

Water-Based EOR in Limestone by Smart Water

A study of surface chemistry

by

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*Dedicated to my wife; to my parents; to my brothers and to my friends
for all their support*

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Reza Rostami Ravari

List of papers

Paper I:

New Method to Clean Carbonate Reservoir Cores by Seawater

Reza Rostami Ravari, Tor Austad, Skule Strand, and Tina Puntervold
Paper SCA2008-15 presented at the International Symposium of the Society of Core Analysts, Abu Dhabi, UAE, October 29-November 02, 2008.

Paper II:

Care Must be Taken to Use Outcrop Limestone Cores to Mimic Reservoir Core Material in SCAL Linked to Wettability Alteration

Reza Rostami Ravari, Tor Austad, and Skule Strand
Paper presented at the 11th International Symposium on Reservoir Wettability, Calgary, Canada, September 6-9, 2010.

Paper III:

Water-Based EOR from a Low-Permeability Fractured Limestone by Wettability Alteration

Reza Rostami Ravari, Tor Austad, and Skule Strand
Paper presented at the 16th European Symposium on improved oil recovery IOR 2011, Cambridge, UK.

Paper IV:

Combined Surfactant-Enhanced Gravity Drainage (SEGD) of Oil and the Wettability Alteration in Carbonates: The Effect of Rock Permeability and Interfacial Tension (IFT)

Reza Rostami Ravari, Tor Austad, and Skule Strand
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Symbols and abbreviations

ϕ	Porosity, fraction or %
σ	Interfacial tension, mN/m
ΔH_{hydr}	Change in hydration enthalpy, kcal/mol
A_w	Sulfate adsorption area (Area between thiocyanate and sulfate effluent curves) in the chromatographic wettability test
ASP	Alkaline-polymer-surfactant
AN	Acid number, mg KOH/g
BET	Braunauer-Emmett-Teller
BN	Base number, mg KOH/g
C/C_o	Relative concentration of effluent ions
$C_{12}\text{TAB}$	Cationic surfactant Dodecyltrimethylammonium bromide
COBR	Crude/oil/brine/rock
D	Core diameter, cm
DI	Deionized water
D_m	Diffusion coefficient, m^2/s
EDS	Energy dispersive spectrometry
EDL	Edwards outcrop limestone
EOR	Enhanced oil recovery
FI	Forced imbibition
FW	Formation brine
G-AB	Gravity, acid and base number
IFT	Interfacial tension, mN/m
IOR	Improved Oil Recovery
IS	Ionic strength, mole/l
J^*	Leverett dimensionless entry pressure
k	Absolute permeability, mD
L	Core length, cm
MeOH	Methanol
NB^{-1}	Inverse Bond number
NSO	Nitrogen, sulfur and oxygene compounds
OOIP	Original oil in place
P_c	Capillary pressure, psi
pH	$-\log [H_3O^+]$
PV	Pore volume, ml
Res1 limestone	Type I reservoir limestone cores
Res3 limestone	Type III reservoir limestone cores
Res4 limestone	Type IV reservoir limestone cores

<i>SEGD</i>	<i>Surfactant-enhanced gravity drainage</i>
<i>SI</i>	<i>Spontaneous imbibition</i>
<i>Silica</i>	<i>Various forms of crystalline and amorphous SiO₂</i>
<i>S_{or}</i>	<i>Residual oil saturation, %</i>
<i>SW</i>	<i>Synthetic Seawater</i>
<i>SWOCa</i>	<i>Synthetic Seawater without Ca²⁺</i>
<i>S_{wi}</i>	<i>Initial water saturation, %</i>
<i>SWOT</i>	<i>Synthetic seawater without SCN and SO₄²⁻</i>
<i>SW1/2T</i>	<i>Synthetic seawater where the concentrations of SCN and SO₄²⁻ are 0.012 mole/l</i>
<i>SWIT</i>	<i>Synthetic seawater where the concentrations of SCN and SO₄²⁻ are 0.024 mole/l</i>
<i>t_d</i>	<i>Dimensionless time</i>
<i>T</i>	<i>Temperature, °C</i>
<i>T_{res}</i>	<i>Reservoir temperature, °C</i>
<i>TDS</i>	<i>Total dissolved solid, g/l</i>
<i>TOL</i>	<i>Total outcrop limestone</i>
<i>wt.%</i>	<i>Weight %</i>

Contents

Acknowledgements.....	IV
List of papers	V
Symbols and abbreviations.....	VI
Contents.....	VIII
1. Introduction.....	1
1.1. Oil recovery from carbonate rocks	1
1.2. Wettability of carbonates.....	1
1.2.1. Crude oil components affecting the wettability	2
1.2.2. Mineral composition affecting the wettability.....	2
1.2.3. Parameters affecting the initial wetting of chalks.....	3
1.3. EOR mechanisms of fractured carbonate reservoirs	4
1.3.1. Miscible methods	5
1.3.2. Thermal methods.....	5
1.3.3. Chemical methods	5
1.3.4. Smart water.....	6
1.4. History of chemical flooding and wettability alteration in carbonates	7
1.5. Water-based EOR in chalk by smart water	9
2. Objectives.....	12
3. Materials and methods	14
3.1. Materials	14
3.1.1. Porous media.....	14
3.1.2. Oils.....	16
3.1.3. Brines.....	16
3.1.4. Additional chemicals	17
3.2. Core preparation.....	17
3.2.1. Initial core preparation.....	17
3.2.2. Core cleaning by hot seawater and surfactant.....	18
3.2.3. Initial water saturation, S_{wi}	18
3.2.4. Oil saturation and aging	18

3.3.	Methods.....	19
3.3.1.	Determination of acid and base numbers	19
3.3.2.	IFT measurement	19
3.3.3.	EDS analysis.....	19
3.3.4.	Chromatographic wettability test	19
3.3.5.	Ionic composition analysis	20
3.3.6.	Zeta potential measurements.....	20
3.3.7.	Chromatographic studies/surface reactivity	21
3.3.8.	Oil recovery by spontaneous imbibition	21
3.3.9.	Oil recovery by forced imbibition	22
4.	Main results and discussion	23
4.1.	Cleaning of carbonate reservoir cores by seawater.....	23
4.2.	Seawater induced wettability modification of outcrop limestones	27
4.2.1.	Initial core preparation	27
4.2.2.	Affinity of SO_4^{2-} towards the carbonate surface	28
4.2.3.	Substitution of Ca^{2+} by Mg^{2+} at the rock surface.....	30
4.2.4.	Oil recovery by spontaneous imbibition and forced displacement.	33
4.2.5.	Surface charge on chalk, reservoir limestone and outcrop limestone when exposed to potential determining ions.....	36
4.3.	Seawater induced wettability modification of reservoir limestones	37
4.3.1.	Affinity of Ca^{2+} , Mg^{2+} and SO_4^{2-}	37
4.3.2.	Effect of oil acid number, AN	39
4.3.3.	SW as wettability modifier in limestone	40
4.4.	The effect of permeability and interfacial tension on the SEG D process in limestones	41
4.4.1.	High permeable Limestone core.....	41
4.4.2.	Low permeable Limestone core.....	43
4.4.3.	Diffusion of surfactant	44
5.	Concluding remarks	46
5.1.	Conclusions	46

5.2. Future work	48
6. References	49
Paper I	57
Paper II	71
Paper III	97
Paper IV	107

1. Introduction

1.1. Oil recovery from carbonate rocks

About half of world's known oil reserves are in carbonate reservoirs (Treiber et al., 1972). Total oil recovery does not exceed generally 30%. Such reservoirs are often characterized by high-permeability fractures and a low-permeability matrix medium. Most of the injected water will pass through the fracture network and displaces only the oil residing in the fracture (Cuiec, 1984; Treiber et al., 1972).

The production from the highly fractured Spraberry field in west Texas in the early 1950s (Brwonscombe and Dyes, 1952), introduced the mechanism referred to as spontaneous imbibition of water into the matrix blocks. Under water injection or aquifer drive, subsequent recovery of oil from the rock matrix is mainly dependent on spontaneous imbibition of water.

Unfortunately, ~90% of the carbonate reservoirs are neutral to oil-wet, which implies that spontaneous imbibition of water will not occur. The capillary pressure is positive if the rock is water-wet and negative in the oil-wet case. If reservoirs are partially or completely oil-wet, the water pressure exceeds the oil pressure inside the matrix blocks, thus preventing the spontaneous imbibition of water. The Ghaba North field in Oman which is a highly fractured, oil-wet carbonate reached a recovery of 2% after more than 20 years of production (Al-Hadhrami and Blunt, 2001). Thus, changing the wettability from oil-wet to water-wet which leads to higher capillary pressure would then be the best way to increase recovery from carbonate rocks (Tabary et al., 2009).

1.2. Wettability of carbonates

Wettability is a very important parameter in oil recovery processes, because it has strong impact on the distribution, location and flow of oil and water in the reservoir during production (Anderson, 1986b; Anderson, 1987a; Anderson, 1987b; Anderson, 1987c; Cuiec, 1991; Hjelmeland and Torsaeter, 1980; Morrow, 1990). Water will occupy the narrowest pores and oil will reside as small droplets in the middle of the pores in a uniform water-wet system. The reverse fluid distribution will be the case in an oil-wet reservoir.

It was generally believed that all reservoir rocks were strongly water-wet (Morrow, 1990). But, the evaluation of the wetting state for different reservoirs indicated that most of the carbonate reservoirs were neutral to oil-wet, up to 65% of the carbonate rocks were oil-wet and 12% were intermediate-wet (Chilingar and Yen, 1983; Cuiec, 1984; Treiber et al., 1972).

Apparently, the original wetting-state of carbonate rocks has been changed to oil-wet when exposed to crude oil.

1.2.1. Crude oil components affecting the wettability

Research studies have shown that the main crude oil fractions affecting the wettability in porous rock are the asphaltenes and resins (Buckley, 2001; Buckley et al., 1996; Xie et al., 2000), which are rich in polar elements such as nitrogen, sulfur and oxygen (NSO-compounds).

It has been experimentally found that a smaller group of components from the asphaltene/resin fractions are more important regarding wettability alteration. These components are polar compounds of acidic and basic nature. (Anderson, 1986b; Crocker and Marchin, 1988; Cuiec, 1984).

Buckley and co-authors have recognized four different mechanisms for wetting alteration by crude oil. These mechanisms are linked to the asphaltenes content in the oil, acid number, base number and brine composition.

- Polar binding: if no water is present in the porous medium, the adsorption of polar components is likely to happen between polar surface sites and molecules containing polar atoms (NSO-compounds).
- Surface precipitation: Precipitation of asphaltenes occurs when the oil is a poor solvent for the heavy fraction.
- Acid/base interactions: This interaction takes place between sites of opposite electrical charge.
- Ion binding: Divalent or other multivalent ions in the brine are likely to bind to both the mineral surface and the oil/brine interface creating bridges.

It was shown by Buckley and Liu (1998) that the ability of a crude oil to alter wettability is dependent on the G-AB profile of the oil (the API gravity, Acid number and Base number) together with the rock material, i.e., sandstone vs. carbonate rock.

1.2.2. Mineral composition affecting the wettability

It has been experimentally observed that the way polar compounds change the rock wettability is dependent on the type of the rock. Carbonate rocks have been found less water-wet than sandstones (Chilingar and Yen, 1983; Treiber et al., 1972). The carbonate surface is positively charged at basic conditions ($\text{pH} < 9.5$) (Pierre et al., 1990) and is able to adsorb negatively charged acidic groups. Sandstone rock is in general negatively charged above

pH of 2 and therefore becomes more oil-wet after being exposed to the basic components (Menezes et al., 1989). Thus, due to opposite surface charges, the organic acids of crude oil (AN) have the largest effect on carbonates wettability while the wettability of sandstones is more affected by the organic bases (BN) (Anderson, 1986a; Lord et al., 2000; Thomas et al., 1993).

There are other factors affecting the wettability alteration of the COBR system including brine chemistry (salinity and pH) (Anderson, 1986a; Buckley et al., 1989; Tang and Morrow, 1997), multivalent cations in the brine (Anderson, 1986a; Castor et al., 1981; Yan et al., 1997), capillary pressure and thin film forces (disjoining pressure) (Hirasaki, 1991), water solubility of polar oil components and diffusion through water films (Anderson, 1986a), stabilization of heavy components by oil (Buckley, 1995; Buckley et al., 1997), temperature (Al-Maamari and Buckley, 2000; Buckley et al., 1997; Liu and Buckley, 1997), pressure (Al-Maamari and Buckley, 2000) and initial water saturation (Jadhunandan and Morrow, 1995; Salathiel, 1973; Yan et al., 1997).

1.2.3. Parameters affecting the initial wetting of chalks

The initial wetting condition for a carbonate rock is related to the stability of the water film between the rock and the oil. The water film stability is dictated by value and sign of the zeta potentials of the oil-water and the water-rock interfaces (Hirasaki and Zhang, 2004). The oil-water interface is usually negatively charged due to the content of carboxylic acid in the crude oil, while the water-rock interface is positive due to $\text{pH} < 9.5$ and a high content of Ca^{2+} in the formation brine. The water film then becomes unstable, and the carboxylic group adsorbs strongly onto the carbonate surface by displacement of water (Buckley et al., 1998; Legens et al., 1999; Liu and Buckley, 1997; Madsen and Lind, 1998; Thomas et al., 1993). Thus, the acid number, AN, of the crude oil has been shown to be a crucial factor for the wetting state of carbonates and it was observed that the water-wetness decreases as the AN increases (Standnes and Austad, 2003b). In contrast to most of the sandstone reservoirs, It has been observed that the water-wetting condition of carbonate reservoirs increases as the temperature of the reservoir increases (Rao, 1999). The reservoir temperature is important because the acid number in the actual crude oil decreases as the temperature increases. In carbonate reservoir, CaCO_3 will act as a catalyst to decompose carboxylic materials. The catalytic effect of CaCO_3 speeds up a very slow reaction so that it becomes significant during the geological time but not during the aging period of the cores in the experiment (Zhang and Austad, 2005). The wetting properties of aged chalk cores in crude oils of different AN at different temperatures confirmed that the

wettability of a carbonate oil reservoir is dictated mainly by the AN of the crude oil and that temperature plays a minor role.

A recent study has shown that the chemical properties of the acids present in the crude oil have also impact on the wetting properties of chalk. It was confirmed that cores saturated with oil depleted in water-soluble acids were somewhat more water-wet, indicating that water-soluble acids may affect the stability of the initial water film between the rock and the oil (Fathi et al., 2010b).

Natural petroleum bases, that are large molecules, behave in a different manner. As the amount of base is increased, the degree of water-wetness increases (Punternvold et al., 2007). Due to steric hindrance, these molecules are probably not able to co-adsorb with the carboxylates onto the chalk surface. Instead, they seem to be forming acid-base complexes with the carboxylates in the oil phase, and thereby preventing the carboxylates from adsorbing onto the rock.

It has been shown experimentally, that for a given AN, the temperature and the amount of sulfate present in the formation water will affect the wetting condition significantly. The concentration of sulfate in the formation water is usually low due to a high amount of Ca^{2+} , and anhydrite, $\text{CaSO}_4(\text{s})$, is precipitated at high temperatures. The amount of sulfate present in the pore water, $\text{SO}_4^{2-}(\text{aq})$ appeared to be the active sulfate species to increase the water-wetness (Shariatpanahi et al., 2011).

1.3.EOR mechanisms of fractured carbonate reservoirs

Oil recovery from fractured oil-wet or mixed-wet carbonate rock has been proven to be a great challenge. Most of the injected water will pass through the fracture network and displaces only the oil residing in the fracture, which in some cases may be only a few percent of OOIP (Al-Hadhrami and Blunt, 2001).

In order to enter the oil-wet matrix block, the injected fluid must overcome the entry pressure or capillary barrier of the matrix block. The capillary entry pressure can be estimated using the Leverett J-function:

$$P_c = \sigma \sqrt{\frac{\phi}{k}} J^*$$

Where P_c is the capillary pressure, σ is the interfacial tension (IFT), ϕ is the porosity, k is the permeability and J^* is the Leverett dimensionless entry pressure with a value usually around 0.25. The capillary entry pressure barrier can be reduced/eliminated by lowering the interfacial tension between the

Introduction

fluids, or altering the wetting state of the rock. Some methods also take advantage of the viscous or gravitational forces to overcome the capillary entry pressure (Al-Hadhrami and Blunt, 2001).

Thermal, miscible and chemical methods are the most frequently applied EOR methods in fractured carbonate reservoirs. The main purpose of applying thermal or miscible methods is generally to enhance the fluid flow in the reservoir rock by changing the oil properties, especially the viscosity.

1.3.1. Miscible methods

Gas injection involves using the gravitational forces to overcome the capillary entry pressure in a gravity drainage process. Near-miscible gas injection is also another approach to lower the IFT between the oil and gas. The use of near-miscible gas lowers the capillary entry pressure, and at the same time, the viscosity of the oil will be reduced (Høgnesen, 2005).

1.3.2. Thermal methods

Al-hadhrami and Blunt (2001) observed wettability alteration of carbonates by injecting hot water/steam (240 °C). They explained the wetting alteration by desorption of asphaltenic materials from the carbonate surface without any experimental verifications. They also proposed to inject steam or hot water to heat the matrix in the giant fractured carbonate field, Ghaba North field in Oman, in order to thermally induce wettability alteration and improve oil recovery. Tang and Kovsky (2002) have also observed increased spontaneous imbibition into diatomic material containing heavy crude oil by hot-water injection. It was concluded from experimental observations that diatomic fines were detached with increasing temperature, and the authors suggested that fresh water-wet pore surfaces were created.

1.3.3. Chemical methods

The chemical methods are aimed to either increase the areal sweep efficiency at the macroscopic scale by changing the mobility ratio, or increase the displacement efficiency at the microscopic scale by reducing the interfacial tension, or altering the rock wettability (Standnes and Austad, 2003b). Since carbonate reservoirs are highly fractured, the use of chemical flooding to increase the macroscopic sweep efficiency is very difficult, because the injected fluid will pass through the fractures rather than the matrix blocks. Thus, in fractured carbonate reservoirs, the chemical EOR methods should focus on mobilizing the trapped oil at pore scale. Improved spontaneous imbibition of water into matrix block has been considered as the

main mechanism for oil production in such reservoirs (Austad et al., 2005). In a fractured reservoir, injection of surfactant will reduce the IFT and thereby the gravity can dominate the fluid flow. A lower IFT decreases the capillary entry pressure, making water imbibition from the fractures easier. However, the capillary forces also decrease, and depending on the permeability, the oil recovery rate may either decrease or increase, although ultimate recovery tends to increase (Austad et al., 1998; Chen et al., 2000; Milter and Austad, 1996b). It has been also shown that surfactants can be used to take advantage of both lowering the oil-water IFT and the effect of altering the carbonate wettability towards a more water-wet state (Austad and Standnes, 2003; Hirasaki and Zhang, 2004; Seethepalli et al., 2004; Standnes and Austad, 2000b). Although many pilot tests and a few field tests have been conducted, the economics of surfactant injection have rarely been favorable (Spinler et al., 2000). Published field tests showed that it was possible to have an economic surfactant process at low surfactant concentrations (Downs, 1989; Inks, 1968).

1.3.4. Smart water

A new EOR method for chalk and possibly an applicable method for all carbonates is wettability alteration by seawater. Austad and co-workers have shown that seawater can act as a “Smart Water” to improve the water-wetness of chalk at high temperatures causing enhanced oil recovery by spontaneous imbibition (Strand et al., 2006a; Zhang and Austad, 2006; Zhang et al., 2006). The great success in oil recovery by injection of seawater into the highly fractured, mixed-wet Ekofisk chalk field is an example of the efficiency of seawater as a smart EOR fluid (Sulak, 1991).

Seawater injection has been proven to be a key factor in oil recovery from low-permeable, high porosity and fractured chalk reservoirs in North Sea (Punternold, 2008). Seawater is able to alter the chalk wettability from oil-wet to intermediate to water-wet, and therefore, water imbibition into the rock matrix is facilitated. In addition to wettability alteration, the compaction of the rock caused by seawater is also an important drive mechanism for oil recovery. Smart water flooding has several advantages compared to other EOR methods (Kokal and Al-Kaabi, 2010):

- It can achieve higher ultimate oil recovery with minimal investment in current operations, assuming that a water-flooding infrastructure is already in place.
- It can be applied during the early life cycle of the reservoir.
- The payback is faster, even with small incremental oil recovery.

Having considered these highly important and interesting features regarding injection of seawater into chalk, the possible extension of using seawater as an EOR fluid for limestone was investigated which will be discussed in this thesis.

1.4. History of chemical flooding and wettability alteration in carbonates

Mobilization of oil trapped by capillary action during water floods was the main objective of enhanced oil recovery by chemical flooding (Morrow and Mason, 2001). Surfactants have been used to enhance recovery of oil from fractured carbonates. Cationic, anionic and nonionic surfactant have been used to alter the wettability of originally oil-wet carbonate rocks (Adibhatla and Mohanty, 2008; Austad et al., 1998; Gupta and Mohanty, 2011; Hirasaki and Zhang, 2004; Milter and Austad, 1996a; Milter and Austad, 1996b; Seethepalli et al., 2004; Standnes and Austad, 2000b; Standnes et al., 2002).

In a research study conducted by Hirasaki and Zhang (2004) the positively charged carbonate surface ($\text{pH} < 9$) was altered to negatively charged in the presence of a low concentration of alkali (Na_2CO_3) when an anionic surfactant was used. Seethepalli et al. (2004) found that solutions of 0.3 M sodium carbonate and 0.05 wt% alkylarylsulfonate promoted imbibition into limestone cores with up to 50% production of OOIP. The solutions had low IFT (~ 0.001 mN/m) and a pH equal to approximately 10. The most probable mechanism of wettability reversal is reaction of sodium carbonate with the rock surface causing release of the calcium-polar compound followed by saponification of the polar molecule. The saponified polar compounds will be slightly soluble in water but will play a larger part at the oil-water interface by lowering the IFT and interfacial oil viscosity. The role of the alkylarylsulfonate is reduction of IFT to a very low value that in turn lowers the threshold pressure for entry of the aqueous solution into the pores and contributes to some emulsification of the oil, thus facilitating its displacement. The alteration of wettability from oil-wet to water-wet changes the capillary pressure from negative to positive, which initiates spontaneous imbibition (Donaldson and Alam, 2008).

Austad and co-workers have shown that cationic surfactants of the type alkyl trimethyl ammonium bromide, $\text{R-N}-(\text{CH}_3)_3\text{Br}$ (C_nTAB), alkyl ammonium chloride, $\text{C}_{10}\text{NH}_3\text{Cl}$ and bioderivatives from the coconut palm, called Arquard and Dodigen can act as wettability modifiers in chalk (Standnes and Austad, 2003a), limestone (Strand et al., 2008) and dolomite (Standnes et al., 2002). Flooding with cationic surfactant is quite attractive because they bear the same charge as the surface of the carbonate surface. The

Introduction

mechanism was described as a specific interaction between the monomer of the cationic surfactant and strongly adsorbed negatively charged carboxylic material from the crude oil. The strong electrostatic and hydrophobic interaction between the species forms a complex usually termed as “cat-anionic surfactant” (Høgnesen et al., 2004). The complex is released from the surface and dissolved either in the oil phase or in the surfactant micelles in the aqueous phase. A positive capillary pressure is created and spontaneous imbibition can occur. The decrease in the interfacial tension (IFT) between the injected surfactant solution and the oil was moderate, showing values in the range of 0.1-1.0 mN/m.

Surfactant can improve oil recovery by either altering the wettability of the matrix and enhances spontaneous imbibition of water, or reducing interfacial tension between oil and water and thus enhances oil-water gravity drainage or both. Surfactant-enhanced gravity drainage (SEGD) is a process, which is different from conventional surfactant flooding or alkaline-polymer-surfactant flooding. The target for SEG D is un-swept/un-drained oil in the matrix, while for conventional surfactant or ASP process the target is to reduce the waterflood remaining oil saturation. In SEG D there is no need for an ultra-low IFT between surfactant solution and crude oil. A reduction in IFT in the order of ~ 10 - 20 would cause gravity force to exceed the capillary pressure of the matrix block (Masalmeh and Oedai, 2009).

Experimental studies in low-permeable chalk, 1-3 mD, were performed when C_{12} TAB dissolved in seawater was used as the imbibing fluid at 40 °C (Høgnesen et al., 2006). At the start, the oil recovery rate from the side and bottom surfaces was significantly higher than that from the top surface. Later, the oil recovery rate from the top surface increased and became much higher than that from the other surfaces. Thus, the test clearly demonstrated the impact of both gravity and capillary forces, due to wettability alteration, in the spontaneous imbibition process.

Diffusion of the surfactant into the porous medium will play an important role in this process. In the lab experiments, the diffusion rate of the surfactant will probably not be the rate determining step in the process. In field situations, however, diffusion of surfactant into the porous medium may be the rate determining factor for oil displacement. Upscaled simulations performed by Stoll et al. (2007) using cationic surfactant in low permeable chalk showed, that for a 1 m³ matrix block, it would take about 200 years for full penetration of the imbibing fluid. It must be mentioned that the upscaling was performed by neglecting the impact of gravity forces.

Masalmeh and Oedai (2009) investigated the impact of initial water saturation on the process of surfactant-enhanced gravity drainage, SEG D, in carbonates. From experimental tests using centrifuge, they concluded that

initial water showed little or no impact on the measured surfactant water-oil P_c -curves. They also concluded that molecular diffusion of surfactant alone could not explain the rate and volume of oil recovered by the SEG D process; because the oil recovery was too high.

Mohanty and co-workers (2008) have done extensive studies, both experimental and numerical simulations, on up-scaling of oil recovery from fractured carbonates by surfactant-aided gravity drainage. They used anionic surfactants dissolved in an optimum salt solution of Na_2CO_3 to give low interfacial tension, IFT, about 10^{-2} mN/m, and to reduce the adsorption of surfactant onto the carbonate surface. Injection of a solution of Na_2CO_3 into a fractured carbonate reservoir containing a high concentration of Ca^{2+} in the formation water is, however, questionable due to precipitation of CaCO_3 in the mixing zone and possible decrease in permeability. They observed decrease in the oil recovery rate as the permeability of the rock decreased, which was scaled by gravitational dimensionless time indicating a process governed by gravity forces. Furthermore, at the field scale, it was modeled that 50% of recoverable oil could be recovered in about 3 years with a fracture spacing of 1 m. Thus, by knowing optimum conditions for the SEG D process in naturally fractured carbonates, it should be possible to recover a significant amount of recoverable oil within a reasonable time frame.

1.5. Water-based EOR in chalk by smart water

Improved imbibition of water into neutral to preferential oil-wet chalk by means of a wettability alteration process has been observed using cationic surfactants of the quaternary ammonium type, $\text{R-N}(\text{CH}_3)_3\text{Br}$ (Standnes and Austad, 2000b). Later, it was documented that the wettability process was catalyzed if the imbibing fluid contained sulfate (Strand et al., 2003). Sulfate can adsorb on the water-wet sites of the chalk surface and reduce the positive charge density. Then, desorption of negatively charged carboxylic material is facilitated. It was also experimentally documented that sulfate can act as a wettability modifier alone, without any expensive surfactant present (Austad et al., 2005; Zhang and Austad, 2004). Sulfate is, in fact, a very strong potential determining ion towards $\text{CaCO}_3(\text{s})$ (Pierre et al., 1990), and knowing that the concentration of sulfate is about twice the concentration of Ca^{2+} in seawater, it may change the zeta potential of the carbonate surface. Spontaneous imbibition even increased with increased concentration of sulfate.

Co-adsorption of Ca^{2+} onto chalk in the presence of sulfate increases the concentration of Ca^{2+} close to the chalk surface, which facilitates a reaction with the carboxylic group. Temperature is also an important parameter. The

Introduction

imbibition rate and oil recovery increases as the temperature increases due to a stronger adsorption of SO_4^{2-} and Ca^{2+} onto the chalk surface (Strand et al., 2006a). In addition to SO_4^{2-} and Ca^{2+} , Mg^{2+} is also an important potential determining ion. The Mg^{2+} ion is small with a high charge density, and it is therefore strongly solvated in water (Burgess, 1978). As the temperature increases, Mg^{2+} becomes more reactive due to partial dehydration of the ion (Strand et al., 2008). Korsnes et al (2007) and Zhang et al (2007) have experimentally shown substitution of Ca^{2+} by Mg^{2+} at the chalk surface at high temperatures, >90-100 °C, when flooding seawater slowly through an outcrop chalk core. Interactions between the potential determining ions, Ca^{2+} , Mg^{2+} and SO_4^{2-} , and the chalk surface appeared to be the chemical mechanism for the wettability alteration (Zhang et al., 2007). During the study of the wettability alteration mechanism, some criteria for the interaction must be present, Figure 1.1, in order to obtain the enhanced oil recovery:

- Sulfate must adsorb onto the positively charged chalk surface, and the adsorption increases as the temperature increases.
- Co-adsorption of Ca^{2+} will take place due to decrease in the positive surface charge of the rock caused by the adsorption of SO_4^{2-} .
- Sometimes Mg^{2+} is able to substitute Ca^{2+} at the surface lattice at high temperature.

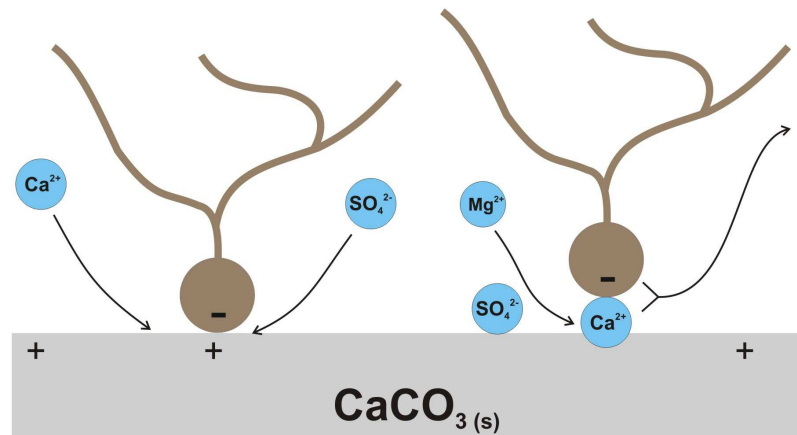


Figure 1.1 Schematic model of the suggested mechanism for the wettability alteration induced by seawater. (a) Proposed mechanism when Ca^{2+} and SO_4^{2-} are the active species. (b) Proposed mechanism when Mg^{2+} , Ca^{2+} and SO_4^{2-} are the active at higher temperature (Zhang et al., 2007).

Introduction

In summary, seawater is able to act as a wettability modifier to improve spontaneous imbibition of water into oil-wet chalk. The key parameters are high temperature and the potential determining ions in seawater: Ca^{2+} , Mg^{2+} , and SO_4^{2-} .

In a recent study, the effect of salinity and ionic composition of smart water on oil recovery at different temperatures was studied (Fathi et al., 2009). It was confirmed that not only is the concentration of the active ions Ca^{2+} , Mg^{2+} and SO_4^{2-} important for wettability alteration to take place, but also the amount of non-active salt, such as NaCl, has an impact on the wettability alteration process, which is discussed as a double-layer effect at the chalk surface. Seawater depleted in NaCl appeared to have the greatest effect on the wetting properties by increasing the water-wet area by 29% compared to the effect of ordinary SW.

Seawater acts as an IOR fluid in Chalk in two ways: (1) As a wettability modifier (smart water) (2) As a pore compaction agent. Due to the high porosity of chalk, compaction takes place during the primary production phase. In Ekofisk, the contribution in the drive mechanism due to compaction was estimated to be in the order of about 40% (Zhang et al., 2007). Korsens et al. (2007) suggested a mechanism for the enhanced-chemically induced weakening of chalk. Substitution of Ca^{2+} by Mg^{2+} at the inter-granular contacts reduces the mechanical strength of chalk. Due to this chemical substitution, the mechanical strength of the chalk decreased by a factor of 2.7 when the cores were flooded with seawater compared to the distilled water or other aqueous solutions free from Mg^{2+} and SO_4^{2-} ions (Korsnes et al., 2006).

2. Objectives

It has been verified by a number of papers that seawater can act as a “smart water” to improve oil recovery from chalk by wettability alteration towards more water-wet conditions by both spontaneous and forced imbibition (Strand et al., 2006a; Zhang and Austad, 2006; Zhang et al., 2006) and a mechanism has been suggested (Zhang et al., 2007). The great success in oil recovery by injection of seawater into the highly fractured mixed-wet Ekofisk chalk field is an example of the efficiency of seawater as an EOR fluid (Sulak, 1991). Chalk is pure biogenic material, and it has a much larger surface area compared to limestone ($\approx 2 \text{ m}^2/\text{g}$ compared to $\approx 0.3 \text{ m}^2/\text{g}$ for limestone, Table 4.1). Even though the chemical composition of chalk and limestone is similar, CaCO_3 , the response against the potential determining ions present in seawater may be different with regard to wettability modification. Thus, it was interesting to see if the results obtained for chalk were also applicable to limestone. In a very preliminary study, Strand et al. (2008) showed that the surface reactivity of reservoir limestone cores towards Ca^{2+} , Mg^{2+} and SO_4^{2-} had a similar trend as that of the chalk surface.

As an extension of the research studies conducted on water-based EOR in chalk, this project was the first attempt to address the limestone surface chemistry with emphasis on the water-based EOR methods.

This research study was aimed at evaluating the potential of using seawater as a wettability modifier in limestone. It was also investigated to present a systematic procedure for analysis of the potential of SW as a wettability modifier in different limestone reservoirs. The main objectives of this study include:

- **SW as core cleaning solvent**

The first part of this thesis concerns the ability of seawater to improve the cleaning of carbonate cores. It is nearly impossible to use traditional solvents to clean the carbonate surface. A chemical interaction under irreversible thermodynamic conditions is needed to remove the adsorbed acidic material from the carbonate surface. Thus, the question asked was: “*Can seawater be used as a cleaning agent to improve the water-wetness after performing the traditional cleaning using toluene and methanol?*”

- **Outcrop limestone as model rock for reservoir limestone**

The objective of the second part of the thesis is to investigate if the mechanism for wettability alteration of the chalk surface by smart water is also applicable to limestone. Since the carbonate surface is more reactive compared to sandstone, it is difficult to restore carbonate core material for

Objectives

parametric studies after being contacted with crude oil. It was therefore decided to study the outcrop limestone as a model for reservoir rock in water-based EOR by wettability modification. The objectives are as follow:

- Evaluate the sensitivity of the new chromatographic wettability test (Strand et al., 2006b) on limestone.
- Study the surface chemistry of limestone and investigate the affinity of potential determining ions in seawater towards limestone at different temperatures.
- Investigate potential of using seawater as a wettability modifier in outcrop limestone material.
- Investigate potential of using seawater as a wettability modifier in reservoir limestone material.

- **Possible SEG D process in limestone**

In the third part of the thesis the SEG D process in limestones was studied and the effect of rock permeability and interfacial tension (IFT) on the oil displacement process was investigated.

3. Materials and methods

3.1. Materials

3.1.1. Porous media

The selected properties of core materials used are summarized in Table 3.1. In the experiments, two types of outcrop limestone and three types of reservoir limestone cores have been used.

TOTAL limestone: This outcrop material was supplied by TOTAL, and it should be representative for an actual oil-bearing formation. The main characteristics of the material can be summarized as:

- Mainly calcite, 94 mole %.
- Small amounts of Al and Si, 0.86 and 1.37 mole %, respectively, which indicated low clay content. One of the tested cores contained about 3.7 mole% iron, but other cores did not contain iron.
- Porosity of 12-16%, including about 50% micro and 50% macro porosity, as reported by TOTAL.
- Permeability in the range of 8-30 mD.
- BET N₂-surface area was 0.18 m²/g.

Edward limestone: Edwards (GC) is a cretaceous limestone from West Texas, and it is also known as West Texas Crème, Cedar Hill cream, or Valencia Ivory building stone (Tie and Morrow, 2005). The main characteristics of the material can be summarized as:

- Mainly calcite, 96 mole %.
- Small amounts of Al and Si, 0.74 and 1.31 mole%, respectively, which indicates low clay content.
- Porosity about 17%.
- Permeability about 6 mD.
- BET N₂-surface area was 0.13 m²/g.

Table 3.1 Core properties

Core number	L (cm)	D (cm)	Porosity (%)	k (mD)	S _{wi} (%)
Total outcrop limestone (TOL)					
TOL# 1	5.03	3.78	15.0	10.5	-
TOL# 6	5.04	3.79	12.8	9.6	10
TOL# 7	5.03	3.78	13.0	-	10
TOL# 10	5.01	3.78	13.1	27	-
TOL# 13	5.03	3.79	12.8	11.7	10
TOL# 15	5.04	3.78	12.8	7.9	-
Edwards outcrop limestone (GC) (EDL)					
EDL# 1	6.13	3.84	17.4	7.3	-
EDL# 3	5.9	3.83	17.4	6.9	-
EDL# 4	6.08	3.84	16.1	5.1	10
Res1 limestone					
C# 20A	4.88	3.78	26.0	8.5	-
C# 33A	4.67	3.78	28.6	6.2	-
C# 46A	4.76	3.78	27.8	2.5	-
Res3 limestone					
Res# 4-12	5.63	3.8	16.7	0.5	10
Res# 5-17	5.52	3.8	17.1	0.2	10
Res4 limestone					
Res# 52	4.77	3.73	28.0	364	10

Res3 limestone: Core materials sampled from the same well in a naturally-fractured limestone reservoir. The porosity was in the range of 17%, and the permeability 0.1-1.0 mD. The BET-N₂ surface area was determined to be 0.29 m²/g.

Materials and methods

3.1.2. Oils

A crude oil was diluted with heptane in a volume ratio of 40/60, heptane/crude, resulting in a high acidic crude oil (AN=1.84 mg KOH/g). A fraction of the oil was treated with silica gel to obtain a crude oil with low AN (AN=0.02 mg KOH/g). Both the low and high acidic oils were centrifuged and filtered through a 5 μm Millipore filter. No precipitation of asphaltenes was observed after diluting with heptane and during the storage. New crude oils, RES40-0.1 with AN=0.10 and RES40-0.57 with AN=0.57 mg KOH/g were made by mixing the high and low AN oils in a proper ratio. Chemical and physical properties of the crude oils used are listed in Table 3.2.

Table 3.2 Selected properties of oil samples

Crude Oil	AN (mg KOH/g)	BN (mg KOH/g)	density ^a (g/cm ³)	viscosity ^b (cP)
RES40	1.84	0.43	0.804	3.14
RES40-0.1	0.1	0.1	0.81	2.95
RES40-0.57	0.57	0.25	0.81	3.1

^{a,b} Measured at 20 °C

3.1.3. Brines

The composition of the brines used is listed in Table 3.3. The brines are prepared using deionized water and different amount of NaCl, Na₂SO₄, KCl, NaHCO₃, MgCl₂·6H₂O and CaCl₂·2H₂O. KSCN and LiCl are used as tracers in the chromatographic tests. All chemicals were PA-graded and delivered by Merck. The terminology is as follows:

- SW is synthetic seawater.
- SW0Ca is SW without Ca²⁺.
- SW0T is SW without SO₄²⁻ and tracer SCN⁻, used in the chromatographic tests.
- SW½T is SW containing 0.012 mole/l of SO₄²⁻ and SCN⁻, used in chromatographic tests.
- SW1T is SW containing 0.024 mole/l of SO₄²⁻ and SCN⁻.

All the brines were filtered through a 0.22 μm Millipore filter and vacuumed to remove dissolved gas prior to use.

Table 3.3 Synthetic brine composition

	FW	SW	SW0Ca	SW0T	SW1/2T	SW1T
Ions	mole/l	mole/l	mole/l	mole/l	mole/l	mole/l
HCO ₃ ⁻	0.009	0.002	0.002	0.002	0.002	0.002
Cl ⁻	1.066	0.525	0.524	0.583	0.538	0.492
SO ₄ ²⁻	0.000	0.024	0.024	0.000	0.012	0.024
SCN ⁻	0.000	0.000	0.000	0.000	0.012	0.024
Mg ²⁺	0.008	0.045	0.045	0.045	0.045	0.045
Ca ²⁺	0.029	0.013	0.000	0.013	0.013	0.013
Na ⁺	0.997	0.450	0.475	0.460	0.427	0.393
K ⁺	0.005	0.010	0.010	0.010	0.022	0.034
Li ⁺	0.000	0.000	0.000	0.000	0.012	0.024
TDS (g/l)	62.83	33.39	33.39	33.39	33.39	33.39
IS (mole/l)	1.112	0.66	0.64	0.64	0.64	0.65

3.1.4. Additional chemicals

Heptane: Used as the oil phase in cores representing a completely water-wet condition.

Decane: Used as the oil phase in cores representing a completely water-wet condition.

Toluene (water-saturated): Used for the cleaning of the limestone reservoir cores.

Methanol: Used for the removal of Toluene and water in the limestone reservoir cores during the cleaning process.

Surfactants: The cationic surfactant C₁₂-N(CH₃)₃Br, termed C₁₂TAB, was obtained from Sigma and used without further purification. Dodigen 5462 containing approximately 50% C₁₂-N(CH₃)₃Cl, 24% C₁₄-N(CH₃)₃Cl, 11% C₁₆-N(CH₃)₃Cl and 13% C₁₈-N(CH₃)₃Cl was obtained from Hoechst AG, Germany, and was used without further purification.

3.2. Core preparation

3.2.1. Initial core preparation

Outcrop limestone cores: Prior to the systematic studies of the surface reactivity towards the actual potential determining ions, the cores were flooded with approximately 8 PV's of deionized water, DI, in order to

Materials and methods

remove dissolvable inorganic salts. Since the outcrop cores have not been exposed to crude oil, the traditional cleaning by toluene and methanol was skipped.

Reservoir limestone cores: The cores were cleaned by flooding the cores at room temperature with water-saturated toluene until the effluent became colourless (Thomas et al., 1993). Thereafter, the cores were flooded with several PVs of methanol to remove toluene and water. Then the core was dried out at 90 °C to evaporate methanol.

3.2.2. Core cleaning by hot seawater and surfactant

During the course of this PhD work, as the results will show, it was found that SW at high temperature is able to increase the water-wetness of the limestone surface. Previously, it has been shown that sulfate present in the brine doped with cationic surfactant, C₁₂TAB, improved the water-wetness of the carbonate surface (Standnes et al., 2002; Strand et al., 2008; Strand et al., 2003).

After initial core preparation, the cores were also flooded with SW+1.0 wt% C₁₂TAB at 130 °C at a rate of 3 PV/D for 3 days. Finally, the cores were flooded with DI water to remove surfactant and salt, and the effluent was checked for SO₄²⁻. As sulfate adsorbs onto the rock, it is most difficult to displace, therefore the core was flooded with DI water until the effluent was free from sulfate, as tested by using BaCl₂. The cores were dried to a constant weight at 90 °C.

3.2.3. Initial water saturation, S_{wi}

The dried cores were saturated with 10 times diluted formation water, under vacuum, and the initial water saturation of 10% was established by use of a dessicator (Springer et al., 2003).

3.2.4. Oil saturation and aging

The cores used in the oil recovery experiments, were saturated and flooded by the corresponding oil (low, medium or high AN oil), 2 PVs in each direction, and finally aged at 90 °C for 2 weeks. The cores were wrapped in Teflon tape to avoid unrepresentative adsorption of polar components onto the surface during the aging process (Standnes and Austad, 2000a).

3.3. Methods

3.3.1. Determination of acid and base numbers

The oil samples acid and base numbers were determined by the use of a Mettler Toledo DL55 automatic titrator. The device performs potentiometric titration using an internal standard. The measurements were according to the modified versions of ASTM D2896 for base number titration and ASTM D664 for acid number titration (Fan and Buckley, 2006).

3.3.2. IFT measurement

The IFT measurements were performed using a Kruss SITE04 spinning drop tensiometer with a small sample volume set installed. The IFT measurements between the crude oil and the surfactant solutions were performed at 50 °C, and the value reported in Table 3.4 is the average of at least three measurements.

Table 3.4 IFT measurement at 50 °C

Oil	Brine	Surfactant	Surfactant Concn. (wt %)	IFT (mN/m)
RES40-0.57	SW	C ₁₂ TAB	1.0	0.67±0.03
RES40-0.57	SW	Dodigen	0.5	0.34±0.03

3.3.3. EDS analysis

Elemental composition of the limestone samples was obtained by Energy Dispersive Spectrometry (EDS) carried out on a Zeiss Supra 35VP scanning electron microscope. An area of the rock sample with a typical grain size distribution was selected and the EDS analysis was applied at a low magnification, normally 400 times. The sample was analyzed for the elements Ca, Mg, K, Si and Fe and the atomic% was calculated. EDS analyses were also performed on single rock grains of interest at a high magnification.

3.3.4. Chromatographic wettability test

A chromatographic technique to determine the water-wet surface fraction of chalk has recently been published (Strand et al., 2006b). The chromatographic technique can be used to monitor changes in wetting conditions after exposing the core to various fluids. The principle of the test is based on the chromatographic separation of the non-adsorbing tracer, SCN⁻, and adsorbing SO₄²⁻ at water-wet sites in the porous system.

Materials and methods

The actual core was flooded to S_{or} at room temperature using SW0T at the rate of 0.1 ml/min. Then, SW $\frac{1}{2}$ T was injected as the chromatographic brine at the same rate. Small fractions of the effluent were collected using a fraction collector and analyzed for the concentration of SCN^- and SO_4^{2-} . The relative ion concentration, C/C_o , was plotted against the number of PVs injected and the area between the effluent curves was calculated. The accuracy of the calculated area in the wettability test has been previously determined to be about $\pm 5\%$ (Strand et al., 2006b).

3.3.5. Ionic composition analysis

An ion-exchange chromatograph, ICS-3000 Reagent-freeTM produced by Dionex Corporation, USA was used to analyze the ionic concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} and SCN^- . In order to stay in the linear region, the effluent samples were diluted 1:50 or 1:200 by deionized water prior to the analysis, and the ion concentrations were calculated based on an external standard (Paper I).

3.3.6. Zeta potential measurements

Sample preparation: The rock materials (outcrop chalk core, reservoir limestone core and outcrop limestone core) were wet-milled with MeOH using a planetary ball mill and dried at 90 °C. In order to investigate the affinity of potential determining ions towards the rock surface, the aqueous rock powder suspension was prepared by mixing pure NaCl brine with 4wt% milled rock powder. The suspension was then stirred for 24 hours before use.

Zeta potential: Zeta potential was measured using a Colloidal Dynamics AcoustoSizer II that worked based on electro-acoustic and ultrasonic attenuation measurements.

The effect of divalent ions in seawater, (SO_4^{2-} , Ca^{2+} and Mg^{2+}) at different concentrations on the charge of carbonate surface in NaCl solution with the salinity of seawater, (33.39 g/l) was analyzed.

For each single divalent ion, a new batch was prepared. The 4wt% carbonate powder suspension in a 100% NaCl brine was stirred for 24 hours. Different molar concentration of SO_4^{2-} , Ca^{2+} and Mg^{2+} was obtained by adding Na_2SO_4 , $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$, respectively. Then the surface charge was measured at different molar concentration of each single divalent ion. For each measurement, the pH was kept constant, equal to 8.4 by adjusting with small amounts of concentrated HCl or NaOH. The carbonate suspensions

Materials and methods

were stirred for 15 minutes after new chemicals were added in order to achieve a new equilibrium before the measurement.

3.3.7. Chromatographic studies/surface reactivity

A 100% water-saturated carbonate core was mounted in a Hassler core holder, with a confining pressure of 25 bars. A back pressure of 11 bars was used to ensure constant pore pressure, and to prevent the fluid from boiling at high temperatures. The core was flooded at constant rate. Samples of the effluent were taken using a fraction collector and the ionic compositions were analyzed.

Affinity of SO_4^{2-} : Affinity of SO_4^{2-} towards the surface of different limestone samples at room temperature was studied using SW1/2T, seawater with equal amounts of SCN^- and SO_4^{2-} at half the seawater concentration of SO_4^{2-} . Before the test, the core was flooded with at least 5 PV's of seawater without SCN^- and SO_4^{2-} (SW0T).

Substitution of Ca^{2+} by Mg^{2+} : Due to the increase in reactivity of Mg^{2+} at $T > 90^\circ\text{C}$, it has been observed that Mg^{2+} is able to displace Ca^{2+} from the carbonate surface lattice, by a substitution reaction. In the presence of SO_4^{2-} , Mg^{2+} is also able to act as a wettability modifier (Zhang et al., 2007). Thus, the substitution of Ca^{2+} by Mg^{2+} is believed to be part of the wettability alteration process. SW was slowly flooded through the cores at a rate of 1.0 PV/D at different temperatures and the concentration of Ca^{2+} , Mg^{2+} , and SO_4^{2-} was plotted versus the PV injected.

3.3.8. Oil recovery by spontaneous imbibition

The spontaneous imbibition tests at low temperatures were performed using 100% heptane-saturated cores in standard Amott cells.

The spontaneous imbibition tests at 130°C on carbonate cores with 10% initial water saturation and aged in crude oil were performed in sealed steel cells. The cores were surrounded by the imbibing brine with a backpressure of ~ 11 bars. The amount of oil produced, quantified as % of OOIP, was collected in a burette and recorded as a function of time. The reported oil recovery also includes thermal expansion of fluids due to the increase in temperature, from 20 to 130°C .

3.3.9. Oil recovery by forced imbibition

Single core flooding: The forced imbibition test on TOL# 13 was performed at 130 °C. A confining pressure of 25 bars and a back pressure of 11 bars were used. First FW was injected at a rate of 0.2 PV/D, and the amount of oil produced, % of OOIP, was collected in a burette and recorded as a function of time. After reaching the plateau, the flooding rate was step-wise increased up to 1.6 PV/D to check possible end effects before switching to SW. Then the rate was decreased to 0.2 PV/D, and the flooding was continued by SW at the same temperature.

Composite core flooding: After SI tests on TOL# 6 and 7, the cores were combined as a composite core and flooded by different brines at a rate of 0.5 PV/D. The test was performed at 130 °C with a confining pressure of 25 bars and a back pressure of 11 bars. In order to increase the capillary number, the flooding rate was increased in steps.

4. Main results and discussion

4.1. Cleaning of carbonate reservoir cores by seawater

All the reservoir limestone cores used in these tests had previously been exposed to crude oil and used in core flooding experiments. Then, the cores have been cleaned in the traditional way using toluene and MeOH. The objective of the experiments is to document that seawater at high temperature is able to improve the water-wetness of the cores after core cleaning in the traditional way. Three sets of experiments were conducted.

The water-wet fraction of core C# 46A was determined by the chromatographic wettability test before and after the core was used for various tests at both low and high temperatures with SW (Puntervold, 2008; Strand et al., 2008). The wettability tests were performed at room temperature using the brine termed SW $\frac{1}{2}$ T. The initial chromatographic separation between SCN $^-$ and SO $_4^{2-}$ before the core was exposed to SW at high temperatures is shown in Figure 4.1(a). The area between the tracer curve and the elution curve for SO $_4^{2-}$, which is proportional to the water-wet area, was determined to be $A_w=0.107$. The fact that the tracer curve passes through the coordinate (1.0, 0.5) indicates that the total pore volume of the core was connected and flooded by the injected fluid. The wettability test of the same core after the core had been exposed to SW at high temperature (the core was flooded with at least 6 PVs of SW at 130 °C), is shown in Figure 4.1(b). The separation between the tracer and sulfate curves increased to $A_w=0.141$, which corresponded to an increase in the water-wet surface area of 32 %.

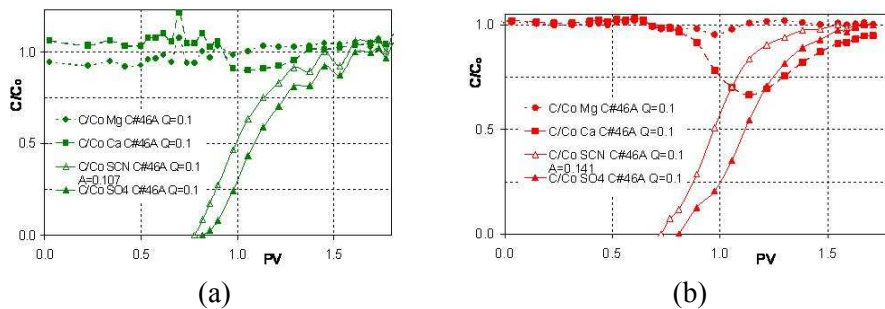


Figure 4.1 Chromatographic wettability test on core C# 46A (a) before exposure to SW at high temperature, and (b) after exposure to SW at high temperature. The core was flooded with SW $\frac{1}{2}$ T at a rate of 0.1 ml/min (Strand et al., 2008).

Main results and discussion

The limestone core termed C# 20A showed very low separation between the elution curves for the tracer and sulfate after cleaning with toluene and MeOH, as illustrated in Figure 4.2. The core was then flooded with seawater at 130 °C for 1 day at a rate of 3 PV/D. After removing the sulfate by flooding with seawater without sulfate at ambient temperature, a new chromatographic wettability test showed good separation between the tracer and the sulfate curve, Figure 4.2. Thus, the water-wet surface area was increased significantly. After flooding the core a second time with seawater at high temperature for 3 days (9 PV), the chromatographic test did not show any significant increase in the water-wet surface area, as illustrated by the fact that the two elution curves for sulfate were similar, Figure 4.2. It is, however, not correct to conclude that the core has obtained a completely water-wet condition, but there is no doubt that seawater at high temperature is able to remove strongly adsorbed carboxylic materials from the carbonate surface.

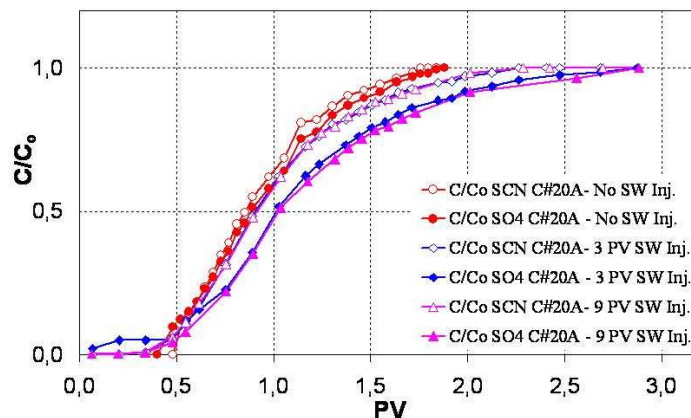


Figure 4.2 Three Chromatographic wettability tests on core C# 20A. The core was flooded with SW $\frac{1}{2}$ T at a rate of 0.1 ml/min. The results shows the water wet area before exposure to SW at high temperature, and after 3 PV (1 day) and after 9 PV (2 days) injection of SW.

In the third set of tests with limestone cores, the core termed C# 33A showed a very large separation between the tracer and sulfate in the initial wettability test, Figure 4.3, which indicated that the core surface was highly reactive. The area between the two curves was $A_w=0.14$. After flooding the core with distilled water to remove easily-removable salts, the core was dried at 110 °C, and saturated with decane. The core was then imbibed with SW0T

Main results and discussion

at 70 °C, and the oil recovery reached a plateau of about 3.3% of oil in place, Figure 4.4.

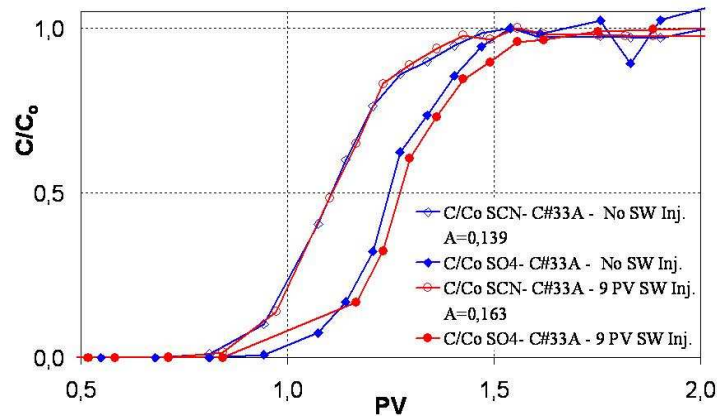


Figure 4.3 Chromatographic wettability tests on core C# 33A. The core was flooded with $SW_{1/2T}$ at a rate of 0.1 ml/min. The results shows the water-wet area before exposure to SW at high temperature and after 9 PV (3 days) injection of SW.

The core was then dried and washed with SW_{0T} prior to a new injection of SW at high temperature. The core was flooded 9 PV (3 PV/D, 3 days) with seawater at 130 °C. A new wettability test only showed a slight increase in the area between the tracer and sulfate curve, $A_w=0.16$, which corresponded to an increase in water-wet area of about 14%, Figure 4.3. Finally, the core was subjected to a new imbibition test using 100% decane and the same core preparation as in the first imbibition test. As seen in Figure 4.4, the oil recovery increased compared to the first test prior to the high temperature flooding with seawater, from 3.3 % to about 8 %. Thus a rather small increase in the water-wet surface area also increased the oil recovery in a spontaneous imbibition process and improved the water-wetness of the core.

It appears to be a discrepancy between the low oil recovery by spontaneous imbibition and wettability. It has, however, previously been observed that chalk samples containing significant amount of silica appeared to be very water-wet by using the chromatographic test, but the imbibition of water was very low (Strand et al., 2007). It is likely that this core also contained some silica.

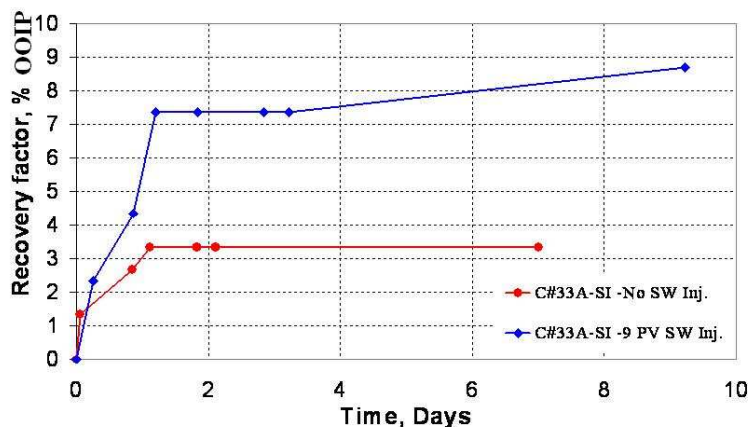


Figure 4.4 Spontaneous imbibition at 70 °C of decane-saturated core C# 33A before exposure to SW at high temperature and after 9 PV's (3days) injection of SW.

Previous studies have shown that seawater acts as an EOR fluid in chalk (Punternold, 2008; Zhang, 2006). Preliminary chemical tests have also indicated that seawater may act as an EOR fluid in limestone. The same chemical interaction between divalent ions in seawater and the rock surface was observed in both cases, but the reactivity towards limestone surface was somewhat lower than for chalk (Strand et al., 2008). The recently obtained results support these observations, and seawater can even be used to improve the cleaning of reservoir limestone cores.

Carboxylates from the crude oil are strongly adsorbed onto the carbonate surface, and traditional cleaning of reservoir carbonate cores by using toluene and methanol will not remove all the adsorbed material. Obviously, each of the limestone cores showed different wetting properties after being cleaned with toluene and MeOH. The reason may be that some of the cores have been used in previous experiments in combination with the cationic surfactant, C₁₂TAB, as wettability modifier. It is previously documented that this surfactant is able to improve the water-wetness in chalk and dolomite (Standnes and Austad, 2000b; Standnes et al., 2002).

4.2. Seawater induced wettability modification of outcrop limestones

This part of the thesis presents a systematic parametric study of the potential of wettability alteration by seawater in outcrop limestone cores. In general, limestone core material is rather inhomogeneous, and it is difficult to use core material from different locations for water-based EOR studies. In order to minimize the variation in core properties, it was suggested to use outcrop cores from the same block for parametric studies. Wettability alteration during a water flood is related to surface reactivity of the rock towards active ions in the injected fluid. The question asked was: “*Is the surface reactivity of outcrop limestone exposed to aerobic conditions comparable to the reactivity observed for reservoir limestone exposed to anaerobic conditions?*” In that case, outcrop limestone could be used as model rock in parametric EOR studies.

4.2.1. Initial core preparation

Figure 4.5 shows that the initial content of dissolvable potential determining ions in both rock types, TOTAL (TOL) and Edward (EDL), is very low compared to ordinary seawater, which contains 520, 1080 and 2310 mg/l of Ca^{2+} , Mg^{2+} , and SO_4^{2-} , respectively. Thus, no interference between ions present in the core and seawater as injection fluid is expected. None of the outcrop cores appeared to contain anhydrite, CaSO_4 .

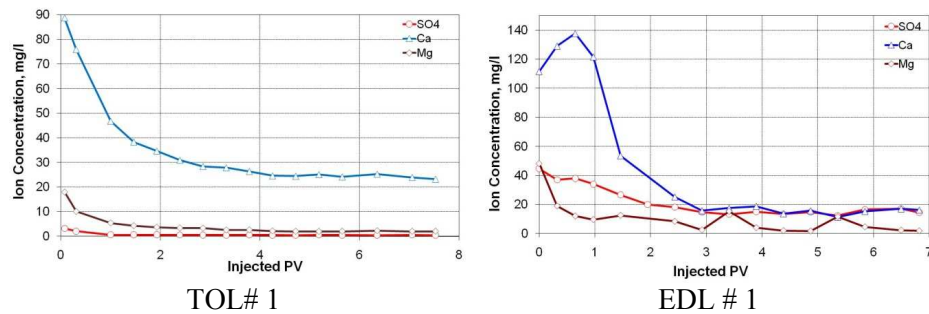


Figure 4.5 Content of Ca^{2+} , Mg^{2+} , and SO_4^{2-} initially present in TOL# 1 and EDL# 1. The cores were flooded with DI at a rate of 0.1 ml/min at ambient temperature.

4.2.2. Affinity of SO_4^{2-} towards the carbonate surface

TOL# 1: The chromatographic test is shown in Figure 4.6(a). The tracer showed a symmetric S-shaped curve, indicating good connectivity between the porous network. The chromatographic separation between SCN^- and SO_4^{2-} is extremely small, and the area between the curves was calculated to be only 0.041. No significant change in the relative concentration of Ca^{2+} and Mg^{2+} was detected. Based on the fact that the chromatographic separation between SCN^- and SO_4^{2-} takes place at the water-wet sites, it is relevant to conclude that the core must act rather oil-wet, which is unreasonable, or the water-wet carbonate surface is for other reasons not reactive towards sulfate. After flooding the core with SW at 130 °C, a new wettability test was performed, and an increase in the chromatographic separation between the tracer and sulfate curve was observed, area 0.075, Figure 4.6(b). In this case, a small decrease in the concentration of Ca^{2+} was noticed, which has been interpreted as co-adsorption of Ca^{2+} onto the carbonate surface due to the decrease in the positive surface charge by adsorption of sulfate (Strand et al., 2006b). Finally, after flooding the core with SW+C₁₂TAB at 130 °C, no increase in the area separating the effluent curves of SCN^- and SO_4^{2-} was observed, indicating no changes in wetting properties, Figure 4.7.

EDL# 1&4: The affinity of sulfate towards Edward cores was also tested using EDL# 1 & 4. The asymmetric shape of the S-formed elution curve of the tracers is also evident in these cores, confirming heterogeneity of the porous medium, i. e. the presence of both micro and macro porosity, Figure 4.8. In both cores, the calculated area slightly increased from 0.049 to 0.079 in EDL# 1 and from 0.085 to 0.133 in EDL# 4 after being exposed to SW at 130 °C.

Regarding wetting conditions, the chromatographic separation between SCN^- and SO_4^{2-} is not only related to water-wet fraction of the rock, but also on the available surface area. It is noticed from Table 4.1 that the BET N₂ surface areas of TOTAL and Edwards cores are rather low, 0.18 and 0.133 m²/g, respectively, compared to other reservoir limestone. As discussed later, after performing oil recovery tests, it is not reasonable to believe that the small chromatographic separation between the tracer and sulfate is due to lower surface area of the outcrop material.

Main results and discussion

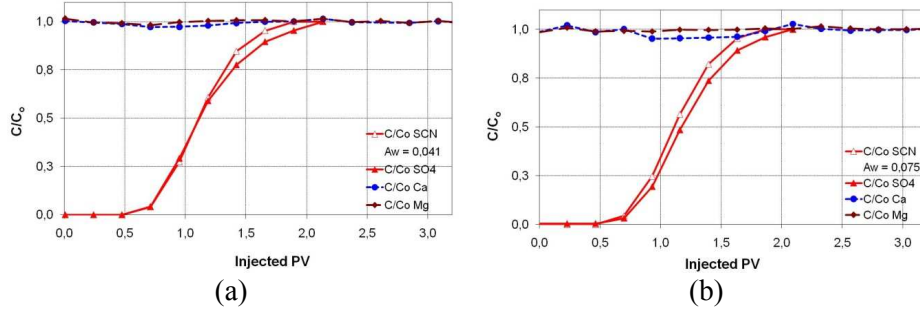


Figure 4.6 Chromatographic wettability test on core plug TOL# 1 (a) before & (b) after exposure to SW at high temperature. The core was flooded with $SW^{1/2}T$ ($[SCN] = [SO_4^{2-}] = 0.012$ mole/l) at a rate of 0.1 ml/min.

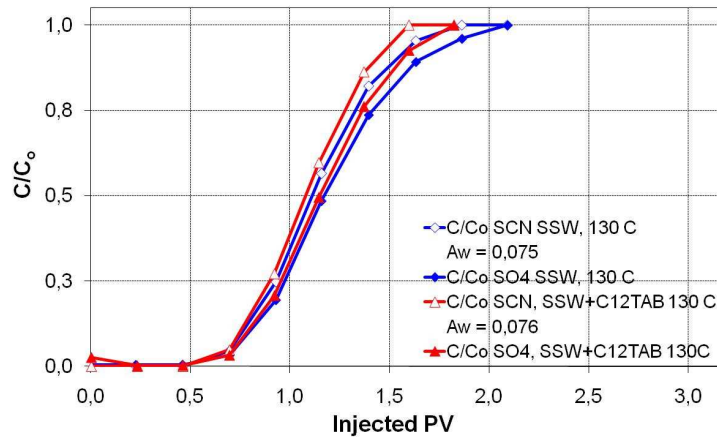


Figure 4.7 Chromatographic wettability test on core plug TOL# 1 after exposure to $SW+C_{12}TAB$ at high temperature. The core was flooded with $SW^{1/2}T$ ($[SCN] = [SO_4^{2-}] = 0.012$ mole/l) at a rate of 0.1 ml/min.

Main results and discussion

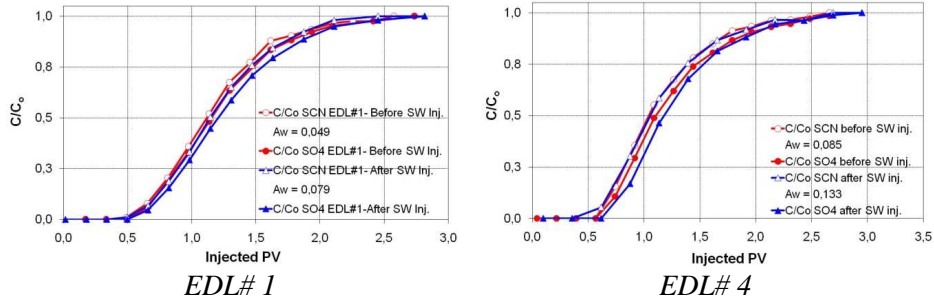


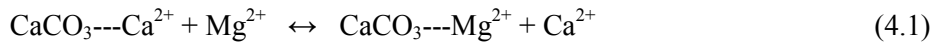
Figure 4.8 Chromatographic wettability test on core plugs EDL# 1 & 4 before & after exposure to SW at high temperature. The core was flooded with SW $_{1/2T}$ ($[SCN^-] = [SO_4^{2-}] = 0.012$ mole/l) at a rate of 0.1 ml/min.

Table 4.1 BET analysis results on different limestone cores

Core Description	Core #	BET, m ² /g	BET C-value
Total outcrop limestone	TOL# 1	0.18	26
Edwards outcrop limestone	EDL# 2	0.133	24
Res1 limestone	Res# 1- 43A	0.772	35
Res 2 limestone	Res# 2-AP14	0.696	40
Res 3 limestone	Res# 3- 2	0.286	28
Stevens Klint outcrop chalk	SK	1.70	40

4.2.3. Substitution of Ca²⁺ by Mg²⁺ at the rock surface

For chalk and reservoir limestone it has been observed that Mg²⁺ will substitute Ca²⁺ at the rock surface in a 1:1 reaction when the core is flooded slowly with seawater at temperatures above 70 °C (Strand et al., 2008; Zhang et al., 2007).



The equilibrium is moved to the right as the temperature is increased. It is hard to believe that the substitution is in the Stern layer because no equilibrium was established even after flooding many PVs at a rate of 1

Main results and discussion

PV/D. Therefore, the substitution may take place in the ionic structure of $\text{CaCO}_3(\text{s})$ or that $\text{MgCO}_3(\text{s})$ is formed.

TOL# 1: The core was flooded slowly with SW, 1 PV/D at different temperatures, Figure 4.9. The surface reactivity of TOL# 1 towards Ca^{2+} , Mg^{2+} , and SO_4^{2-} appeared to be very low. The concentration of all the ions remained quite similar to the initial concentration of SW. At 130 °C, a very small decrease in the concentration of Mg^{2+} was noticed, which corresponded to a small increase in Ca^{2+} , but compared to previous studies using chalk and reservoir limestone cores, the effect is negligible (Strand et al., 2008; Zhang et al., 2007). At 150 °C, it is a small decrease in Mg^{2+} concentration. The concentration of Ca^{2+} first increased a little, and then decreased probably due to precipitation of anhydrite, $\text{CaSO}_4(\text{s})$, which is supported by the continuous decrease in the concentration of SO_4^{2-} . The contact time between the rock and the injected fluid was doubled by flooding the core with a rate of 0.5 PV/D at 130 °C, but this did not increase the substitution of Ca^{2+} by Mg^{2+} , confirming that reaction rate is not a limiting parameter for substitution.

EDL# 3: The same test on the EDL# 3 core at 130 °C also showed that the surface reactivity of this material is very low as shown by Figure 4.10. It is, however, a significant increase in Ca^{2+} and decrease in Mg^{2+} .

Obviously, the outcrop limestone shows a different surface behavior towards the active ions compared to the reservoir limestone, and the reason may be:

1. The outcrop limestone is acting oil-wet without being in contact with oil, which is very unlikely.
2. The outcrop limestone acts water-wet, but chemically, the surface appears nearly non-reactive towards the actual ions due to structural differences compared to reservoir limestone, or the surface is adsorbed by polymeric hydrophilic material like humus acids, polysaccharides etc.

The water-wet nature of the surface can be tested by spontaneous imbibition of water into cores saturated with a model oil.

Main results and discussion

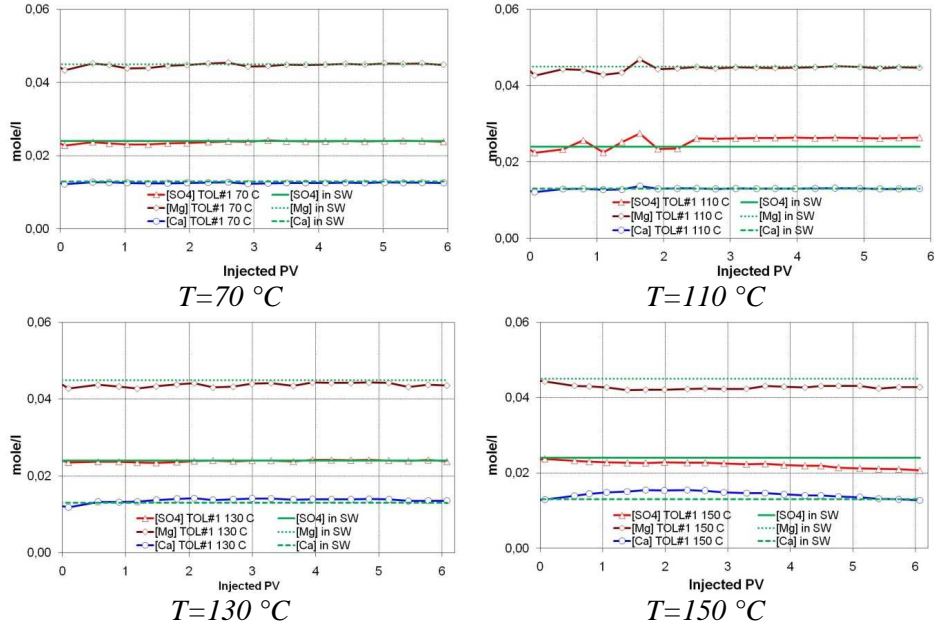


Figure 4.9 Changes in molar concentrations of Ca^{2+} , Mg^{2+} , and SO_4^{2-} when flooding SW through the limestone TOL# 1 at different temperatures. The dashed lines represent the initial concentration of ions in SW. Flow rate was 1 PV/D.

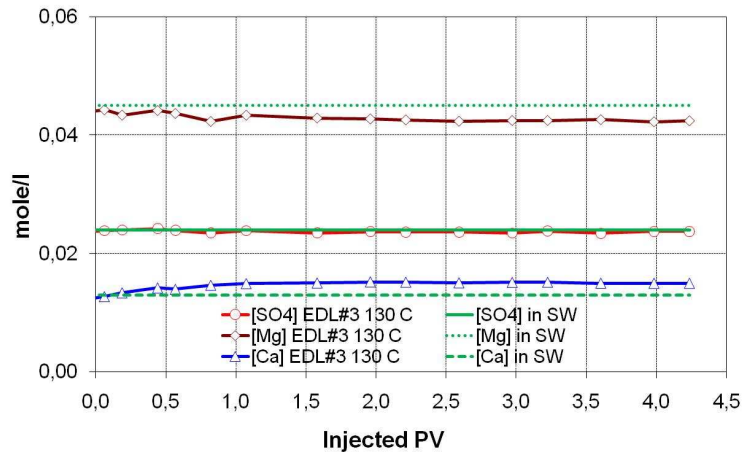


Figure 4.10 Changes in molar concentrations of Ca^{2+} , Mg^{2+} , and SO_4^{2-} when flooding SW through the limestone EDL# 3 at 130 °C. The dashed lines represent the initial concentration of ions in SW. Flow rate was 1 PV/D.

4.2.4. Oil recovery by spontaneous imbibition and forced displacement

The surface reactivity of the Total and Edwards outcrop cores was very low and not encouraging regarding improved oil recovery by wettability alteration. The capillary forces created by the porous medium were tested by saturating TOL# 10 and EDL# 1 with heptane without any initial water present and performing spontaneous imbibition using seawater without sulfate at room temperature, Figure 4.11. About 32% of OOIP was produced from each of the cores very quickly, indicating that capillary forces were active, and that the water-wet surface was present. Spontaneous drainage of the core TOL# 15 at $S_{or} = 0.56$ only produced traces of water indicating that the Amott oil index is close to 0. Thus, even though the outcrop cores from an imbibition point of view appeared preferential water-wet, the chromatographic wettability test using SCN^- and SO_4^{2-} indicated very low separation between the curves. This can only be explained by low reactivity of the outcrop limestone surface.

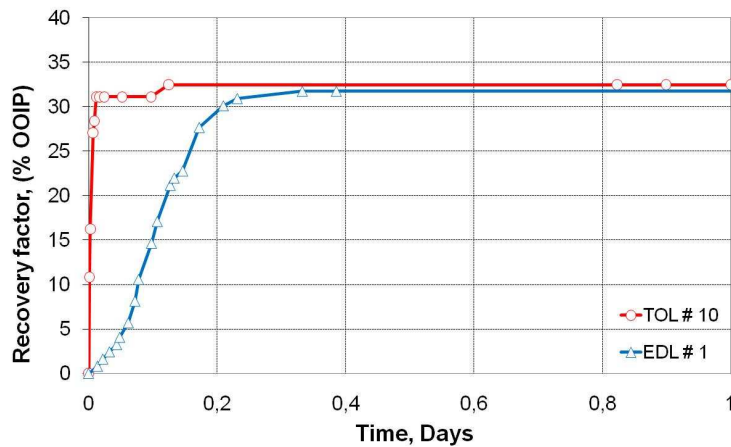


Figure 4.11 Spontaneous imbibition at ambient temperature of SWOT (without SO_4^{2-}) into outcrop limestones TOL# 10 and EDL# 1. Cores were 100% saturated with heptane.

Now, the actual question is: “Will a crude oil with a significant amount of acidic material be able to change wetting properties of outcrop core material, or will the low surface reactivity maintain water-wet conditions?”

A composite core was made by putting TOL# 6 and 7 together. First, each of the cores were subjected to spontaneous imbibition using FW at 130 °C, and then the composite core was flooded with FW followed by SW, Figure

Main results and discussion

4.12. The oil recovery by spontaneous imbibition, about 7-8 %, was mainly due to thermal expansion. Forced imbibition with FW increased the recovery to 30% using a flow rate of 0.5 PV/D. Switching to SW did not produce any extra oil even though the flooding rate was increased to 4.0 PV/D.

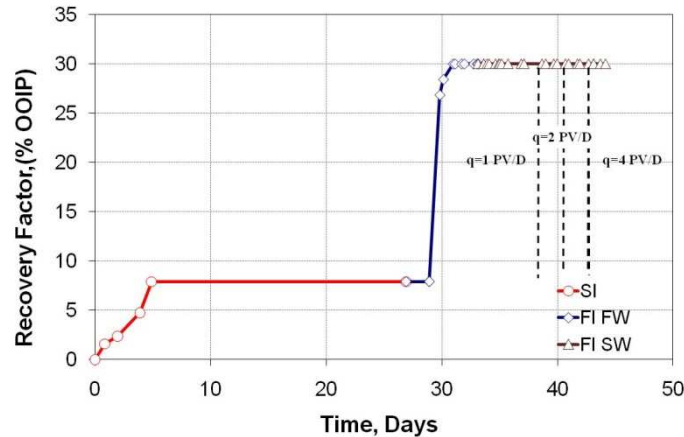


Figure 4.12 Forced imbibition at 130 °C of FW and SW into composite cores TOL # 6 and 7 using crude oil with AN=1.8 mg KOH/g. Initial flooding rate was 0.5 PV/D. $S_{wi}=0.1$.

It is well known that the water-wetness decreases as the AN of the crude oil increases (Standnes and Austad, 2000a). The crude oil used in the oil recovery tests had a very high AN, 1.80 mg KOH/g, and it was therefore decided to perform oil recovery tests with a crude oil of lower AN, i.e. AN=0.5 mg KOH/g, , Figure 4.13. No oil was recovered by spontaneous imbibition with FW at 130 °C. Forced imbibition with formation water increased the oil recovery to slightly below 30%, and no improvements were obtained by switching to SW.

The oil recovery from Edward outcrop core, EDL# 4, was tested using an initial FW saturation of $S_{wi}=10\%$ and the crude oil with AN=0.5 mg KOH/g. The spontaneous imbibition tests were performed using FW and SW at 130 °C. The low oil production <10% could mostly be linked to thermal expansion, Figure 4.14.

Main results and discussion

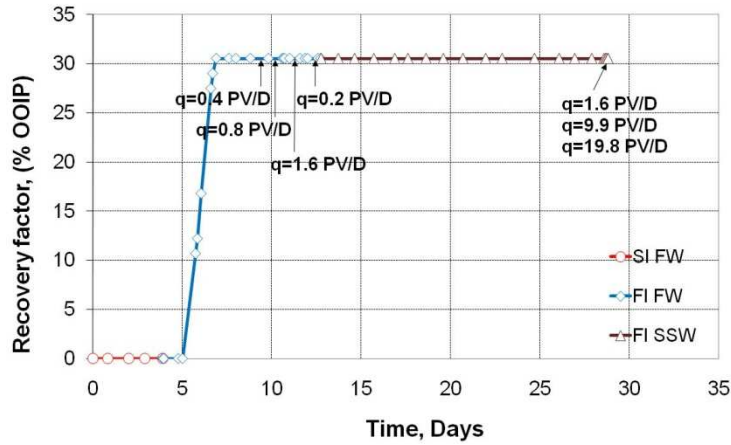


Figure 4.13 Spontaneous imbibition with FW followed by Forced imbibition with FW and SW at 130 °C on TOL# 13 using crude oil with AN=0.5 mg KOH/g. Initial flooding rate was 0.2 PV/D. $S_{wi}=0.1$.

Even though the surface reactivity of the Total and Edward outcrop limestone is very low towards active ions like Ca^{2+} , Mg^{2+} , and SO_4^{2-} , acidic crude oils are able to change the wetting property from initial water-wet to the preferential oil-wet. Seawater, which can act as a wettability modifier towards chalk and reservoir limestone at high temperature, is not able to enhance oil recovery from Total and Edward outcrop limestone, neither by spontaneous imbibition nor by forced imbibition.

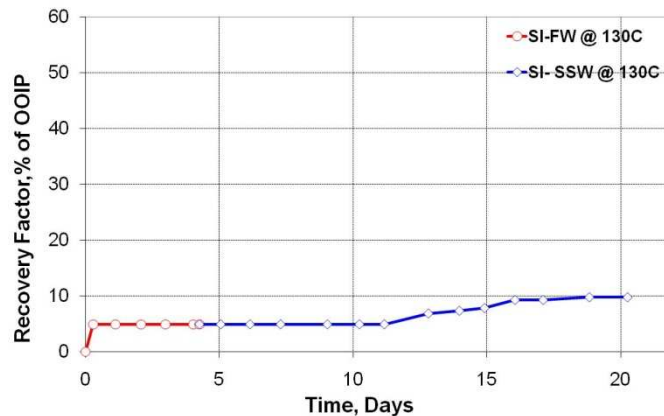


Figure 4.14 Spontaneous imbibition at 130 °C of FW and SW into EDL# 4 using crude oil with AN=0.5 mg KOH/g. $S_{wi}=0.1$.

4.2.5. Surface charge on chalk, reservoir limestone and outcrop limestone when exposed to potential determining ions

In order to have a better understanding of the electric charge properties of carbonates, zeta potential of outcrop limestone cores was measured and compared to that of chalk and reservoir limestone (high reactive material). For each series of measurements, the concentration of one divalent ion present in seawater, i.e. SO_4^{2-} , Ca^{2+} or Mg^{2+} , was changed in the bulk suspension and the results are shown in Figures 4.15 and 4.16. At constant pH ($\text{pH}=8.4$), an increase of Ca^{2+} or Mg^{2+} concentration in the both outcrop chalk and reservoir limestone suspension increased the zeta potential of the rock surface. SO_4^{2-} ions changed the surface charge in a similar trend, and it appeared to decrease linearly with increasing sulfate concentration in the range of 0-0.1 mole/l. The effect of potential determining ions on the surface charge of outcrop chalk and reservoir limestone is in line with the high reactivity of their surface as was observed previously (Strand et al., 2008; Zhang et al., 2007).

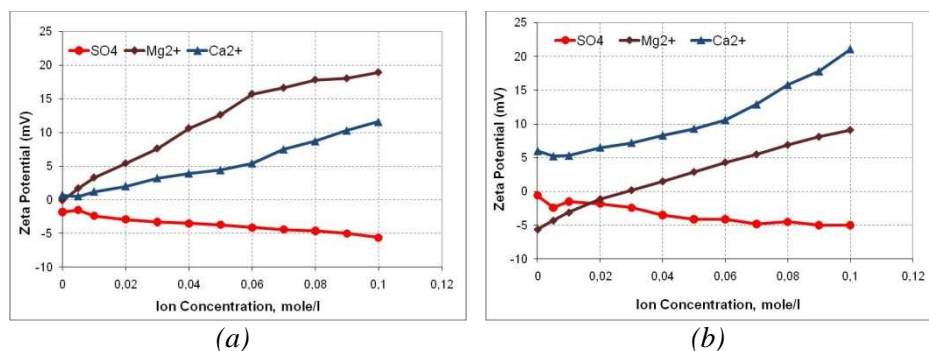


Figure 4.15 Impact of divalent ions in seawater on surface charge of (a) Outcrop chalk (b) reservoir limestone, $\text{pH}=8.4$, $T=25^\circ\text{C}$

The same series of measurements on the outcrop limestone surface shows the similar effect for Ca^{2+} and Mg^{2+} ions, Figure 4.16. But an increase in sulfate concentration up to 0.1 mol/l is not able to decrease the surface charge to negative values as was observed for both outcrop chalk and reservoir limestone (high reactive rock surfaces).

Therefore, the low reactivity of the outcrop limestone, which has been already observed in the parametric studies and oil displacement tests, is also confirmed by surface charge measurements.

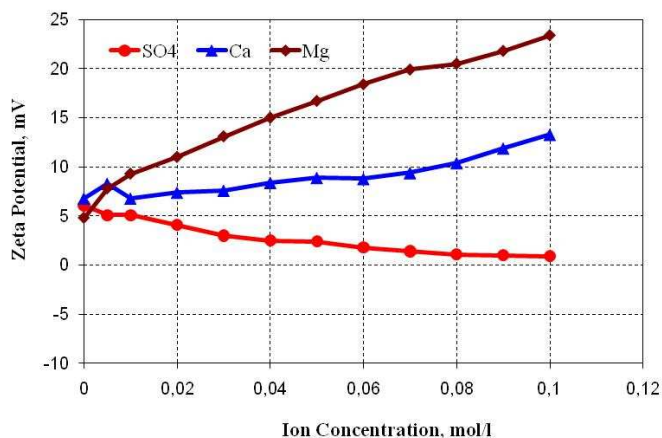


Figure 4.16 Impact of divalent ions in seawater on surface charge of Outcrop limestone, $pH=8.4$, $T=25^{\circ}C$

4.3. Seawater induced wettability modification of reservoir limestones

4.3.1. Affinity of Ca^{2+} , Mg^{2+} and SO_4^{2-}

In order to illustrate the great difference between outcrop and reservoir limestone regarding surface reactivity and oil recovery by wettability modification with SW, the experimental study was performed on core materials sampled from the same well in a naturally-fractured limestone reservoir. The porosity was in the range of 17%, and the permeability 0.1-1.0 mD, Table 3.1.

The reservoir limestone core termed Res# 5-17 was cleaned by distilled water, toluene and methanol prior to the wettability test. The BET- N_2 surface area of the core was $0.29 \text{ m}^2/\text{g}$, which is somewhat higher than that of the tested outcrop limestone cores, Table 4.1. The chromatographic separation between the tracer and sulfate is much larger compared to the results from the outcrop cores, which indicated strong affinity of sulfate towards the surface and a water-wet surface, Figure 4.17. Initially, the core was flooded with SW0T (SW without tracer and sulfate). Then the core was flooded with SW1T (SW with tracer and sulfate). It is interesting to note that the presence of sulfate results in increased adsorption of Ca^{2+} and desorption of Mg^{2+} probably due to reduced activity of Mg^{2+} because of ion-pair formation with sulfate (Carlberg and Matthews, 1973).

Main results and discussion

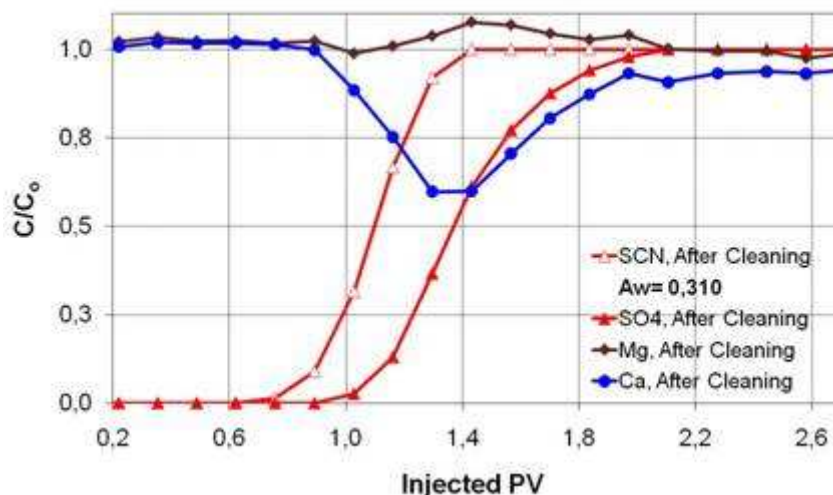


Figure 4.17 Chromatographic affinity test of sulfate towards the surface of the water-wet reservoir limestone core Res# 5-17 (Shariatpanahi et al., 2010).

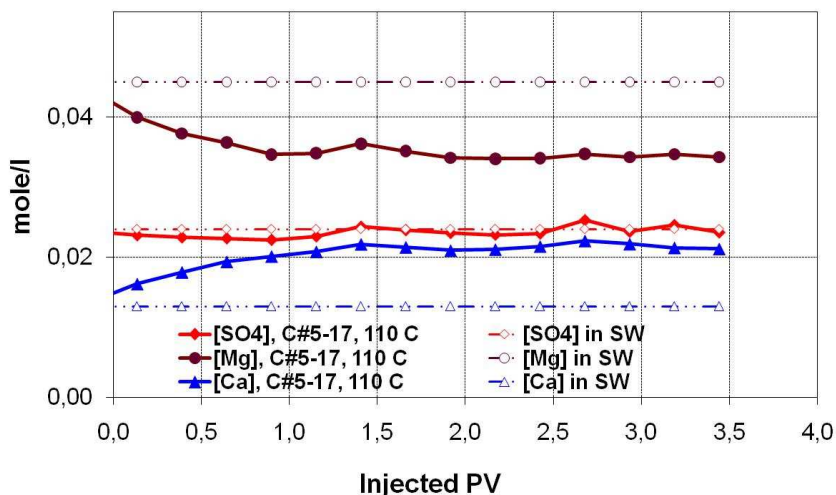


Figure 4.18 Ca^{2+} is substituted by Mg^{2+} dissolved in seawater in the reservoir limestone core Res# 5-17 at 110 °C in a 1:1 reaction. Flooding rate 1 PV/D (Shariatpanahi et al., 2010).

Main results and discussion

The same limestone reservoir core showed that Ca^{2+} from the carbonate rock was substituted by Mg^{2+} from the SW at 110 °C in a 1:1 process when flooding the core slowly with SW, Figure 4.18.

4.3.2. Effect of oil acid number, AN

Different wetting conditions were obtained by saturating the reservoir cores with crude oils with different acid number. RES40-0.1 and RES40-0.57 were prepared from the same crude oil as described in the experimental part, giving crude oils that contained the same type of acidic material and with similar physical properties, Table 3.2. It has previously been shown that the initial wetting conditions, and consequently, the ability of seawater to act as a wettability modifier depended somewhat on the type of acidic material present, i.e. the presence of partly water-soluble acids (Fathi et al., 2010b). By using crude oils with the same type of acidic material, the difference in initial wetting and wettability alteration by seawater can be discussed in terms of amount of acidic material and not in relation to the type of acids present.

Core Res# 5-17: The core with $S_{wi}=0.1$ was aged with RES40-0.1 (AN=0.1 mg KOH/g). The oil recovery in a spontaneous imbibition process using FW reached the plateau of 18% of OOIP after 14 days, Figure 4.19. Then the imbibing fluid was changed to SW, which resulted in a sudden increase in oil recovery and reached a plateau of 38% of OOIP after 45 days. The oil recovery was further increased to 42% of OOIP by adding 1.0 wt% C_{12}TAB to the SW. It is previously verified that cationic surfactant of the type C_{12}TAB is an excellent wettability modifier in carbonates in combination with SW (Standnes and Austad, 2000b; Standnes et al., 2002). Previous studies with outcrop chalk material and the same crude oil with AN=0.10 mgKOH/g only resulted in a moderate decrease in the water-wetness of the rock. Therefore, the next test was performed using a crude oil with higher AN=0.57 mgKOH/g.

Core Res# 4-12: The core with $S_{wi}=0.1$ was aged with RES40-0.57 (AN=0.57 mgKOH/g). As expected, the core appeared less water-wet when the AN of the crude oil was increased from 0.10 to 0.57 mgKOH/g. Only $\approx 9\%$ of OOIP was produced after spontaneous imbibition with FW for 14 days, compared to core Res# 5-17, Figure 4.20. Introduction of SW as the imbibing fluid increased the oil recovery immediately, and the oil recovery stabilized at 37% of OOIP after about 28 days.

Even though the initial wetting conditions were different for the two cores as indicated by different degree of imbibitions with FW, the final oil recovery

Main results and discussion

by spontaneous imbibition with SW from the two cores appeared to be quite similar, 37-38% of OOIP.

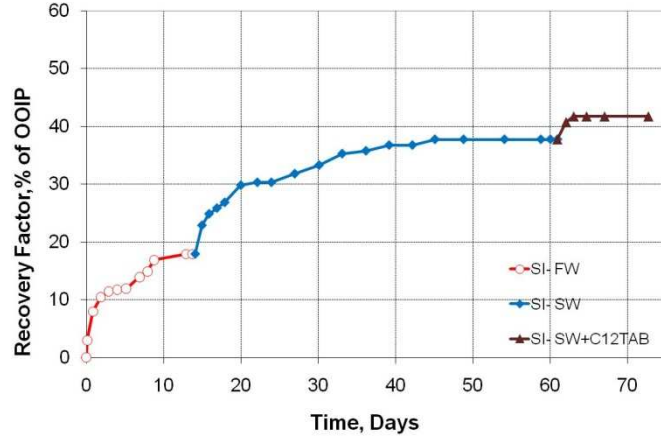


Figure 4.19 Spontaneous imbibition into Res# 5-17 with FW and SW at 130 °C. The core had a $S_{wi}=0.1$ and was saturated and aged with RES40-0.1.

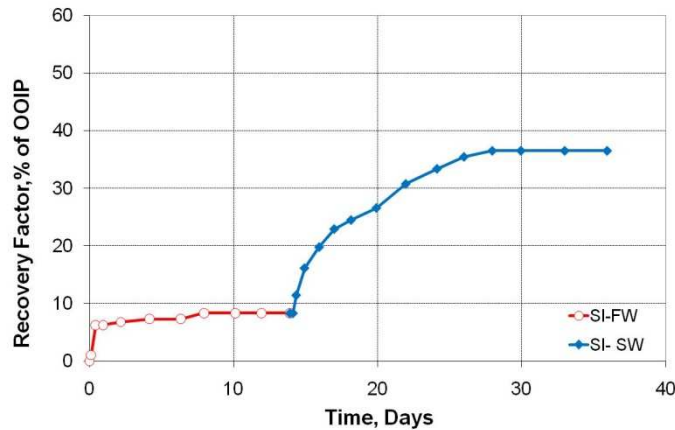


Figure 4.20 Spontaneous imbibition into Res# 4-12 with FW and SW at 130 °C. The core had a $S_{wi}=0.1$ and was saturated and aged with RES40-0.57.

4.3.3. SW as wettability modifier in limestone

This is the first experimental verification that seawater will also act as a wettability modifier in limestone and oil recovery would be increased significantly in a spontaneous imbibition process at high temperatures. The reactivity of reservoir limestone surface towards potential determining ions in

seawater can vary significantly between different limestone reservoirs. It has been experienced completely oil-wet limestone reservoir cores, where none of the cleaning methods used in this thesis were able to increase the wetting conditions significantly, including C₁₂TAB in SW at high temperature (Fathi et al., 2010a).

It is also interesting to note that the two limestone outcrops showed a completely different surface reactivity compared to reservoir limestone, and care must be taken when using outcrop material to mimic reservoir rock in experimental studies related to wettability modification.

4.4. The effect of permeability and interfacial tension on the SEG D process in limestones

In this part of the thesis, the SEG D process is studied using two different cationic surfactants, which are able to act as wettability modifiers and at the same time give a moderate decrease in IFT, 0.34 and 0.67 mN/m, Table 3.4. Under those conditions, the fluid flow during the oil displacement process will be determined by both capillary and gravity forces. The test will be performed on two limestone cores of quite different permeability, 0.46 and 364 mD, and the results will be discussed in relation to our previous study on 1-3 mD chalk using a similar type of surfactant (Høgnesen et al., 2006). To avoid differences in core properties, the same cores were used for both of the surfactant systems, C₁₂TAB and Dodigen. Thus, the objective is to study the effect of rock permeability on the oil displacement process at two different IFT values, which are still high enough to activate capillary forces.

The carboxylic material in the crude oil, as quantifies by the acid number (AN), is the most important wetting parameter in carbonates (Standnes and Austad, 2000a). The AN of the crude oil used in this study was 0.57 mg KOH/g, and the initial saturation of formation water was 10%. When using cleaned cores without traces of sulfate, carbonate cores aged in crude oil of AN>0.5 mg KOH/g would act neutral to slightly oil-wet. Therefore, the cores were first imbibed with formation water without sulfate to confirm low water-wetness, thereafter the imbibing fluid was exchanged to ordinary seawater containing cationic surfactant. No optimization of the salinity to obtain low IFT is needed for the surfactant to work properly.

4.4.1. High permeable Limestone core

The oil recovery from the high permeable core using C₁₂TAB and Dodigen is shown in Figures 4.21-4.23. In both cases, no oil was recovered by using formation water as imbibing fluid, confirming very low water-wetness of the

Main results and discussion

rock. The oil was displaced spontaneously from the core as the imbibing fluid was switched to seawater containing surfactant. An ultimate oil recovery of 49% of OOIP was recovered within about 6 days for the $C_{12}TAB$ system, while the Dodigen system needed about 20 days to reach the plateau recovery of 57% of OOIP. For comparison, the oil recovery profile was plotted in the same diagram, as shown in Figure 4.23. About 30% of OOIP was recovered within less than 8 hours for both of the surfactants. With reference to the previous study on chalk, the high rate of oil recovery at the start must be linked to wettability alteration and activation of capillary forces. In the case of $C_{12}TAB$, the oil recovery curve appeared to contain three distinct sections, which can be related to changes in the drive mechanism for the fluid flow, i. e. (1) Mainly capillary forces; (2) Both capillary and gravity forces; (3) Mainly gravity forces. Also for the Dodigen system, $IFT=0.34$ mN/m, it appeared to show a similar trend. The timeframe, where both capillary and gravity forces were active, appeared to be smaller, and gravity forces seemed to take over earlier due to the lower IFT. The ultimate oil recovery was higher, and about 18% of OOIP was produced by mainly gravity forces compared to about 9% for the $C_{12}TAB$ system. Thus, due to the impact of capillary forces by wettability alteration, about 70 % of the producible oil could be recovered within 1-2 days under lab conditions.

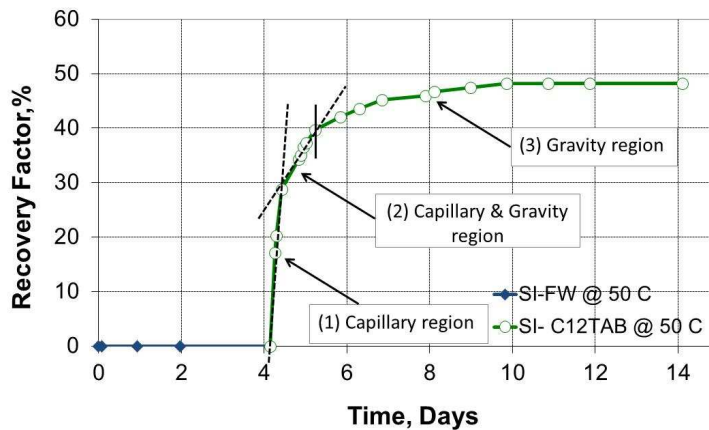


Figure 4.21 Spontaneous imbibition at 50 °C of FW and SW+1wt% $C_{12}TAB$ into core Res# 52 using oil with $AN=0.57$ mg KOH/g (first Restoration).

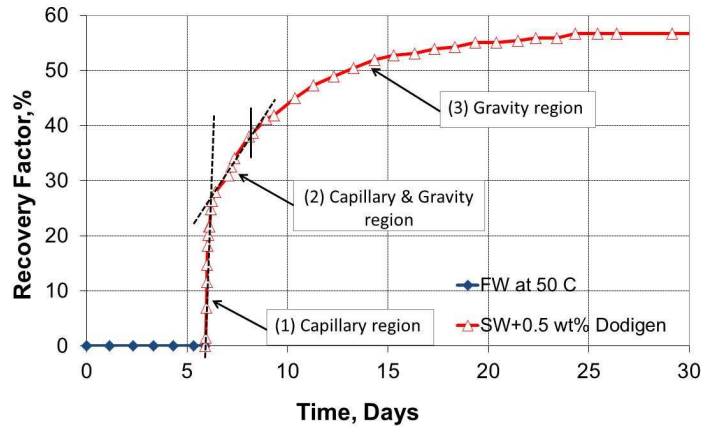


Figure 4.22 Spontaneous imbibition at 50 °C of FW and SW+0.5wt% Dodigen into core Res# 52 using oil with AN=0.57 mg KOH/g (second Restoration).

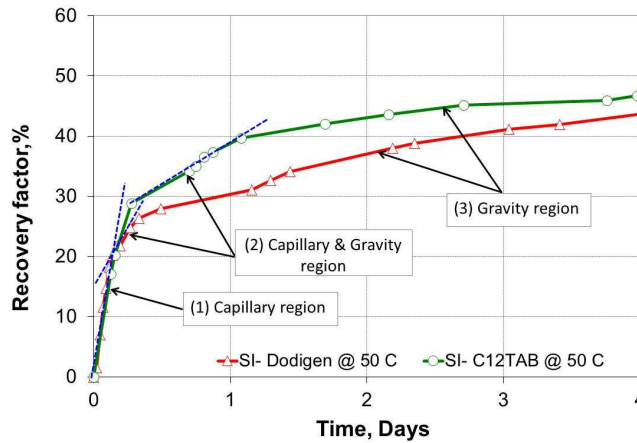


Figure 4.23 Spontaneous imbibition at 50 °C into core Res# 52. Comparison of C₁₂TAB with Dodigen.

4.4.2. Low permeable Limestone core

The oil recovery from the low permeable, 0.46 mD, limestone core is shown in Figure 4.24. Spontaneous imbibition by FW only resulted in 4 % recovery, which to some extent could be related to fluid expansion by increasing the temperature from room temperature to 50 °C. No significant increase in oil recovery was observed by switching the imbibing fluid from FW to SW

Main results and discussion

containing $C_{12}TAB$. The IFT was decreased from 0.67 to 0.34 mN/m by exchanging $C_{12}TAB$ by Dodigen, but no response in oil recovery was noticed. The imbibing fluid was again switched to $C_{12}TAB$ and the temperature was increased to 70 and 90 °C without any oil production. Slightly above 20% of OOIP was recovered as the temperature was increased to 110 °C. The oil recovery was determined at room temperature, and it was not corrected for possible oil recovery due to thermal expansion.

The vertical permeability of the carbonate matrix rock appeared to be crucial when using surfactant to combine capillary forces by wettability alteration and gravity forces in an imbibition process. In this case, it is impossible to discuss the impact of capillary and gravity forces on the fluid flow in terms of the inverse Bond number, NB^{-1} , because the wettability is changed during the imbibition process (Schechter et al., 1994).

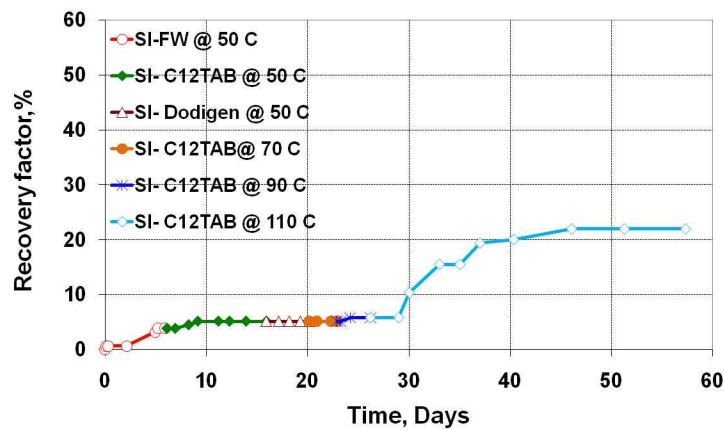


Figure 4.24 Spontaneous imbibition at 50 °C of FW, SW+1wt% $C_{12}TAB$ and SW+0.5 wt% Dodigen into core Res# 4-12 using oil with AN=0.57 mg KOH/g.

4.4.3. Diffusion of surfactant

The transport of surfactant into the matrix blocks appeared to be the critical rate determining step for the field applications. The question is: “How is the surfactant, micelles and monomers, transported to the imbibition front to create wettability modification?” Stoll and co-workers (2007) suggested that the wettability modification was limited to the rate of molecular diffusion of the surfactant. In low permeable chalk (1-3 mD) at low initial water saturation, they estimated a diffusion coefficient in the order of $D_m=10^{-11}$ m²/s. The mechanism for wettability alteration cannot be related to diffusion of

Main results and discussion

surfactant through the initial formation water because the process is also taking place in porous medium without initial water present (Høgnesen et al., 2004). Masalmeh and Oedai (2009) also concluded from their experimental data, that molecular diffusion alone can not explain the rate and volume of oil recovered by cationic surfactant-assisted oil recovery from fractured carbonate. If that should be the case, the diffusion coefficient should be at least a factor of 10 higher than the calculated value. The rate and efficiency of the wettability alteration process by cationic surfactants are related to the monomeric concentration of the surfactant and the presence of sulfate at the imbibing water front.

Within 1-2 days, about 70% of producible oil was recovered from the Res# 52 core using C₁₂TAB and Dodigen, mostly by capillary forces due to wettability alteration. The molecular diffusion coefficient for C₁₂TAB and Dodigen, as calculated by the method described by Stoll et. al. (2007), was determined to be 5.04×10^{-10} and 8.23×10^{-10} m²/s, respectively. By applying these conservative values, the time required to achieve 40% oil recovery (70% of recoverable oil) from a 1 m³ reservoir block would be in the order of 2 and 4 years for C₁₂TAB and Dodigen, respectively.

5. Concluding remarks

For the first time it, has been verified experimentally that seawater is able to act as a wettability modifier in limestone cores and increase oil recovery in a spontaneous imbibition process. Special focus was made on surface reactivity towards active ions like Ca^{2+} , Mg^{2+} , and SO_4^{2-} , which are present in seawater and known to play an important role in the wettability alteration process. Outcrop limestones have also been investigated to mimic reservoir limestone material in special core analysis related to water-based oil recovery by wettability modification. Finally, experimental studies have been performed to mimic oil recovery from naturally fractured limestone by using cationic surfactants dissolved in seawater to impose combined effects of capillary and gravity forces.

5.1. Conclusions

The main conclusions drawn from this study were:

- The water-wetness of reservoir limestone cores pre-cleaned with toluene and MeOH can be drastically improved by flooding with seawater at 130 °C. It is therefore interesting to note that SW can also act as a cleaning solvent.
- The two outcrop limestones tested showed similar surface reactivity, which was completely different from reservoir limestone.

Even though the outcrop limestones appeared to be preferential water-wet, the surface affinity of sulfate was negligible. Water-wet reservoir limestone showed strong affinity to sulfate.

Opposite to reservoir limestone, Mg^{2+} present in seawater was not able to substitute Ca^{2+} at the outcrop limestone surface in a 1:1 reaction, confirming the lower reactivity of the outcrop limestone.

The outcrop limestone showed strong capillary forces as confirmed by spontaneous imbibition of water into cores saturated with model oil.

Acidic crude oils (AN=0.5 and 1.84 mg KOH/g) made the outcrop limestone preferential oil-wet, and negligible oil was produced in a spontaneous imbibition process using formation water.

Opposite to reservoir limestone, no extra oil was recovered from outcrop limestone by using seawater as wettability modifying fluid, neither in a spontaneous imbibition nor in a forced imbibition process, even at 130 °C.

Concluding remarks

The reason why outcrop limestone behaved differently from reservoir limestone is not solved yet, and it is a matter for further studies. Therefore, care must be taken when using outcrop limestone as a model reservoir material in water-based EOR studies.

- Extra oil recovery can be obtained by a tertiary spontaneous imbibition process of seawater into reservoir limestone cores first imbibed by formation water in a secondary process.

The initial water-wetness of the rock decreased as the acid number of the crude oil increased. The oil recovery by spontaneous imbibition of formation water decreased from 18 to 9% of OOIP when the acid number of the crude oil was increased from 0.10 to 0.57 mgKOH/g.

The oil recovery, in the tertiary process, with seawater appeared to be independent of the acid number of the crude oil used. The recovery increased to 37-38% of OOIP.

- Cationic surfactant of the type alkyl trimethyl ammonium, $R-N(CH_3)_3^+$, will give an IFT-value in the range of 0.1-1 mN/m between the injected surfactant solution (surfactant dissolved in seawater) and the actual crude oil.

The oil recovery by spontaneous imbibitions into the high permeable core (364 mD) indicated three different regimes for oil displacement: (1) Oil recovery by capillary forces due to wettability alteration; (2) Oil recovery by combined capillary and gravity forces; (3) Oil recovery by gravity forces. The impact of gravity forces increased as the IFT decreased. About 40% of OOIP could be recovered within 1-2 days by capillary and combined capillary and gravity forces (Regimes 1 & 2). In the regime dominated by gravity forces (Regime 3), about 9% additional oil was recovered at IFT=0.67 mN/m, while 18% extra oil was produced at IFT=0.34 mN/m.

No oil was recovered from the low permeable core (0.46 mD); indicating that permeability of the rock is crucial for oil recovery by surfactant in a spontaneous imbibition process.

The fast recovery of oil from the high permeable core indicated that a significant amount of producible oil can also be recovered in the field using surfactant provided that the rock permeability is reasonably high, $k > 300$ mD.

The time scale for a diffusion process is linked to the square of the length scale of the medium. The time required to achieve 70% of the recoverable oil from the core plug in the laboratory was 1 day. Applying the upscaling equation, the corresponding time required to

Concluding remarks

achieve 70% of the recoverable oil from a 1 m³ reservoir block, would be in the order of 2 years.

A combined effect of surfactant-enhanced gravity drainage (SEGD) and the wettability alteration in fractured, highly permeable oil-wet carbonate rock can provide an economically interesting opportunity.

5.2. Future work

The experimental work presented in this thesis, has given a systematic procedure for analysis of the potential of SW as a wettability modifier in different limestone reservoirs. In the light of the interesting results obtained, the following studies should be conducted:

- Develop a data base including the experimental data on water-based EOR in different carbonate rock types. The data base will be used to find possible correlations among key important parameters and/or among different rock types. The data base will also be used during screening process for a potential candidate for smart water flooding.
- Investigate the reason why the outcrop limestone is not reactive towards potential determining ions, especially SO₄²⁻.
- Develop a numerical simulation software applying the chemical reactions at the carbonate surface during wettability alteration by seawater.

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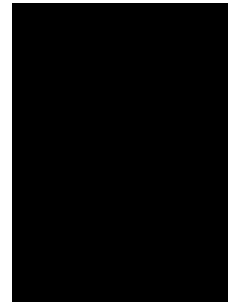
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Paper I:

New Method to Clean Carbonate Reservoir Cores by Seawater

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NEW METHOD TO CLEAN CARBONATE RESERVOIR CORES BY SEAWATER

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ABSTRACT

It was recently documented, that modelling of carbonate reservoirs for predicting waterflood performance, could be done by obtaining a reliable P_c curve based on primary drainage, which forms the basis for oil in place calculations and for modelling the imbibition P_c curve. Furthermore, a reliable primary drainage P_c curve was only obtained when the carbonate core was properly cleaned to improve the water-wet fraction significantly. Carboxylic material present in crude oil is bonded very strongly onto the carbonate surface. It is nearly impossible to use traditional solvents to clean the surface. A chemical reaction under irreversible thermodynamic conditions is needed to remove the material. A series of preferential oil-wet limestone cores from a Middle Eastern oil reservoir was first cleaned by the traditional technique using toluene and methanol. Thereafter, the cores were flooded with different PVs of synthetic seawater, SW, at 130 °C. The newly developed chromatographic wettability test showed that the water-wet fraction can increase by about 30% after flooding with SSW at high temperature. Seawater is, however, known to act as a wettability modifier in chalk, which will improve oil recovery by spontaneous imbibition. It is therefore interesting to note that SW also can act as a cleaning solvent. It is also confirmed that a rather small increase in the water-wet area may have a significant effect on oil recovery by spontaneous imbibition.

INTRODUCTION

Seawater is known to act as an EOR-fluid towards chalk in the sense that it is able to improve water wetness, which will increase oil recovery during a water flood (Zhang and Austad 2006; Zhang et al. 2006). The chemical mechanism has been described as an interaction between active ions in seawater (Ca^{2+} , Mg^{2+} , SO_4^{2-}) and the rock surface. Some of the strongly adsorbed carboxylic material is then removed from the chalk surface (Zhang et al. 2007). The efficiency of the wettability alteration process is sensitive to the temperature, and a temperature above 90-100 °C appeared to be needed. Cleaning of carbonate cores has always been an issue for debate, because of the very strong interaction between the carboxylic components and the calcite surface. It was recently documented, that modelling of carbonate reservoirs for predicting waterflood performance could be done by obtaining a reliable P_c curve based on primary drainage, which forms the basis for oil in place calculations and modelling of the imbibition P_c curve (Masalmeh and Jing 2007). Furthermore, a reliable primary drainage P_c curve was only obtained when the carbonate core was properly cleaned to improve the water-wet fraction significantly.

The question that we ask in this paper is: “Can seawater be used to improve the cleaning of carbonate cores, i.e. to improve the water wetness after performing the traditional cleaning procedure using MeOH and toluene ?”

EXPERIMENTAL

Carbonate rocks

In the experiments outcrop chalk and reservoir limestone cores have been used.

Chalk cores: All chalk cores were prepared from the same Stevns Klint chalk block and used in the experiments. The chalk consists of 98 % pure biogenic CaCO₃ with high porosity (45-50 %) and low matrix permeability (2-3 mD). It has a reactive large surface area of about 2 m²/g (Frykman 2001; Røgen and Fabricius 2002). The age and properties of the chalk are quite similar to those observed for the North Sea chalk oil reservoirs. The data for the cores are given in Table 1.

Limestone cores: The physical properties of the reservoir limestone cores from a field in the Middle East are summarized in Table 2. Prior to use, the cores were cleaned at ambient temperature by flooding with water-saturated toluene (at least 5 PV) at a rate of 0.1 ml/min until the effluent was colorless (min. 3 PV). Thereafter, the cores were flooded with 3 PV of methanol also at ambient temperature, and finally dried at 110 °C to constant weight.

Brines

Artificial formation water, VB, related to the Valhall field was used as initial brine in the imbibition and wettability experiments on the chalk cores. The compositions of synthetic seawater, SW, and the chromatographic fluids SW-U, SW¹/₂M and SW-M are given in Table 3.

Oils

Two different oils have been used in the experiments. Heptane was used as a reference oil to represent a water-wet core. A reservoir stock tank oil diluted with 40 vol% n-heptane, centrifuged, and filtered through a 5 µm Millipore filter, was used in the chalk experiments with neutral-wet chalk cores. This mixture has been used in many previous experiments, and no precipitation of asphaltenic material was detected on standing. Heptane was used to keep the viscosity of the oil closer to reservoir conditions. The oil was termed RES40~1.6, and the acid number, AN, was 1.6 mg KOH/g, the density was 0.805 g/cm³, and the viscosity was 2.5 cP. The high AN of the oil made the carbonate rock neutral to oil-wet.

Preparation of the chalk cores

The chalk cores were prepared according to the method described in a previous paper (Punternold et al. 2007). The cores were flooded with distilled water to remove any dissolvable salts, especially sulfates, and then saturated with formation water VB. Initial water saturation was established by flooding the cores in a Hassler core holder with 1.5 PV of oil in each direction. The crude oil saturated cores were wrapped in Teflon tape and

aged in the oil at 90 °C for 4 weeks in a sealed steel container. The core data are listed in Table 1.

Spontaneous imbibition

The oil saturated cores were transferred to a sealed steel imbibition cell and surrounded with the imbibing fluid. The spontaneous imbibition test (SI) was performed at the specified temperature with a constant back pressure of ~10 bar. The produced oil was collected in a burette, and the volume was recorded as a function of time.

Chromatographic wettability test

The chromatographic wettability test, developed by (Strand et al. 2006), which determines the water-wet surface area of a chalk core, was used to determine changes in the wetting condition. The same test is also valid for limestone cores (Punternvold 2008; Strand et al. 2008). The oil saturated carbonate core was placed inside a Hassler core holder and flooded with SW brine without sulfate (SW-U) to obtain residual oil saturation, S_{orw} . Next, the core was flooded with SW brine containing both SO_4^{2-} and SCN^- as a tracer (SW-M or SW $\frac{1}{2}$ M) at a constant rate. The effluent was collected using a fraction collector. Each fraction was analyzed for SO_4^{2-} and SCN^- , and the concentration relative to the initial concentration was plotted against injected pore volumes, PV. Chromatographic separation between the non-adsorbing tracer SCN^- and the adsorbing SO_4^{2-} takes place at the water-wet sites of the chalk surface, and the area between the elution curves of the two components is directly proportional to the water-wet area inside the core. Completely water-wet condition is assumed when using heptane as the oil phase in outcrop cores not exposed to oil.

Chemical analysis

The ionic concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} , and SCN^- in the effluent fraction from the chromatographic wettability test were analysed using an ion-exchange chromatograph, ICS-3000 Reagent-free™ produced by Dionex Corporation, USA. The effluent samples were diluted 1:10 or 1:20 by deionised water prior to the analyses, and the ionic concentration was calculated by the use of external standards.

RESULTS AND DISCUSSIONS.

This section is organized by first presenting the results from core studies using outcrop chalk to document the potential of seawater to change wetting condition. Then, the potential of seawater as a core cleaning fluid will be presented using reservoir limestone cores.

Seawater as wettability modifier in chalk

Three similar outcrop cores from the same block were used. One of the cores was used as a reference core for a water-wet system by using heptane as the oil phase. The chromatographic wettability test was used, and the validation of this test for carbonates has been reported previously (Strand et al. 2006) The area for the chromatographic separation

between the tracer and sulfate when flooding seawater with tracer, SCN^- , was calculated to be $A=0.170$, Fig. 1.

The two other cores were saturated under vacuum with Valhall reservoir brine (VB) without any SO_4^{2-} . The initial water saturation was decreased to $S_{wi} \sim 0.25$ by flooding, 1.5 PV in each direction, using a crude oil with a high acid number ($\text{AN} = 1.60 \text{ mgKOH/g}$). Finally, the cores were aged in the crude oil at 90°C for 4 weeks.

After aging, one of the cores (VF#35) was flooded to residual oil saturation, $S_{or} = 0.25$, at room temperature using seawater without any sulfate (SW-U) and the wettability was determined chromatographically. The area between the tracer and the sulfate curve was determined to be, $A=0.103$, Fig. 1, which corresponds to a water-wet fraction of $\text{WI} = (0.103/0.170) = 0.61$.

After aging, the third core (VF#32) was imbibed by Valhall brine at 90°C , and the oil recovery was very low, less than 10% of OOIP, Fig. 2. No improvement in oil recovery was detected when the imbibing fluid was switched to seawater (SW) at 90°C . When the temperature was increased to 130°C , seawater imbibed spontaneously, and the plateau recovery was slightly below 50 % of OOIP. Obviously, the temperature of 90°C is too low for wettability alteration in an imbibition process.

The core was removed from the imbibition cell and flooded to S_{or} with SW-U. The flooding continued until no sulfate was detected at the outlet using a BaCl_2 solution. Finally, the new wetting condition was determined chromatographically, and the area between the tracer curve and sulfate curve was calculated to be, $A=0.188$, Fig. 1, which corresponds to a water wet fraction of $\text{WI} = (0.188/0.170) = 1.1$. Thus, by exposing the core to SW at 130°C for about 20 days, the wetting condition has been changed drastically. The wetting properties appeared to be quite similar to the reference water-wet core saturated with heptane, which was supposed to be completely water-wet.

Wettability modification by seawater in limestone

All the reservoir limestone cores used in these tests were pre-flooded with toluene and MeOH. Thus, the objective of the experiments is to document that seawater at high temperature is able to improve the water wetness after cleaning the cores in the traditional way. Three sets of experiments were conducted.

The wetting state of the 46A core was determined by the chromatographic technique before and after the core was used for various tests at both low and high temperatures with SW (Puntervold 2008; Strand et al. 2008). The wettability tests were performed at room temperature using the brine termed SW $\frac{1}{2}$ M. The chromatographic separation between SCN^- and SO_4^{2-} before the core was exposed to SW at high temperatures is shown in Fig. 3. The area between the tracer curve and the elution curve for SO_4^{2-} , which is proportional to the water-wet area, was estimated to be $A=0.107$. The fact that the tracer curve passes through the coordinate (1.0, 0.5) indicates that the total pore volume of the core was connected and flooded by the injected fluid. The wettability test of the same core after the core had been exposed to SW at both low and high temperatures (the core was flooded with at least 6 PVs of SW at 130°C), is shown in Fig. 4. The water-wet surface area has

increased because the calculated area between the tracer and sulfate curve was increased to $A=0.141$, which corresponded to an increase in the water wetness of 32 %.

The limestone core termed C#20A appeared to be nearly completely oil-wet after cleaning with toluene and MeOH since the separation between the elution curve for the tracer and sulfate is negligible, as illustrated in Fig. 5. The core was flooded with seawater at 130 °C for 1 day, which corresponds to 3 PVs. After removing the sulfate by flooding with seawater without sulfate at ambient temperature, the chromatographic wettability test showed good separation between the tracer and the sulfate curve, Fig. 5. Thus, the water-wet area was increased significantly. After flooding the core a second time with seawater at high temperature for 3 days (9 PV), the chromatographic test did not show any significant increase in the water-wet area, as illustrated by the fact that the two elution curves for sulfate were similar, Fig. 5. It is, however, not correct to conclude that the core has obtained a completely water-wet condition, but there is no doubt that seawater at high temperature is able to remove strongly adsorbed carboxylic materials from the carbonate surface.

In the third set of wettability tests with limestone, the core termed C#33A showed a very large separation between the tracer and sulfate in the wettability test, Fig. 6, which indicated that this core appeared to be rather water-wet. The area between the two curves was $A=0.14$. After flooding the core with distilled water to remove salt, the core was dried at 110 °C, and saturated with decane. The core was then imbibed with SW-U at 70 °C, and the oil recovery reached a plateau of about 3.3% of oil in place, Fig. 7.

The core was then dried and washed with SW-U prior to a new injection of SW at high temperature. The core was flooded 9 PV (3 days) with seawater at 130 °C. A new wettability test only showed a slight increase in the area between the tracer and sulfate curve, $A=0.16$, which corresponded to an increase in water wet area of about 14%, Fig. 6. Finally, the core was subjected to a new imbibition test using decane and the same core preparation as in the first imbibition test. As seen in Fig. 7, the oil recovery increased compared to the first test prior to the high temperature flooding with seawater, from 3.3 % to about 8 %. Thus a rather small increase in the water-wet area may have an effect on oil recovery in a spontaneous imbibition process.

It appears to be a discrepancy between the low oil recovery by spontaneous imbibition and wettability. We have, however, previously observed that chalk samples containing significant amount of silica appeared to be very water-wet by using the chromatographic test, but the imbibition of water was very low (Strand et al. 2006). May be this core contained some silica, but this is only speculations.

General comments

Previous studies have shown that seawater acts an EOR fluid in chalk (Zhang 2006; Puntervold 2008). Preliminary chemical tests have also indicated that seawater may act as an EOR fluid in limestone. The same chemical interaction between seawater and the rock is observed in both cases, but the reactivity towards limestone is somewhat slower than for

chalk (Strand et al. 2008). The results from the present paper support these observations, and seawater can even be used to improve the cleaning of reservoir limestone cores.

Carboxylates from the crude are strongly adsorbed onto the carbonate surface, and traditional cleaning of reservoir carbonate cores by using toluene and methanol will not remove all the adsorbed material. Obviously, each of the limestone cores showed different wetting properties after being cleaned with toluene and MeOH. The reason may be that we have used some of the cores in previous experiments in combination with the cationic surfactant, C12TAB, as wettability modifier. It is previously documented that this surfactant is able to improve the water wetness in chalk and dolomite (Standnes and Austad 2000; Standnes et al. 2002).

During the restoration of the wetting condition of a pre-cleaned carbonate core, it is very important to be aware of the strong impact of sulfate on the final wetting properties. If the initial water saturation is established by drainage using water saturated N_2 gas and porous plate, the concentration of sulfate in the residual water will increase due to the adsorption of sulfate onto the carbonate surface. Sulfate in combination with divalent ions like Ca^{2+} and Mg^{2+} increases the water wetness of the core (Punternvold et al. 2007). This is clearly demonstrated in Fig. 8. One of the chalk cores was pre-flooded with distilled water to remove traces of sulfate initially present, and the core appeared less water wet compared to the core not pre-flooded with distilled water.

CONCLUSIONS

The strong chemical interaction between seawater and calcite surface is further documented in this paper, and the following conclusions can be made:

- Chalk of neutral wetting condition will act as completely water-wet after exposing to seawater at 130 °C in a spontaneous imbibition process.
- The water-wetness of reservoir limestone cores pre-cleaned at ambient temperature with toluene and MeOH can be drastically improved by flooding with seawater at 130 °C.
- The observed wetting modification with seawater in limestone supports previous observations that seawater can act as an EOR-fluid also in limestone

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Table 1. Core data for chalk cores.

Core ID	L [cm]	D [cm]	V_b [cm ³]	Φ [%]	k [mD]	PV [ml]	S_{wi} [%]	Oil [ml]	S_{or} [%]
VF#20	6.72	3.81	76.6	48.8	~2	37.49	35	Heptane	30
VF#32	6.77	3.79	76.3	47.5	~2	36.3	22	Crude	29
VF#35	6.79	3.79	76.6	48.5	~2	37.1	27	Crude	24

Table 2. Core data for reservoir limestone cores.

Core ID	L [cm]	D [cm]	V_b [cm ³]	Φ [%]	k [mD]	PV [ml]
20A	4.88	3.78	54.76	25.95	8.47	14.21
33A	4.67	3.78	52.41	28.57	6.22	14.97
46A	4.76	3.78	53.42	27.8	2.47	14.8

Table 3. Composition and properties of the brines used.

Ions	VB mole/l	SW mole/l	SW-U mole/l	SW ^{1/2} M mole/l	SW-M mole/l
HCO_3^-	0.009	0.002	0.002	0.002	0.002
Cl^-	1.066	0.525	0.623	0.574	0.525
SO_4^{2-}	0.000	0.024	0.000	0.012	0.024
SCN^-		0.000	0.000	0.012	0.024
Mg^{2+}	0.008	0.045	0.045	0.045	0.045
Ca^{2+}	0.029	0.013	0.013	0.013	0.013
Na^+	0.997	0.450	0.500	0.475	0.450
K^+	0.005	0.010	0.010	0.022	0.034
IS	1.11	0.66	0.68	0.68	0.68
TDS, g/l	62.83	33.39	35.72	35.72	35.7

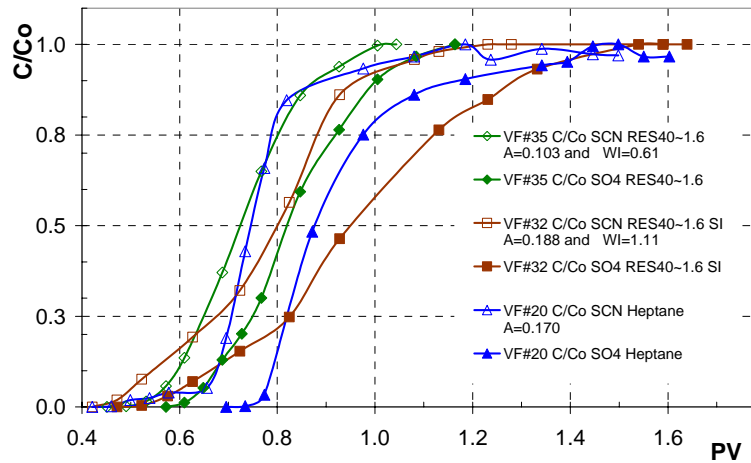


Figure 1. Comparable wettability indices for cleaned chalk cores, before (VF#35) and after (VF#32) SI at 130 °C. $S_{wi} \sim 0.25$. Crude oil with AN = 1.6 mg KOH/g. The heptane saturated core, VF#20, is used as a reference for a water wet core ($A = 0.17$). The cores were flooded with SW-M at a rate of 0.2 ml/min

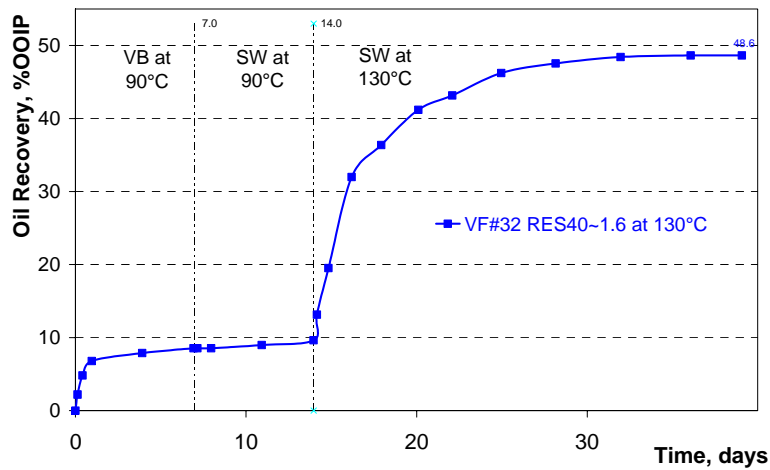


Figure 2. Stevns Klint core VF#32 ($S_{wi} \sim 0.25$) saturated with RES40 oil with AN~1.6 and aged for 4 weeks at 90 °C. The core have been SI at 130°C giving an oil recovery of 49%

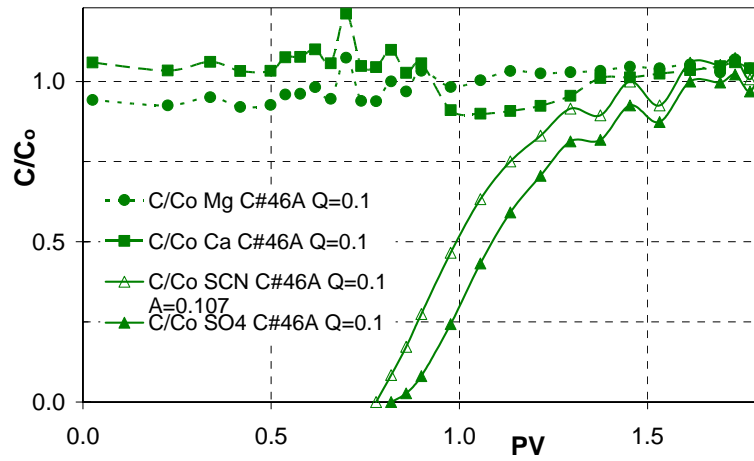


Figure 3. Chromatographic wettability test on core 46A before exposure to SW at high temperature. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. (Strand et al. 2008)

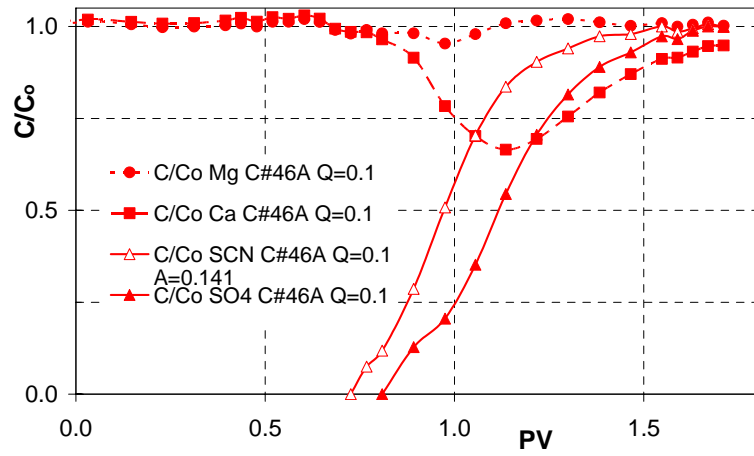


Figure 4. Chromatographic wettability test on core 46A after exposure to SW at high temperature. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. (Strand et al. 2008)

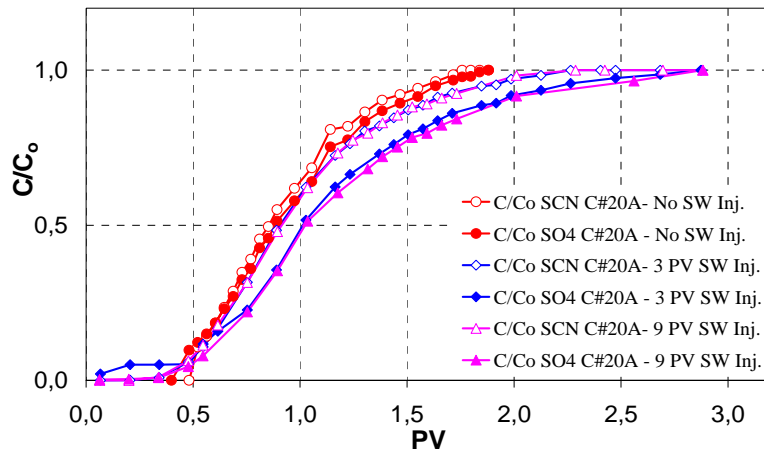


Figure 5. Three Chromatographic wettability tests on core C#20A. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. The results shows the water wet area before exposure to SW at high temperature, and after 3 PV (1 day) and after 9 PV (2 days) injection of SW.

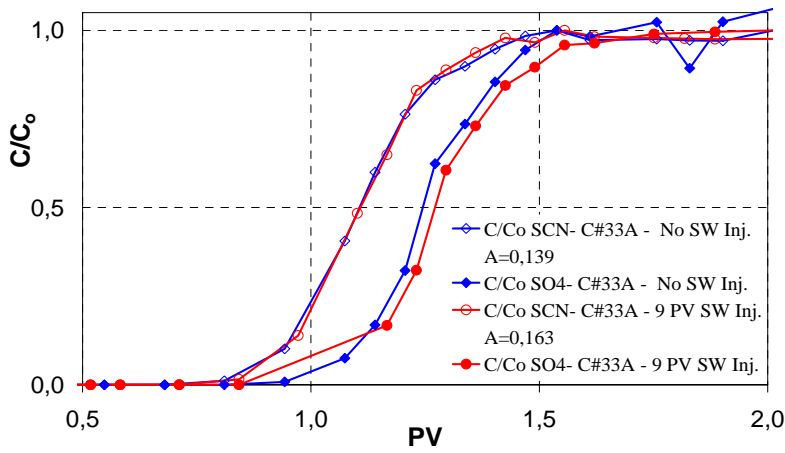


Figure 6. Chromatographic wettability tests on core C#33A. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. The results shows the water wet area before exposure to SW at high temperature and after 9 PV (3 days) injection of SW.

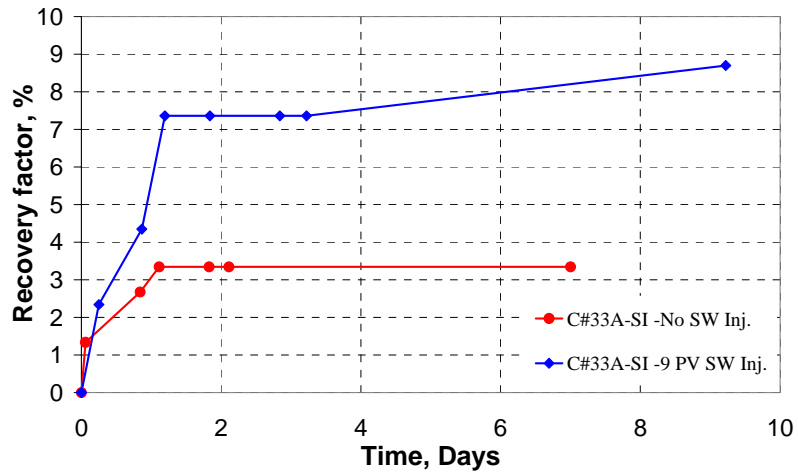


Figure 7. Spontaneous imbibition at 70 °C of decane saturated core C#33A before exposure to SW at high temperature and after 9 PV (3 days) injection of SW.

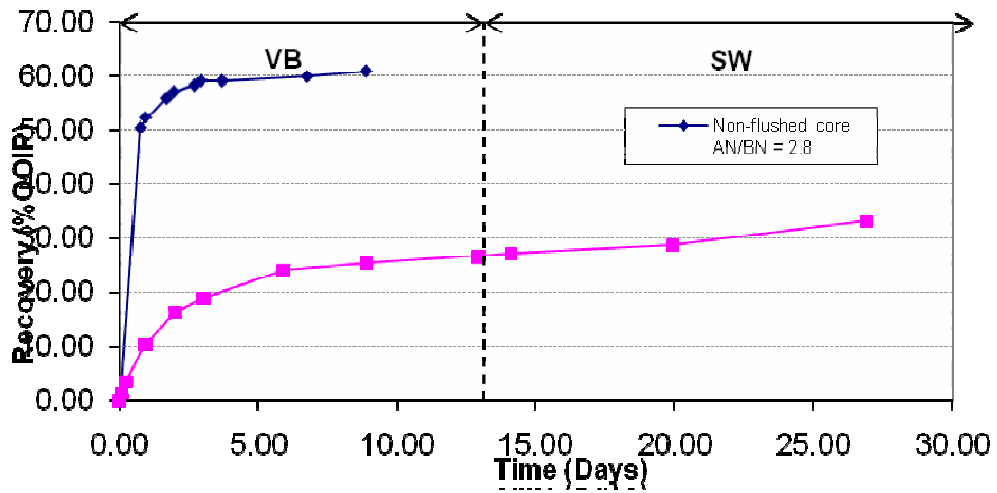


Figure 8. Imbibition at 90 °C into non-cleaned and cleaned cores. The cores were first imbibed with formation brines (VB), followed by SW. The cleaned core appeared to be much less water-wet than the non-cleaned core. $S_{wi} \sim 0.1$. Crude oil with AN = 0.5 mg KOH/g (Puntervold et al. 2007).

Paper II:
**Care Must be Taken to Use Outcrop Limestone Cores to Mimic
Reservoir Core Material in SCAL Linked to Wettability
Alteration**

Reza Rostami Ravari, Tor Austad, and Skule Strand

Paper presented at the 11th International Symposium on Reservoir
Wettability, Calgary, Canada, September 6-9, 2010.

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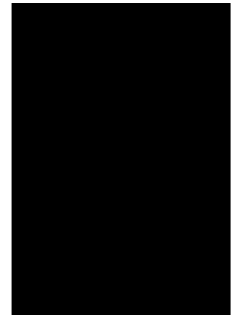
Paper III:

**Water-Based EOR from a Low-Permeability Fractured
Limestone by Wettability Alteration**

Reza Rostami Ravari, Tor Austad, and Skule Strand

Paper presented at the 16th European Symposium on improved oil
recovery IOR 2011, Cambridge, UK.

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Paper IV:

Combined Surfactant-Enhanced Gravity Drainage (SEGD) of Oil and the Wettability Alteration in Carbonates: The Effect of Rock Permeability and Interfacial Tension (IFT)

Reza Rostami Ravari, Tor Austad, and Skule Strand

Energy & Fuels **2011**, 25 (5), pp 2083-2088.

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Paper IV