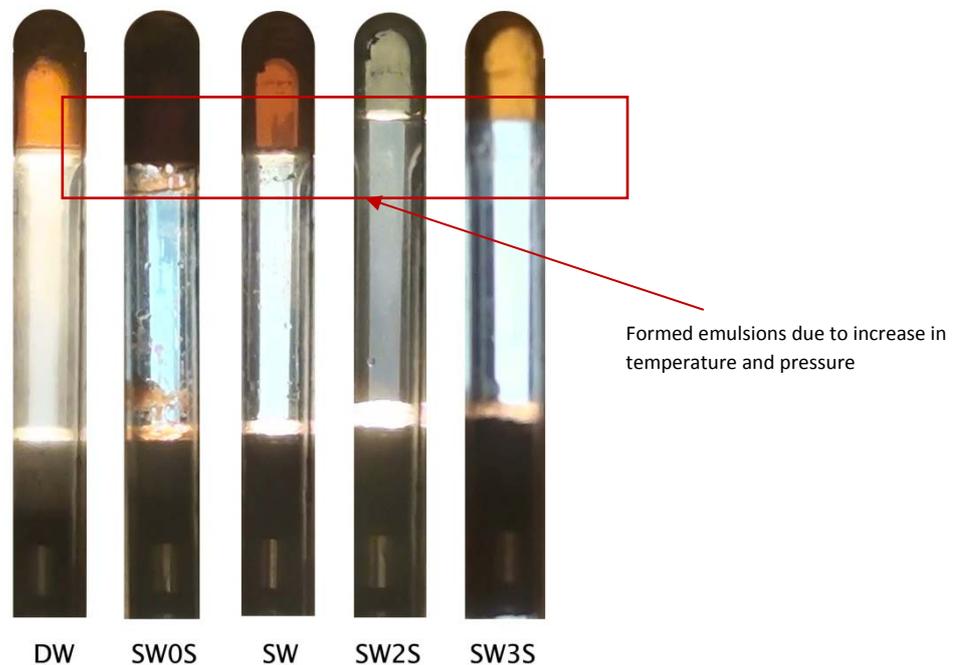


Figure 5.8 Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 110 °C and 300 bar. All samples shows formed emulsions. The emulsions are formed as the temperature and pressure has been increased.

After removal from the cell the heptane/brine systems were stored in a sample bottle and later examined for any changes. A significant color change in the heptane/ brine system was observed.



Figure 5.9 Heptane with different brine solutions after processing in the JEFRI cell at ambient temperature and atmospheric pressure. From left to right heptane with DW (not processed in the JEFRI cell), SW2S and SW3S.

As can be seen in figure 5.9, the system is completely colorless at the beginning of an experiment. The heptane and water phases remain transparent throughout the operation in the high pressure cell, but heptane containing phase changes from colorless to yellow or brown. As the system is exposed to higher temperatures and pressures, the change in color becomes more intense and as figure 5.9 shows, the color of the heptane phase persists after the experiment.

5.3.5 Turbiscan

Initially the crude oil and brine solution were mixed in a glass tube appropriate for the Turbiscan MA 2000 with 30/70 vol% ratio. During mixing the oil/brine system by hand shaking, it was immediately observed that the system changed from a two-phase liquid system to a single gel-like phase (very sticky, jelly and basically immobile). This observation was the same for both crude oils. This effect was never observed under high pressures and temperatures (in the PVT cell). Therefore, the new system was investigated more thoroughly.

Initially the gel-like phase was observed over a period of time to find out whether the system would eventually return to the original two-phase form. As no change was observed after one week, it was concluded that at room temperature and atmospheric pressure the 'gel' phase was stable. In figure 5.10 the 'gel' formations produced by both crude oils are pictured.



Figure 5.10 Picture of the formation of a 'gel' phase occurring from hand shaking crude oil and brine solution together. This form is stable as long as the glass tubes are at room temperature and atmospheric pressure. The formed phase is sticky and jelly-like. It is immobile, even though it is not completely solid.

After one week, the gel-like phases were exposed to heat. At 50 °C the crude oil/brine systems reformed back to their original two phase liquid-liquid form and stayed in this state during cooling to room temperature. The effect of pressure on the gel-like phase was not considered in this work.

Light scattering analysis from the Turbiscan confirms that the stabilities of the oil/brine emulsions may be different. The emulsions formed by crude oils and DW are less stable than those from the crude oils and SW3S. For both crude oils the presence of brine rather than distilled water results in a larger emulsion phase which also persists for longer.

The Latin American crude oil mixed with distilled water was chosen to conduct further research on the gel-like phase formation. Different WOR were tested: 50/50 vol%, 20/80 vol% and 10/90 vol%. The gel-like behavior was observed for all the tested systems. A way to avoid the formation of a gel phase was to mix the crude oil and water in a tube of a larger diameter, (1.5 cm rather than 1.1 cm).

Four further experiments were conducted with 30/70 vol% WOR: two experiments with the Middle East Crude mixed with DW and SW3S and two with the Latin American Crude mixed with DW and SW3S. This time the glass tubes were only shaken gently, in order not to reach the 'gel' state, and immediately placed in the Turbiscan. They were operated for 2 hours and the samples were scanned every two minutes.

For the Latin American crude, separation of oil and brine takes longer in the case of DW compared with SW3S. This is in agreement with the observations of the phase separation of the samples. This indicates also that the sulfate ions in the SW3S solution act as emulsion destabilizing ions. Similar results were obtained in the experiments with the Middle East crude and DW and SW3S, where the separation of oil and water is faster in the case with no sulfate ions. It should be mentioned that these four experiments may have a significant margin of error due to the inherent uncertainty of the mixing procedure.

5.4 Discussion

5.4.1 Viscosity Variation of Crude oil

In the previous work [72] it was found that decrease in viscosity and formation of an emulsion phase could be a possible reason for the observed increase in oil recovery under high salinity flooding. In the SARA analysis it was observed that the Latin American crude oil exhibited greatest viscosity variation on contact with brine. Since this oil has a higher amount of heavy components (aromatics, resins and asphaltenes) compared to the Middle East crude oil, this suggests that viscosity of a crude oil with a high percentage of heavy components will vary most after interaction with brine solutions.

However, the GC analysis of the Latin American crude oil samples did not show any significant compositional change before and after contacting with the brine solutions in the PVT cell. Based on this finding, we propose that variation of viscosity of the crude oil, after contact with the brine solutions at high temperature and pressure, could be explained by a change in shape of heavy petroleum molecules in contact with the different ions. This happens in polymer solutions. Many authors reported decrease in viscosity of polymer solution when salt is added to solution [67, 68].

5.4.2 Emulsion Formation

SARA analysis revealed that the Middle East crude oil has a relatively high amount of light hydrocarbons. Furthermore, the GC analysis of the Middle East crude oil before and after interacting with the brine solutions in the PVT JEFRI cell showed that this oil originally had a higher content of light components compared to the oil after the experiment. The light components were possibly consumed by the emulsion phase formed. This indicates that formation of emulsions is correlated to the lighter components of the crude oil. In the heptane/brine interaction study, we observed formation of a significant emulsion phase after interacting with the brine solution in the PVT JEFRI cell. This also supports the hypothesis that the emulsions are formed by the lighter components of the crude oil.

A significant change in color of heptane was observed in the heptane/brine study in the PVT JEFRI cell. The heptane changed from colorless to yellow or brown after interacting with brine solutions with high sulfate concentration. The possibility of impurities in the equipment has been excluded: its cleaning has been carried out very thoroughly, and the color change was observed in repeated experiments with the same intensity of yellow or brown. Fernø et al. [14] also observed a color change in decane (from transparent to dark yellow) during high temperature spontaneous imbibition experiments with a brine solution having high sulfate concentration. Liberation of carboxylic components of crude oil from the chalk surface, by ion exchange or dissolution, was reported to be a reason for the color change. However, in our experiments the color changed in the absence of a porous medium, solely by interaction with the brine solution. The reason behind this change is not clear yet. However, the effect is pronounced and repeatable.

From the light scattering measurements it was observed that the crude oil/brine samples produced larger and more stable emulsions compared to crude oil/DW samples. This confirms that sulfate participates in mechanisms that control emulsion formation. Furthermore, the unexpected observation of a 'gel-like' phase formed from DW and crude oil creates a basis for speculation as to whether the crude oil/brine system could possibly act similarly under reservoir or production conditions. Formation of such a phase might be a problem for oil recovery. Unfortunately, due to the blackness of the crude oils, it was not possible to extract information about the droplet sizes of the dispersed phase in the Turbiscan experiments.

Emulsions of crude oil and water have been encountered at different stages of oil production (drilling, producing, transporting, processing etc.). These emulsions may be dispersions of water

particles in oil (W/O) or fine dispersions of oil in water (O/W), in some cases multiple emulsions may also be found [79, 80]. Pressure gradients over chokes and valves introduce high shear stress that causes dispersion of oil drops. Generally, crude oil components like asphaltenes, resins, waxes and naphthenic acids are considered to be surface active natural emulsifiers that are responsible for producing stable emulsions [80]. However, the emulsion phase (related to lighter components of the crude oil) that we observed in our experiments is apparently formed by a different mechanism. First, it is not produced under high shear stresses; its formation requires only gentle shaking. Secondly, it is formed without participation of heavy and complex petroleum components, which is confirmed in experiments with pure n-heptane. Our experiments show that formation of emulsions in the reservoirs and during production might be a much more widespread phenomenon, and probably much more important for petroleum recovery, than was previously believed.

5.5 Conclusions

1. SARA analysis of Latin American crude oil revealed that a crude oil with high amounts of heavy components exhibits viscosity decrease after contact with brine solutions.
2. No significant compositional change in GC analysis of the Latin American crude oil suggested that viscosity variation is possibly because of change of conformations of the heavy molecules like in polymer solutions [67].
3. SARA analysis of the Middle East crude oil and compositional changes in the range of lighter components in the GC analysis demonstrated that formation of emulsions is related to lighter components of a crude oil.
4. The heptane-brine systems formed emulsions in the JEFRI cell. But no change in heptane viscosity was observed. This may support the conclusion that viscosity variation in crude oil is attributed to the presence of heavy components, while formation of emulsions is related to lighter components.
5. The measurements in the Turbiscan confirmed that the presence of sulfate in the brine facilitates creation of the water-brine emulsions. A new observation was the formation of a 'gel-like' single phase under shaking the oil/brine samples in the course of their preparation for the Turbiscan. This may be an important, previously overseen mechanism affecting oil production.

5.6 Acknowledgements

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Paper IV

Zahid, A.; Shapiro, A. A.; Stenby, E. H. and Yan, W.

Managing Injected Water Composition to Improve Oil Recovery: A Case Study of North Sea Chalk Reservoirs

Submitted to Energy & Fuels (2011)

Seawater Flooding: A Case Study of North Sea Chalk Reservoirs

Abstract

In recent years, many core displacement experiments of oil by seawater performed on chalk rock samples have reported SO_4^{2-} , Ca^{2+} and Mg^{2+} as potential determining ions for improving oil recovery. Most of these studies were carried out with outcrop chalk core plugs. The objective of this study is to investigate the potential of the advanced waterflooding process by carrying out experiments with reservoir chalk samples. The study results in better understanding of the mechanisms involved in increasing the oil recovery with potential determining ions. We carried out waterflooding instead of spontaneous imbibition, which has been applied in most of the previous studies. Two different flooding schemes (with and without aging) were used for flooding North Sea reservoir chalk samples. For comparison, two tests were also carried out with Stevns Klint core plugs. The flooding tests were carried out with the following injecting fluids: distilled water, brine with and without sulfate, and brine containing only magnesium ions. The total oil recovery, recovery rate and interaction mechanisms of ions with rock were studied for different injecting fluids at different temperatures and wettability conditions. Studies of the temperature dependence of the oil recovery indicated that the interaction of the ions contained in brine with the rock cannot be the only determining mechanism of enhanced recovery. We observed no substitution of Ca^{2+} ions with Mg^{2+} ions at high temperatures for both rocks. Not only the injection brine composition, but also the formation water composition affected the oil recovery at high temperatures from the Stevns Klint chalk rock.

6.1 Introduction

Waterflooding has been the most widely used oil recovery method for many decades. Historically, the injected brine salinity was not considered as an important factor influencing the amount of oil recovered. However, over the last decade many studies have shown that waterflooding can be significantly improved by manipulating the injected brine chemistry both for sandstone and carbonate reservoirs [1, 59, 81-83]. The exceptional success of seawater injection in the Ekofisk chalk reservoir[32] has been the motivation for a number of

experimental studies to understand complex crude oil/water/rock chemical interactions for carbonate reservoirs.

Several laboratory experimental studies of water injection were carried out by Austad and co-workers, who used different core plugs and studied recovery as a function of brine composition and temperature [1, 17-20]. It was observed that SO_4^{2-} , Ca^{2+} and Mg^{2+} are the potential determining ions for improving the oil recovery in chalk reservoirs at high temperatures (above 90 °C). It was also reported that these ions must act together, because neither of them alone had an effect on spontaneous imbibition. Based on these experimental results, wettability alteration was proposed to be a key reason for the improvement of oil recovery. A schematic model of the chemical mechanism for wettability modification was suggested. According to this model, the ions adsorb to the rock surface, which changes the surface charge so that the adsorbed crude oil may be removed from the rock.

Webb et al. [84] presented a comparative study of the oil recovery from a North Sea carbonate core sample with simulated SO_4^{2-} free brine and with seawater containing SO_4^{2-} under reservoir conditions. The imbibition tests were performed with live oil. It was concluded that the wettability alteration of the carbonate rock with the SO_4^{2-} ion is responsible for the saturation changes.

Fjelde et al. [12] carried out spontaneous imbibition experiments using seawater and formation brine with core plugs from two fractured chalk fields at reservoir temperature. Only a small increase in oil recovery was observed with the seawater as compared to the formation brine (containing no SO_4^{2-}) for reservoir core plugs as compared to Stevns Klint outcrop chalk core plugs. Karoussi et al. [31] investigated extreme cases of waterflooding of Stevns Klint core plugs with ion-free water and water containing just Mg^{2+} or SO_4^{2-} ions. Water saturated with Mg^{2+} ions alone showed the highest oil recovery in the spontaneous imbibition experiments. Madland et al. [42] studied the effect of aqueous chemistry on the mechanical strength of chalk. Hydrostatic creep tests were carried out with continuous flooding of seawater, distilled water, NaCl and MgCl_2 . It was shown that the presence of only Mg^{2+} in the injected brine can deform the rock. Bagci et al. [61] also studied the effect of brine composition on oil recovery by waterflooding. Experiments were carried out with different brine compositions (NaCl, KCl, CaCl_2 and mixed brines such as 2 wt% KCl + 2 wt% NaCl, 2 wt% KCl + 5 wt% CaCl_2 etc). The highest oil recovery (18.8% higher than under distilled water injection) was observed for the 2 wt% KCl brine. No analysis of the reasons for such a recovery variation was presented.

In most of the studies discussed above outcrop chalk core plugs were used. Very few studies have been carried out using reservoir chalk core plugs. To our knowledge, no single study has yet been reported in the open literature about the interaction of potential determining ions with the reservoir rock at different temperatures and under different wetting conditions regarding oil recovery.

The objectives of this study are: (1) to experimentally investigate the oil recovery potential of the advanced waterflooding process for reservoir chalk samples at different wettability and temperature conditions; (2) to investigate reactivity of the potential determining ions towards the reservoir chalk surface; (3) to compare the reservoir chalk and the Stevns Klint outcrop core plugs with respect to oil recovery and reactivity of the potential determining ions under the same experimental conditions.

The flooding tests with North Sea chalk samples were carried out both with and without aging at different temperatures and using different injected brine solutions. For comparison, similar experiments were performed with the Stevns Klint outcrop chalk cores. All the flooding experiments were designed so that we could study both the oil recovery and the affinity of the potential determining ions with the chalk surface.

We carried out waterflooding instead of spontaneous imbibition, which was applied in most of the previous studies. Skauge et al. [85] reported high oil recovery for a carbonate core sample that showed no spontaneous water imbibition. Study of the forced injection is important, since viscous and gravity forces usually prevail over capillary forces at characteristic reservoir scales.

The paper is structured in the following way: The experimental methodology is described in the next section. The subsequent sections provide the results of laboratory core flooding study and detailed discussion. Finally, the conclusions are drawn.

6.2 Experimental

6.2.1 Core Plugs

Outcrop Stevns Klint core plugs and core plugs from two different North Sea chalk reservoirs were used in the experiments.

The outcrop chalk is of Maastrichtian age and has a large specific surface area of around $2 \text{ m}^2/\text{g}$, as determined by the nitrogen adsorption [86]. The porosity is about 46-48% and the permeability about 6-7 mD. The core plugs are very homogenous regarding permeability and porosity, which makes them suitable for parametric studies. The Stevns Klint core plugs were

3.6-3.8 cm in diameter and 7-8 cm in length. The core plugs were provided by the Danish Geotechnical Institute (GEO).

The core plugs from two different North Sea chalk reservoirs (1L and RE05) has a specific surface area of 2.06 and 2.10 m²/g, respectively, as determined by BET. The detailed properties of all the core plugs used in this study are given in Table 6.1. In order to confirm the homogeneity of the cores and absence of fissures, X-ray computer tomography (CT) scan analysis was performed on each core plug.

Table 6.1 Core Plug properties

Name of Plug	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (mD)
North Sea(1L)	5.79	2.57	31.74	0.97
North Sea (RE05)	7.47	3.72	37.87	0.83
Stevns Klint - 1	7.70	3.69	47-50	6.48
Stevns Klint - 2	7.86	3.82	47-50	6.96

6.2.2 Crude Oil

We used North Sea dead crude oil for this study. Density, acid number, base number and viscosity of the crude oil are given in Table 3.1.

6.2.3 Brine Solutions

The synthetic brine solutions were prepared by adding different amounts of NaCl, NaHCO₃, KCl, MgCl₂·6H₂O, CaCl₂·2H₂O and Na₂SO₄ to distilled water. Three different brine solutions were prepared for injection: 1) synthetic seawater without sulfate ions (SW0S); 2) sulfate concentration three times larger than in the synthetic seawater (SW3S); 3) 0.1M MgCl₂ (0.1M Mg). The total dissolved solid amounts for the first two brine solutions was made similar by adjusting the amount of NaCl. North Sea synthetic formation water (FW) was also prepared for using as initial water in the tests. The detailed compositions of all the brine solutions are given in Table 6.2.

Table 6.2 Different brine compositions.

	SW0S (ppm)	SW3S (ppm)	FW (ppm)
Na⁺	8471.18	7758.46	31022.62
K⁺	390.98	390.98	521.84
Mg²⁺	1093.73	1093.73	664.95
Ca²⁺	521.01	521.01	5667.24
Cl⁻	17459.61	11255.33	60272.08
HCO₃⁻	122.03	122.03	13.07
SO₄²⁻	0.000	6916.32	0.000
TDS(g/L)	33.39	33.39	98.158

6.2.4 Core Preparation

Prior to any flooding experiment, the core plugs from the North Sea reservoirs were cleaned. They were put into a Hassler core holder, flooded with toluene until the effluent was colorless, and then flooded with ethanol. After cleaning, the core plugs were dried in an oven at 90 °C to constant weight. The dried core plugs were flooded with distilled water at 40 °C. The pore volume was calculated by comparing the weights of the dry and the saturated core. We established initial water saturation by flooding the confined core by 5-7 pore volumes (pv) of crude oil at an injection rate of 0.2cc/min at 70 °C. Afterwards, the two different flooding sequences were applied, as shown in Figure 6.1. Flooding sequence 1 was without aging of the plug in crude oil, while flooding sequence 2 involved aging. For aging in flooding sequence 2, three pore volumes of crude oil were flooded from both sides of the core plug. The saturated core was then aged for three days at 80 °C. Flooding sequence 2 was not applied to second North Sea chalk sample RE05. We assumed that solvent cleaned reservoir cores are water wet, and remain so during flooding sequence 1, and that they probably become more oil-wet during sequence 2. This assumption is partly confirmed by appearance of recovery after breakthrough in the flooding sequence 2.

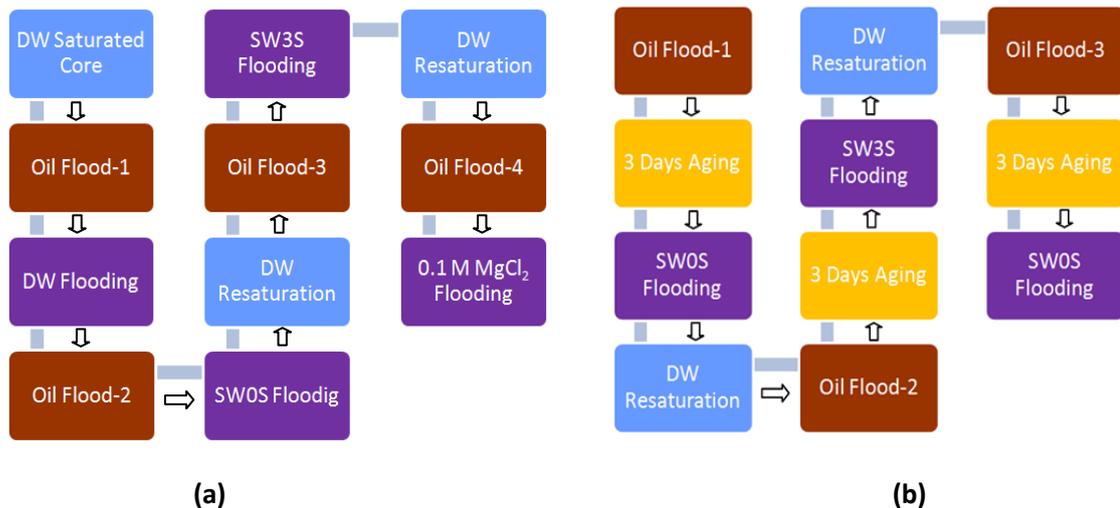


Figure 6.1 (a) Flooding sequence 1 without aging. (b) Flooding sequence 2 with aging. DW (distilled water); SWOS (synthetic seawater without sulfate ions); SW3S (sulfate concentration three times larger than in the synthetic seawater)

The drilled core plugs from Stevns Klint were dried in the oven at 90 °C overnight. Then they were saturated with a brine solution for three hours under vacuum, after which the pore volume was calculated for each core plug. Initial water saturation was established in the same way as for the reservoir core plug. No aging was carried out with the Stevns Klint plugs.

Initial water saturation is high in the core plugs as compared to average saturation in reservoirs. Tang et al.[87] conducted a study on the effect of initial water saturation with Kansas outcrop chalk samples (Kansas outcrop chalk is very similar to the rock matrix of the North Sea fractured chalk reservoirs). They concluded that initial water saturation has a significant effect on water injection in an intermediate-wet chalk. This effect is much less pronounced for a water-wet chalk. In our study, flooding sequence 1 with reservoir chalks and tests with Stevns Klint are at water-wet condition (without aging). So, in these cases, possibly the effect is less pronounced. It could affect the two tests in flooding sequence 2 with reservoir chalk core plug (1L).

6.2.5 Flooding Schemes

In all the experiments, flooding was initially carried out at 40 °C. When no more oil came out, the temperature was increased to 70 °C, and finally to 120 °C. The flooding tests were carried out with a sleeve pressure of 70 bar for the reservoir core plugs and 30 bar for the outcrop core plugs. A back pressure of 12 bar was used for all the experiments to avoid boiling of the liquids. The volume of produced oil was measured as a function of pore volumes injected.

6.2.6 Chemical Analysis

Effluent was collected by means of a fractional collector at different time intervals and analyzed for potential determining ions (SO_4^{2-} , Ca^{2+} and Mg^{2+}). The SO_4^{2-} ion was detected with the ion

chromatograph DX-120 produced by Dionex, USA. The Ca^{2+} and Mg^{2+} ions were analyzed with the ICP (Inductive Coupled Plasma) Varian 720-ES. The effluent samples were diluted with deionized water before the analysis to meet the concentration limits of the equipment.

6.3 Results

6.3.1 North Sea Chalk Reservoir Core Plug (1L)

6.3.1.1 Flooding Sequence 1

In flooding sequence 1, a preliminary flooding test was carried out at 40 °C with a plug initially saturated by oil and distilled water. First, distilled water was injected at a relatively slow injection rate of 2pv/day. When the production stopped, the temperature of the system was increased to 70 °C and finally to 120 °C. As shown in Figure 6.2a, 53.1% OOIP (original oil in place) was recovered after injection of the distilled water at 40 °C. The oil was produced only before the water breakthrough, so that the displacement looked piston-like. Increasing the temperature to 70 and 120 °C produced no additional oil.

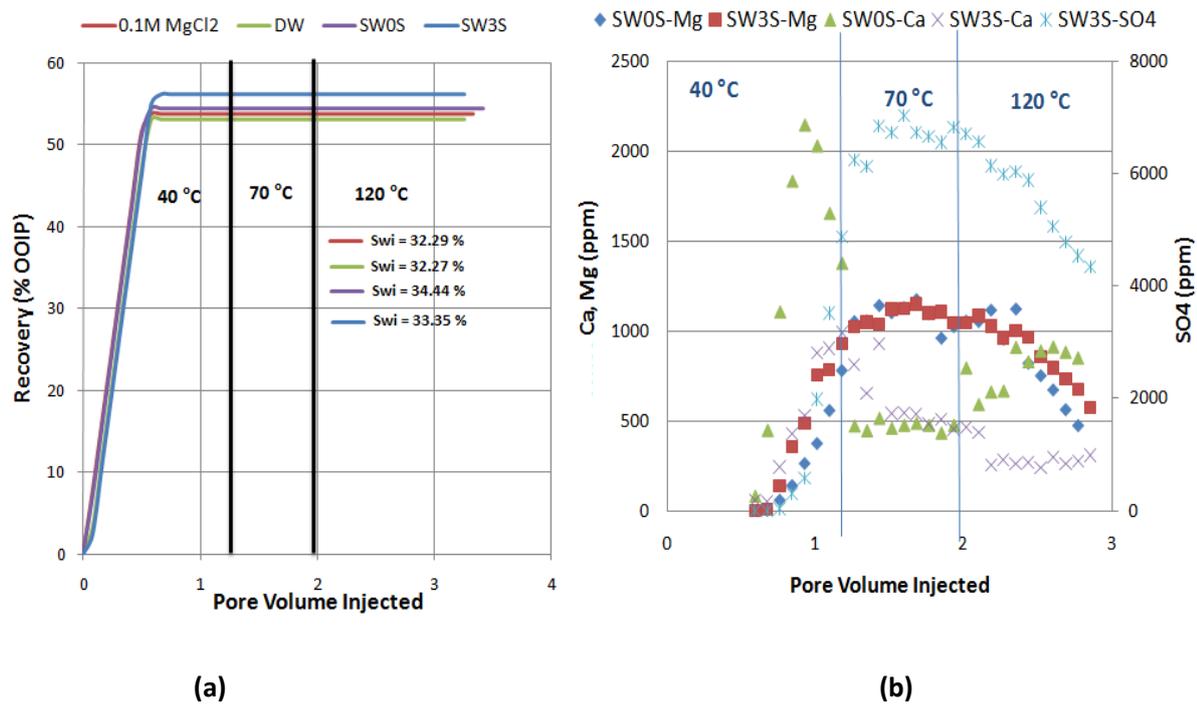


Figure 6.2 (a) Waterflooding in North Sea chalk core plug (1L) without aging, oil recovery (% OOIP) as a function of pore volume injected. (b) Effluent ion concentrations as a function of pore volume injected.

After completion of the first cycle, the core was resaturated with distilled water and afterwards 7 pv of crude oil was injected to establish the initial water saturation. In the second cycle, the core was flooded with SW0S brine at 40, 70 and 120 °C, in the same way as for the first cycle.

Also in this case no oil was produced after water breakthrough, and an increase in temperature to 70 and 120 °C did not result in additional production, as shown in Figure 6.2a. The total amount of oil produced was 54.4% OOIP. The effluent was analyzed for Ca^{2+} and Mg^{2+} ions at different temperatures. The results, plotted in Figure 6.2b, indicate that the concentration of Ca^{2+} and Mg^{2+} ions in the effluent increases with time at 40 °C. This is because at the initial stage of flooding the distilled water, which was initially in the core, comes out of it. The concentration for both ions remains approximately constant at 70 °C, and the concentration of Ca^{2+} increases, while the Mg^{2+} concentration decreases in the effluent at 120 °C.

In the third cycle the core was resaturated with distilled water and then initial water saturation was established in the same way as for the second cycle. In this case, the core was flooded with brine SW3S with the same injection rate of 2 pv/day. This relatively slow injection rate was used in order to allow the different potential determining ions to interact with the chalk matrix. The oil recovery at 40 °C was 56.1% OOIP, which is 1.7% higher than for the SW0S injection. Increasing the temperature to 70 and 120 °C did not improve the oil recovery. The concentration of the different potential determining ions increased with time at 40 °C and remained approximately constant at 70 °C, but at 120 °C the concentration of all the ions decreased in the effluent.

In the fourth cycle, the core was flooded with the 0.1 M MgCl_2 brine solution in the same sequence as above, in order to check the effect of Mg^{2+} ions on the reservoir chalk core plug. 53.8% OOIP of oil was produced in this case, which is less than for the SW3S flooding. Thus, in this case Mg^{2+} ions did not help increasing oil recovery, compared to SO_4^{2-} ions. The effluent was also analyzed for Ca^{2+} and Mg^{2+} ions, and the trend in the Mg^{2+} ion concentration was the same as for the SW3S case.

6.3.1.2 Flooding Sequence 2

After completion of flooding sequence 1, the core was resaturated with distilled water and initial water saturation was established by flooding 3 pv of crude oil from both sides of the core plug. After establishing initial water saturation, the core was aged at 90 °C for three days. In the first cycle of this flooding sequence, the core was flooded with brine SW0S in the same way as in flooding sequence 1. This resulted in a final oil recovery of 50.7% OOIP. As shown in Figure 6.3a, most of the oil was produced before the water breakthrough, but some oil was also produced after the breakthrough. For comparison, no oil was produced after breakthrough in flooding sequence 1. Increasing the temperature to 70 and 120° C did not improve the oil

recovery. The effluent was also analyzed for Ca^{2+} and Mg^{2+} concentrations, which are plotted in Figure 6.3b.

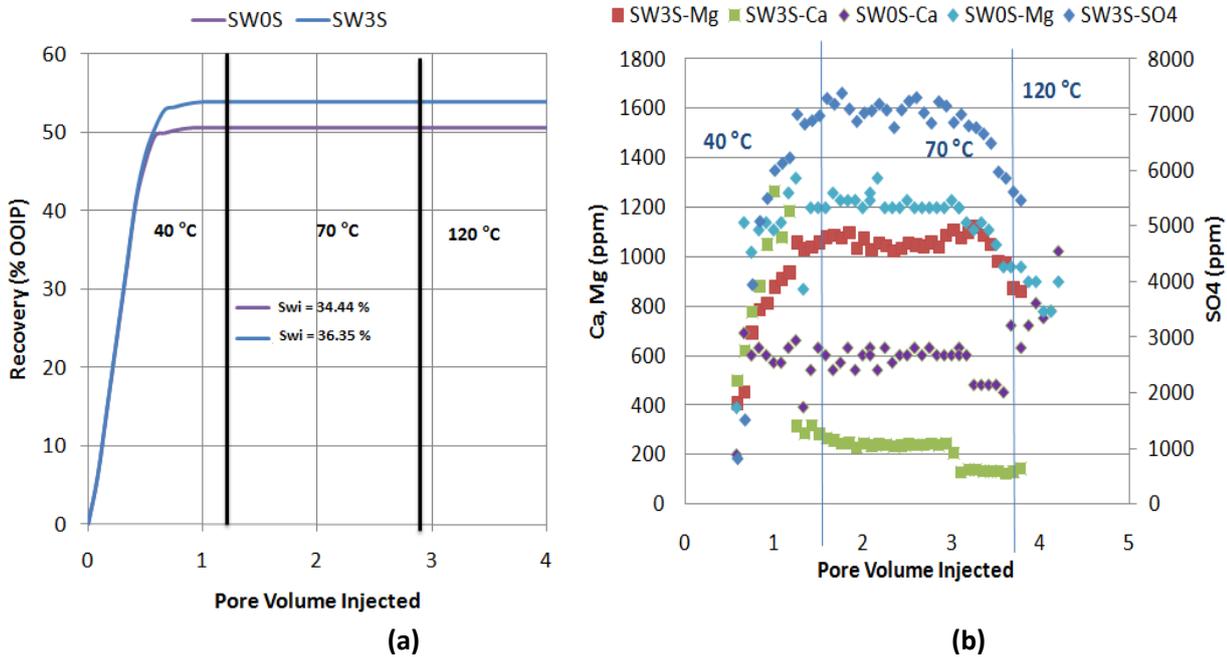


Figure 6.3 (a) Waterflooding in North Sea chalk (1L) core plug with aging, oil recovery (% OOIP) as a function of pore volume injected. (b) Effluent ion concentrations as a function of pore volume injected.

The reactivity trend of these ions with the rock is the same as in flooding sequence 1. The concentration of Ca^{2+} in the effluent increases, while the concentration of Mg^{2+} decreases with time at 120 °C. In cycle 2 of flooding sequence 2, the core was flooded with brine SW3S, which resulted in an oil recovery of 53.4% OOIP. This is around 2.7 % higher than for cycle 1. No more oil was produced with the increase in temperature also in this case. The effluent ion profile of Ca^{2+} , Mg^{2+} and SO_4^{2-} is plotted in Figure 6.3b.

In cycle 3, we flooded the core plug (Swi 35.1%) with SW0S brine again to check the repeatability of the tests. 50.9% OOIP oil was produced, which is very similar to the previous test (not plotted).

6.3.1.3 Formation Brine Composition

In all the flooding tests and flooding sequences described until now, distilled water was used to establish initial water saturation in the cores. One more test was carried out with the North Sea formation brine as initial water to check if this could affect the oil recovery mechanism. After the completion of flooding sequence 2, the core was cleaned with toluene and ethanol and was dried in an oven until constant weight was achieved. The core plug saturated with the North Sea formation brine and crude oil was flooded with the SW3S brine at different

temperatures. As in the previous cases, in this case increase of the temperature did not result in recovery increase, as shown in Figure 6.4a. The effluent was analyzed for potential determining ions (not plotted). The reactivity trend of the ions remained the same as in the case of SW3S injection in flooding sequences 1 and 2.

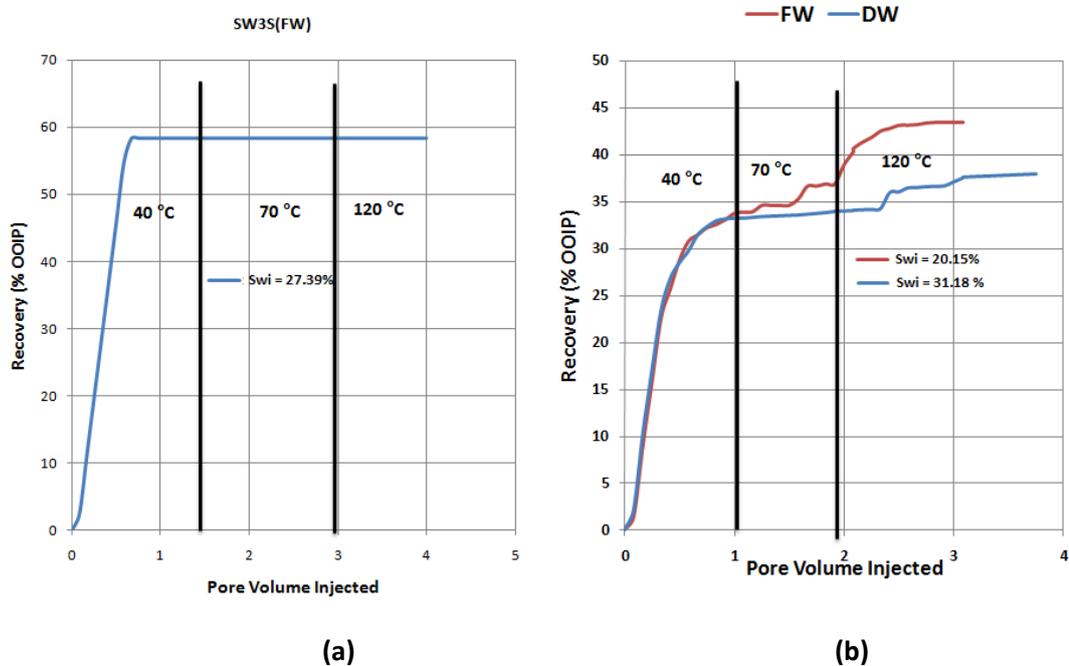


Figure 6.4 (a) SW3S brine injection in North Sea chalk (1L) core plug without aging with North Sea formation brine as initial water. (b) SW3S brine injection in two Stevns Klint chalk core plugs without aging with distilled water and North Sea formation brine as initial water.

6.3.2 Stevns Klint Chalk Plugs

For comparison, two flooding tests were carried out with the Stevns Klint chalk cores. Both tests were carried out with the same injected fluid SW3S, but with the different compositions of water forming initial water saturation. In the first test, the core was saturated with distilled water, after which initial water saturation was established by flooding 7 pv of crude oil. The saturated core plug was then flooded with SW3S at 40 °C. This resulted in an oil recovery of 33.8% OOIP. As shown in Figure 6.4b, the oil production at water breakthrough was 26.1% OOIP, and after water breakthrough an additional 7.7% OOIP was produced. Increasing the temperature to 70 and 120 °C resulted in an additional production of 0.4 and 3.7% OOIP, respectively. Thus, the temperature played an important role in recovering more oil after water breakthrough in the Stevns Klint case, which is in accordance with most of the previous studies [1, 69].

In the second test, a core plug was saturated with the North Sea reservoir formation brine and then initial water saturation was established by flooding with crude oil. Flooding was carried out with brine SW3S at 40 °C and resulted in an oil recovery of 34.6% OOIP. As shown in Figure

6.4b, 8.9% OOIP was produced after water breakthrough. Increasing the temperature to 70 and then to 120 °C resulted in an additional production of 2.3% and 6.6% OOIP, respectively.

The effluent was analyzed for the three potential determining ions for both tests, and the concentration profiles are presented in Figure 6.5.

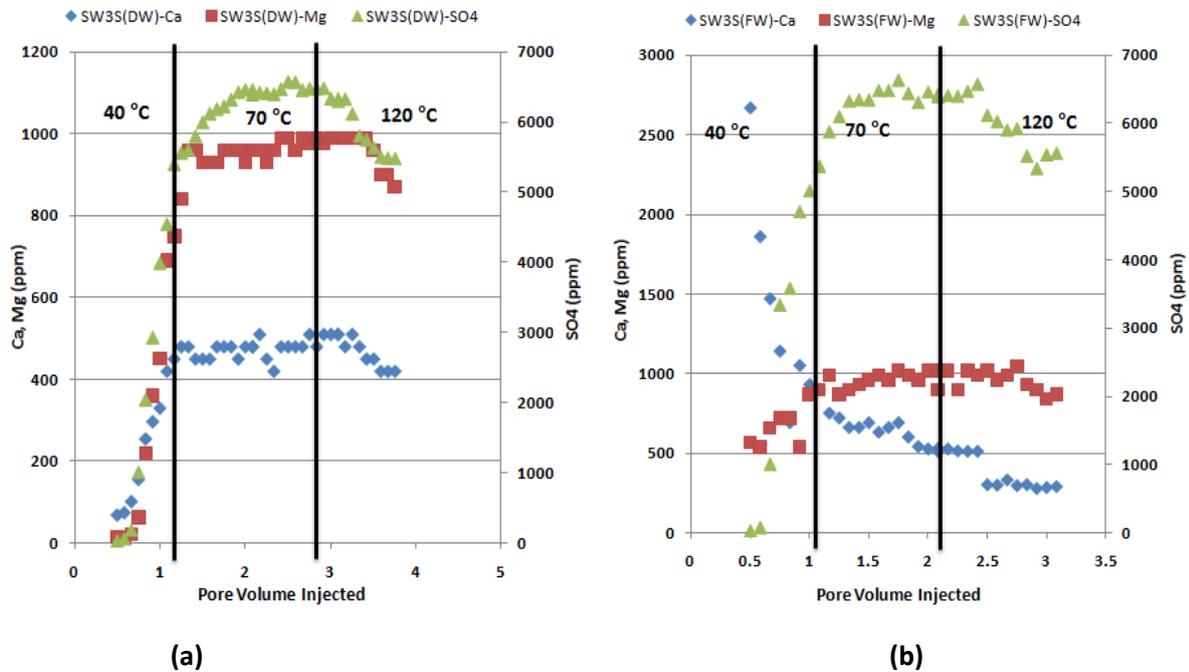


Figure 6.5 (a) Effluent ion concentrations during SW3S brine injection in Stevns Klint chalk core plugs with distilled water as initial water. (b) Effluent ion concentrations during SW3S brine injection in Stevns Klint chalk core plugs with North Sea formation brine as initial water.

In Figure 6.5a, at 40 °C the concentration of all the ions increases with time (because initial formation water is distilled), remains approximately constant at 70 °C and decreases at 120 °C. In Figure 6.5b, the calcium ion concentration decreases at 40 °C because the formation water already has a high calcium concentration as compared to the injected brine SW3S. The reactivity trend of rest of the ions at different temperatures is the same as for the first test.

6.3.3 North Sea Chalk Reservoir Core Plug (RE05)

6.3.3.1 Flooding Sequence 1

Another coreflood experiment was conducted using a different reservoir chalk core plug RE05 to check especially the effect of temperature on oil recovery. The core was first flooded with brine SW0S under different temperatures, in the same way as in flooding sequence 1 for first North Sea chalk sample (1L). As shown in Figure 6.6, 50.9% OOIP was recovered after injection of SW0S at 40 °C. A significant amount of oil was produced after water breakthrough. Increasing the temperature to 70 and 120 °C resulted in an additional production of 2.2% OOIP.

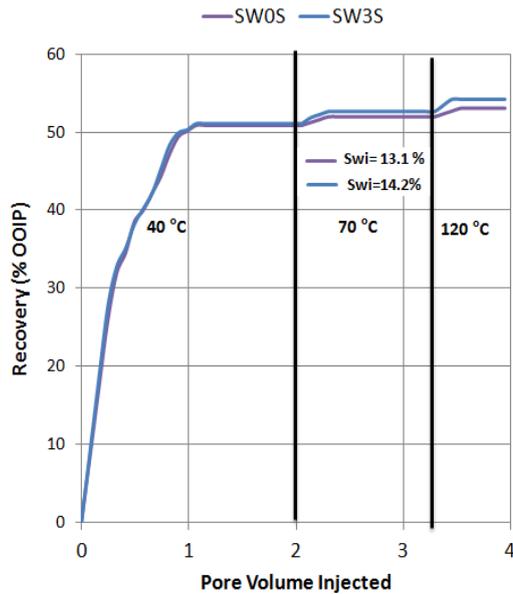


Figure 6.6 Waterflooding in North Sea chalk (RE05) core plug without aging, oil recovery (% OOIP) as a function of pore volume injected.

In the second cycle, the core was flooded with the SW3S brine solution with the same injection rate and temperature sequence as was adopted for the first cycle. The oil recovery at 40 °C was 51.1% OOIP. Increasing the temperature to 70 and then to 120 °C resulted in an additional production of 3.1% OOIP. For both cycles, oil production at 40 °C is approximately the same, as shown in Figure 6.7. However, at 70 and 120 °C the core plug flooded by SW3S brine produced approximately 0.7% and 1.2% OOIP more oil, respectively, as compared to the core plug flooded with SW0S brine.

6.4 Discussion

6.4.1 Effect of Reactivity of Potential Determining Ions

It has been established that seawater is an excellent injection fluid for high temperature chalk reservoirs because of the presence of potential determining ions (SO_4^{2-} , Ca^{2+} and Mg^{2+}) [69]. We have carried out all the experiments at both low and high temperatures to investigate the potential of seawater flooding. We observed no increment in oil recovery with increase in temperature for both flooding sequences (with and without aging) for reservoir chalk sample 1L. On the contrary, experiments with the Stevns Klint outcrop chalk showed a very clear effect of the temperature. Increasing the temperature produced additional 4.1 % and 5.2% OOIP oil for the first and second test, respectively (see Figure 6.4b). For another reservoir rock sample RE05, increasing the temperature resulted an additional oil recovery of 2.2 and 3.1 % OOIP during SW0S and SW3S brines flooding, respectively.

Strand et al.[19] mentioned reactivity of potential determining ions with chalk surface (of rock-fluid interactions and symbiotic interactions between the three ions: Ca^{2+} , Mg^{2+} and SO_4^{2-} or mutual affinity of the ions towards the rock) as a necessary condition for improving the oil recovery. This reactivity increases with increase in temperature for reservoir (1L) and outcrop rock. Meanwhile, recovery in our experiments increased with the temperature only for reservoir rock RE05 and for the outcrop chalk samples. The effect for the reservoir rock was RE05 was considerably lower than for the outcrop chalk. No effect of temperature on oil recovery was observed in case of reservoir rock 1L.

One explanation for the observed differences might be that potential determining ions did not react in the same way with the reservoir chalk (1L) as with the Stevns Klint rock. However, Figures 6.2b, 6.3b, 6.5a and 6.5b show that the reactivity trend of potential determining ions at different temperatures is the same for both 1L and Stevns Klint cores. Thus, it is possible that in some rock the potential determining ions react with the internal porous surface, but this has no effect on the recovery. For such reservoir rocks it is not the ion interaction which controls the oil recovery process. For the outcrop chalks and for other reservoir rocks like RE05 it could be one of the controlling mechanisms for the oil recovery process.

In general, concentration of all potential determining ions at high temperature decreases in the effluent. This decrease in concentration could be because of high adsorption (Austad et al.[17] reported high adsorption of sulfate at high temperature) or due to in situ precipitation of CaSO_4 .

Lack of extra recovery at high temperature in reservoir rock (1L) cannot be explained by a low acid number of the crude oil (see Table 6.2), since the same crude oil was used for all the rock types (North Sea chalk samples and Stevns Klint cores). Hence, an explanation of the observed effects cannot be based on water-oil interactions alone, but should involve interactions with rock. A more precise explanation should be found in additional studies.

6.4.2 Reactivity of Potential Determining Ions and Effect of Aging

Verification of the aging effect on recovery is achieved by comparison of the flooding experiments with and without aging (see Section 3.1.2). The concentrations of the effluent ions are plotted in Figure 6.7 for both flooding schemes. As shown in the figure, for injection of the SW3S brine the ion interaction behavior is similar with and without aging, but a lesser loss of ions is observed in the case of aging. Possibly, the oil layer formed on the rock surface by aging hinders or prevents reaction. The results are similar for injection of SW0S (not plotted).

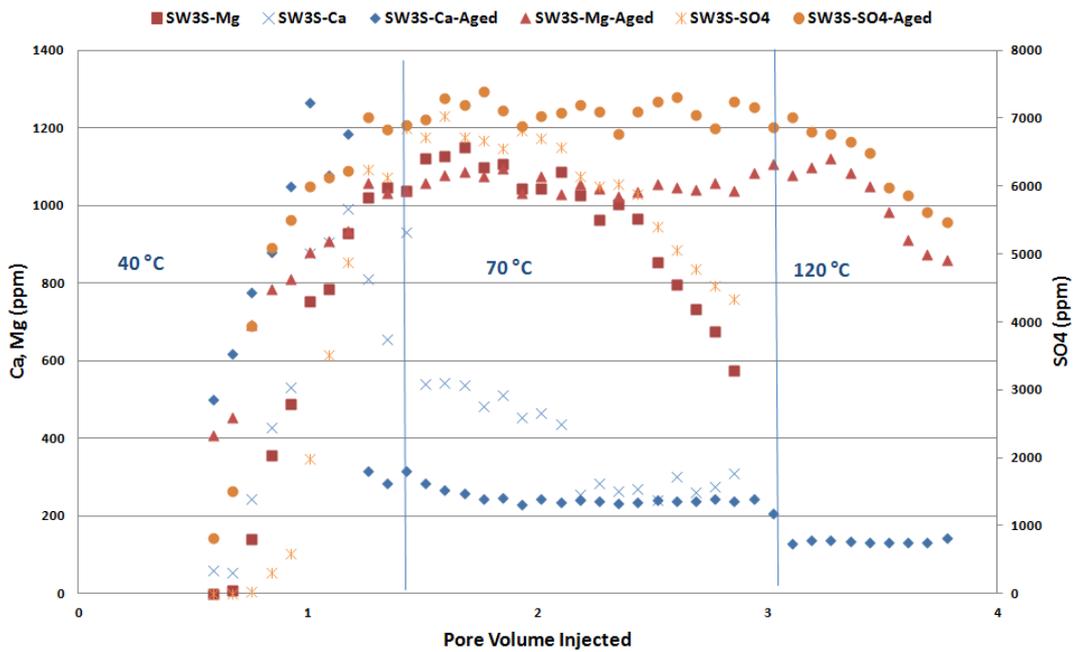


Figure 6.7 Effluent ion concentrations during SW3S brine injection at different wetting conditions in North Sea chalk core plug (1L). Comparatively, lesser loss of ions is observed in the case of aging.

6.4.3 Substitution Reaction

Zhang et al.[20] reported an increase in the effluent calcium concentration during seawater flooding in Stevns Klint cores at the temperatures above 100 °C. This effect was interpreted as a result of substitution of Ca^{2+} by Mg^{2+} ions on the internal rock surface. This substitution reaction is reported as a possible reason for an increment in oil recovery.

In our experiments, we did not observe this substitution reaction during SW3S flooding, neither with Stevns Klint rock, nor with the reservoir chalk (1L). Unexpectedly, an increase of the Ca^{2+} ion concentration in the effluent was observed during SWOS flooding above 100 °C in reservoir chalk (1L), for both flooding sequences, but a reason for this is not clear.

6.4.4 Effect of the Composition of Formation Brine

The effect of the composition of the formation brine was studied and tested in the two experiments with the Stevns Klint core plugs. The initial water saturation was formed by the distilled water for the first plug ($S_{wi} = 31.18\%$), and by the reservoir brine for the second plug ($S_{wi} = 20.15\%$), as described in Section 3.2. This significant difference in initial water saturations shows that initial water composition also affects drainage: the water displacement by the crude oil. This was also observed for the reservoir core 1L (5 % difference in initial saturations). For both tests with the Stevns Klint plugs, the oil production at 40 °C is approximately the same, as shown in Figure 6.4b. However, at 70 and 120 °C the core plug initially saturated by formation brine produced approximately 2% and 3.2% OOIP more oil, respectively, compared to the core

plug saturated with distilled water. This indicates that not only the injection brine composition, but also different ions in the formation brine can increase the oil recovery at high temperatures. This difference in oil recovery may not be attributed to the difference in initial water saturations, since if this was the reason then there should have been a difference in oil recoveries also at 40 °C. Possibly, at high temperatures some ions in the formation water affect the recovery. For the reservoir chalk core 1L, high temperatures did not help to improve the oil recovery for the different compositions of the formation brine.

6.4.5 Outcrop Chalk as a Substitute in Flooding Tests

The outcrop rock was used in many studies as a model for reservoir rock because of easy availability and good rock characterization. We used both the reservoir and outcrop rocks for this study. Experimental results demonstrate that the oil recovery mechanism at high temperatures is different for the different rocks, although they have similar surface area and reactivity of potential determining ions. Enrichment of the brine by sulfate ions increased oil recovery under water wetting conditions, but a comparatively less recovery increment was observed for the reservoir core plugs than for the Stevns Klint outcrop chalk samples. Recovery in the experiments with the outcrop chalk is strongly temperature dependent[19]. Meanwhile, the experiments with the reservoir chalk rocks showed relatively less effect of temperature as compared to Stevns Klint in one case (RE05) and no effect of temperature in another case (1L). This indicates that the rock may also determine whether the effect of the temperature on the recovery is observed. It should also be remarked that a much lower recovery at 40 °C from the outcrop chalk cores (less than 35% OOIP) could contribute to additional recovery at higher temperatures compared to the reservoir core plugs (which had already established quite high recovery > 50% at 40 °C). The reservoir rock, unlike the outcrop chalk, has stayed in contact with oil under reservoir pressure and temperature for many years. This could be the reason for the different responses of these rocks on flooding. Thus, care should be taken in using outcrop chalk as a model for reservoir chalk and, in particular, for the water based IOR.

6.5 Conclusions

1. Temperature did not affect oil recovery in experiments with one reservoir rock sample and showed relatively insignificant effect for another reservoir rock sample, while flooding of the Stevns Klint outcrop chalk rock was strongly affected by the temperature.
2. Interaction of different ions with rock depends on the temperature, meanwhile for the recovery this is not always the case. This indicates that in some rocks, interaction of the ions with rock is not the main controlling factor for the oil recovery process. However for other reservoir rocks, it could be the controlling parameter.

3. In the two different flooding schemes (with and without aging of core plug), the trend of interaction of ions with reservoir rock remains the same, but a comparatively smaller loss of ions was observed in the aged core.
4. Enrichment of the brine by sulfate ions increased oil recovery under water wetting conditions, but the comparative recovery increment was less for the reservoir core plugs than for the Stevns Klint outcrop chalk.
5. No substitution of Ca^{2+} ions by Mg^{2+} ions was observed under high temperatures for the Stevns Klint cores.
6. The initial brine composition showed an effect on oil recovery under high temperatures for the outcrop chalk, but not for the reservoir rock.
7. Care should be taken when using outcrop chalk as a model for reservoir chalk and, in particular, for the water based IOR. Since the mechanisms for efficiency of this IOR method are not totally clear, it should be checked every time with exactly that type of rock where it will be applied.

6.6 Acknowledgements

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Paper V

Zahid, A.; Shapiro, A. and Skauge, A.

Experimental Studies of Low Salinity Waterflooding in Carbonate Reservoirs

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Experimental Studies of Low Salinity Waterflooding in Carbonate Reservoirs

Abstract

In recent decade, laboratory waterflood and successful field tests have showed that low salinity waterflooding can improve the oil recovery in sandstone reservoirs. However, low salinity effect has not been thoroughly investigated for carbonates. Most recently, Saudi Aramco reported significant increase in oil recovery by low salinity waterflooding in Saudi Arabian carbonate reservoirs. The experimental data on carbonates is very limited, so more data plus mechanistic studies is needed to understand and utilize this method for carbonate reservoirs. In this paper, we have experimentally investigated the oil recovery potential of low salinity water flooding for carbonate rocks. We used the reservoir carbonate and outcrop chalk core plugs. The flooding experiments were carried out initially with the seawater, and afterwards the contribution to oil recovery was evaluated by sequential injection of various diluted versions of the seawater. The total oil recovery, interaction of the different ions with the rock, and the wettability changes were studied both at the room and the high temperature. No low salinity effect was observed for the reservoir carbonate core plug at the room temperature, but increase of the pressure drop over the core plug is detected. On the contrary, a significant increase in oil recovery was observed under low salinity flooding of the reservoir carbonate core plugs at 90 °C. An increase in pressure drop was also observed in this case, possibly related to migration of fines or dissolution. The Aalborg chalk core plugs did not show any low salinity effect, both at the room and at a high temperature. In the light of experimental results, discussions are made about possible mechanisms for improving oil recovery in carbonate reservoir as a function of change in brine salinity.

7.1 Introduction

In the last decade, low salinity waterflooding has been emerged as a very prospective EOR method. An extensive laboratory research carried out by Morrow and coworkers showed that low salinity waterflooding can improve the oil recovery for both outcrop and reservoir rocks

[21-24]. Successful field tests and field wide analysis also documented increase in oil recovery by injecting brine of low salinity [14, 25-27]. Many recent examples of increased in oil recovery by low salinity waterflooding also confirmed this emerging trend [15, 48]. In most of these studies, 15-20 % extra oil recovery from low salinity waterflooding is reported.

In most of the reported low salinity waterflooding studies, sandstone core plugs were used. Very few studies have been carried out using carbonate core plugs. The reason is that the low salinity effect was mainly attributed to interaction with the clay minerals, which are lacking in carbonates[13]. Doust et al. [28] reported however a different chemical mechanism may also be responsible for the effect: it is the crude oil adsorption onto positively charged calcite surface and negatively charged quartz surface.

Fathi et al. [9] carried out spontaneous imbibition and flooding tests with low salinity brine solutions using Stevens Klint outcrop chalk core plugs at 110 and 120 °C. A negative impact of diluting the seawater to low salinity was reported which significantly decreased oil recovery in spontaneous imbibition. Tertiary diluted seawater flooding also did not help in producing any extra oil. Decrease in the concentration of the active ions (SO_4^{2-} , Ca^{2+} and Mg^{2+}) was reported as a reason for drastic decrease in oil recovery.

Contrary to these results, Saudi Aramco reported 16-18 % OOIP increase in oil recovery by low salinity waterflooding in composite rock samples from Saudi Arabian carbonate reservoirs[29]. Experiments were carried out using live oil and at a reservoir temperature of 212 °F. Wettability alteration (determined by NMR T2 distribution and contact angle measurement) was reported as a key mechanism for increment in oil recovery.

The objectives of the present study are: (1) to experimentally investigate low salinity effect for carbonate core samples; (2) to study wettability alteration using NMR; (3) to investigate reactivity of the potential determining ions towards the rock surface.

We used Middle East carbonate reservoir carbonates and Aalborg chalk core plugs for this study. The flooding experiments were carried out initially with seawater, and afterwards the contribution to oil recovery was evaluated by sequential injection of the differently diluted seawater. Total oil recovery, ion interaction and wettability change were studied for both the rocks at the room and at a high temperature.

7.2 Experimental

7.2.1 Core Plugs

Three core plugs from Middle East carbonate reservoir and three outcrop Aalborg chalk core plugs were used in the experiments.

The outcrop chalk is of Maastrichtian age and has high non-carbonate content. Strand et al.[88] reported 6 wt. % silicates in the form of quartz and opal-CT. The high silica content indicates the high water-wet surface fraction and the wetting condition of the core. The porosity of the cores is about 32-34% and the permeability is about 2-4 mD. The core plugs are very homogenous regarding permeability and porosity. They are 3.77 cm in diameter and 6-7 cm in length.

The core plugs from the Middle East carbonate reservoir are of Lower Cretaceous age and have a specific surface area of 2.02 m²/g, as determined by BET. The porosity of this material is 25% and the permeability is 0.973 mD. The detailed properties of all the core plugs used in this study are given in Table 7.1.

Table 7.1 Core plug properties

Name of Plug	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (mD)
<i>Middle East carbonate reservoir core plugs</i>				
ME-1	4.48	3.78	19.4	245
ME-2	3.81	3.78	19.4	308
ME-3	5.58	3.79	19.2	275
<i>Aalborg reservoirs core plugs</i>				
AA-04	6.46	3.77	33.3	3.1
AA -05	6.47	3.77	33.4	3.2
AA -06	6.51	3.77	33.3	3.1

X-ray diffraction (XRD) analyses of both rock samples (Middle East carbonate reservoir and Aalborg chalk) were carried out to identify the chemical composition. The crushed material of both rock samples is composed of mainly calcite with some quartz. There was no dolomite and anhydrite in both samples.

7.2.2 Crude Oil

Crude oil from Middle East carbonate reservoir has been used for this study. Acid and base numbers of the crude oil were measured using Metrohm 702 SM Titrino by the methods developed by Fan and Buckley[89] (modified versions of ASTM D2896 for the base number titration and of ASTM D664 for the acid number titration). Density, acid number, base number and viscosity of the crude oil are given in Table 7.2.

Table 7.2 Crude oil properties

	Density @ 22 C (g/cm ³)	Acid number (mg KOH/g)	Base number (mg KOH/g)	Viscosity (cp)
Middle East carbonate reservoir oil	0.838	0.96	0.15	3.21

7.2.3 Brine Solutions

Two different brine solutions were prepared: 1) formation water (FW) to establish initial water saturation; 2) synthetic seawater (SSW) as an injecting brine solution to displace crude oil. The total dissolved solids (TDS) for FW and SSW is 213,734 and 57,670 ppm, respectively. In addition to these, three different dilutions of seawater were also prepared to study the low salinity effect. The twice, ten times and twenty times diluted seawater will be denoted by LS-2, LS-10 and LS-20, correspondingly. The detailed composition of all the brine solutions, their density and viscosity are given in Table 7.3 and Table 7.4.

Table 7.3 Brine compositions and ions concentration

Component	FW (ppm)	SSW (ppm)	LS-2 (ppm)	LS-10 (ppm)	LS-20 (ppm)
Na ⁺	59,491	18,300	9150	915	45.75
Mg ²⁺	2439	2110	1055	105.5	5.28
Ca ²⁺	19,040	650	325	32.5	1.63
Cl ⁻	132,060	32,200	16100	1610	80.5
HCO ₃ ⁻	354	120	60	30	1.5
SO ₄ ²⁻	350	4290	2145	214.5	10.73
TDS	213,734	57,670	33.39	33.39	33.39

Table 7.4 Density and viscosity of brine solutions

Property	FW	SSW	LS-2	LS-10	LS-20
Density (g/cm ³)	1.425	1.044	1.026	1.011	1.009
Viscosity (cp)	0.933	0.767	0.745	0.725	0.716

7.2.4 Core Preparation

The core plugs from the Middle East carbonate reservoir were cleaned by flooding toluene and then with ethanol. After cleaning, the core plugs were dried in an oven at 90 °C to constant weight. The drilled Aalborg chalk core plugs were also dried in the oven at 90 °C overnight. All the dried core plugs were saturated with FW under vacuum and allowed 3 days to get ionic equilibrium between ions and rock. The pore volume was calculated by saturation weight method and brine permeability was measured by flooding FW at 3 constant rate and recording the pressure drop. Afterwards, initial water saturation was established by drainage with 5-7 pore volumes (pv) of pre-filtered (2 µm online filter) Middle East carbonate reservoir crude oil at an injection rate of 0.2cc/min at room temperature. After establishing initial water saturation, core plugs enclosed in core holder were aged at 90 °C for 4 weeks. Fresh crude is flooded most of the time during aging with a very slow rate to make the wettability alteration process more efficient.

7.2.5 Flooding Schemes

In most of the experiments, flooding was initially carried out at with the SSW. In the second step, the contribution to oil recovery was evaluated by the sequential injection of various diluted versions of SSW. For every injecting brine solution, a nominal injection rate of 0.1cc/min was used and then injection rate was increased to 0.5 and 1c/min to remove the mobile oil. The flooding tests were carried out with a sleeve pressure of 30 bars for the Middle East carbonate reservoir core plugs and 40 bars for the Aalborg outcrop core plugs. A back pressure of 5 bars was used to avoid the formation of air. Pressure drop is continuously measured with the FUJI pressure transducers placed at inlet and outlet of the core. A fraction collector was used at constant time interval to acquire the production profile of oil and water. The volume of produced oil was measured as a function of pore volumes injected.

7.2.6 Chemical Analysis

Effluent collected using fractional collector at constant time intervals were analyzed for Na^{2+} , Ca^{2+} and Mg^{2+} ions. They were analyzed with the 2100 DV ICP-OES, ICP (Inductively Coupled Plasma) acquired from Perkin Elmer. The effluent samples were diluted with nitric acid (suprapure grade) before the analysis to meet the concentration limits of the equipment.

7.2.7 Laboratory NMR Tests

NMR experiments were performed to study the effect of ionic composition on the rock samples. All the core plugs with connate water saturation were first flooded with SSW and then sequentially with low salinity brines LS-2, LS-10, LS-20 and LS-100. NMR scan was performed at different stages for most of the flooding tests.

All the NMR tests were run on 12 MHz Maran DRX rock-core analyzer from Resonance Instruments, with a gradient probe giving access to gradient strengths of up to 225 G/cm. The instrument was running at 35 °C and ambient pressure. To avoid any evaporation, all the samples were preheated in dominating saturating fluid at 35 °C prior any test.

7.3 Results and Observations

7.3.1 Middle East Carbonate Reservoir Core Plugs

7.3.1.1 Test 1: Core ME-1

A preliminary flooding test was carried out with core ME-1 at room condition. First, SSW was injected at an injection rate of 0.1cc/min. When the production stopped, injection rate was increased to 0.5 and finally to 1cc/min to make sure that there is no mobile oil. As shown in Figure 7.1a, 27.14% OOIP (original oil in place) was recovered at an injection rate of 0.1cc/min. 21.85 % OOIP oil was produced before the water breakthrough (WBT). Oil recovery after WBT resulted in a considerable increase in recovered oil (5.29 % OOIP). Increasing the injection rate to 0.5 and 1 cc/min produced additional 8.16 % and 1.95% OOIP oil, respectively.

After SSW injection, three brine solutions with different dilution of seawater were subsequently injected in the same way as for SSW injection. The second step of flooding was carried out with LS-2 brine solution at three different injection rates. This did not result in significant additional oil production (0.51 % OOIP). Third and fourth step of flooding was finished with an injection of LS-10 and LS-20 brine solutions at an additional recovery of 1.15% and 0.23 % OOIP, respectively.

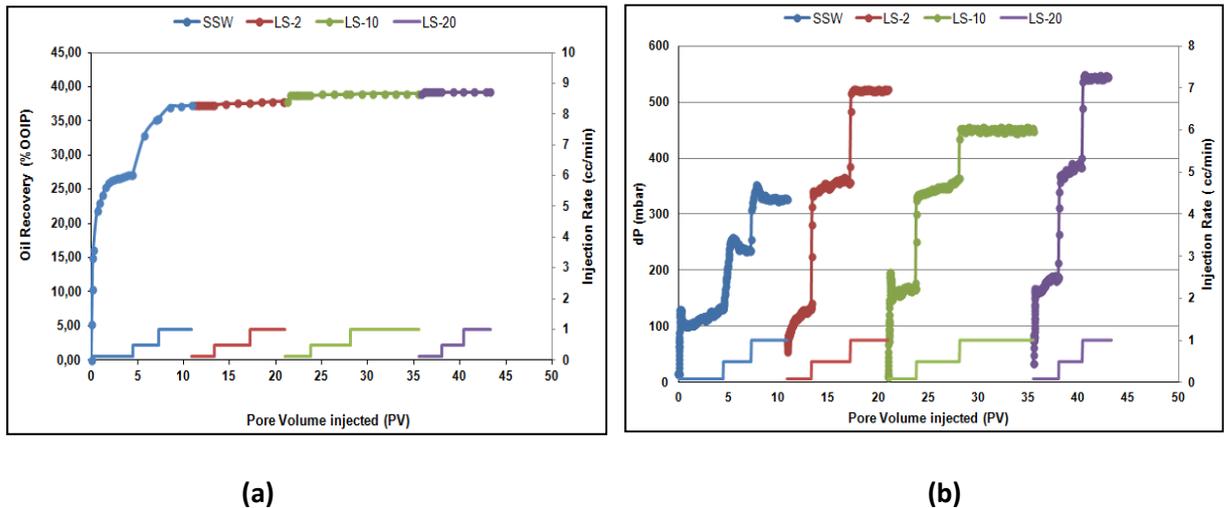


Figure 7.1 (a) Oil recovery (% OOIP), injection rate as a function of pore volume injected (PV) for core ME-1 @ 22 °C. (b) Pressure drop variation (ΔP), injection rate as a function of pore volume injected (PV) for core ME-1 @ 22 °C.

The pressure drop variation across the core for all the injection brine is shown in the Figure 7.1b. The general trend is that as the salinity of injecting brine decreases, the pressure drop across the core increases. This increased pressure drop could be attributed to the migration of fines[90]. The concentration profile of Mg^{2+} , Ca^{2+} and Na^+ in the effluent is presented in Figure 7.2a. There was a constant production of Ca^{2+} in the effluent during SSW flooding at an injection rate of 0.1cc/min. But increasing the injection rate to 0.5 and 1 cc/min stopped this additional production of Ca^{2+} . Concentrations of Mg^{2+} and Na^+ are in good agreement with the concentrations of these ions in injecting fluid. The trend of concentration profile for Mg^{2+} , Ca^{2+} and Na^+ in the effluent during LS-2, LS-10 and LS-20 is same as in the case of SSW flooding.

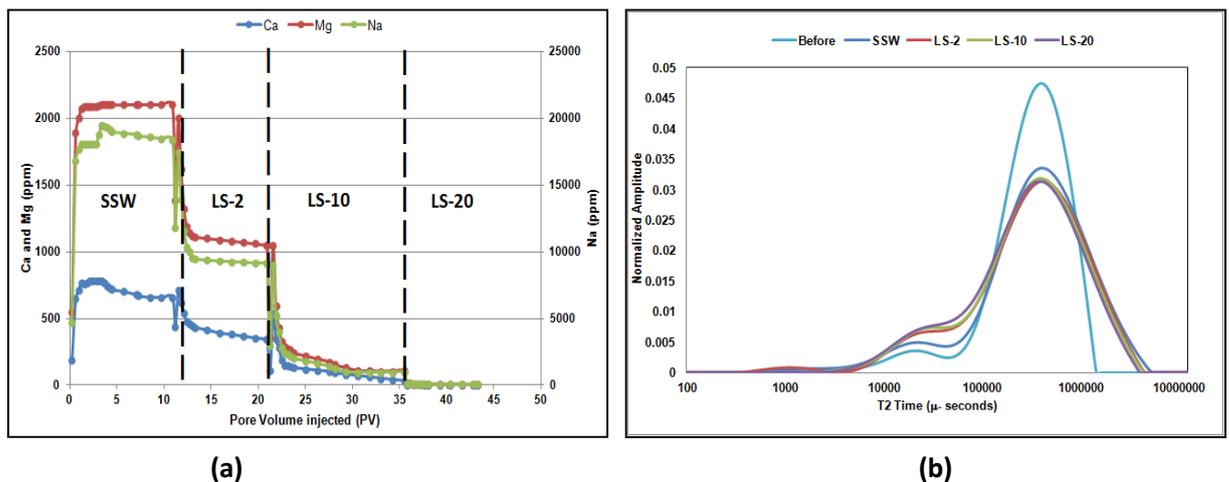


Figure 7.2 (a) Concentration profiles for Mg^{2+} , Ca^{2+} and Na^+ (ppm) in the effluent as a function of pore volume injected (PV) from core ME-1 @ 22 °C. (b) NMR T_2 distribution for core ME-1 at each step of different brines flooding @ 22 °C.

Figure 7.2b shows the NMR T2 distribution results for rock sample after flooding every brine solution. There was no apparent significant shift in the position of T2 distributions between NMR results for different injection brines.

7.3.1.2 Test 2: Core ME-2

The second test was carried out with core ME-2 at 90 °C with the same flooding and injection rate sequence as was adopted for the first test. SSW resulted in a final oil recovery of 26.31% OOIP at an injection rate of 0.1 cc/min. Injection rate was increased to 0.5 and 1cc/min to remove any mobile oil and this produced 2.57 and 1.8% OOIP additional oil, respectively. In the second step, LS-2 brine was injected and oil recovery increased to 36.19% OOIP (6.03% OOIP additional oil). In the third step, injection of LS-10 brine solution produced 11.68% OOIP additional oil. The fourth step of flooding was finished with LS-20 injection and this resulted in a minor increase in recovered oil (1.28 % OOIP). Figure 7.3b shows the pressure drop variation across the ME-2 core plug. An increase in pressure drop was also observed in this case with the decrease in salinity of injecting brine and that is probably due to migration of fines.

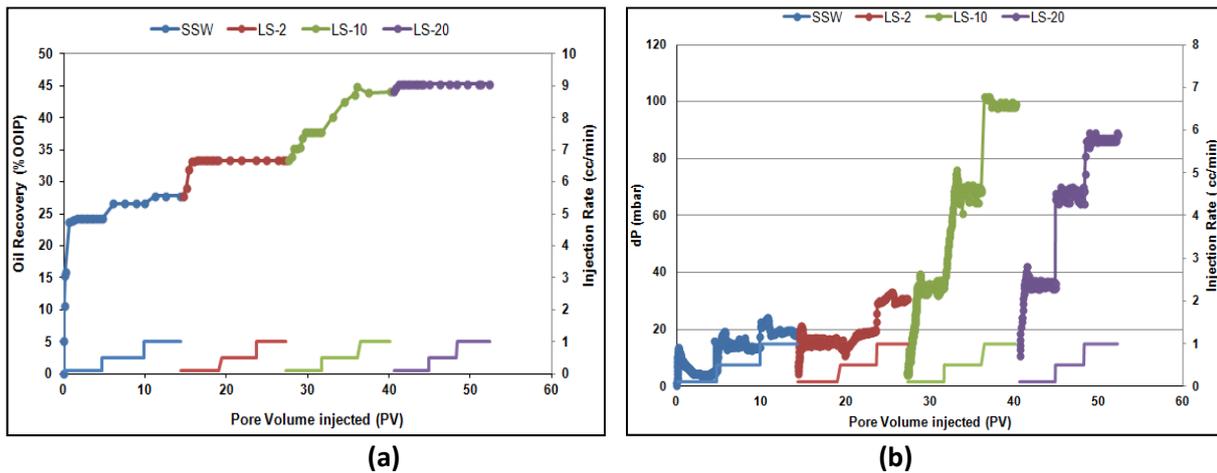
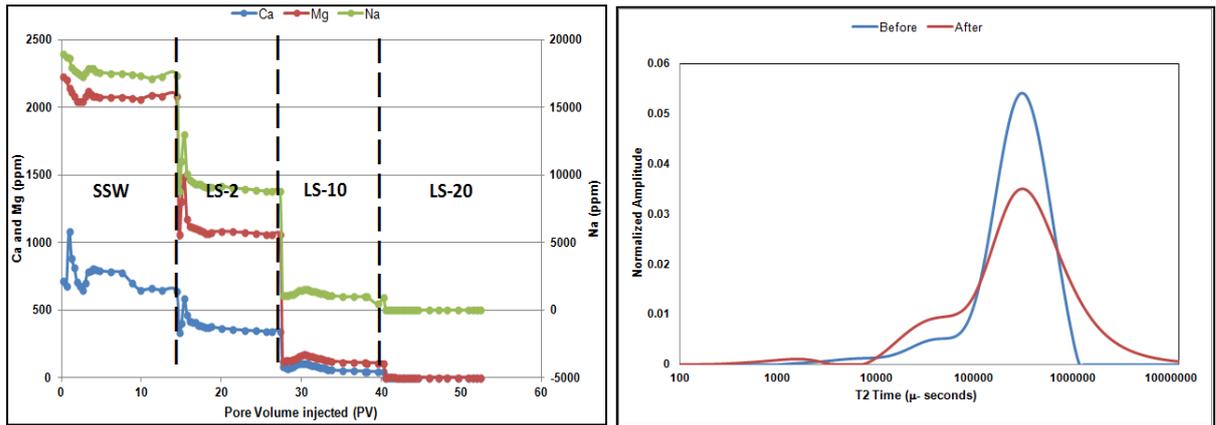


Figure 7.3 (a) Oil recovery (% OOIP) and injection rate as a function of pore volume injected (PV) for core ME-2 @ 90 °C. (b) Pressure drop variation (ΔP) and injection rate as a function of pore volume injected (PV) for core ME-2 @ 90 °C.

The concentration profiles for the different ions in the effluent for ME-2 core are shown in Figure 7.4a. The trend for concentration profiles of Mg^{2+} and Na^+ is the same as it was in the test 1 with Middle East carbonate reservoir core plug, and does not vary with the injected fluids. There is a constant production of Ca^{2+} in the effluent during all the experimental steps and injection rates, except for the SSW injection, where additional Ca^{2+} production stopped when injection rate increased to 0.5 and 1cc/min.



(a)

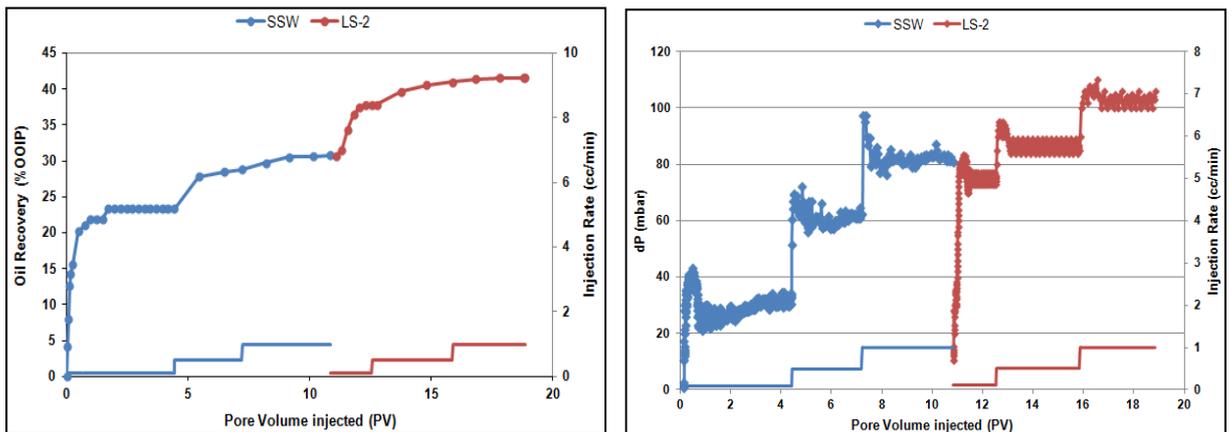
(b)

Figure 7.4 (a) Concentration profiles for Mg²⁺, Ca²⁺ and Na⁺ (ppm) in the effluent as a function of pore volume injected (PV) from core ME-2 @ 90 °C. (b) NMR T₂ distribution for core ME-2 before and after flooding @ 90 °C.

The NMR T₂ distribution profiles before and after flooding are shown in Figure 7.4b. No apparent shift was observed in the position of the T₂ distributions before and after the coreflood experiment.

7.3.1.3 Test 3: Core ME-3

Another coreflooding experiment was conducted at 90 °C using a new core plug ME-3 to confirm and validate the increased oil recovery observed with the different low salinity brine solutions. Figures 7.5a and 7.5b illustrate the oil recovery and pressure drop variation, respectively for all injected slugs.



(a)

(b)

Figure 7.5 (a) Oil recovery (% OOIP) and injection rate as a function of pore volume injected (PV) for core ME-3 @ 90 °C. (b) Pressure drop variation (ΔP) and injection rate as a function of pore volume injected (PV) for core ME-3 @ 90 °C.

Increase in oil recovery with low salinity brine and the pressure profiles are consistent with the previous test where ME-2 core plug was used. As shown in Figure 7.5a, 30.7% OOIP was recovered with SSW injection. On the second step, injection of LS-2 resulted in a final oil recovery of 41.5% OOIP (10.7% OOIP additional oil). We did not flood the plug with other diluted versions of the seawater because it was broken. Still, this experiment validated the significant low salinity effect with carbonate core plug at 90 °C. No effluent analysis and NMR scan was carried out in this case.

7.3.2 Aalborg Outcrop Chalk Core Plugs

7.3.2.1 Test 1: Core AA-05

The low salinity flooding potential was also investigated for the outcrop chalk rock samples. This was necessary in order to compare the effects of the low salinity flooding for the different rocks and to test whether the outcrop chalk samples might serve as “models” for the reservoir rocks. The first test was carried out at 90 °C with the same flooding but with different injection rate sequence as was adopted for the Middle East carbonate reservoir core plugs. First, SSW was injected at a relatively low injection rate of 0.04cc/min, because of low permeability of the chalk core plugs. When the production stopped, injection rate was increased to 0.2 cc/min, to make sure that there is no mobile oil. Continuous injection of the SSW at the two different injection rates resulted in a final recovery of 76.6 % OOIP (see Figure 7.6a).

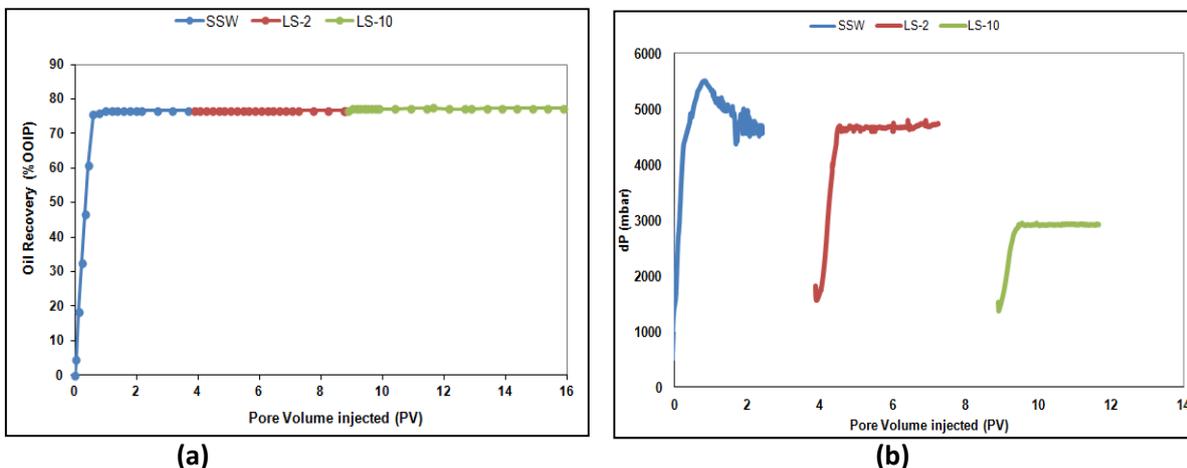


Figure 7.6 (a) Oil recovery (% OOIP) as a function of pore volume injected (PV) for core AA-05 @ 90 °C. (b) Pressure drop variation (ΔP), injection rate as a function of pore volume injected (PV) for core AA-05 @ 90 °C.

After the SSW injection, the two different dilutions of seawater (LS-2, LS-10) were subsequently injected in the same order as for SSW injection. Both injection procedures did not result in significant oil production (0.59 % OOIP). The pressure drop variation for this test is shown in Figure 7.6b. This time no increase in pressure drop was observed with the decrease in salinity

of the injected brine. Figures 7.7a and 7.7b show the effluent ion concentration and the NMR T₂ distribution profile.

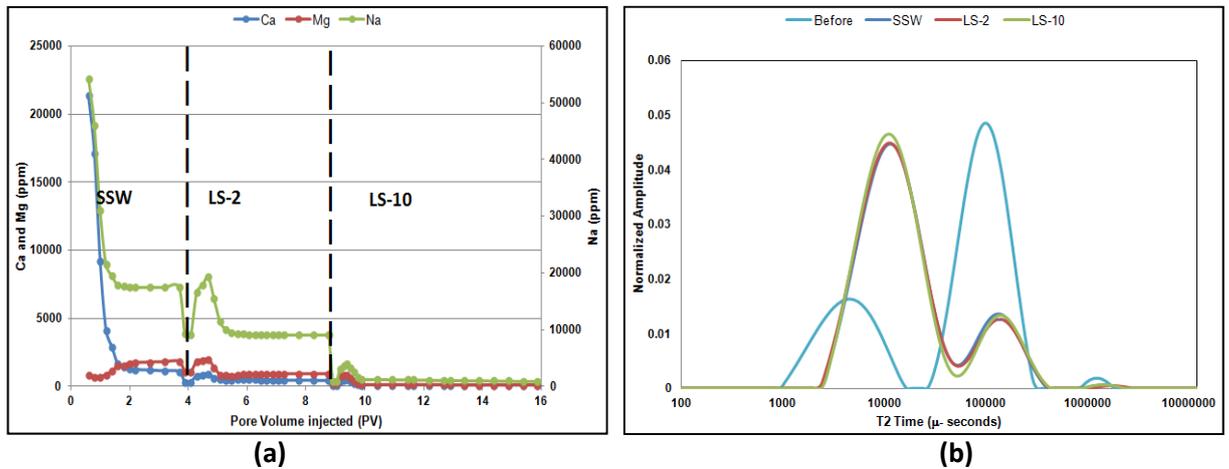


Figure 7.7 (a) Concentration profiles for Mg^{2+} , Ca^{2+} and Na^{+} (ppm) in the effluent as a function of pore volume injected (PV) from core AA-05 @ 90 °C. (b) NMR T₂ distribution for core AA-05 at each step of different brines flooding @ 90 °C.

The connate water has a high concentration of Na^{+} and Ca^{2+} ions. That is why gradually decreasing concentrations of these ions are observed during SSW flooding up to approximately 1.9 pore volumes injected. At this stage, it may be assumed that all the ions present in the connate water have been exchanged, either with the injected water or with the surface. After this moment the concentration of Na^{+} becomes in agreement with the injected fluid (SSW), but concentration of Mg^{2+} in the effluent is noticeably lower. A significant concentration of Ca^{2+} in the effluent is observed, probably, due to dissolution of chalk. The trends of concentration histories for Mg^{2+} , Ca^{2+} and Na^{+} in the effluent during LS-2 and LS-10 flooding are the same as for the SSW flooding. As previously, we did not observe any apparent shift in the positions of the T₂ distributions after injecting different brines.

7.3.2.2 Test 2: Core AA-06

In the second test with the outcrop chalk plug, a diluted version of seawater (LS-10) was flooded from the start to check if this could give high oil recovery compared to the previous test, where flooding started with SSW injection. Figures 7.8a and 7.8b illustrate the oil recovery and the pressure drop variation. Injection of LS-10 resulted in the final recovery of 75.9 % OOIP, which is very close to the oil recovery by the SSW injection in previous test (76.6 % OOIP). The SSW was flooded after LS-2 injection, but this flooding was not able to produce any additional oil (see Figure 7.8a). No increase in pressure drop was observed in this case. Effluent ion concentrations and NMR T₂ distribution profiles are shown in Figures 7.9a and 7.9b. The same

trends as in test 1 were observed for concentrations profile for of Mg^{2+} , Ca^{2+} and Na^+ in the effluent. No apparent shift in T2 distribution peak was observed in this case.

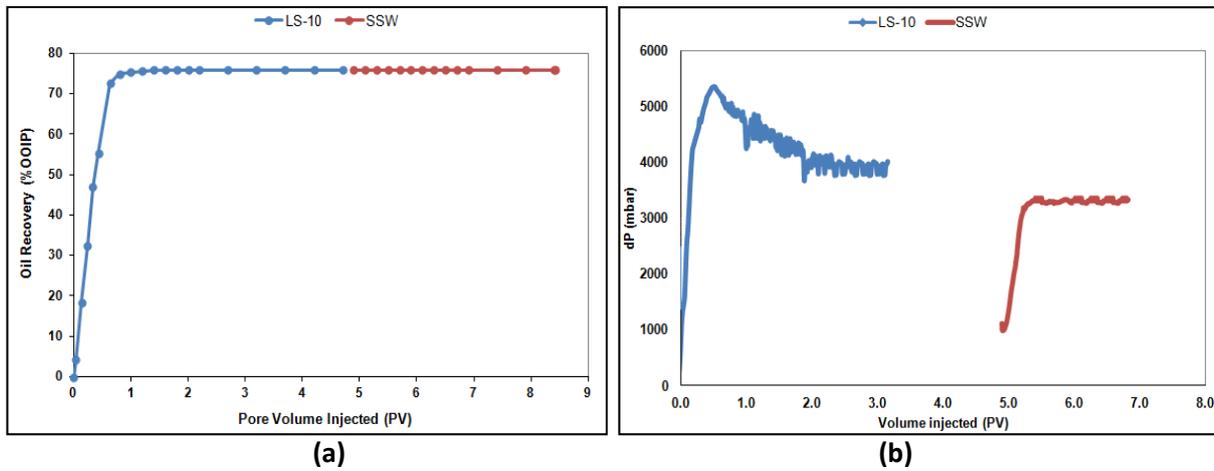


Figure 7.8 (a) Oil recovery (% OOIP) as a function of pore volume injected (PV) for core AA-06 @ 90 °C. (b) Pressure drop variation (ΔP), injection rate as a function of pore volume injected (PV) for core AA-06 @ 90 °C.

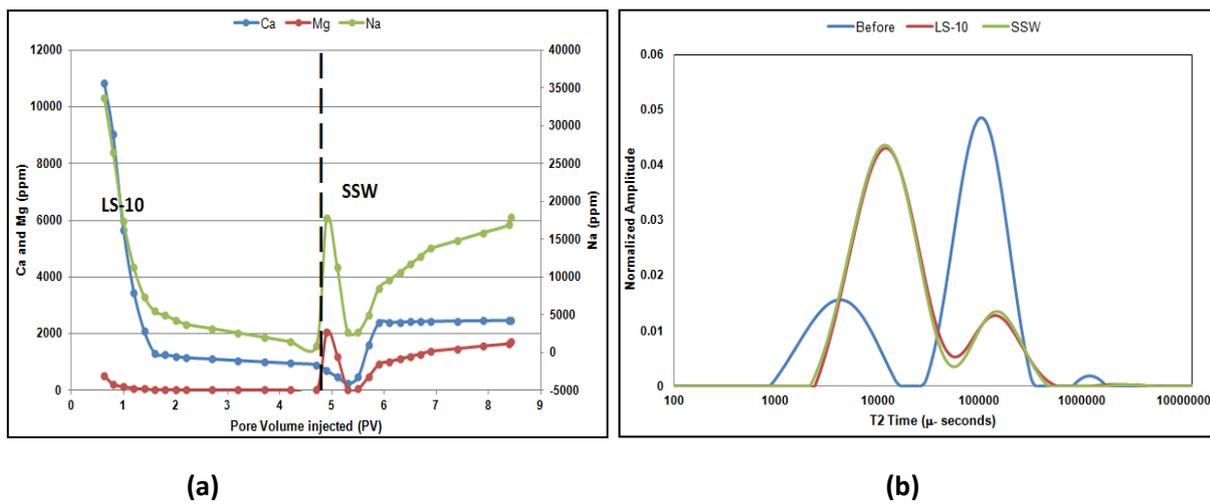


Figure 7.9 (a) Concentration profiles for Mg^{2+} , Ca^{2+} and Na^+ (ppm) in the effluent as a function of pore volume injected (PV) from core AA-06 @ 90 °C. (b) NMR T_2 distribution for core AA-06 at each step of different brines flooding @ 90 °C.

7.3.2.3 Test 3: Core AA-04

The SSW flooding produced 76.6 % OOIP in the first test at 90 °C with Aalborg chalk so there was not that much potential left for low salinity flooding. The new test was run at 40 °C in order to give more room for low salinity brines to recover additional oil. As shown in Figure 7.10a, 60.4% OOIP was recovered by the SSW injection on the first step. Afterwards the additional recovery was attempted by sequential injection of the two diluted versions of seawater (LS-2 and LS-10). Both low salinity brines were not able to produce significant additional oil (0.61 % OOIP). Thus, low salinity waterflooding was not able to produce any additional oil from the

chalk rock irrespective of an order of injected fluids and of the temperature. No increase in pressure was observed (see Figure 7.10b). The general trend for the pressure drop variation in the outcrop chalk rock is that as the salinity of seawater decreases, pressure drop across the core plug also decreases (probably, due to decreasing viscosity of the water). No effluent analysis and NMR scan was carried out for this test.

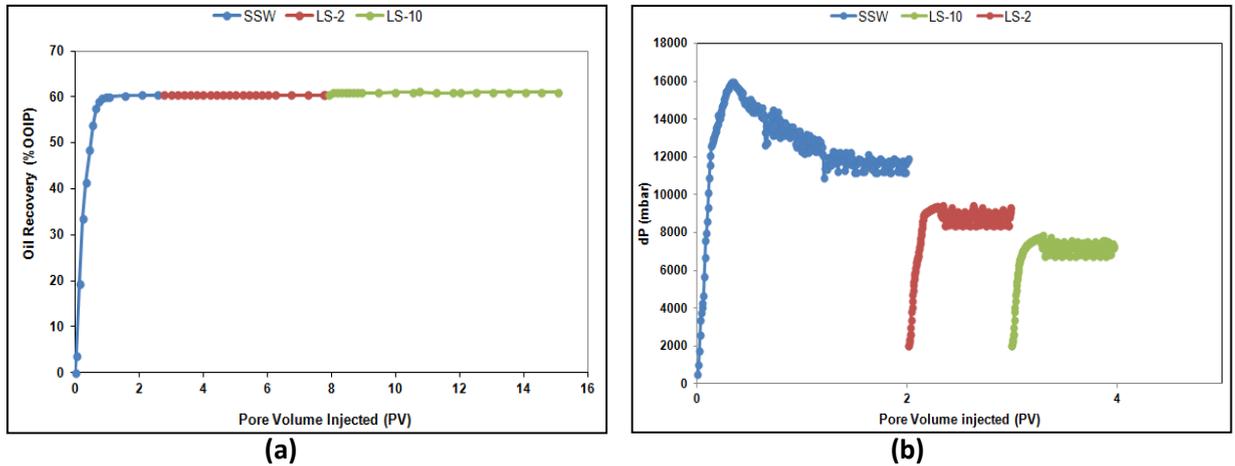


Figure 7.10 (a) Oil recovery (% OOIP) as a function of pore volume injected (PV) for core AA-04 @ 22 °C. (b) Pressure drop variation (ΔP), injection rate as a function of pore volume injected (PV) for core AA-04 @ 22 °C.

7.4 Discussion

The effect of low salinity waterflooding in sandstone was usually associated with the wettability alteration of the clay minerals[47]. But this mechanism cannot explain the oil recovery in our case (carbonate reservoirs) due to the lack of the clay minerals in the rock.

Seawater flooding may improve the oil recovery from a chalk reservoirs. The effect was associated with the capability of the active ions contained in seawater (SO_4^{2-} , Ca^{2+} and Mg^{2+}) to alter the rock wettability and was also attributed to viscosity change of the crude oil and emulsion formation [1, 72]. However, these effects could not explain, either, the enhanced oil recovery in our experiments, under flooding with the diluted seawater.

Saudi Aramco reported significant increment in oil recovery with low salinity brines from the Saudi Arabian carbonate reservoirs [29]. Wettability alteration was reported as a driving mechanism for substantial increase in oil recovery. This was indicated by apparent shift in the position of T2 distribution between NMR results before and after injecting different salinity slugs of seawater. However, in our study no apparent shift in T2 distribution peak was observed in any of the tests.

Most recently, Austad et al.[50] also reported a rather small low salinity effect in the experiments with low permeable limestone cores from the aqueous zone of an oil reservoir. The observed increment in oil recovery was attributed to the amount of anhydrite present in the rock matrix. The chemical mechanism behind this increment was claimed to be the same as previously reported for the seawater flooding in chalk reservoirs (sulfate ions adsorb to the rock surface, which changes the surface charge so that the adsorbed crude oil may be removed from the rock). The only difference is that sulfate is produced in the matrix due to the dissolution of anhydrite. This could not explain, either, significant low salinity effect observed from Middle East carbonate reservoir core plugs at 90 °C, since the XRD analysis showed no anhydrite present in the rock matrix.

A significant increase in pressure drop across the Middle East carbonate reservoir core plugs was observed with the decrease in the salinity of injecting. This increased pressure drop could be attributed to the migration of fines. Tang et al.[47] suggested that low salinity waterflooding in sandstone could release clay particles (so called fines) that could improve water wetness of the clay minerals. Even more importantly, it could block the pore throats and divert the flow to nonswept zones to improve microscopic efficiency [91]. This could be a possible mechanism for observed increment in oil recovery in the Middle East carbonate reservoir core plugs. However, increase in the pressure drop (possibly migration of fines) was also observed in test 1 at the room temperature, where no increment in oil recovery was observed (see Figure 7.1a). Thus, microscopic migration of fines probably does not always results in additional recovery. Additionally, in test 2 (ME-2) there is a constant production of Ca^{2+} in the effluent during diluted versions of seawater flooding at all the three different injection rates at 90 °C. This production of Ca^{2+} stops at higher injection rates (0.5 and 1 cc/min) during diluted seawater flooding in test 1 at room temperature. This indicates that rock dissolution may also be the possible mechanism for recovery increment. The fact that one of the core plugs was damaged (ME-2, see Figure 7.11) in the experiment also confirms the combined fine migration and dissolution effects as a possible reason for additional recovery.

Zhang et al.[1] reported an increase in the effluent calcium concentration during seawater flooding of the Stevns Klint outcrop chalk cores at temperatures above 100 °C. This effect was interpreted as a result of substitution of Ca^{2+} by Mg^{2+} ions on the internal rock surface. This substitution reaction was reported as a main possible reason for an increment in oil recovery. In our experiments, we observed this substitution reaction during SSW and low salinity brines flooding with the Aalborg chalk core plugs, but not with Middle East carbonate reservoir core

plugs (see Figure 7.2a, 7. 4a, 7.7a and 7.9a). This reaction did not give any increment in oil recovery from the Aalborg chalk core plugs. This indicates that substitution reaction is not always the mechanism behind the increment in oil recovery.



Figure 7.11 (a) Middle East carbonate reservoir core plug (ME-2) before flooding. (b) Middle East carbonate reservoir core plug (ME-2) after flooding @ 90 °C.

7.5 Conclusions

1. No low salinity effect was observed from Middle East carbonate reservoir core plug at room temperature.
2. A substantial increase in oil recovery was achieved with diluted versions of seawater from Middle East carbonate reservoir core plugs at 90 °C.
3. No low salinity effect was detected in Aalborg chalk core plugs both at room and reservoir temperature.
4. NMR measurements indicated that low salinity brines did not significantly change the surface relaxation of both used carbonate rocks.
5. Migration of fines, dissolution and destruction of rock particles are possible mechanisms of oil recovery increment with low salinity brines from Middle East carbonate reservoir core plugs at 90 °C.
6. Substitution reaction is not always the mechanism which controls the oil recovery process in chalk core plugs.

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Conclusions and Future work

Smart waterflooding is a promising technique for improving oil recovery. Although extensive research has been carried out, the governing physical and chemical mechanisms for this increase in recovery are not yet clear. This thesis adds more important information to the fundamental understanding of the mechanisms behind the smart waterflooding method in carbonate reservoirs. The overall conclusions of this work are summarized in this chapter.

Recovery Mechanisms of HSW in Chalk Reservoirs

In most of the reported studies, wettability alteration of the porous surface towards more water wetting conditions was reported as a key reason for oil recovery improvement [8, 11, 12]. Our results show that increment in oil recovery with sulfate ions cannot be explained just by the rock wettability alteration. Injection of sulfate rich brine may lead to additional recovery even under completely water wet conditions. Crude oil/brine interaction study suggests that crude oil viscosity reduction and formation of an emulsion phase between sulfate-enriched brine and oil at high temperature and pressure could also be the possible reasons for the observed increase in oil recovery. On the other hand, seawater flooding study in North Sea chalk reservoirs indicates that the rock may also determine whether the effect of the temperature on the recovery is observed. Thus, brine/crude oil interaction alone may be insufficient to explain all the mechanisms.

Substitution of Ca^{2+} by Mg^{2+} ions on the internal rock surface was also reported as a possible reason for an increment in oil recovery [1]. In LSW experiments with Aalborg chalk, we observed this substitution reaction but without any increment in oil recovery. On the other hand, in HSW experiments with Stevens Klint chalk, we observed increment in oil recovery but without substitution reaction. This indicates that substitution reaction is not always the mechanism behind the increment in oil recovery.

IFT decrease also seems to be insufficient to account for the observed increment in oil recovery. Probably, oil recovery increment is a result of the different mechanisms acting together.

Outcrop Rock as a Model for Reservoir Rock

The outcrop rock is used in many studies as a model for reservoir rock because of easy availability and good rock characterization. We used both the reservoir and outcrop rocks for

this work. Experimental results demonstrate that the oil recovery mechanisms under HSW and LSW at high temperature may be different for outcrop and reservoir rocks. Thus, care should be taken in using outcrop chalk as a model for reservoir chalk and, in particular, for the water based IOR.

Important Parameters Influencing Oil Recovery

HSW in reservoir and outcrop chalk core plugs and crude oil/brine interaction study show that temperature, brine composition (both injected and formation brine composition) and crude oil composition are key parameters of this method. The oil recovery increases as the sulfate concentration and temperature increases. The newly observed phenomena (effect of crude oil and initial water composition) cannot be explained right now. Further investigations are needed in order to exactly understand the causes for them.

Crude Oil-High Salinity Brine Interactions

Our results showed that sulfate ions could help decreasing the viscosity of one of the crude oils when brine is contacted with it at high temperature and pressure. For the other crude oil, sulfate ions in brine could be responsible for creation of an emulsion phase at the interface between crude oil and brine. This viscosity variation is possibly explained by changes of conformations of the heavy molecules, like it is observed in polymer solutions [67]. Our experiments suggest that viscosity variation in crude oil is attributed to the presence of heavy components, while formation of emulsions is related to lighter components.

Recovery Mechanisms of LSW in Carbonate Reservoirs

The mechanisms for the improved oil recovery under low salinity waterflooding in carbonates are different from those for sandstones. This is due to the lack of the clay minerals in the rock and decrease in the concentration of the active ions (SO_4^{2-} , Ca^{2+} and Mg^{2+}) in the injected brine solutions. Increase in the pressure drop (possibly due to migration of fines) and constant production of Ca^{2+} in the effluent (seemingly, rock dissolution) during diluted seawater flooding are the possible mechanisms for recovery increment. Temperature is a decisive parameter for the process.

Suggestions for Future Work

- Analysis of the mechanisms leading to the enhanced recovery under high and low salinity waterflooding should continue.
- Crude oil/high salinity brine solution interaction study was one of the first to understand the underlying mechanism leading to an increase in oil recovery. This

may substantially increase our knowledge about EOR. This study should be extended to other crude oils and also to low salinity brine solutions.

- Most recently Exxon Mobil reported that borate and phosphate ions can give better oil recovery compared to sulfate ions from Middle East carbonate reservoir [92]. The potential of both these ions should be further explored.
- The effect of the composition of the formation brine should also be investigated.

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