# Waterflooding of carbonate reservoirs

## EOR by wettability alteration

Doctorial Thesis by

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# Acknowledgements

# List of papers

**Paper I:**

**Water flooding of carbonate reservoirs: Effects of a model base and natural crude oil bases on chalk wettability**
Tina Puntervold, Skule Strand and Tor Austad
*Energy & Fuels* 21 (3) (2007) 1606-1616.


**Paper II:**

**New method to prepare outcrop chalk cores for wettability and oil recovery studies at low initial water saturation**
Tina Puntervold, Skule Strand and Tor Austad
*Energy & Fuels* 21 (6) (2007) 3425-3430.


**Paper III:**

**Injection of seawater and mixtures with produced water into North Sea chalk formation: Impact of fluid-rock interactions on wettability and scale formation**
Tina Puntervold and Tor Austad
Journal of Petroleum Science and Engineering (in press)


**Paper IV:**

**Co-injection of seawater and produced water to improve oil recovery from fractured North Sea chalk oil reservoirs**
Tina Puntervold, Skule Strand and Tor Austad
Journal of Petroleum Science and Engineering (under review)

## Paper V:

**Effect of temperature on enhanced oil recovery from mixed-wet chalk cores by spontaneous imbibition and forced displacement using seawater**
Skule Strand, Tina Puntervold and Tor Austad
Energy & Fuels (under review)


## Paper VI:

**"Smart water" for oil recovery from fractured limestone: A preliminary study**
Skule Strand, Tor Austad, Tina Puntervold, Eli J. Høgnesen, Martin Olsen and Sven Michael F. Barstad
Energy & Fuels (in press)

# Symbols and abbreviations

| | |
|---|---|
| $\Delta H_{hydr}$ | Change in hydration enthalpy, kcal/mol |
| $\Delta P$ | Pressure gradient |
| $\Delta S_{OF}$ | Change in oil saturation by forced drainage |
| $\Delta S_{OS}$ | Change in oil saturation by spontaneous drainage |
| $\Delta S_{WF}$ | Change in water saturation by forced imbibition |
| $\Delta S_{WS}$ | Change in water saturation by spontaneous imbibition |
| $\phi$ | Porosity, % |
| $\theta$ | Contact angle, ° |
| $\sigma$ | Interfacial tension, mN/m |
| $\sigma_{os}$ | Interfacial tension between oil and solid, mN/m |
| $\sigma_{ow}$ | Interfacial tension between oil and water, mN/m |
| $\sigma_{ws}$ | Interfacial tension between water and solid, mN/m |
| A | Area between the $SCN^-$ and $SO_4^{2-}$ curves |
| $A_{Heptane}$ | Area between the $SCN^-$ and $SO_4^{2-}$ curves using heptane as oil phase – representing a completely water-wet system |
| AN | Acid number, mgKOH/g oil |
| API | American Petroleum Institute |
| ASTM | American Society for Testing and Materials |
| $A_{Wett}$ | Area between the $SCN^-$ and $SO_4^{2-}$ curves using crude oil |
| BN | Base number, mgKOH/g oil |
| $C/C_o$ | Relative concentration of effluent ions |
| $C_{12}TAB$ | Cationic surfactant Dodecyl Trimethyl Ammonium Bromide |
| COBR | Crude oil brine rock |
| D | Diameter, cm |
| DW | Distilled water |
| EF | Ekofisk brine |
| EOR | Enhanced oil recovery |
| FI | Forced imbibition |
| FW | Formation water |
| G-AB | Gravity, Acid and Base number |
| GOR | Gas oil ratio |
| $I_{AH}$ | Amott-Harvey relative displacement index |
| IFT | Interfacial tension, mN/m |
| $I_o$ | Displacement by oil ratio |
| IOR | Improved oil recovery |
| $I_w$ | Displacement by water ratio |

| | |
|---|---|
| $J^*$ | Dimensionless entry pressure, often 0.25 |
| k | Permeability, mD |
| L | Length, cm |
| NaCl-M | NaCl brine with equal amounts of $SCN^-$, $Ca^{2+}$ and $Mg^{2+}$ corresponding to seawater $Ca^{2+}$ concentration |
| NSO | Nitrogen Sulphur Oxygen |
| OOIP | Oil originally in place |
| PA | For Analysis |
| $P_c$ | Capillary pressure, psi |
| $pK_a$ | Acid constant |
| PV | Pore volume |
| PV/D | Pore volume per day |
| PW | Produced water |
| $(PW)_{calc}$ | Calculated PW composition, mol/l |
| $(PW)_{exp}$ | Experimentally measured PW composition, mol/l |
| $PW_{EF}$ | Ekofisk produced water |
| $PW_{VH}$ | Valhall produced water |
| PW1SSW1 | Mixture of 1 part PW and 1 part SSW |
| PW1SSW2 | Mixture of 1 part PW and 2 parts SSW |
| PW1SSW4 | Mixture of 1 part PW and 4 parts SSW |
| PW1SSW8 | Mixture of 1 part PW and 8 parts SSW |
| PW2SSW1 | Mixture of 2 parts PW and 1 part SSW |
| PW-SSW | Mixtures of seawater and produced water |
| PWxSSWy | Mixture of x parts PW and y parts SSW |
| Q | Flow rate |
| SEM | Scanning electron microscope |
| SI | Spontaneous imbibition |
| $S_{or}$ | Residual oil saturation |
| SSW | Synthetic seawater |
| SSW/US | Seawater without sulphate |
| SSW½M | Seawater with equal amounts sulphate and thiocyanate, corresponding to half the amount of the sulphate concentration in seawater |
| SSW2S | Seawater with twice the seawater sulphate concentration |
| SSW4S | Seawater with four times the seawater sulphate concentration |
| SSW-M | Seawater with equal amounts of sulphate and thiocyanate, corresponding to seawater concentration of sulphate |
| SSW-U | Seawater without sulphate and thiocyanate |
| STB | Standard barrels |
| $S_w$ | Water saturation |
| $S_{wi}$ | Initial water saturation |

| | |
|---|---|
| $S_{wr}$ | Residual water saturation |
| T | Temperature, °C |
| TDS | Total dissolved solids, g/l |
| USBM | United States Bureau of Mines |
| VB | Valhall brine |
| VF | Viscous flooding |
| $V_b$ | Bulk volume, cm$^3$ |
| VB/US | Valhall brine without sulphate |
| WI | Wetting index |
| $WI_{New}$ | New wetting index |
| wt% | Weight percent |

# Contents

# 1 Introduction

## 1.1 Oil recovery from carbonate rocks

Oil production is generally divided into three stages, primary recovery, secondary recovery and tertiary recovery. In primary recovery, which is usually (but not necessarily) the first production stage, the natural energy of the reservoir is used to displace the oil from the reservoir. The drive mechanisms are pressure depletion of the reservoir pressure, in the form of solution-gas drive, gas cap drive, natural water drive, or fluid and rock expansion, or gravity drainage. In this stage, only 10-30 % of the OOIP (oil originally in place) is produced (Castor et al., 1981).

Secondary recovery is usually initiated when primary production is declining, adding additional energy to the reservoir in order to maintain pressure or provide a more efficient oil displacement. Gas injection and waterflooding are two secondary methods, the latter being the most common. The recovery factor after the secondary stage is usually 30-50 % of OOIP (Castor et al., 1981).

The tertiary recovery stage, comprising miscible gas injection, chemical injection and thermal energy methods, typically takes over when secondary recovery becomes uneconomical. However, oil production does not always follow this chronological order. Therefore, the term 'Enhanced Oil Recovery' (EOR) is nowadays more widely used than 'tertiary recovery'. Another term, IOR (Improved oil recovery) is also often seen, and in addition to EOR this term includes reservoir characterization, reservoir management and infill drilling (Green and Willhite, 1998). The EOR methods most commonly target the oil left in the waterflooded reservoir, which especially in carbonate reservoirs can be a substantial amount. There are five categories of EOR processes (Green and Willhite, 1998): mobility-control (polymers, foams), chemical (surfactants, alkaline agents), miscible (hydrocarbon solvents, $CO_2$), thermal (steam, in-situ combustion) and other processes, such as microbial EOR, immiscible $CO_2$ etc. Seawater injection should perhaps be categorized under other processes, as it is a superb EOR fluid to chalk. This will be discussed later in chapter 3.

Approximately 50 % of all the petroleum reserves in the world are found in carbonate reservoirs (Treiber et al., 1972). Oil recovery from these reservoirs is generally very low, usually below 30 %. The reason for this is that most carbonate rocks are fractured, of low permeability and of low water-wetness (Cuiec, 1984; Treiber et al., 1972). Chilingar and Yen (1983) reported that out of 161 carbonate rocks studied, 15 % were strongly oil-wet,

65 % were oil-wet, 12 % were of intermediate wettability and 8 % were water-wet.

The presence of fractures in a porous, low permeable rock matrix provides a relatively high permeability flow path from the injector to the producer. The permeability of fractures is often 50 times higher than the permeability of the chalk matrix. This means that secondary waterfloods are less effective because the injected water follows the least resistance path to the producer, only displacing the oil residing in the fractures, which is only a few percent of OOIP. In fractured and low permeable carbonate reservoirs, oil displacement from the matrix blocks by spontaneous imbibition of the injection fluid, constitutes the main drive mechanism to obtain high recovery. However, being mostly neutral to oil-wet, oil recovery from carbonates by spontaneous imbibition of water is limited. The unfavourable wetting state prevents spontaneous uptake of water into the matrix due to a negative capillary pressure. Thus, in order to achieve high recoveries from carbonate rocks, the capillary pressure should be increased through a wettability alteration of the rock surface towards a less oil-wet state, in that way promoting spontaneous imbibition of water to expel the oil. Seawater has the ability to do just that.

## 1.2 Carbonate rock classification

Carbonates are formed by the sedimentation of calcareous plant and animal debris. They are therefore often referred to as biogenic, i.e. containing mostly organic material produced by living organisms. If the sediment material is fragmented, the rock is classified as a clastic rock, while a non-clastic rock consists mostly of intact sediments. A bioclastic rock is a rock type composed of fragmented or detrital organic material, that has not been fully homogenized by chemical processes (Skinner and Porter, 1991). Limestone and dolomite can be classified as either clastic or non-clastic rocks.

Geologists generally classify rocks containing at least 50 % carbonate minerals as a carbonate rock (Mazzullo et al., 1992). There are several kinds of carbonate minerals, differentiated by their ionic composition and/or structure, the most important are Calcite ($CaCO_3$), Aragonite ($CaCO_3$), Siderite ($FeCO_3$), Magnesite ($MgCO_3$), Dolomite ($CaMg(CO_3)_2$) and Ankerite ($CaFe(CO_3)_2$) (Bjørlykke, 2001). Carbonate rocks are mostly composed of either calcite, dolomite or a combination of these minerals. Limestone is defined as a sedimentary carbonate rock containing more than 50 % of calcite. Dolomite, on the other hand, is defined as a sedimentary carbonate rock containing at least 50 % of the mineral dolomite (Mazzullo et al., 1992). The

dolomite mineral, $CaMg(CO_3)_2$, is made up of layers of $CO_3^{2-}$ with alternating layers of $Ca^{2+}$ and $Mg^{2+}$ in between. Dolomite is not formed directly, but is formed gradually by a "dolomitization" process in which the $Ca^{2+}$-ions of $CaCO_3$ (calcite or aragonite) is substituted by $Mg^{2+}$-ions according to the following equation:

$$2\ CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \hspace{3cm} (1.1)$$
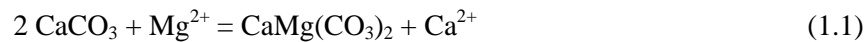
Chalk is classified as a limestone, and it originated from the deposition and sedimentation of calcareous skeletal debris from the unicellular planktonic algae coccolithophorid, plus a small amount of foraminiferal material (Milter, 1996). The coccolithophorid algae consist of many spherical coccospheres (2-20 μm diameter), which are built up by coccolithic ring structures (3-15 μm diameter), which in turn are composed of ring fragments or platelets consisting of calcite crystals (0.25-1 μm diameter). Figure 1.1 shows clearly a coccolithic ring and ring fragments, intact and non-intact.
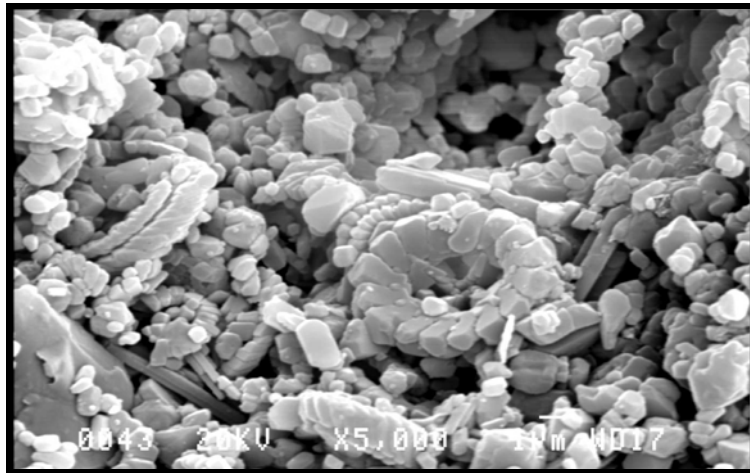


*Figure 1.1 SEM picture of chalk showing the coccolithic rings, ring fragments and pore space*

Chalk is finely grained and is usually highly porous because of small pores between the skeletal constituents, seen as the black spaces in Figure 1.1, but with low permeability because of the microscopic size of the constituents.

## 1.3 Outcrop material

In wettability and rock mechanical studies in the laboratory, outcrop chalk material is often used to represent the reservoir rock. Contrary to real reservoir rock samples, outcrop chalk is cheap and readily available. Prior to any experimental studies, it is important to decide on the type of outcrop material to be used, because they may behave differently despite having similar lithology (Milter and Øxnevad, 1996; Strand et al., 2007). Especially silica type and content have been shown to affect the wettability and the mechanical strength of the rock. (DaSilva et al., 1985; Strand et al., 2007) The geological descriptions of four types of outcrop chalks, Stevns Klint, Aalborg, Liége and Beer Stone are summarized in Table 1.1.

**Table 1.1** *Geological descriptions of Stevns Klint, Aalborg, Liége (Strand et al., 2007) and Beer Stone (Milter and Øxnevad, 1996)*

|  | Stevns Klint | Aalborg | Liége | Beer Stone |
|---|---|---|---|---|
| Origin | Sigerslev, Denmark | Roerdal, Denmark | Halembaye, Belgium | Beer, England |
| Geologic age | Maastrichtian | Maastrichtian | Campanian | Turonian |
| Silica content (wt%) | ~ 1 | 2-7 | < 2 | - |
| Porosity (%) | 45-50 | 45 | 40 | 24-30 |
| Permeability (mD) | 2-5 | 3-5 | 1-2 | 1-2 |
| Specific surface area ($m^2$/g) | ~ 2 | ~ 2 | ~ 2 | 1 |

## 1.4 Wettability

Wettability can be defined as the tendency one fluid has to spread on or adhere to a solid surface in the presence of another immiscible fluid (Craig Jr., 1971). The reservoir rock wettability is an important property determining the success of a waterflood, because it has a great influence on the location, flow and distribution of the fluids in the reservoir. In a system at equilibrium, the wetting fluid is located on the pore walls and occupies the smallest pores while the non-wetting fluid is located in the pore bodies. Thus, in a water-wet system, water is found at the pore walls and oil in the pore bodies. Vice-versa,

in an oil-wet system the oil is located at the pore walls and water in the pore bodies.

A relatively fast way to evaluate the wettability of the system is by measuring the contact angle ($\theta$) between a solid and the two immiscible fluids, Figure 1.2. The contact angle reflects the equilibrium between the interfacial tensions of the two fluid phases and their individual adhesive attraction to the solid. The contact angle is by convention measured through the denser phase, which in Figure 1.2 is the water phase.

In a system containing a reservoir rock, oil and water, Figure 1.2, the rock is typically preferentially water-wet if water occupies the smallest pores and is the spreading fluid ($\theta < 90°$), and preferentially oil-wet if oil is the spreading fluid ($\theta > 90°$) occupying the smallest pores. The rock is intermediate (neutral)-wet when the rock has no strong preference for either fluid and both fluids can be the spreading fluid ($\theta = 90°$).
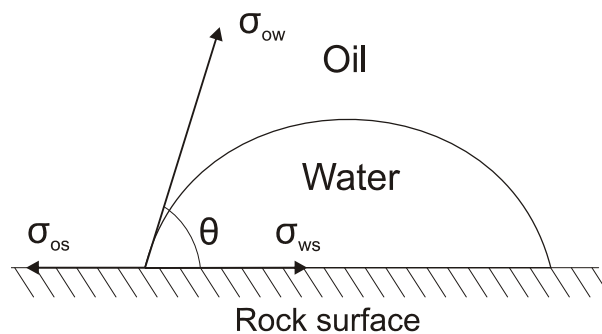


**Figure 1.2** *Wettability of a system between oil water and rock. (Craig Jr., 1971)*

Not all reservoirs have uniform wettability throughout the reservoir, but rather a heterogeneous wettability. Fractional, spotted or dalmatian wettability are terms that are often seen representing a heterogeneously wetted reservoir (Anderson, 1986a). In this type of rock wettability, some areas of the rock are strongly oil-wet, while the rest is strongly water-wet. A special type of fractional wettability was introduced by Salathiel (1973) as "mixed wettability". In mixed wettability fine pores and grain contacts are preferentially water-wet and contain no oil, whereas the oil-wet surfaces form continuous paths through the largest pores and contain all of the oil. Thus, oil

permeability exists down to very low oil saturations during waterflooding, and higher recovery was seen than for either uniformly water-wet or oil-wet conditions (Salathiel, 1973).

### 1.4.1 Wettability measurement methods

There are several methods, qualitative or quantitative, that can be used for wettability measurements (Anderson, 1986b). Quantitative methods are: contact angle measurements, Amott (imbibition and forced displacement), and the USBM method. Qualitative methods are: imbibition rates, microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillarimetric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance and dye adsorption.

In this thesis work, wettability has been measured by spontaneous and forced imbibition (incomplete Amott), and by a newly developed chromatographic wettability test for chalk (Strand et al., 2006b). The principles of these two methods will be explained in the following.

#### 1.4.1.1 Amott method

In the Amott method (Amott, 1959) imbibition and forced displacement (by centrifuging) are combined in order to measure the average wettability of a core (Anderson, 1986b). The wetting fluid of a system will generally imbibe spontaneously into the core, displacing the nonwetting fluid. The ratio of spontaneous imbibition to forced imbibition is used to reduce the influence of e. g. relative permeability, viscosity and initial saturation of the rock.

A complete Amott test is a rather time consuming method, resulting in "displacement-by-oil-ratio", $I_o$, and "displacement-by-water-ratio", $I_w$. The first expression is the ratio of the water volume displaced by spontaneous imbibition (drainage) of oil to the total displacement from spontaneous and forced imbibition (drainage) of oil. Likewise, the latter expression gives the ratio of the oil volume displaced by spontaneous imbibition of water to the total displacement from spontaneous and forced imbibition.

The Amott-Harvey method is a modification of the Amott test method. Figure 1.3 shows a complete test cycle for the Amott-Harvey method.
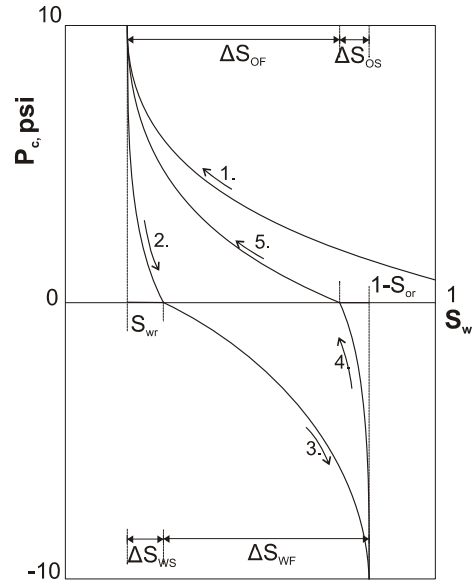
**Figure 1.3** *Capillary pressure curve for Amott and Amott-Harvey test method.*

The test cycle is divided into five segments:

1. Primary drainage of water by oil to establish initial water saturation, $S_{wi}$

2. Spontaneous imbibition of water

3. Forced imbibition of water

4. Spontaneous imbibition (drainage) of oil

5. Forced imbibition (drainage) of oil

The Amott-Harvey method gives a relative displacement index, $I_{AH}$ (Anderson, 1986b), which is related to the Amott indices to oil and water, $I_o$ and $I_w$, respectively, through:

$$I_{AH} = I_w - I_o \tag{1.2}$$

The Amott wetting indices are found by saturation changes in the following way:

$$I_w = \frac{\Delta S_{WS}}{\Delta S_{WS} + \Delta S_{WF}} \qquad\qquad (1.3)$$

$$I_o = \frac{\Delta S_{OS}}{\Delta S_{OS} + \Delta S_{OF}} \qquad\qquad (1.4)$$

Thus, the Amott-Harvey index gives a single value for the wettability of a system. The index ranges from -1 for a completely oil-wet system to +1 for a completely water-wet system. Cuiec (1984) supplemented the index range by stating that $-1 \leq I_{AH} \leq -0.3$ is an oil-wet system, $-0.3 < I_{AH} < 0.3$ is an intermediate-wet system and $0.3 \leq I_{AH} \leq 1$ is a water-wet system.

The limitation using the Amott test and its modification is that these methods are insensitive near neutral wettability (Anderson, 1986b), they do not discriminate between systems that reach residual non-wetting phase without change in sign of imbibition capillary pressure (Ma et al., 1999) or distinguish well enough between degrees of strong water wetness (Morrow, 1990).

### 1.4.1.2    Chromatographic wettability test

This test method was developed by Strand et al. (2006b) and it is based on chromatographic separation between sulphate, $SO_4^{2-}$, and the tracer thiocyanate, $SCN^-$, during core flooding. $SO_4^{2-}$ adsorbs on the water-wet chalk surface, but $SCN^-$ acts as a non-adsorbing agent. This property is used to quantify the water-wet surface area of the chalk. An oil-saturated chalk core is first flooded to $S_{or}$ with a brine without $SO_4^{2-}$ and $SCN^-$, then second by a brine containing equal amounts of both $SO_4^{2-}$ and $SCN^-$. The effluent is collected in fractions and analysed for the ionic compositions of $SO_4^{2-}$ and $SCN^-$. Relative ion concentration is plotted against pore volume injected, Figure 1.4, and the area between the curves is calculated. This area is directly proportional to the water-wet surface area of the core.
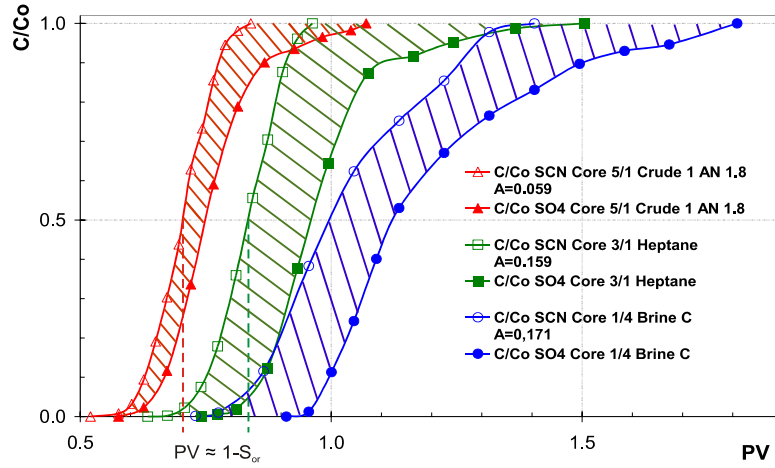
**Figure 1.4** *Chromatographic separation of $SO_4^{2-}$ and $SCN^-$ for a preferential oil-wet core. Completely water-wet conditions are assumed using heptane as oil or at 100 % water saturated condition (Strand, 2005).*

A wetting index, ($WI_{New}$), describing the fraction of water-wet area inside the core, is calculated according to the following equation:

$$WI_{New} = \frac{A_{Wett}}{A_{Heptane}} \tag{1.5}$$

Where:

$A_{Heptane}$ and $A_{Wett}$ are the areas between the $SCN^-$ and the $SO_4^{2-}$ curve for a completely water-wet system using heptane as the oil phase and the actual crude oil system, respectively. The area is calculated using the trapezoidal rule. According to the definition of $WI_{New}$:

$WI_{New} = 1.0$         represents a completely water-wet system
$WI_{New} = 0.5$         represents a neutrally wetted system
$WI_{New} = 0.0$         represents a completely oil-wet system

### 1.4.2 Wetting alteration by crude oil

Originally, all reservoir rocks were thought to be water-wet. Sandstone reservoirs were formed by deposition in an aqueous environment. Most sedimentary rocks are therefore water-wet by nature. In carbonates, water played a large role in the development of porosity. At a later stage oil migrated into both reservoir types. However, it was shown that most carbonate rocks are intermediate to oil-wet (Chilingar and Yen, 1983; Cuiec, 1984; Treiber et al., 1972). Thus, the original reservoir rock wettability has been altered from water-wet to oil-wet by the contact with crude oil. There are several factors that have an impact on this alteration of the COBR (crude oil/brine/rock) system.

Adsorption of surface-active polar compounds from the crude oil results in a less water-wet rock. These hydrocarbon compounds have a polar group containing oxygen, nitrogen or sulphur, and they adsorb with the polar end onto the rock surface, orientating the hydrocarbon end outwards, and thus make the surface oil-wet (Anderson, 1986a; Denekas et al., 1959). Although surface-active compounds exist over a wide range of molecular weights, it is generally accepted that the heavier fractions of the crude oil, asphaltenes and resins, have the largest effect on wettability (Anderson, 1986a; Buckley, 2001; Cuiec, 1984; Denekas et al., 1959; González and Travalloni-Louvisse, 1993; Yan et al., 1997). A group of components from the asphaltene/resin fraction has been found to be especially important regarding wettability alteration, and they are polar compounds of acidic and basic nature (Anderson, 1986a; Cuiec, 1984; Denekas et al., 1959), sulphur compounds, oxygen compounds and nitrogen compounds. Four mechanisms by which the polar compounds can adsorb onto the rock surface have been identified (Al-Maamari and Buckley, 2000; Buckley and Liu, 1998; Buckley et al., 1998), and they are:

- Polar interactions between the oil and solid predominate in the absence of a water film, resulting in adsorption of the polar oil components onto the polar surface sites.

- Surface precipitation is dependent on the ability of the oil to solvate the asphaltenes.

- Acid/Base interactions in the presence of water control the surface charges of the oil/water and solid/water interfaces. The net charge affects the stability of the water film, and the ionized acidic/basic sites influence adsorption.

- Ion-binding is an interaction between charged sites at the mineral surface and higher valency ions in the brine, creating bridges between like charges.

By assessing the rock type and the characteristic properties of the crude oil, such as the API gravity, acid number (AN) and base number (BN), the so-called G-AB parameters, the mechanism by which the crude oil is likely to alter the rock wettability, can be evaluated (Buckley et al., 1998).

The ability of the different polar compounds to alter the rock wettability depends on the rock type. It has been found that carbonate rocks are typically less water-wet than sandstone reservoirs (Chilingar and Yen, 1983; Treiber et al., 1972). Experiments have shown that silica (sandstone), is negatively charged above pH 2 (Menezes et al., 1989), while calcite (carbonate) is positively charged below pH 8 (Pierre et al., 1990). Thus, because of opposite surface charges the rocks will respond differently to acidic and basic material. For instance, the wettability of silica is more affected by the organic bases, while carbonates are more affected by the organic acids (Anderson, 1986a; Lord et al., 2000; Thomas et al., 1993) .

Brine chemistry is another important parameter that can influence the rock wettability, because the salinity and pH of the brine strongly affects the surface charge of the rock and fluid interfaces, hence affecting the adsorption as mentioned in the above paragraph (Anderson, 1986a; Buckley et al., 1989; Tang and Morrow, 1997). Also the presence of multivalent cations in the brine can affect wettability (Anderson, 1986a; Castor et al., 1981; Yan et al., 1997).

Other factors, than the above described, that have effect on the wettability alteration of the COBR system are (Standnes, 2001):

- Capillary pressure and thin film forces, disjoining pressure (Hirasaki, 1991)
- Water solubility of polar oil components and diffusion through water films (Anderson, 1986a; Kaminsky and Radke, 1998)
- 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)
- Initial water saturation (Jadhunandan and Morrow, 1995; Salathiel, 1973; Yan et al., 1997)

### 1.4.3 Initial wetting of chalk

Initially, the water-wet chalk surface was in equilibrium with the surrounding brine containing a high concentration of $Ca^{2+}$-ions. If the pH of the formation brine is $< 8$, the chalk surface is positively charged (Pierre et al., 1990). This has been verified experimentally by zeta-potential measurements (Legens et al., 1999; Zhang and Austad, 2006). When crude oil, containing surface-active polar compounds, invaded the chalk reservoir, the oil/brine interface became negatively charged as a result of partial dissociation of the carboxylic material of the crude oil in contact with the water phase.

The wettability of the rock depends largely on the strength of the wetting film, and to what extent the wetting molecules are displaced from the rock surface (Milter, 1996). The film strength is affected by the oil-brine and brine-rock interface charges, and whether the interfaces attract or repel each other. The disjoining pressure, the total pressure between two particles or interfaces at very small distances (Derjaguin et al., 1987), involves electrostatic interactions, steric forces (hydration forces) and London dispersion forces (Hirasaki, 1991). When the disjoining pressure is positive, the two particles or interfaces repel each other, and the wetting film remains stable. On the other hand, when the disjoining pressure is negative, the two particles or interfaces attract each other, and the film becomes thinner. At one point, the film thickness will reach a critical level and become unstable. The film ruptures, and the non-wetting fluid will directly contact the rock surface (Buckley et al., 1989; Kaminsky and Radke, 1998; Legens et al., 1999).

In chalk, the two interfaces were oppositely charged, i.e. they attracted each other. A negative disjoining pressure was formed between the positively charged brine/rock interface and the negatively charged oil/brine interface. This led to a thinning of the water film between the oil and rock, film rupture, and oil was able to contact parts of the rock. Carboxylic material adsorbed onto the rock surface, and made it less water-wet (Thomas et al., 1993). The carboxylic material is very strongly bonded to the $Ca^{2+}$-ions at the rock surface and is thus not easily removed by solvents, but it can be removed by chemical reactions.

Molecular modelling of binding energies of benzoic acid and a water molecule to a model calcite surface, has been performed by Legens et al. (1999). Both binding energies were similar, -52.9 and -54.0 kcal/mol for benzoic acid and water, respectively, meaning that their affinities for the calcite surface were almost identical. It was concluded that in presence of excess water, the surface would be mostly hydrated, and that in excess oil organic phase adsorption of benzoic acid was favoured. These predictions were also confirmed experimentally (Legens et al., 1999).

The most important parameters affecting the chalk wettability are AN, temperature and zeta potentials of the COBR interfaces. It is known that the wettability of carbonates is very strongly related to the AN of the crude oil, Figure 1.5 (Standnes and Austad, 2000a). A higher AN corresponds to less water-wet chalk.
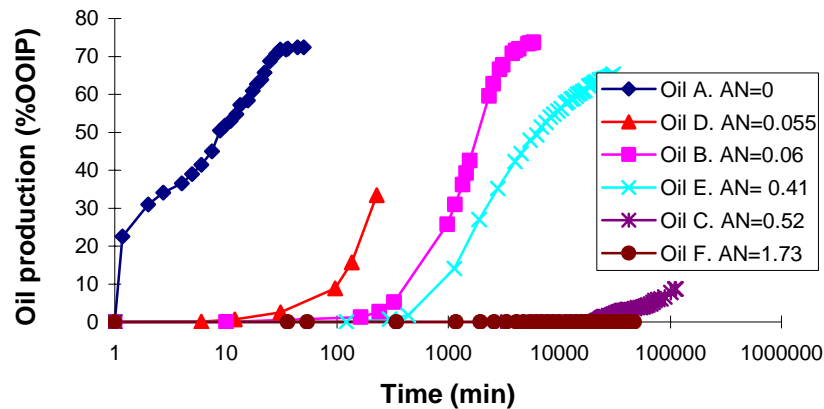


**Figure 1.5** *The influence of AN on oil recovery from chalk by spontaneous imbibition at 40 °C. (Standnes and Austad, 2000a)*

It is a general observation for carbonate reservoirs that the water-wetness increases as the reservoir temperature increases (Rao, 1999). At high temperatures, the AN is reduced by decarboxylation, a reaction that is even catalyzed by $CaCO_3$ (Shimoyama and Johns, 1972). Decarboxylation is a slow process, meaning that it does not take place during the time frame of the laboratory experiments. Wettability tests by aging chalk cores in crude oils of different AN at different temperatures confirmed that the AN played the major role concerning wetting conditions, while no correlation to the aging temperature was observed, i.e. the temperature appeared to play a minor role (Zhang and Austad, 2005).

Strong correlations between the asphaltene content and BN have been experienced (Barth et al., 2005; Skauge et al., 1999), and Skauge et al. (1999) found that the amount of acids and bases were proportional to the amount of asphaltenes and NSO-compounds (nitrogen, sulphur, oxygen), and that a high AN usually corresponded to a high BN. The latter finding does not agree with the results from Dubey and Doe (1993) who found that most oils tested had a

significant higher BN than AN. This disagreement may be caused by the reservoir temperature, i.e. because of decomposition of the carboxylic acids at high temperatures, > 90-100 °C, the AN of the oil is decreased over geological time. The bases have not been reported to decompose at high temperature, and therefore the BN remains the same. Thus, the AN of the oils that we measure today, such as

Ekofisk:    T = 130 °C;    AN = 0.10 mgKOH/g;   BN = 1.5 mgKOH/g;

Valhall:    T =  90 °C;    AN = 0.20 mgKOH/g;   BN = 2.4 mgKOH/g;

may not be the AN of the oil that originally wetted the reservoir rock, because of decomposition and also adsorption. Many experiments have been performed on the effect of AN on chalk, but little has been done on BN. Can BN have an effect on the initial wetting of chalk?

## 1.5 North Sea chalk reservoirs

The chalk formations in the North Sea are highly porous due to an early invasion of hydrocarbons in the pores, but these reservoirs are also of low matrix permeability, and were therefore not expected to produce oil and gas economically. However, one of the greatest successes in Norwegian oil history is the development and production of the Ekofisk field. The recovery success from Ekofisk is quite unique for this type of field. The presence of a fracture network, with approximately 50 times higher permeability than the matrix, drastically increased the effective permeability of the field. The fractures work as transport routes for the injection fluid, as well as for the produced fluid. Another important reason for the success of the Ekofisk recovery has been the use of seawater as injection fluid, in combination with the high Ekofisk reservoir temperature, 130 °C. The reason why will be further discussed in chapter 3.

### 1.5.1   Ekofisk

The Ekofisk field, located in the southern part of the Norwegian sector in the North Sea, was discovered in 1969 and put on production in 1971. The initial reservoir pressure was 7135 psia at 10400 ft depth and reservoir temperature was 268 °F (~130 °C) (Hermansen et al., 2000; Kvendseth, 1988). The Ekofisk field consists of two low-permeable (0.1 – 10 mD) fractured chalk formations, Ekofisk (120 m) and Tor (60 m). The overlying

Ekofisk formation is of Danian age and the underlying Tor formation is of Maastrichtian age, Table 1.2, and both have a fairly high porosity 30-45 % and low initial water saturation <10 %. These two formations are separated by a 15-30 m tight limestone zone. Field wettability varies from the preferentially water-wet Tor formation, to the moderately water-wet Lower Ekofisk and to the neutral to slightly oil-wet Upper Ekofisk Formation (Hamon, 2004; Torsaeter, 1984).

**Table 1.2** *Stratigraphic nomenclature of the chalk group in the Greater Ekofisk area (Dangerfield and Brown, 1987)*

| STAGE | GROUP | FORMATION | ZONATION |
|---|---|---|---|
| PALEOCENE | MONTROSE | MAUREEN EQ. | MAUREEN FORMATION EQUIVALENT |
| | CHALK | EKOFISK | UPPER POROUS ZONE |
| | | | TOMMELITEN TIGHT ZONE |
| | | | REWORKED DANIAN ZONE |
| | | | REWORKED MAASTRICHTIAN ZONE |
| | | | EKOFISK TIGHT ZONE |
| MAASTRICHTIAN TO TURONIAN | | TOR | UPPER |
| | | | MIDDLE |
| | | | LOWER |
| | | HOD | UPPER |
| | | | MIDDLE |
| | | | LOWER |
| CENOMANIAN | | PLENUS MARL HIDRA | |

The field contains an estimated 7 billion STB hydrocarbons and the recovery factor was at first estimated to be 17-18 % OOIP based on primary depletion with gas re-injection. In order to increase the recovery factor, the water flooding potential was evaluated, as a secondary recovery method. A pilot waterflood of the Tor formation (Hallenbeck et al., 1991; Thomas et al., 1987) initiated in 1981 confirmed laboratory studies that showed high water imbibition into chalk cores. These promising results led to waterflood pilots in the Lower Ekofisk formation in 1985 (Hallenbeck et al., 1991; Sylte et al.,

1988), and in the Upper Ekofisk formation in 1990, both with promising results. Full field water injection into the Tor formation commenced in 1987 and was in 1988 expanded to the Lower Ekofisk formation and in 1992-93 water flooding was extended to the Upper Ekofisk formation (Christian et al., 1993). Water flooding of the Ekofisk field has contributed to significant increased oil recovery, increased oil rates, reduced water cut and reduced GOR since the start of water injection in 1987 (Hermansen et al., 2000).

Production by pressure depletion reduced the reservoir pressure from slightly above 7000 psi in 1971 to 4000 psi in 1985 (Dangerfield and Brown, 1987). The weight of the overburden layers exerted a stress on the chalk reservoir that could not be supported by the pore pressure and matrix strength. This resulted in pore collapse of the chalk which led to compaction of the rock by deformation of the chalk matrix (Johnson and Rhett, 1986). 10 ft subsidence of the seafloor was detected at the Ekofisk field in 1984. To mitigate the subsidence and stop compaction, water flooding with seawater for pressure support was initiated in 1987. This only partly solved the problem. The compaction rate had been reduced, but there was still chalk deformation. This has later been explained as a water weakening of chalk phenomena (Korsnes, 2007; Madland, 2005) and will be discussed later in this thesis, in chapter 3.

Seawater injection proved to be a very successful injection fluid, displacing oil very efficiently from the Ekofisk field and increasing the reserves estimates. Water injection optimization and high activity is expected to prolong the life of Ekofisk for many years to come, until 2050 according to the latest prognoses (Olje- og energidepartementet and Oljedirektoratet, 2007).

### 1.5.2 Valhall

Valhall was discovered in 1975 and production commenced in 1982. The field is an overpressured, undersaturated Upper Cretaceous chalk reservoir, located in the southern part of the North Sea. It is located at a depth of 2400 m and produces from two chalk formations, Tor and Hod. About two-thirds of the oil and the majority of the production comes from Tor, which is a soft and very pure (95-98 % calcite) chalk formation with high porosity (up to 50 %) and with high oil saturations (>90 %) (Ruddy et al., 1989). Matrix permeability is low (1-15 mD) (Hermansson and Gudmundsson, 1990), but the effective permeability is higher due to natural fractures in the reservoir. Originally the recovery driving force was pressure depletion with compaction drive, which as for Ekofisk, caused subsidence of the seafloor, and predicted

primary recovery was very low, 24 % OOIP (Ali et al., 1994). A pilot waterflood operation began in 1990 (Ali et al., 1994) and positive results led to the initiation of water injection in 2004. After 20 years of production, the estimated recovery factor had in 2003 increased to 40 %, and approximately 50 % of the drive mechanism is owed to rock compaction (Barkved et al., 2003). By 2007 waterflooding of the Valhall reservoir has resulted in a generally good performance, and waterflood expansion to new areas of the field is planned by 2008 (Tjetland et al., 2007).

# 2   Objectives

Carbonate reservoirs hold nearly 50 % of the petroleum reserves in the world, and due to unfavourable wetting conditions, oil recovery from carbonate reservoirs is below 30 % OOIP. A wettability alteration of the rock surface to a less oil-wet state is necessary to increase recovery by spontaneous imbibition of water. Past studies have shown that the most important wetting parameters regarding chalk wettability are the acid number (AN) of the oil, temperature, and the zeta potential of the rock-brine and oil-brine interfaces. Many studies have been done on the impact of the AN on the wetting conditions in chalk, but little has been done on base number (BN).

The first part of this thesis concerns the impact of BN, both natural bases and a model base, on the wetting conditions of chalk. Effects of temperature, initial water saturation, imbibition fluid and the wetting mechanism were studied.

The objectives of the second part of this thesis were to investigate the rock wettability alteration potential by injection of mixtures of seawater (SSW) and Valhall produced water (PW). Because of strict environmental policies in the North Sea, all the produced water should be cleaned by expensive methods before deposition to sea is allowed. Therefore, it is desirable to re-inject PW into the reservoir as it is. Seawater injection has been a huge success into the mixed-wet, fractured oil chalk reservoir at the Ekofisk field. Could it be possible to dilute seawater with some produced water and still be able to achieve high oil recoveries? First, the compatibility of the brines was tested by a modelling study, where the precipitation of sulphate salts, $CaSO_4$, $BaSO_4$ and $SrSO_4$, was investigated versus temperature. Second, the EOR-potential of mixtures of produced water and seawater (PW-SSW) was studied experimentally by spontaneous imbibition and viscous flooding (forced imbibition) of outcrop chalk cores.

Finally, in the third part of the thesis, a preliminary study on limestone was performed. The objective was to find out if the mechanisms for wettability alteration of the chalk surface are also applicable to limestone, and if it is possible to use seawater injection as an EOR method for limestone reservoirs as well. Another objective was to look at cleaning of reservoir carbonate cores, which is a challenging task. The potential determining ions in seawater are able to desorb organic carboxylic material from the chalk surface. If they can do the same in limestone, is seawater then a better reservoir core cleaning fluid than the more traditional method using toluene and methanol?

# 3   Water based EOR in carbonates

Waterflooding has traditionally been categorized as a secondary drive mechanism, maintaining reservoir pressure and improving reservoir sweep efficiency. In a secondary waterflood, the injected water has the same composition as the water that is present in the reservoir, i.e. the formation water. If the injected water has a different composition than the formation water, e.g. seawater, and increased oil recovery is experienced, this can be regarded as a tertiary recovery method.

Seawater has proven to be an exceptional EOR-fluid and a compaction fluid in chalk reservoirs (Austad et al., 2005; Austad et al., 2007). A number of studies performed by Austad and coworkers (Høgnesen, 2005; Korsnes, 2007; Madland, 2005; Milter, 1996; Standnes, 2001; Strand, 2005; Zhang, 2006) has led to an understanding of the mechanism behind the high recovery factor at the Ekofisk field. Initially, when the field was put on production in 1971, 17 % oil recovery had been estimated. Nowadays the prognoses have been increased to an amazing 50-55 %. In comparison, most carbonate reservoirs produce well below 30 % OOIP.

In several ways seawater plays a very active role in oil recovery from low permeable, high porosity and fractured chalk reservoirs in the North Sea. It improves the wettability of the chalk from oil-wet to intermediate to water-wet, thereby facilitating water imbibition into the rock matrix. Seawater weakens the chalk causing compaction of the rock, which is an important drive mechanism for oil recovery. At high temperatures, sulphate is stripped from seawater, which decreases possible scale formation. And last, but not least, seawater may also play an environmental role regarding the "zero-discharge" policy. These highly important and interesting features regarding injection of seawater into chalk will be discussed further in this thesis, and a possible extension of seawater as an EOR-fluid for limestone will be investigated.

## 3.1 EOR from carbonate reservoirs

EOR from carbonates has proven to be a great challenge due to the unfavourable wetting conditions of the rock that prevent spontaneous uptake of water and hence the oil is not expelled from the rock, but rather maintained inside. The fact that most carbonate rocks are highly fractured is another challenge. The matrix has a low permeability whereas the fractures have a relatively higher permeability, often 50 times higher than the matrix. The injected fluid will therefore favour the path of least resistance, i.e. the highest

permeability track from injector to producer. The injected fluid follows the fractures and displaces only the oil residing in the fractures, which in some cases is only a few per cent of OOIP (Al-Hadhrami and Blunt, 2001). Thus, the matrix, where most of the oil is held, is bypassed. Oil recovery from carbonate reservoirs is therefore usually very low, < 30 %. The goal of water-based EOR in carbonates is to imbibe water into the matrix and with that, displace the oil into the fractures where it is further transported to the producer.

In order for the injected water to imbibe from the fractures into the intermediate to oil-wet matrix blocks a capillary pressure threshold, expressed by the Leverett *J*-function, must be overcome or in some cases reduced.

$$P_c = \sigma \sqrt{\frac{\phi}{k}} J^*$$
(3.1)

Here $P_c$ is capillary pressure, $\sigma$ is oil-water interfacial tension, $\phi$ is porosity, k is permeability and $J^*$ is a dimensionless entry pressure, 0.25 is a value often used. The capillary entry pressure barrier can be overcome by viscous forces or by gravity forces, alternatively it can be reduced/eliminated by reducing the interfacial tension between the fluids using traditional methods such as surfactant flooding, gas injection, miscible gas injection or by altering the rock wettability (Al-Hadhrami and Blunt, 2001).

### 3.1.1  Surfactant flooding

Oil recovery by surfactant injection was originally aimed at the mobilization of capillary trapped oil after waterflooding (Morrow and Mason, 2001). The surfactant solution lowers the interfacial tension (IFT) between water and oil, deforming the residual oil drops so that these can be mobilized and displaced through the pore throats by viscous forces (Green and Willhite, 1998).

By using surfactants in fractured reservoirs, a lower IFT decreases the capillary entry pressure according to the Leverett *J*-function (3.1), 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. Another objective of using surfactants is to alter the rock wettability towards more water-wet, in that way also to enhance imbibition (Standnes et al., 2002).

Unfortunately, surfactant flooding is a rather expensive EOR-method, which is probably its biggest limitation.

### 3.1.2  Gas injection and miscible gas injection

Gas injection, which is the oldest EOR-method, is also an expensive method, and application of this method depends on gas availability and cost. Typical gases to be injected are nitrogen and flue-gases, the cheapest gases. Other more expensive gases are hydrocarbons and $CO_2$.

Gas injection utilizes gravitational forces in form of density differences between the oil and gas, to overcome the capillary entry pressure in order to displace the oil. Gas is non-wetting to oil, and the IFT between the oil and gas (~20 mN/m) is lower than that between oil and water (~50 mN/m) (Al-Hadhrami and Blunt, 2001). The gas is able to enter the matrix at the top of the reservoir and expel the oil from the bottom. The problem with gas injection is that it can be difficult to establish and maintain a gas column in the reservoir, because gas may channel through fractures at the top of the reservoir, which can lead to excessive gas production.

Miscible or near-miscible gas injection is another method that lowers the gas/oil IFT, which results in a lower capillary barrier. This method also decreases the viscosity of the oil, facilitating oil flow.

### 3.1.3  Rock wettability alteration

By altering the wettability of the rock from oil-wet, that prevents imbibition of water, to water-wet, that promotes imbibition of water, the capillary forces become positive, water is imbibed and oil can be expelled. Wettability alteration can be achieved by thermal methods and by use of surfactants. However, a rather "new" EOR-method for chalk, and possibly an applicable method for all carbonates, is wettability alteration by seawater. This will be the topic for the rest of the thesis.

## 3.2 Injection of seawater into chalk reservoirs

### 3.2.1  Seawater as a wettability modifier

Because of large permeability contrasts between the fractures and the matrix, the injected water follows the fractures to the producer without displacing oil from the matrix. Spontaneous imbibition of water from

fractures into the matrix blocks is regarded as an important drive mechanism for recovery in fractured oil-wet reservoirs. Some of the early work that looked into the spontaneous imbibition mechanism in chalk, was performed with surfactants, anionic, cationic and non-ionic (Austad et al., 1998; Milter and Austad, 1996a; Milter and Austad, 1996b; Standnes and Austad, 2000b; Standnes et al., 2002). It was found that the cationic surfactant $C_{12}TAB$ (dodecyl-trimethyl-ammonium-bromide) was the most successful due to the chemical interactions between the surfactant and the carboxylates adsorbed at the chalk surface (Standnes and Austad, 2003). The wettability of chalk was improved towards less oil-wet conditions, and oil was then displaced by spontaneous water imbibition into the rock. During the work with cationic surfactant, it was discovered that sulphate ($SO_4^{2-}$) present in the imbibing fluid influenced the wettability alteration process by improving spontaneous imbibition into chalk (Strand et al., 2003). This was explained by the influence of sulphate on the surface charge of chalk. Sulphate is a potential determining ion toward chalk (Pierre et al., 1990), i.e. it can adsorb on the water-wet surface of chalk and reduce the positive charge density. Desorption of negatively charged carboxylic material is then facilitated. Work was next initiated to look at the potential of sulphate as a wettability alteration agent for oil-wet chalk cores, in the absence of surfactant, using seawater as the imbibing fluid (Strand et al., 2006a). Seawater contains a large amount of sulphate, 0.024g/mol. Spontaneous imbibition tests showed that seawater alone was able to change the wetting of chalk, improving oil recovery. Spontaneous imbibition even increased with increased concentration of $SO_4^{2-}$. Temperature is also an important parameter in wettability alteration by $SO_4^{2-}$, because the affinity of $SO_4^{2-}$ for the chalk surface increases with temperature (Strand et al., 2006a). In addition to $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ are also important potential determining ions. All three ions are highly involved in the wettability alteration process of oil-wet chalk. However, $SO_4^{2-}$ is the most important parameter and must be present together with either $Ca^{2+}$ or $Mg^{2+}$ or both. A chemical mechanism of the wettability alteration of chalk by seawater has been suggested and it is shown in Figure 3.1 (Zhang et al., 2007).

Briefly explained, negatively charged carboxylic material is adsorbed on the positively charged chalk surface, and the system is in equilibrium with the formation water containing an excess of $Ca^{2+}$. When seawater, containing a lot of $SO_4^{2-}$, is injected into the reservoir the equilibrium is disturbed. $SO_4^{2-}$ adsorbs on the chalk surface, thus lowering the positive charge density. Due to less electrostatic repulsion, more $Ca^{2+}$ ions can approach the surface (Strand et al., 2006a), and displace some of the carboxylic material by ion-bonding (Figure 3.1A). Seawater also contains a lot of $Mg^{2+}$ ions. The smaller $Mg^{2+}$-ion is strongly solvated/hydrated in water, $\Delta H_{hydr} = -459$ kcal/mol (Burgess,

1978), but will be partly dehydrated as the temperature increases. At high temperatures, >90-100 °C, $Mg^{2+}$ is also involved in the wettability alteration. Experiments have shown that $Mg^{2+}$ is able to substitute $Ca^{2+}$ from the chalk surface when flooding seawater slowly through an outcrop chalk core at high temperatures (Korsnes et al., 2007; Zhang et al., 2007). Thus, $Mg^{2+}$ should be able to displace the carboxylate-bonded $Ca^{2+}$-ion as well (Figure 3.1B), making the surface less oil-wet.
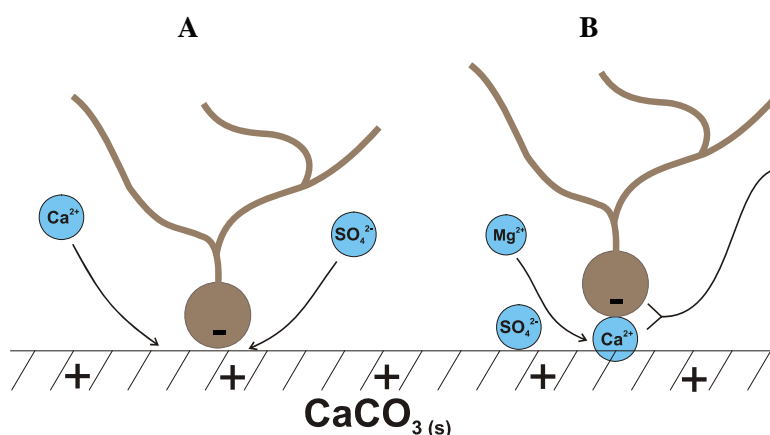


**Figure 3.1** *Suggested mechanism for the wettability alteration induced by seawater.* **A:** *Proposed mechanism when $Ca^{2+}$ and $SO_4^{2-}$ are active.* **B:** *Proposed mechanism when $Mg^{2+}$, $Ca^{2+}$ and $SO_4^{2-}$ are active at higher temperatures (Zhang et al., 2007).*

In consequence, the ability of seawater to act as a wettability modifier of the oil-wet chalk surface is much dependent on the potential determining ions in combination with high temperature.

### 3.2.2 Seawater as a compaction fluid

Compaction is an important drive mechanism for oil recovery from porous chalk reservoirs, and it is present in Ekofisk, Valhall and other chalk fields in the North Sea. At the Valhall field, simulation studies have indicated that 50 % of the oil production is owed to the rock compaction recovery mechanism (Cook and Jewell, 1996). Compaction is seen at the surface as subsidence, a deformation or a sinking of the seafloor. 3.5 m subsidence was discovered at Ekofisk in 1984, which resulted in expensive rig remediation

(Sulak, 1991). Compaction in the reservoir has been defined as the process in which the compressive strength of the rock is exceeded and plastic deformation occurs, resulting in irreversible reduction of porosity and permeability (Settari, 2002). Excluding thermal effects or chemical effects, such as dissolution, reservoir compaction is governed by the effective stress, reservoir thickness and rock compressibility (Nagel, 2001).

Chalk is a relatively soft reservoir rock, and early invasion of hydrocarbons into the reservoir prevented strengthening and compaction by diagenesis, maintaining instead a high porosity. The chalk strength is influenced by the porosity and by silica content (DaSilva et al., 1985). The type of pore fluid is also important as water saturated chalk is much weaker than oil saturated chalk (Madland et al., 2002; Newman, 1983). This has been described as a water weakening effect. Field and laboratory observations show evidence of water-induced compaction that may have affected the Valhall reservoir performance during waterflooding (Cook et al., 2001). The mechanism behind the water weakening of chalk has previously been mostly linked to physical interactions between chalk grains, and the chalk mechanical stability has been related to capillary forces (Delage et al., 1996). Early laboratory results suggested that the compaction behaviour of chalk was very much dependent on the water chemistry of the saturation fluid, causing chalk dissolution (Newman, 1983). As seawater is injected into the reservoir, the existing chemical compositional equilibrium between chalk and formation water is disturbed. Recent research has shown that water weakening is chemically enhanced by seawater-chalk interactions, such as dissolution of $CaCO_3$ and precipitation of $CaSO_4$ due to the removal of one or both common ions of chalk, $Ca^{2+}$ and $CO_3^{2-}$, and by thin film chemistry at the inter-granular contacts (Heggheim et al., 2005; Madland et al., 2006). Seawater contains potential determining ions towards chalk, $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ (Pierre et al., 1990), that are able to alter the wettability of chalk towards more water-wet conditions as described in the previous section (Zhang et al., 2007). Interesting rock mechanical experiments have revealed that the same ions are responsible for the water weakening of chalk by seawater, and hence chalk compaction (Korsnes et al., 2006a; Korsnes et al., 2006b). It was found that $Mg^{2+}$ from seawater was able to substitute $Ca^{2+}$ from the chalk surface, and that this substitution increased with temperature. A mechanism for the enhanced chemically induced weakening of chalk was suggested (Korsnes et al., 2007), and is illustrated in Figure 3.2.
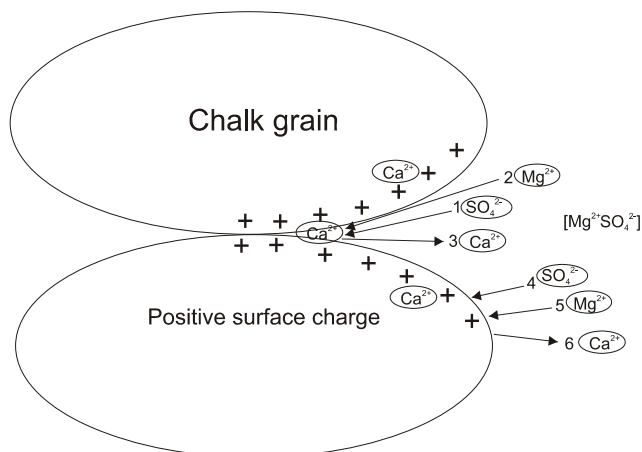
**Figure 3.2** *Schematic illustration of the suggested mechanism of enhanced water weakening of chalk by seawater (Korsnes et al., 2006a).*

Initially the chalk surface is positively charged, and in the thin water film at the inter-granular contacts the surface charge influences the ionic balance. When $SO_4^{2-}$ is absent in the brine, $Mg^{2+}$ substitutes $Ca^{2+}$ in the pore body, but not at the grain contacts. No enhanced weakening of the chalk is experienced. In the presence of $SO_4^{2-}$, the mechanical strength of chalk is decreased due to substitution of $Ca^{2+}$ by $Mg^{2+}$ at the inter-granular contacts. This substitution is catalyzed by $SO_4^{2-}$, which is attracted to the inter-granular contacts by electrostatic interactions. Because of the ion-pair formation between $SO_4^{2-}$ and $Mg^{2+}$ in solution, $Mg^{2+}$ is able to move closer to the grain contacts, and substitute $Ca^{2+}$ from the surface. Formation of $MgCO_3$ reduces the chalk mechanical strength as a result of different atomic sizes of $Ca^{2+}$ and $Mg^{2+}$.

### 3.2.3   Co-injection of seawater and produced water

During the waterflooding operation of a field, the amount of produced water will continuously increase. This water contains environmentally toxic components, such as low molecular weight aromatic material. Because of strict environmental regulations and "zero discharge" requirements, the operating companies in the North Sea are obliged to properly clean the produced water before it can be discharged to sea. These cleaning methods are rather expensive, and it is therefore of interest to inject the produced water back into the reservoir. In some cases this is already being done. On the Valhall field, where there is ongoing seawater injection, the produced water is injected into the reservoir through a separate injection well to avoid scale.

According to Bader (2006) there are three possible water sources for oilfield injection operations, seawater, produced water and aquifer water. He states that by using seawater, sulphate must be removed to avoid scale problems. However, removing sulphate means removing the most important wettability alteration parameter for chalk, which would limit enhanced oil recovery. As a second and third approach, he proposes to mix treated produced water either with sulphate-free seawater to decrease sulphate removal costs or with saline aquifer water. Again, that would mean no enhanced oil recovery from chalk by wettability alteration. A possible optimal solution is thus perhaps to co-inject produced water with seawater containing sulphate, and with that being environmentally friendly, and at the same time achieve enhanced oil recovery by wettability alteration of the chalk surface.

The produced water composition varies with time. In a water injection process, it has been shown that the fluid residing in the pores, e.g. the formation water, is banked up at the front and displaced by the injection water (Nielsen et al., 2000). Consequently, the produced water is initially pure formation water. As time passes, the produced water composition is modified through several liquid – rock and liquid – liquid interactions, such as ion exchange by adsorption of $SO_4^{2-}$ and $Ca^{2+}$ on the chalk surface (Strand et al., 2006a; Zhang et al., 2007), ion substitution at the chalk surface of $Ca^{2+}$ by $Mg^{2+}$ (Korsnes et al., 2006a; Korsnes et al., 2006b; Zhang et al., 2007), and precipitation of $CaSO_4$ in the formation at high temperatures. Furthermore, the injected seawater may also release/dissolve traces of $Ba^{2+}$ and $Sr^{2+}$ present in the chalk formation as carbonates. The concentration of these ions in the produced water will normally not increase beyond the value in the initial formation water because of precipitation of sulphate salts in the reservoir.

In order to co-inject seawater and produced water into the reservoir, it is necessary to investigate the water compatibility to prevent scale formation in and around the injection well that will impair the injectivity (Bader, 2007). Hence, for economical and environmental purposes, two related questions have been put forward in this thesis: Is it possible to co-inject produced water and seawater through the same injection well without injectivity impairment, and would enhanced oil recovery by wettability alteration of the chalk surface, still be achieved?

### 3.2.4   Scale problems related to seawater injection

By injecting sulphate-containing seawater or mixtures with produced water into a chalk reservoir with a $Ca^{2+}$-rich formation water, scale potential has to be considered. A chemical equilibrium has existed between the chalk

surface and the formation water for millions of years. The formation water contains a lot of $Ca^{2+}$-ions due to the dissolution of chalk in the water. It also contains some $Ba^{2+}$, $Sr^{2+}$ and in some cases $Ra^{2+}$. When cold seawater or seawater/produced water mixtures, with compositions different from the formation water, is injected into the reservoir, the existing chemical equilibrium is disturbed and a temperature gradient is formed. Component exchange processes, which are temperature sensitive, take place by dissolution of chalk, substitution and adsorption at the chalk surface and precipitation of sulphate salts. Injection of seawater into chalk reservoirs is thus a complex system.

Field data from a North Sea chalk field have shown that there is sulphate ion stripping in the reservoir due to scale formation when the injected seawater mixes with the formation water (Jordan and Mackay, 2007; Mackay and Jordan, 2003). Injection water sulphate ions did break out eventually, but the seawater fraction at which it occurred, varied (Jordan and Mackay, 2007). In sandstones, barium stripping has been commonly observed, however, recent results have shown that also sulphate stripping takes place in sandstone due to $CaSO_4$ formation (Mackay et al., 2006). As the injection fluid moves through the chalk reservoir, $SO_4^{2-}$ may also be stripped off by adsorption. $SO_4^{2-}$ has a high affinity for the chalk surface, especially at high temperatures (Strand et al., 2006a). $SO_4^{2-}$ adsorbs onto the surface and promotes wettability alteration towards a less oil-wet state. Sulphate stripping due to seawater injection into a hot reservoir thus reduces the scaling potential at the production well, and in addition, due to adsorption, enhanced oil recovery may be observed by wettability alteration of the chalk surface.

Even though $SO_4^{2-}$ is strongly retained in the chalk formation, serious scale problems have been observed in hot producing wells (T = 130 °C). Some of these scale problems may be linked to the fact that seawater has been widely used in well treatments like HCl acid stimulation operations and scale inhibitor squeeze tests. Seawater injection into a hot well causes precipitation of $CaSO_4$ (Austin et al., 1975). Calcium sulphate can crystallize as anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) or gypsum ($CaSO_4 \cdot 2H_2O$). At temperatures above 40-50 °C, the anhydrite is the most stable form, i.e. with the lowest solubility. The meta-stable hemihydrate is the most soluble, while gypsum has a solubility in between the former two (Carlberg and Matthews, 1973). All three forms have decreasing solubilities with increasing temperatures above ~ 40 °C (Lu and Fabuss, 1969). The formation water contains only traces of $SO_4^{2-}$, but small amounts of $Ba^{2+}$ and $Sr^{2+}$, which will precipitate in the presence of $SO_4^{2-}$. Back-production of the injected fluid from the production well with formation water containing $Ba^{2+}$ and $Sr^{2+}$ will convert some of the precipitated $CaSO_4$ into $BaSO_4$ and $SrSO_4$ scale due to a

lower solubility of the two latter compounds. Thus, $BaSO_4$, which is the most feared scale component, is probably self-induced in the production well. If the well treatments had been performed with fresh water instead of seawater, the scale potential would most likely be drastically reduced due to sulphate stripping in the reservoir.

## 3.3 Injection of seawater into limestone reservoirs

Chalk is a fairly rare reservoir rock. Ordinary limestone reservoirs are far more abundant around the world. Generally, oil recovery from carbonate rocks is very low, due to very unfavourable wetting conditions for a successful waterflood as a secondary recovery method. However, injection of seawater into the chalk reservoir, Ekofisk, has been an enormous success, as a result of wettability alteration of the rock surface as explained in section 3.2.1. Chalk is a very homogeneous and pure biogenic $CaCO_3$ rock with a rather large specific surface area. Limestone is less homogeneous, regarding both porosity and permeability. In consequence, the reactivity of the rock surface towards the potential determining ions of seawater $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ is expected to be higher for chalk than for limestone. However, the adsorbed carboxylic material from the crude oil is the same, and even a small improvement of wettability can result in increased oil recovery. Based on the positive results from chalk, it is of great interest to investigate if increased recovery from limestone can be obtained by a wettability alteration of the rock surface using seawater in the same way as for chalk.

# 4 Materials and Methods

In this section the materials used, oil, brine, rock etc. and experimental methods will be briefly described. A more detailed description can be found in the different papers.

## 4.1 Materials

### 4.1.1 Rock material

Most of the work in this thesis has been performed on Stevns Klint outcrop chalk material. This 98 % pure biogenic chalk of Maastrichtian age is highly porous (45-50 %) and of low matrix permeability (1-2 mD), and has a rather reactive surface area of around 2 m$^2$/g (Frykman, 2001; Røgen and Fabricius, 2002).

Reservoir limestone cores from a Middle Eastern field were used in the limestone experiments. The core properties are listed in Table 4.1.

*Table 4.1 Reservoir limestone core properties.*

| Core | L | D | $V_b$ | $\phi$ | k | PV |
|------|------|------|-------------|------|------|-------|
|      | [cm] | [cm] | [cm$^3$] | [%] | [mD] | [ml] |
| 2-21 | 4.91 | 3.78 | 55.25 | 24.7 | 2.7 | 13.65 |
| 46A | 4.76 | 3.78 | 53.42 | 27.8 | 2.47 | 14.85 |
| 20A | 4.88 | 3.78 | 54.76 | 26.2 | 3.03 | 14.35 |

### 4.1.2 Oils

In order to obtain the correct initial wetting conditions in the different experiments at different temperatures it was necessary to manipulate crude oils. The acid number is the most important wetting parameter for chalk, thus by changing the acid number it is possible to vary the initial wetting of the chalk core. Therefore, Heidrun oil with AN ~3.0 mgKOH/g oil and BN ~1.0 mgKOH/g oil was used to vary the acid number, and Valhall oil with AN ~0.2 mgKOH/g oil and BN ~2.4 mgKOH/g oil was used to adjust the base number. The Heidrun oil was diluted with n-Heptane in a ratio 60:40, then centrifuged and filtrated through a 5 μm Millipore filter. No asphaltenes were precipitated during storage. The resulting oil was termed Oil A (AN ~1.9 mgKOH/g oil,

BN ~0.50 mgKOH/g oil). Oil A was treated with silica gel to remove surface-active polar components, i.e. acidic and basic components, centrifuged and filtrated through a 5 μm Millipore filter. The resulting oil was termed Oil B (AN ~0.20 mgKOH/g oil, BN ~0.10 mgKOH/g oil). The Valhall oil, Oil C, was centrifuged and filtrated through an 8 μm Millipore filter to remove solids. The oil properties are given in Table 4.2.

**Table 4.2** *Oil properties*

| Oil | AN (mgKOH/g oil) | BN (mgKOH/g oil) | Density g/cm$^3$ |
|-----|------------------|------------------|------------------|
| A | 1.9 | 0.50 | 0.808 |
| B | 0.20 | 0.10 | 0.801 |
| C | 0.20 | 2.4 | 0.856 |

Oils A, B and C were mixed in different ratios to obtain oils with desired AN and BN ratios.

### 4.1.3 Brines

All brines that have been used are artificial, made by dissolving different amounts of the following salts in distilled water, NaCl, $Na_2SO_4$, KCl, $NaHCO_3$, $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$. KSCN have also been used as tracer in the chromatographic tests. All chemicals were PA-grade and provided by Merck. For use in experiments, $Fe^{2+}$, $Ba^{2+}$ and $Sr^{2+}$ and other trace components have been left out from the brines in order to successfully perform core flooding experiments. Table 4.3 contains brines used in spontaneous imbibition and viscous flooding experiments. Table 4.4 contains brines that were used in the chromatographic tests and in the modelling studies.

**Table 4.3** *Molar compositions (mol/l) of brines used in experimental spontaneous imbibition and viscous flooding studies*

|  | SSW | SSW/US | SSW2S | SSW4S | VB | VB/US | EF | PW$_{VH}$ |
|---|---|---|---|---|---|---|---|---|
| HCO$_3^-$ | 0.002 | 0.002 | 0.002 | 0.002 | 0.009 | 0.009 | - | 0.013 |
| Cl$^-$ | 0.525 | 0.597 | 0.453 | 0.309 | 1.065 | 1.066 | 1.196 | 1.096 |
| SO$_4^{2-}$ | 0.024 | - | 0.048 | 0.096 | 0.001 | - | - | 0.001 |
| Mg$^{2+}$ | 0.045 | 0.045 | 0.045 | 0.045 | 0.008 | 0.008 | 0.025 | 0.008 |
| Ca$^{2+}$ | 0.013 | 0.013 | 0.013 | 0.013 | 0.029 | 0.029 | 0.231 | 0.031 |
| Na$^+$ | 0.450 | 0.474 | 0.426 | 0.378 | 0.996 | 0.996 | 0.684 | 1.027 |
| K$^+$ | 0.010 | 0.010 | 0.010 | 0.010 | 0.005 | 0.005 | - | 0.005 |
| Ionic strength | 0.657 | 0.657 | 0.657 | 0.657 | 1.112 | 1.112 | 1.452 | 1.150 |
| TDS (g/l) | 33.4 | 34.2 | 32.6 | 31.0 | 62.8 | 62.8 | 68.0 | 65.0 |

**Table 4.4** *Molar composition (mol/l) of brines used in the chromatographic tests and in the modelling studies*

|  | SSW -U | SSW -M | SSW ½M | NaCl | NaCl -M | SSW | PW$_{VH}$ | PW$_{EF}$ |
|---|---|---|---|---|---|---|---|---|
| HCO$_3^-$ | 0.002 | 0.002 | 0.002 | - | - | 0.002 | 0.013 | 0.008 |
| Cl$^-$ | 0.623 | 0.525 | 0.574 | 0.571 | 0.556 | 0.525 | 1.096 | 0.765 |
| SO$_4^{2-}$ | - | 0.024 | 0.012 | - | - | 0.024 | 0.001 | 0.007 |
| SCN$^-$ | - | 0.024 | 0.012 | - | 0.013 | - | - | - |
| Mg$^{2+}$ | 0.045 | 0.045 | 0.045 | - | 0.013 | 0.045 | 0.008 | 0.021 |
| Ca$^{2+}$ | 0.013 | 0.013 | 0.013 | - | 0.013 | 0.013 | 0.031 | 0.049 |
| Na$^+$ | 0.500 | 0.450 | 0.475 | 0.571 | 0.504 | 0.450 | 1.027 | 0.635 |
| K$^+$ | 0.010 | 0.034 | 0.022 | - | 0.013 | 0.010 | 0.005 | 0.007 |
| Ba$^{2+}$ | - | - | - | - | - | - | - | 8.2E-06 |
| Sr$^{2+}$ | - | - | - | - | - | - | - | 2.2E-03 |
| Li$^+$ | - | - | - | - | - | - | - | 9.8E-04 |
| Ionic strength | 0.683 | 0.681 | 0.683 | 0.571 | 0.595 | 0.657 | 1.150 | 1.150 |
| TDS (g/l) | 35.7 | 35.7 | 35.7 | 33.4 | 33.4 | 33.4 | 65.0 | 45.8 |

### 4.1.4   Additional chemicals

**Benzyl amine:** This model base, a primary amine, which is not normally found in crude oil, was added to a crude oil in different amounts to get oils with varying BN.

**$C_{12}$TAB:** The cationic surfactant, Dodecyl trimethyl ammonium bromide, was added to a seawater brine to see the effect of the surfactant.

**n-Heptane:** Completely free from surface-active components n-Heptane was used as the oil phase in cores representing a completely water-wet situation.

**Toluene (water-saturated)**: Used for core cleaning of limestone reservoir cores

**Methanol**: Used for core cleaning of limestone reservoir cores

## 4.2  Core preparation

In order to mimic the real reservoir as closely as possible, it is necessary that the working conditions in the lab are as close as possible to the reservoir conditions. In addition, to be able to compare the results from different tests, it is important that the starting point is the same, i.e. core plugs are prepared in the same way every time, giving reproducible results. When working with real reservoir cores that contain oil and formation water, it is common practice to clean the cores with water-saturated toluene and methanol prior to core preparation.

### 4.2.1   Outcrop chalk cores

The chalk material that has been used in this work is outcrop chalk from Denmark. A standard core preparation procedure developed by Standnes and Austad (2000a) was utilized with some modifications. All cores in an experiment series were drilled from the same chalk block by an oversized bit, then shaped in a lathe to a diameter ~38 mm and cut by a diamond saw to a length ~65 mm. The cores were dried at 120 °C to constant weight and were then ready for establishment of initial water saturation ($S_{wi}$). Different initial water saturations were used in this project and a modification of Standnes and Austad's method was necessary (Puntervold et al., 2007). Further core preparation varied according to the desired $S_{wi}$.

An oil-saturated core with high $S_{wi}$ (30-50 %) used in the model base experiments, was obtained by saturating the core with the formation water

under vacuum followed by oil flooding in a Hassler cell, 1.5 PV at a rate of 1.0 ml/min, in both directions to get a uniform wettability.

An oil-saturated core with low $S_{wi}$ (~10%) was established by saturating the core with formation water under vacuum, followed by drainage with water-saturated $N_2$-gas, gradually increased in pressure up to 10 bar, on a confined porous plate. After drainage, the core was flooded in a Hassler cell with 1.5 PV of oil in both directions at a rate of 1.0 ml/min at 90 °C in the base number experiments, and at a rate of 0.4 ml/min at 50 °C in the remaining experiments, using a backpressure of 6-10 bar.

Because this chalk is rather weak, the confining pressure in the Hassler cell did not exceed 25 bar. After flooding, the cores were wrapped in Teflon tape to avoid adsorption of unrepresentative organic material on the chalk surface, immersed in oil inside a sealed steel container, and aged at 90 °C for 4 weeks. Some of the cores were not wrapped in Teflon tape before aging. These cores had 2 mm removed (by lathe and saw) from all sides after aging. Having finished the aging period, the cores were ready for wettability studies.

During the course of this thesis work, as the results will show, it was found that the outcrop chalk material contained initial sulphate. Knowing the wettability altering ability of sulphate toward the chalk surface, clearly the initially present sulphate would have an effect on the initial wetting establishment. From the point of discovery and onwards, all outcrop core material was, prior to any wettability studies, pre-flushed with at least 4 PV of distilled water (DW) at 50 °C to remove dissolvable sulphate salts from the core.

### 4.2.2 Limestone reservoir cores

The reservoir cores were, prior to any experiments, cleaned at room temperature by flooding at a rate of 0.1 ml/min at least 5 PV of water-saturated toluene until the effluent was colorless (min. 3 PV). Thereafter, the cores were flooded with 3 PV of methanol, and then dried at 110 °C to constant weight. Afterwards the cores were evacuated and saturated with the actual fluids. The porosity was determined by weight difference of wet and dry core.

In the adsorption studies the affinities of the potential determining ions in seawater, $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$, towards the limestone surface were studied chromatographically.

## 4.3 Methods

### 4.3.1 Determination of acid and base numbers

A Mettler Toledo DL55 automatic titrator was used to determine acid and base numbers by potentiometric titrations using an internal standard. The methods used were developed by Fan and Buckley (2006), and they are modified versions of ASTM D2896 for base number titration and ASTM D664 for acid number titration.

### 4.3.2 Spontaneous imbibition

At low temperatures (50-70 °C) spontaneous imbibition was performed in standard Amott glass cells, while at higher temperatures (90-130 °C) sealed steel containers with ~10 bar back pressure to prevent boiling were used. After aging, and after Teflon tape or 2 mm of the surface had been removed, the core was placed inside the cell and surrounded with imbibition brine. The amount of oil (% OOIP) expelled from the core was recorded versus time in a graded burette.

### 4.3.3 Chromatographic studies

The chromatographic wettability test was developed by Strand et al. (2006b). The test determines the amount of water-wet surface area in a core based on the chromatographic separation between the adsorbing sulphate ($SO_4^{2-}$) and a non-adsorbing tracer, thiocyanate ($SCN^-$). The principles of the test were explained in section 1.4.1.2.

#### 4.3.3.1    Chalk

After aging, and Teflon tape or 2 mm of the surface had been removed, the core was placed inside the Hassler core holder again, with a confining pressure not exceeding 25 bar. 1 PV of SSW-U (seawater without $SO_4^{2-}$ and $SCN^-$) was flooded through the core at a rate of 0.2 ml/min. Another 1 PV SSW-U was flooded through the core at a rate of 0.4 ml/min. Next the core was flooded with at least 2 PV of SSW-M (seawater with both $SO_4^{2-}$ and $SCN^-$) at a rate of 0.2 ml/min. The effluent was collected in fractions of 1-3 ml by use of a fraction collector. The fractions were analysed for concentrations of $SO_4^{2-}$ and $SCN^-$, and the concentration relative to the initial concentration was plotted versus injected PV.

### 4.3.3.2    Limestone

A Hassler core holder was used with a confining pressure of 18 bar. A backpressure valve (7 bar) was used to ensure constant pore pressure, and to prevent the fluid from boiling at high temperatures. Samples of the effluent were taken using a fraction collector and the ionic compositions were analysed. The flow rates in the chromatographic tests were 0.1 and 0.2 ml/min.

The affinity of $SO_4^{2-}$ towards the limestone surface at room temperature was studied using SSW½M, 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 "cleaned" with at least 5 PV of seawater without $SO_4^{2-}$ and $SCN^-$ (SSW-U).

The relative affinities of $Ca^{2+}$ and $Mg^{2+}$ were studied by using NaCl-M, a NaCl-brine with equal amounts of $Ca^{2+}$, $Mg^{2+}$ and $SCN^-$ ions. The tests were conducted at 20, 70, 100, and 130 °C. Before each test, the core was cleaned at ambient temperature by flushing 5 PV pure NaCl-brine with the same salinity through the core.

In order to study the possible substitution of $Ca^{2+}$ by $Mg^{2+}$ at the surface, SSW was injected very slowly into the core at different temperatures: ambient, 80, 100, and 130 °C. The injection rate was about 1 PV/D for at least 7 days. Before each test, the core was cleaned by injecting 5 PV of SSW at a rate of 0.1 ml/min at ambient temperature.

### 4.3.4   Viscous flooding

Viscous flooding, also referred to as forced imbibition/displacement in the literature, was performed in a Hassler core holder. The core was placed in a rubber sleeve inside the Hassler cell with a 20 bar confining pressure and with a constant back pressure, ~10-12 bar, to prevent boiling at temperatures in the range 90-130 °C. Brine, formation water (FW), PW or SSW, was injected slowly into the core at a controlled rate where the differential pressure across the core never exceeded 8 psi, and never went below 1 psi. This procedure gave rates of approximately 10 % of the core PV per day, ~3 ml/day. The produced oil was collected in a burette, and the volume was recorded versus time.

### 4.3.5   Ionic composition analysis

The ionic concentrations of $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, and $SCN^-$ were analysed by an ion-exchange chromatograph, ICS-3000 Reagent-free™ produced by

Dionex Corporation, USA. Calibration curves were stored in the computer system. In order to stay in the linear region of the calibration curve, the effluent samples were diluted 1:10 or 1:20 by distilled water prior to the analyses.

### 4.3.6 Simulation software

The compatibility of PW and SSW was modelled using the OLI Systems Stream Analyzer 1.3, a chemical model software based on thermodynamic equilibrium conditions using published experimental data.

# 5 Main results and discussion

## 5.1 The effect of base number on chalk wettability

It has been shown in previous studies that oil properties, especially the acid number (AN) and the temperature, are important for chalk wettability. The degree of oil wetting of the chalk surface is very much dependent on how much of the acidic material present in the crude oil that is able to adsorb onto the surface. Results have shown that the water wetness and oil recovery by spontaneous imbibition decreased as the AN increased up to a certain limit (Standnes and Austad, 2000a; Zhang and Austad, 2005). However, no systematic studies on the impact of base number (BN) on chalk wettability have been performed. Many crude oils in carbonates contain a high base number, i.e. Valhall oil with BN ~2.4 mgKOH/g oil, consequently it is of interest and importance to investigate the possible impact of base number on the wetting conditions of chalk.

Spontaneous imbibition experiments were performed on outcrop Stevns Klint chalk cores using crude oils with added model base, benzyl amine, or crude oils containing natural petroleum bases. In order to study the effect of the basic material on the chalk wettability, the base number was varied but the acid number was kept constant at AN = 0.5 mgKOH/g oil.

### 5.1.1 Model base

Four chalk cores were flooded to relatively high initial water saturations, $S_{wi}$ ~30-50 %, and saturated with oils with constant acid number (AN = 0.5 mgKOH/g oil), but varying base number. The cores were initially spontaneously imbibed at 70 °C with seawater without sulphate, SSW/US. Later the imbibing fluid was changed. The results from the imbibition tests are shown in Figure 5.1. Taking into account the wettability altering effect of sulphate in seawater, the sulphate was left out from the imbibing fluid initially in order to see the direct influence of BN on the wetting conditions.

The fact that the oil recovery decreased as the content of base increased from AN:BN-ratio 1:0 to 1:4, confirmed that the chalk cores became less water-wet as the content of benzyl amine increased. As the base content increased beyond 1:4, the effect of benzyl amine on the initial wetting appeared to be small, i.e. the oil recovery profiles for the two cores saturated with oils with AN:BN-ratio 1:4 and 1:10 were almost identical. This suggests that there is only a certain amount of acidic material that can be adsorbed onto the surface, and that the surface in these two experiments is saturated with

acidic material. The oil recovery from the core without added base is about twice the amount of oil recovered from the cores saturated with oils with AN:BN-ratio 1:4 and 1:10. Thus, the model base must be an active component in the wetting mechanism in such a way as to increase the organic coating of the chalk surface.
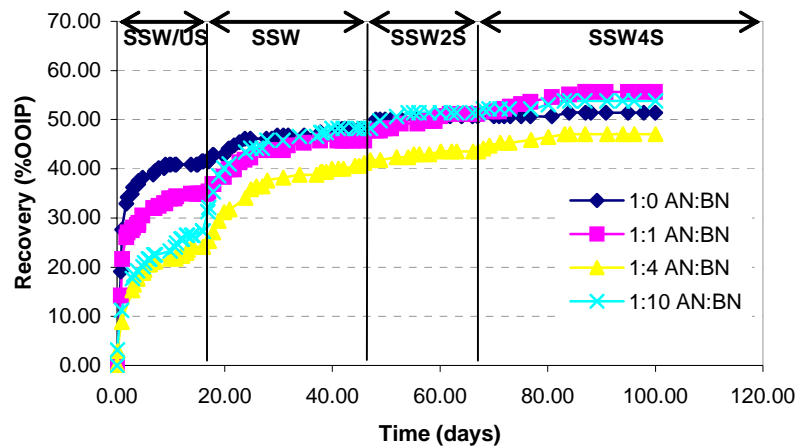


**Figure 5.1** *Spontaneous imbibition experiments with model base at 70 ℃ showing oil recovery as a function of time for chalk cores saturated with different AN:BN-ratio oils. High $S_{wi} \sim 30\text{-}50$ %, EF-brine as initial water.*

In Figure 5.2, the initial water saturation in the cores was reduced to 10-20 % by porous plate drainage using water-saturated $N_2$. For comparison with the high $S_{wi}$ results, these cores were saturated with the same oils and spontaneously imbibed at 70 ℃ with SSW/US. The same trend was observed, i.e. an increase in BN decreased water wetness. However, due to lower $S_{wi}$, the oil recovery was much lower, which agrees with earlier findings (Jadhunandan and Morrow, 1991). At low water saturation, the amount of surface-active material in the crude oil increases due to higher oil saturation, and low water saturation also makes the water film on the chalk surface thinner so that oil can adsorb more easily onto the chalk surface. The results also confirmed that the decrease in wetting conditions as the base content increased beyond 1:4 levelled off.

Furthermore, when the imbibing fluid was increased in sulphate concentration to SSW, SSW2S and SSW4S, there was a jump, although of

varying magnitude, in oil production from all cores, suggesting that wettability alteration takes place in the chalk cores even at high model base content. The same kind of effect of increased sulphate content in the imbibing fluid has been experienced before, though not with these high amounts of base content (Zhang and Austad, 2006).
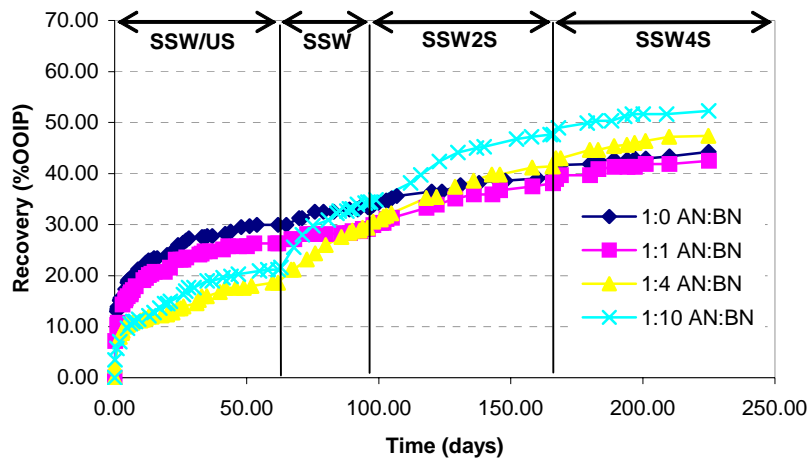


**Figure 5.2** *Spontaneous imbibition experiments with model base at 70 ºC showing oil recovery as a function of time for chalk cores saturated with different AN:BN-ratio oils. Low $S_{wi}$ ~ 10-20 %, EF-brine as initial water.*

Yet, it must be kept in mind that benzyl amine is only a model base and may not be representative for the natural crude oil bases.

### 5.1.2 Natural crude oil bases

In order to study the effect of natural crude oil bases on the initial wetting of chalk, oils with constant AN and varying amount of natural crude oil bases were made by mixing three crude oils, oils A, B and C in Table 4.2, in different volume ratios. Crude oils with constant AN = 0.5 mgKOH/g oil and various AN:BN ratios in the range 0.24 – 4.6 were obtained. The initial water saturation in all cores was kept similar ~10 %. In Figure 5.3, the results from spontaneous imbibition at 70 °C are shown using Valhall brine (VB), containing a very small amount of sulphate, Table 4.3, as the initial formation water and imbibing fluid. The results showed, contrary to the model base

results, that as the content of base in the oil decreased, water wetness decreased. Approximately 15-20 % recovery differentiated the cores saturated with oils with the highest and lowest basic contents, (AN:BN) = 0.32 and 4.6, respectively.
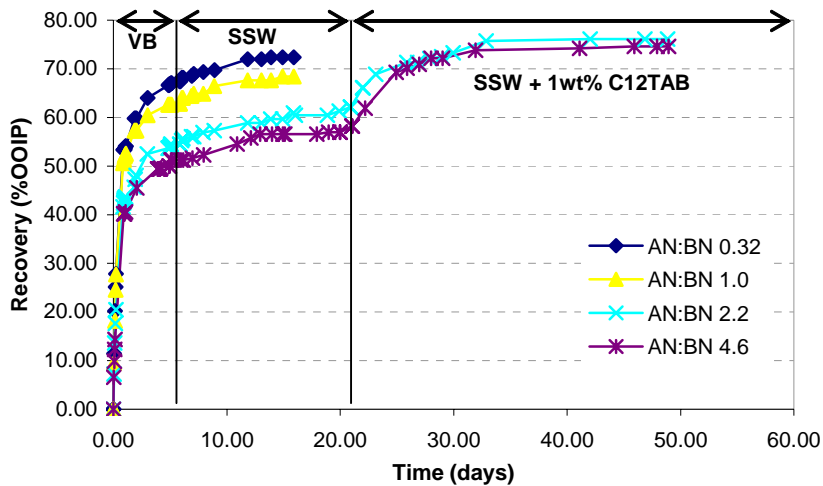


**Figure 5.3** *Spontaneous imbibition experiments with petroleum bases at 70 ºC showing oil recovery as a function of time for chalk cores saturated with oils of different AN:BN-ratios. $S_{wi} \sim 10$ %, VB as initial water.*

By considering the shapes of the imbibition curves in Figure 5.3, and the values of final oil recovery ~50-70 %, using formation water, VB, as the imbibing fluid, these results suggested that the cores were very water-wet. Similar water-wet cores were also observed at 50, 90 and 110 °C. Despite the water wetness, increasing the amount of sulphate in the imbibing fluid by switching to SSW gave a 5-10 % increase in recovery from cores saturated with oils containing rather large amounts of natural crude oil bases. Yet an even more dramatic increase, ~15 %, was observed when adding 1 wt% of the cationic surfactant $C_{12}TAB$ to SSW, which confirmed the chalk surface wettability altering ability of this surfactant, which has been experienced in earlier work with chalk (Standnes and Austad, 2000b).

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### 5.1.3   Wetting mechanisms

The fact that addition of a small model base, benzyl amine, to an acidic crude oil had an opposite effect on the wetting conditions compared to natural crude oil bases, suggests that the wetting mechanism is different in the two cases. Benzyl amine is a model base, which is not found naturally in crude oil. This primary amine is a relatively strong base compared to pyridine-like bases commonly found in crude oils, as shown by the $pK_a$-values for benzyl amine and pyridine: 9.33 and 5.25, respectively. The benzyl amine molecule is also rather small in comparison to the relatively large nitrogen-containing bases, which are mostly present in the asphaltene and resin fractions of the crude oil (Speight, 1991).

It is believed that benzyl amine reacts with carboxylic acids in the crude oil according to the following chemical reaction:

$$Ph\text{-}CH_2\text{-}NH_2 \; + \; R\text{-}COOH \;\; = \;\; Ph\text{-}CH_2\text{-}NH_3^+ \; + \; R\text{-}COO^- \qquad (5.1)$$

The small cationic benzyl ammonium ion, which is soluble in the aqueous phase, appears to co-adsorb onto the chalk surface together with the large anionic carboxylate. Thus, benzyl amine can enhance the adsorption of large carboxylic molecules by co-adsorption onto the chalk surface. Co-adsorption can be facilitated due to little steric hindrance and strong electrostatic interaction between the negatively charged carboxylates and positively charged ammonium ions. Furthermore, the electrostatic repulsion between negatively charged carboxylates at the chalk surface is decreased by the co-adsorption of the cationic benzyl ammonium ion.

The natural petroleum bases, on the other hand, appear to react with the carboxylic material in the crude oil forming acid-base complexes in chemical equilibrium with the acidic and basic material. The complex has a very large molecular weight, and it is very little soluble in the aqueous phase. Moreover, due to steric hindrance close to the positively charged N-atom, the co-adsorption of natural bases together with carboxylic material is limited. Thus, it seems like the natural bases prevent adsorption of carboxylic material onto the positively charged chalk surface.

## 5.2  Core cleaning – initial sulphate in outcrop chalk

Despite using oils with a rather high acid number (AN = 0.5 mgKOH/g oil) to create chalk cores of low water wetness in Figure 5.3, the cores

behaved very water-wet, with high oil recovery in a short time using formation water as imbibing fluid. The amount of acidic material in an oil with AN of 0.5 mgKOH/g oil has in previous studies been sufficient to create less water-wet cores, thus the very water-wet cores resulting from the natural base experiments were a curiosity. The cores used in those experiments were drilled out from a new block of outcrop chalk. This chalk block was taken further down in the Sigerslev quarry in Denmark. This quarry is situated close to sea, and knowing the wettability altering effect of seawater on chalk, a hypothesis was proposed, that there might be sulphate already present in the outcrop chalk as a result seawater influx/contamination.

Usually, the salinity of the reservoir brine is much higher than the expected dissolved salt in the outcrop chalk. Therefore, direct saturation of chalk by the reservoir brine should give a representative composition of the initial water in the core. If the core contains a small amount of sulphate, which is absent in the initial formation brine, the final wetting properties of the core can be changed drastically by preventing organic material adsorption. Thus, it was decided to investigate if sulphate was initially present in the outcrop chalk material. Hence, two dried cores (PV ~34 ml) were flooded at 50 °C with 4 PV of distilled water (DW) to remove all dissolvable sulphate salts from the core. The amount of sulphate ($SO_4^{2-}$) in the effluent was analysed and is plotted in Figure 5.4. On average, 5.3 mg sulphate was eluted from each core.
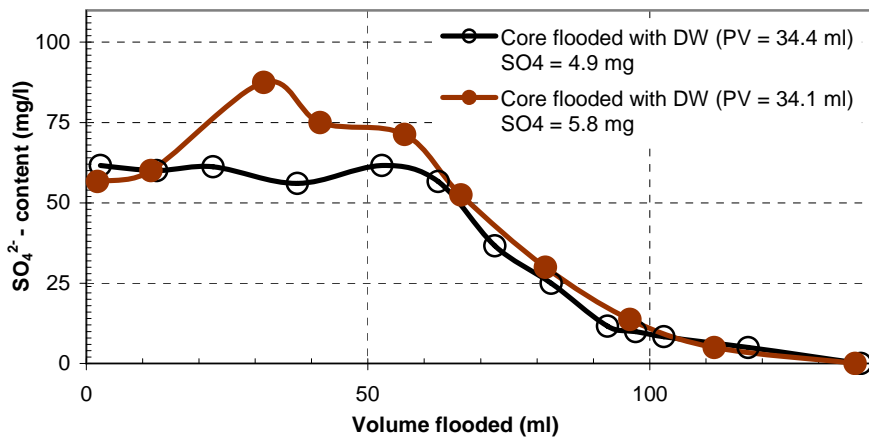


**Figure 5.4** *Effluent sulphate content from two cores flooded with distilled water at 50 °C.*

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To obtain low initial water saturations, $S_{wi}$ ~10 %, the pressurized porous plate technique was used, in which a 100 % water saturated core was drained down to residual water saturation. In this process, if sulphate is present inside the core, the sulphate is adsorbed onto the chalk surface, and as a result of that, sulphate is increased in concentration in the remaining water inside the core. In order to decide how much sulphate that is retained in the core after drainage, 15 cores were drained on the porous plate, and the amount of sulphate was measured in the effluent. The calculated amount of sulphate eluted from one average core is plotted in Figure 5.5. For comparison the eluted amount of sulphate by core flooding of one core is included in the figure.
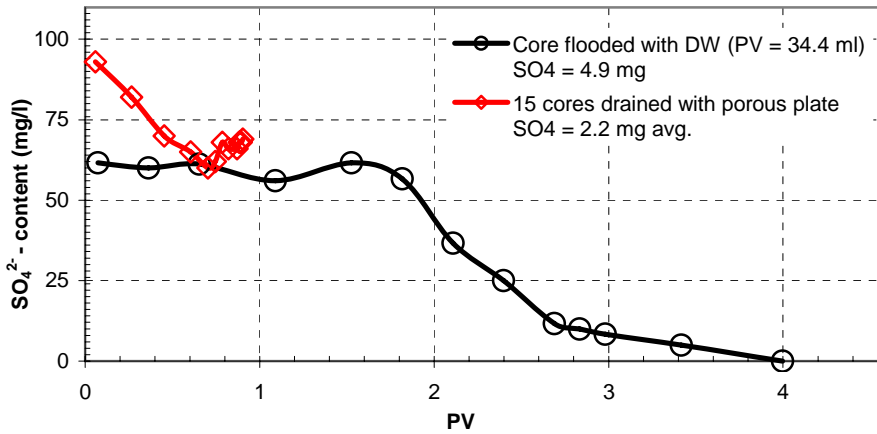


**Figure 5.5** *Difference in effluent sulphate content between core flooding and core drainage.*

The average amount of sulphate drained from each core was determined to 2.2 mg. Thus, the amount of sulphate left in an average core after drainage was: 5.3 - 2.2 mg = 3.1 mg. The residual water saturation for each core was on average 10.4 %. With an average PV of 34 ml, the apparent concentration of sulphate in the residual water was determined to be 0.88 g/l, which corresponds to as much as one-third of the sulphate concentration in seawater. In other words, there is a considerable amount of sulphate initially present in the core. In the presence of $Ca^{2+}$ and $Mg^{2+}$, $SO_4^{2-}$ prevents adsorption of organic material onto the chalk surface, and the chalk remains rather water-wet. In order to achieve reliable, reproducible and comparable results in wettability studies, it is very important that the cores are cleaned properly so

that they have the same initial conditions. Based on these results, all further wettability studies on outcrop chalk were initiated by flushing at least 4 PV of sulphate-free water through the core, in order to remove all dissolvable sulphate salts. The effect of flushing the cores can be seen in Figure 5.6, which shows spontaneous imbibition at 90 °C of one DW-flushed core and one non-flushed core, both saturated with 10 % formation brine and with a crude oil with (AN/BN) = 2.8.
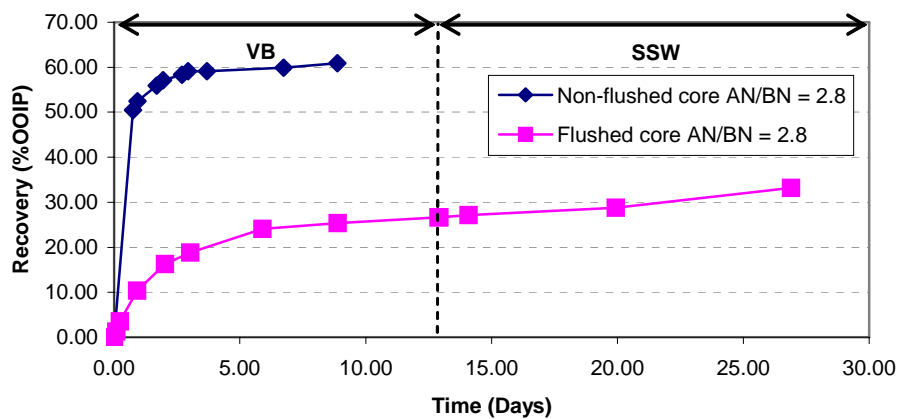


**Figure 5.6** *Spontaneous imbibition at 90 °C into non-flushed and flushed cores. The cores were first imbibed with formation brine, then by SSW.*

There was a 30 % recovery difference between the two cores, and the flushed core behaved less water-wet compared to the non-flushed core. Thus, small variations in the initial concentration of sulphate can result in great differences in wetting properties when using the same crude oil and initial brine.

By determining the water-wet fraction of the chalk surface in one DW-flushed core and one non-flushed core, using the chromatographic wettability test method (Strand et al., 2006b), the effect of flushing on wettability was confirmed, Figure 5.7. The results showed that flushing the cores with distilled water significantly reduced the wetting index (WI), i.e. the water-wet fraction of the surface, from WI = 0.84 to WI = 0.65, in other words from very water-wet to neutral/slightly water-wet.

These results demonstrate the impact that initial sulphate in outcrop chalk material can have on the initial wetting conditions, and the need for proper core cleaning in order to obtain reproducible wetting conditions. The core preparation procedure developed by Standnes and Austad (2000a) was

therefore modified to include flushing of at least 4 PV of sulphate-free water, at 50 °C, through the core prior to establishment of $S_{wi}$, especially when using the porous plate method, which actually increased the sulphate concentration in the remaining initial water even more.
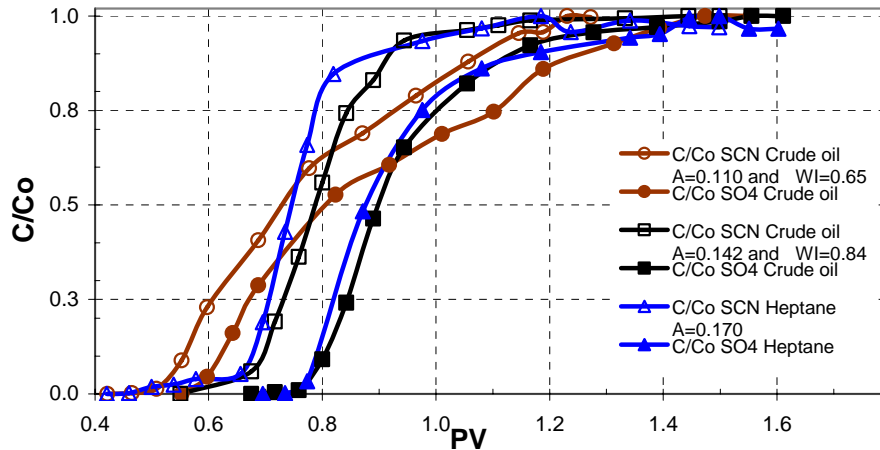


**Figure 5.7** *Comparable wettability indices for a flushed and a non-flushed core. $S_{wi} \sim 10 \%$. Crude oil with AN/BN = 2.8.*

## 5.3 Co-injection of produced water and seawater

As many of the oil fields in the North Sea have reached a mature state, and water injection has been ongoing for years already, the amount of produced water increases. Because produced water contains compounds that are regarded carcinogenic, and that may be bio-accumulated in living marine organisms, strict environmental requirements regarding disposal of this water, have to be met. The produced water must be satisfactorily cleaned, and these cleaning methods are expensive. Alternatively, it can be re-injected into the reservoir in a secondary waterflooding process. At the Valhall field, produced water and seawater are being injected into the reservoir through separate wells to circumvent scale problems. The positive effect on oil recovery from injecting seawater is well known, but dependent on high reservoir temperature. A lower reservoir temperature can to some degree be compensated for by increasing the sulphate concentration in the injection water in order to achieve correspondingly high oil recovery (Zhang and Austad, 2006). A question to be raised is: Is seawater the optimal injection fluid for chalk, or is it possible to inject a mixture of seawater and produced

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water, without impairing the injectivity, but still experience enhanced oil recovery?

### 5.3.1 Compatibility and scale potential

In order to avoid scale problems in the injector, seawater and produced water must be compatible at the injection well temperature. A disadvantage regarding the produced water is that it continuously changes in composition, thus compatibility may be difficult to predict. In the early stages of waterflooding, the injected seawater displaces both oil and the formation water (Nielsen et al., 2000), thus the produced water is mainly formation water. In later stages, the produced water composition is modified through chalk dissolution, precipitation of sulphate salts, and through ionic interactions between seawater and the chalk surface, i.e. substitution of $Ca^{2+}$ by $Mg^{2+}$ and adsorption of $SO_4^{2-}$ at the surface (Strand et al., 2006a; Zhang et al., 2007). Table 4.4 contains recent produced water compositional data from the Valhall field and the Ekofisk field. Water injection at the Valhall field commenced in 2004, and is thus still at as early stage, i.e. no seawater breakthrough, which is confirmed by the negligible amount of sulphate in the produced water composition. Concentrations of $Ba^{2+}$ and $Sr^{2+}$ were not provided in the compositional analysis in Table 4.4, but it is well known that the Valhall formation water contains both ions that will cause significant sulphate scale when mixed with seawater (Jordan et al., 2005; Norris et al., 2001). In consequence, a similar scaling behaviour observed at the Ekofisk field, regarding these two ions, is surely to be expected at the Valhall field, however influenced by a lower reservoir temperature, 90-95 °C.

The compatibilities of different produced water and seawater mixtures from the Vallhall field and Ekofisk field, as a function of temperature, were modelled, and the results are shown in Figure 5.8 – 5.11. Regarding Ekofisk, precipitation of $CaSO_4$, $SrSO_4$ and $BaSO_4$ were considered, while in the case of Valhall, only $CaSO_4$ was considered due to the lack of $Sr^{2+}$ and $Ba^{2+}$ data. The figures show the precipitation of $CaSO_4$, $SrSO_4$ and $BaSO_4$ from produced water and seawater mixtures, PW1SSW1, PW1SSW2, PW1SSW4 and PW1SSW8 (PWxSSWy = x parts PW and y parts SSW), including also pure PW and SSW. The Valhall temperature is 90-95 °C, and according to the results in Figure 5.8, there is no $CaSO_4$ precipitation for any of the brines at temperatures below 100 °C. The solubility of $CaSO_4$ increases when the temperature is lowered. The Ekofisk temperature is 130 °C, and at this temperature the PW is saturated with $CaSO_4$, $SrSO_4$ and $BaSO_4$, Figures 5.9 - 5.11. There will be precipitation of $CaSO_4$ from all the modelled brines in the

reservoir (sulphate stripping), Figure 5.9. In the injection well the temperature is lower, due to injection of cool produced water and/or seawater, and as long as the temperature is kept below 90-100 °C, the injectivity can be maintained.
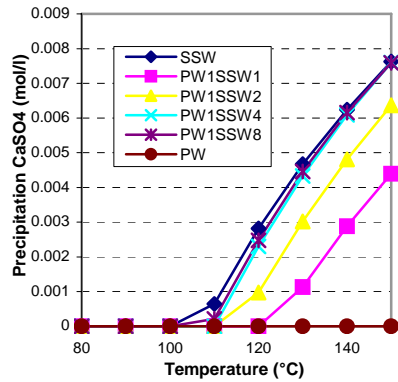


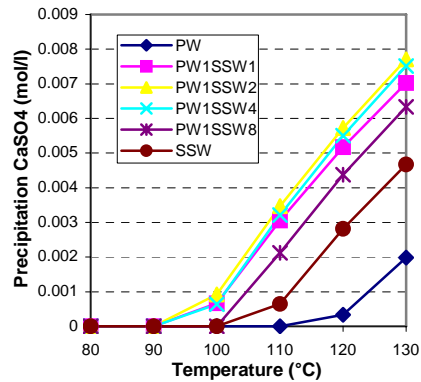**Figure 5.8** *Precipitation of CaSO₄ vs. temperature for mixtures of seawater and Valhall field PW.*



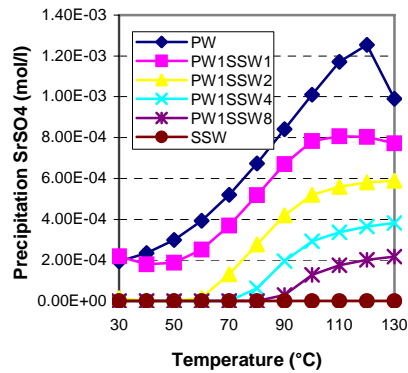**Figure 5.9** *Precipitation of CaSO₄ vs. temperature for mixtures of seawater and PW from Ekofisk field – Ekofisk formation.*



**Figure 5.10** *Precipitation of SrSO₄ vs. temperature for mixtures of seawater and PW from Ekofisk field – Ekofisk formation.*
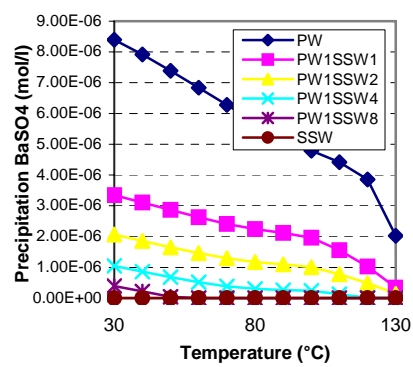


**Figure 5.11** *Precipitation of BaSO₄ vs. temperature for mixtures of seawater and PW from Ekofisk field – Ekofisk formation.*

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The solubility trend of $SrSO_4$ is the same as for $CaSO_4$, i.e. the solubility increases with a decrease in temperature, Figure 5.10, and the solubility seems to go through a minimum at 120 °C for PW, PW1SSW1 and possibly PW1SSW2. Even though the concentration of $Ca^{2+}$ is much larger than that of $Sr^{2+}$ in the PW, there is some precipitation of $SrSO_4$ across the entire temperature range, because of a lower solubility of $SrSO_4$ compared to $CaSO_4$. By increasing the amount of SSW in the mixtures, precipitation can be reduced drastically. Hence, the results show that if the PW is sufficiently diluted with SSW, scale problems related to $SrSO_4$ in the injector can probably be avoided, due to the lower temperature in these wells.

Figure 5.11 illustrates the precipitation of $BaSO_4$ versus temperature. Contrary to the solubility profile of $CaSO_4$ and $SrSO_4$, the solubility of $BaSO_4$ increases with temperature, i.e. precipitation decreases as temperature increases. The PW is saturated with $BaSO_4$ at all temperatures, 30-130 °C, which means that $BaSO_4$ is precipitated in the reservoir. The initial formation water saturations in the North Sea chalk reservoirs are generally very low, 5-7 %, and the concentration of $Ba^{2+}$ in the formation water (FW) is of a magnitude $10^{-6}$ mol/l. By diluting the PW sufficiently with seawater, e. g. PW1SSW8, the scale potential can be avoided or at least reduced to a very minimum, as suggested by the modelling results in Figure 5.11.

The performed compatibility modelling of produced water and seawater show that by diluting the produced water with a sufficient amount of seawater, scaling of the sulphate salts, $CaSO_4$, $SrSO_4$ and $BaSO_4$ in the injector can be minimized and the injectivity maintained, by injecting at relatively low temperatures < 80 °C. Additionally, it has been found that injection wells in fractured reservoirs tolerate a substantial amount of scale deposition before loss of injectivity is experienced (Mackay et al., 2002).

Temperature plays a lead role in predicting scale potential by influencing chalk dissolution, sulphate salt precipitation, and ionic interactions between seawater and the chalk surface, such as substitution of $Ca^{2+}$ by $Mg^{2+}$ and adsorption of $SO_4^{2-}$. In the reservoir, the injected seawater or PW-SSW mixtures are not in equilibrium with the formation, thus component exchange takes place. Chalk dissolution decreases at higher temperatures, while the substitution of $Ca^{2+}$ by $Mg^{2+}$ at the chalk surface increases with higher temperature (Korsnes et al., 2007; Zhang et al., 2007). At 100 °C and 130 °C, core flooding experiments revealed that the amount of $Ca^{2+}$ in the effluent had increased with 20 and 50 % relative to the initial concentration, respectively, because of substitution by $Mg^{2+}$. Analysis of the concentration of $Mg^{2+}$ in the effluent confirmed a 1:1 substitution, by revealing correspondingly reduced

concentrations (Korsnes et al., 2006a; Korsnes et al., 2006b; Zhang et al., 2007). At 70 °C there were no detectable changes in either concentration.

The small $Mg^{2+}$ ion is strongly solvated/hydrated in water, $\Delta H_{hydr} = -459$ kcal/mol (Burgess, 1978), which makes it less reactive at low temperature. The $Mg^{2+}$ ion is partly dehydrated as the temperature increases, and the rate of substitution increases due to the decrease in the activation energy of the reaction. Additionally, in seawater, $Mg^{2+}$ forms an important ion-pair with $SO_4^{2-}$ (Carlberg and Matthews, 1973):

$$Mg^{2+} + SO_4^{2-} = [Mg^{2+} \cdots SO_4^{2-}](aq) \qquad (5.2)$$
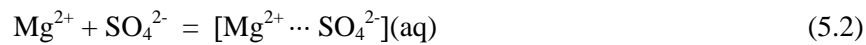
Because $[Mg^{2+}] \sim 2[SO_4^{2-}]$ in seawater, the formed ion-pair will lower the activity of $SO_4^{2-}$ significantly. As the temperature increases, the equilibrium of reaction (5.2) is moved to the right, affecting the solubility of $CaSO_4$ in seawater. By removal of $Mg^{2+}$ from seawater by the substitution process, the activity of $SO_4^{2-}$ is less reduced, and $SO_4^{2-}$ is thus available for sulphate salt precipitation. The effect of substitution of $Ca^{2+}$ by $Mg^{2+}$ from the chalk surface, on $CaSO_4$ solubility, was modelled as a function of temperature, by increasing and decreasing the respective amounts of $Ca^{2+}$ and $Mg^{2+}$ with the same number of moles, Figure 5.12.
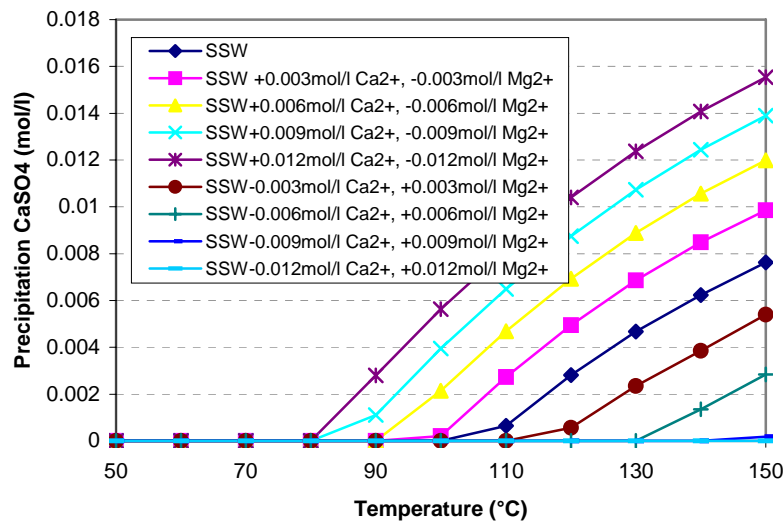


**Figure 5.12** *Precipitation of $CaSO_4$ as a response to varying $[Ca^{2+}]$ and $[Mg^{2+}]$ in SSW as a function of temperature*

Take Ekofisk as an example, with a reservoir temperature of 130 °C. At this temperature a 50 % increase in $Ca^{2+}$ concentration was experienced as a result of substitution by $Mg^{2+}$. The concentration of $Ca^{2+}$ in normal seawater is 0.013 mol/l, thus a 50 % increase corresponds to an increase of 0.0065 mol/l, which in Figure 5.12 is represented by the yellow line (triangle). Interpreting the modelling results shows that substitution of $Ca^{2+}$ by $Mg^{2+}$ at the chalk surface in the Ekofisk reservoir almost doubles the amount of precipitated $CaSO_4$ from 0.005 mol/l from pure seawater, to 0.009 mol/l. Considering the Valhall field, with a reservoir temperature of 90-95 °C, the substitution reaction results in a 20 % increase, at most, of the $Ca^{2+}$ concentration. This corresponds to an increase of 0.003 mol/l of $Ca^{2+}$, which in Figure 5.12 is represented by the pink line (square). As seen from the figure, at 90-100 °C there is no additional precipitation of $CaSO_4$ in the reservoir that is caused by substitution of $Ca^{2+}$ by $Mg^{2+}$ at the chalk surface. Thus, as an overall conclusion from this modelling work, it seems that the Ekofisk field will experience far more sulphate stripping in the reservoir than the Valhall field, due to a higher reservoir temperature. In the future of Valhall, more sulphate scale is probably to be expected compared to Ekofisk.

The modelling results were compared to field experience by doing some simple calculations. Injection of seawater into the Ekofisk field has been going on for more than 20 years, and the PW is therefore a mixture of FW and seawater. The volumetric mixing of FW and seawater can be approximated by assuming that $Na^+$ and $Cl^-$ are inert ions, i.e. they do not react with the formation in any way. Calculations showed that 0.264 litres of FW were mixed with 0.736 litres of SSW resulting in 1.00 litre of PW. Based on these values, the expected concentrations of the other ions in the PW can be calculated, $(PW)_{calc}$, assuming that no interaction with the formation takes place. A comparison to the corresponding experimentally measured composition of PW, $(PW)_{exp}$, will then indicate possible interactions with the formation. Both calculated and measured data can be found in Table 5.1. The differences between measured and calculated concentrations of the various ions in the PW, in Table 5.1, confirmed that substitution of $Ca^{2+}$ by $Mg^{2+}$ at the chalk surface takes place in the reservoir, i.e. $Ca^{2+}$ increased in concentration while $Mg^{2+}$ decreased, which was also observed in the laboratory (Korsnes et al., 2006b; Zhang et al., 2007). A slightly lower decrease in $Ca^{2+}$ compared to a 1:1 substitution may be due to $CaSO_4$ formation. The results in Table 5.1 also show that the actual concentration of $Ba^{2+}$ in the PW is significantly lower than expected, supporting the modelling results, ascribing the results to trapping of $Ba^{2+}$ in the formation by precipitation of $BaSO_4$. The concentration of $Sr^{2+}$ in the PW is similar for both $(PW)_{exp}$ and $(PW)_{calc}$, Table 5.1, reflecting very little interaction with the

formation. $SO_4^{2-}$, on the other hand, is strongly held back in the formation, as documented by a 10 time reduction in measured concentration compared to the calculated concentration, Table 5.1.

*Table 5.1 Composition of PW from the Ekofisk field, experimentally measured and calculated data based on mixing 0.264 litres of FW with 0.736 litres of SSW forming 1.00 litre of PW.*

| Component | $(PW)_{exp}$ (mol/l) | $(PW)_{calc}$ (mol/l) | $[(PW)_{exp}-(PW)_{calc}]$ (mol/l) |
|---|---|---|---|
| $Ca^{2+}$ | 0.049 | 0.036 | + 0.013 |
| $Mg^{2+}$ | 0.021 | 0.039 | - 0.018 |
| $Ba^{2+}$ | 8.2E-6 | 5.3E-4 | - 0.00052 |
| $Sr^{2+}$ | 0.0022 | 0.0024 | - 0,0002 |
| $SO_4^{2-}$ | 0.007 | 0.078 | - 0.071 |

It has been shown earlier, that $SO_4^{2-}$ adsorbs onto the chalk surface, and that the affinity for the chalk surface increases drastically as the temperature increases beyond 100 °C (Strand et al., 2006a). Furthermore, the decrease in $SO_4^{2-}$-concentration can also be linked to precipitation of $BaSO_4$ and $CaSO_4$. It is interesting to see that the interactions between the components in seawater and the chalk surface observed in the laboratory by using outcrop material is similar to observations in the field (Mackay and Jordan, 2003).

### 5.3.2   Co-injection of seawater and produced water as an EOR-technique

In order to evaluate co-injection of seawater and produced water as an EOR-technique for a low-permeable, moderately water-wet chalk reservoir, experimental studies were performed on outcrop chalk cores in the laboratory. The cores were pre-flushed with DW, then saturated with Valhall FW (VB/US) and drained to 10 % $S_{wi}$, before being flooded with and aged in crude oil to obtain sufficiently mixed-wet cores. Subsequently, the cores were spontaneously imbibed with different imbibing fluids with increasing amount of sulphate, Valhall PW, PW2SSW1, PW1SSW1, PW1SSW2, PW1SSW8, and oil production was recorded with time. Some of the cores that were spontaneously imbibed with PW, were also subjected to viscous flooding to

see if that could increase production even more. Valhall FW (VB/US) and PW ($PW_{VH}$) compositions can be found in Table 4.3. Traces of $Ba^{2+}$ and $Sr^{2+}$ have been left out from the brines in these experiments to avoid possible precipitation.

Previously, it has been documented that spontaneous imbibition of SSW by wettability alteration increased with temperature (Zhang and Austad, 2006; Zhang et al., 2006; Zhang et al., 2007). To test the influence of temperature on oil recovery by co-injection, spontaneous imbibition was performed at 50, 70, 90, 110 and 130 °C. At 50 °C, Figure 5.13, an oil with AN = 0.39 mgKOH/g oil was used to wet the cores. The results showed no discrimination or systematic trend for the different brine mixtures used. The cores were moderately water-wet as shown by the rather slow imbibition rate and low ultimate recovery. Thus, it seemed that the temperature was too low to promote a wettability alteration in these tests. The same conclusion was also reached based on the results at 70 °C, Figure 5.14, where an oil with AN = 0.69 mgKOH/g oil was used to wet the cores.
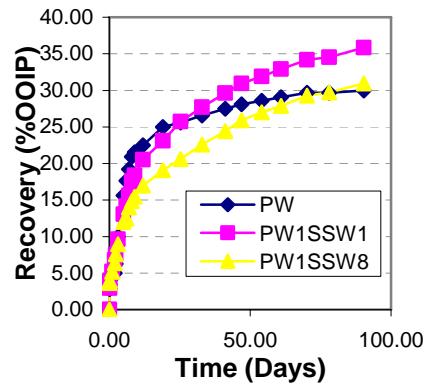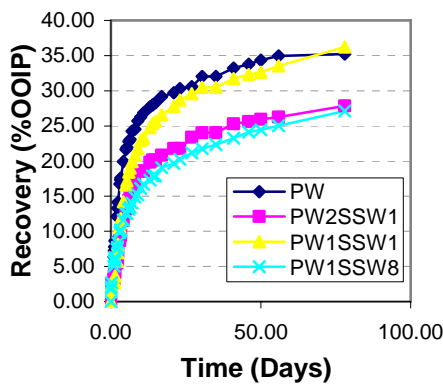


**Figure 5.13** *Spontaneous imbibition of mixtures of PW and SSW into chalk cores at 50 °C saturated with a crude oil of AN = 0.39 mgKOH/g oil*

**Figure 5.14** *Spontaneous imbibition of mixtures of PW and SSW into chalk cores at 70 °C saturated with a crude oil of AN = 0.69 mgKOH/g oil*

It has been quantified experimentally that the affinity of sulphate ions for the chalk surface increases drastically with temperatures above 100 °C (Strand et al., 2006a). At a temperature of 90 °C, a tendency of increased oil recovery with PW-SSW mixtures compared to pure PW was barely

noticeable, but as the temperature was raised to 110 and 130 °C, wettability alteration of the chalk surface was promoted, and the results showed a clear trend pointing towards increased oil recovery when PW was mixed with SSW, compared to pure PW. Figure 5.15 shows the spontaneous imbibition results at 110 °C, but the results at 130 °C showed a similar trend and are therefore also represented by Figure 5.15. However, the original results at 90 and 130 °C are illustrated by figures in Paper IV. At 110 °C, the core imbibed with PW stopped producing at 30 % recovery, which was only half of the recovery from the PW-SSW mixtures, which all produced 60 % OOIP, Figure 5.15. It is obvious that the presence of sulphate is crucial for wettability alteration to take place, and these findings support the results from previous work (Zhang et al., 2007). Because there is nearly no difference in recovery between the three mixtures, it is clear that all three brines contain sufficient amounts of sulphate, calcium and magnesium in order to promote wettability alteration, provided that the temperature is high enough, i.e. > 100 °C.
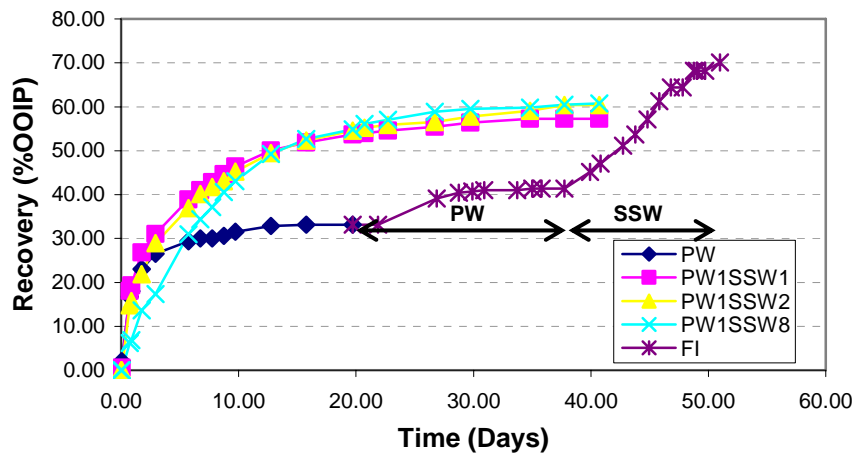


**Figure 5.15** *Spontaneous imbibition of mixtures of PW and SSW into chalk cores at 110 °C saturated with a crude oil of AN = 0.70 mgKOH/g oil. After spontaneous imbibition using PW, viscous flooding was performed with PW and SSW at 110 °C. ΔP = 4 psi.*

When the core imbibed with PW had stopped producing by spontaneous imbibition at 110 °C, it was subjected to viscous flooding (forced imbibition, FI), at the same temperature, with PW and later followed by SSW, to see if a production increase could be observed with a pressure gradient across the

core. Injection of PW gave a 10 % production increase, ending with a cumulative oil recovery of 40 %. What is even more interesting is that when injecting SSW instead of PW, a drastic and immediate 30 % increase was observed, and oil recovery finally reached 70 % OOIP, which is somewhat higher than obtained in a spontaneous imbibition process for a completely water-wet system. Thus, SSW also improved oil recovery by viscous flooding because of its ability to improve the water-wetness of the chalk surface. These results agree with observations using Valhall cores at reservoir conditions (Webb et al., 2005).

Based on the positive response from forced displacement of PW and SSW at 110 °C, Figure 5.15, and considering the low oil recovery at T < 100 °C because of no wettability alteration of the chalk surface, the effect of temperature on the potential for enhanced oil recovery by viscous flooding was investigated. In Figure 5.16 the two cores C#2 and C#3, $S_{wi}$ ~10 % Valhall FW (VB/US in Table 4.3), saturated with an oil with AN = 1.9 mgKOH/g oil were both first spontaneously imbibed (SI) with FW at 90 °C.
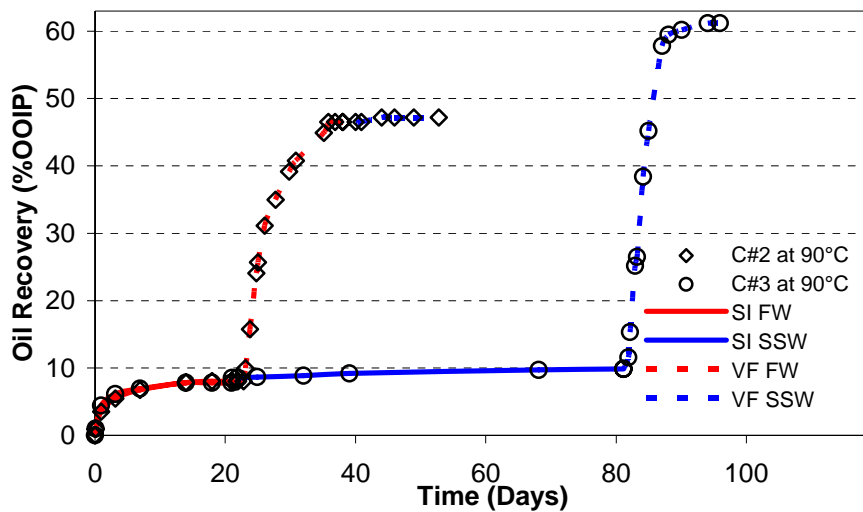


**Figure 5.16** *Oil recovery from the cores C#2 and C#3 at 90 °C by successive spontaneous imbibition (SI) and viscous flooding (VF). The injection rate was in the range of 0.08-0.12 PV/D, and the ΔP across the core varied from 6 psi at the start to 2 psi at the end.  $S_{wi}$ ~ 10 % and AN=1.9 mgKOH/g.*

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Both cores behaved very oil-wet, due to the high AN, and oil recovery by spontaneous imbibition with FW ended at 8.5 % OOIP after approximately 20 days. At that time, core C#2 was subjected to viscous flooding (VF) with FW, and plateau recovery of 46 % OOIP was reached after 0.7 PV injected. At this point, no additional oil was recovered by flooding with SSW, probably because it is difficult to mobilize the residual oil at such a high water saturation. Core C#3 was after spontaneous imbibition with FW, spontaneously imbibed with SSW, but hardly any enhanced oil recovery was experienced. However, by subjecting the same core to viscous flooding with SSW, plateau recovery at 60 % OOIP was reached after 0.7 PV SSW injected, ending at 61.2 % after 1.1 PV injected. Thus, at 90 °C when enhanced oil recovery by spontaneous imbibition of SSW is negligible, oil recovery can be drastically enhanced by performing a viscous flood with SSW. In addition, viscous flooding of SSW gave a 14 % OOIP increase in oil recovery compared to viscous flooding of FW, due to the presence of sulphate in SSW that promotes wettability alteration of the chalk surface.

In order to prove the importance of reservoir temperature on enhanced oil recovery, the same experiments were performed at 110 °C using cores C#4 and C#5, $S_{wi} \sim 10\%$ Valhall FW (VB/US in Table 4.3), saturated with an oil with AN = 1.9 mgKOH/g oil, and the results are given in Figure 5.17.
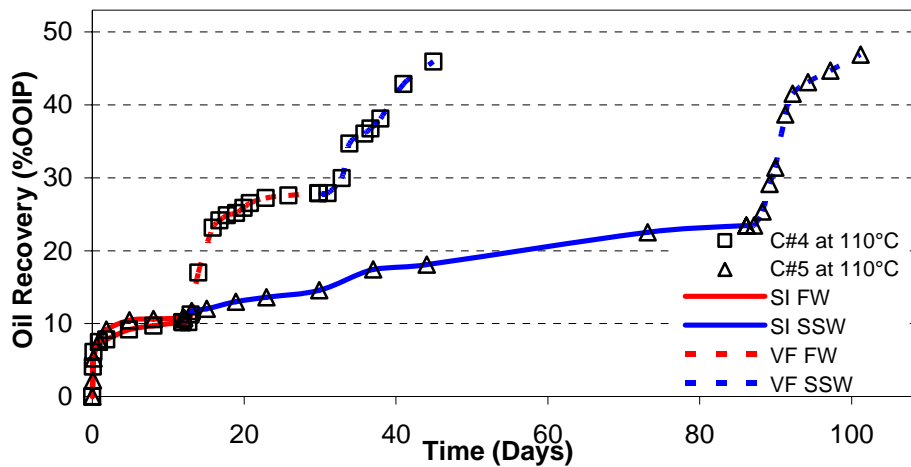


**Figure 5.17** *Oil recovery from the cores C#4 and C#5 at 110 °C by successive spontaneous imbibition (SI) and viscous flooding (VF). The injection rate was in the range of 0.06-0.10 PV/D, and the ΔP across the core varied from 6 psi at the start to 3 psi at the end. $S_{wi} \sim 10$ % and AN=1.9 mgKOH/g.*

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By spontaneously imbibing both cores, C#4 and C#5, with FW, approximately 10 % OOIP was recovered. Core C#4 was then flooded with FW, and cumulative oil production reached almost 30 % after 0.7 PV injected. By subsequently flooding with SSW, oil recovery increased to 46 % after 1.3 PV of SSW injected, and at this point the test was terminated. The other core C#5 was after spontaneous imbibition with FW, spontaneously imbibed again, however, this time with SSW. A temperature of 110 °C has previously been sufficient to promote wettability alteration of the chalk surface when using an oil with AN = 0.7 mgKOH/g oil, Figure 5.15. At 110 °C wettability alteration is also promoted when working with an oil with AN = 1.9 mgKOH/oil, only resulting in lower recovery because of the more oil-wet initial condition. Thus, spontaneous imbibition of SSW increased cumulative oil recovery from core C#5 to 23.5 % OOIP. Finally, the core was flooded with SSW, and the recovery reached 47 % OOIP after 1.4 PV SSW injected. Thus, when using SSW for enhanced recovery at 110 °C, oil recovery is greater by a viscous flood compared to spontaneous imbibition.

These results at 90 and 110 °C show that the temperature is very important for the wettability alteration to take place. Around 100 °C, the hydrogen-bonds that solvate/hydrate $Mg^{2+}$ and $SO_4^{2-}$ in solution break, increasing the reactivity of these ions. The affinity of $SO_4^{2-}$ towards the chalk surface increases (Strand et al., 2006a), and $Mg^{2+}$ can substitute $Ca^{2+}$ from the chalk surface (Zhang et al., 2007). Thus, at T > 100 °C spontaneous imbibition of SSW increases with temperature, nevertheless, a viscous displacement is more efficient by forcing the active ions into the matrix. At temperatures T < 100 °C it seems that significant enhanced oil recovery by wettability modification using SSW can only be achieved through a viscous flood.

### 5.3.3 Compaction

Previously it has been shown that the chemical reactions that promote wettability modification by SSW at high temperatures, also caused enhanced water weakening or compaction of chalk under stress (Korsnes et al., 2006a; Korsnes et al., 2007; Korsnes et al., 2006b) The mechanism behind the chemical weakening of chalk by SSW was described by a substitution of $Ca^{2+}$ by $Mg^{2+}$ at the inter-granular contacts in the presence of $SO_4^{2-}$ (Korsnes et al., 2006a). Thus, injected fluids that promote wettability modification, also promote enhanced mechanical weakening of chalk. Therefore, based on the findings in this study, it is reasonable to conclude that PW-SSW mixtures will behave in similar ways as pure SSW regarding compaction.

Compaction as a drive mechanism is favourable regarding oil recovery, but it is an expensive IOR-method because of costly well damages and rig operations due to subsidence of the seafloor. Compaction can be decreased by removing $SO_4^{2-}$ from SSW or by injecting pure PW, but then oil recovery will be drastically decreased.

## 5.4 Wettability alteration of limestone by seawater – a preliminary study

It is well known that limestone is less homogeneous than chalk, regarding both porosity and permeability. Limestone has therefore a smaller surface area, and the limestone surface is thus expected to be less reactive towards the potential determining ions, $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$, compared to the chalk surface. The chemical component of both chalk and limestone is $CaCO_3$, and the organic material in the oil that adsorbs on both surfaces, is the carboxylic material, hence there is a realistic potential for seawater-induced wettability alteration of the limestone surface. A preliminary study on this topic was initiated and is presented in the following.

### 5.4.1 Affinities of $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ towards limestone

The chromatographic wettability test was used to test the affinity of $SO_4^{2-}$ towards the limestone surface at room temperature using core 2-21, core properties in Table 4.1. The core was flooded with SSW½M, at two different rates, 0.1 and 0.2 ml/min. In both tests there was a time difference in the elution of $SO_4^{2-}$ and the tracer, $SCN^-$, and the area between the two curves is directly proportional to the water-wet surface inside the core, Figure 5.18. As the flow rate was increased from 0.1 to 0.2 ml/min, the area between the curves was increased from 0.112 to 0.173. As expected, the separation between the components in a chromatographic process is depending on the flow rate. A flow rate of 0.1 ml/min gave the better displacement profile, thus in the subsequent tests, the rate was kept at 0.1 ml/min. The fact that there was a delay in the elution of $SO_4^{2-}$, confirmed adsorption of $SO_4^{2-}$ onto the water-wet sites of the limestone surface, in the same way as has been observed for chalk (Strand et al., 2006a).
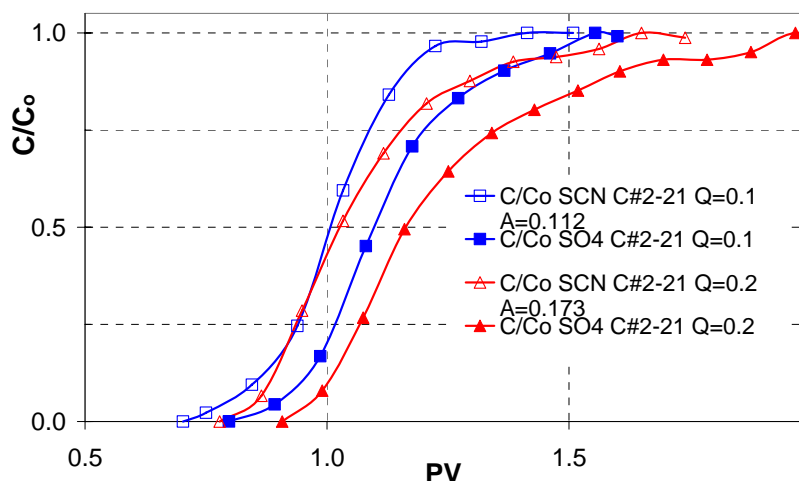
**Figure 5.18** *Effluent curves of relative concentration versus pore volume for SCN⁻ and SO₄²⁻ using SSW½M as chromatographic fluid. The tests were performed at ambient temperature at two different flow rates; Q= 0.1 and 0.2 ml/min, on the core termed 2-21.*

In chalk, the interplay between $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ in seawater is important for wettability alteration (Zhang et al., 2007). $SO_4^{2-}$ is depending on the presence of either or both cations in order to work as a wettability modifying agent. Studies on chalk have revealed that $Ca^{2+}$ and $Mg^{2+}$ also have affinities for the chalk surface, and at temperatures > 100 °C, $Mg^{2+}$ was even able to substitute $Ca^{2+}$ from the chalk surface (Korsnes et al., 2007; Zhang et al., 2006; Zhang et al., 2007).

The competitive adsorption of $Ca^{2+}$ and $Mg^{2+}$ onto the limestone surface was investigated by chromatographic tests at various temperatures on core 2-21, using brine NaCl-M, which contained equal amounts of $Ca^{2+}$, $Mg^{2+}$ and $SCN^-$. The results at 20 and 130 °C are shown in Figure 5.19. Separation between the tracer curve and the effluent curves for $Ca^{2+}$ and $Mg^{2+}$ confirmed adsorption of both ions onto the limestone surface. At 20 °C their relative affinities were identical, whereas when temperature was increased to 130 °C, the affinity of $Mg^{2+}$ was greater than that of $Ca^{2+}$, as seen by a larger area between the tracer curve and the $Mg^{2+}$-curve than that between the tracer curve and the $Ca^{2+}$-curve, Figure 5.19.

The $Mg^{2+}$ ion is small with a high charge density, and it is therefore more strongly solvated in water than $Ca^{2+}$. This is also reflected in the hydration energy of the two ions, -459 and -380 kcal/mol for $Mg^{2+}$ and $Ca^{2+}$, respectively (Phillips and Williams, 1965). This means that $Mg^{2+}$ becomes more reactive as the temperature increases due to partial dehydration of the ion.

At 130 °C, similar studies on chalk revealed a maximum of 75 % increase in $Ca^{2+}$ concentration of the effluent, as a result of the substitution of $Ca^{2+}$ by $Mg^{2+}$ (Zhang et al., 2007). Such an increase is not observed in limestone, Figure 5.19, thus it was concluded that the limestone surface is less reactive compared to chalk.

Substitution of $Ca^{2+}$ by $Mg^{2+}$ was, however, observed at temperatures >100 °C when flooding seawater slowly at a rate of 1PV/D through the limestone core 46A, core properties in Table 4.1. Figure 5.20 shows the changes in molar concentrations of $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ at 130 °C. The



**Figure 5.19** *Competitive adsorption of $Ca^{2+}$ and $Mg^{2+}$ in NaCl-M brine onto limestone core 2-21 at 20 and 130 °C. $[Ca^{2+}] = [Mg^{2+}] = [SCN^-] = 0.013$ mol/l. Flow rate 0.1 ml/min.*

decrease in $Mg^{2+}$, from 0.045 to 0.040 mol/l, was the same as the increase in $Ca^{2+}$, from 0.013 to 0.018 mol/l, which indicated a 1:1 substitution. Based on these observations and experience from previous work on chalk, it is reasonable to believe that SSW should be able to improve the water-wetness of reservoir limestone at high temperature.
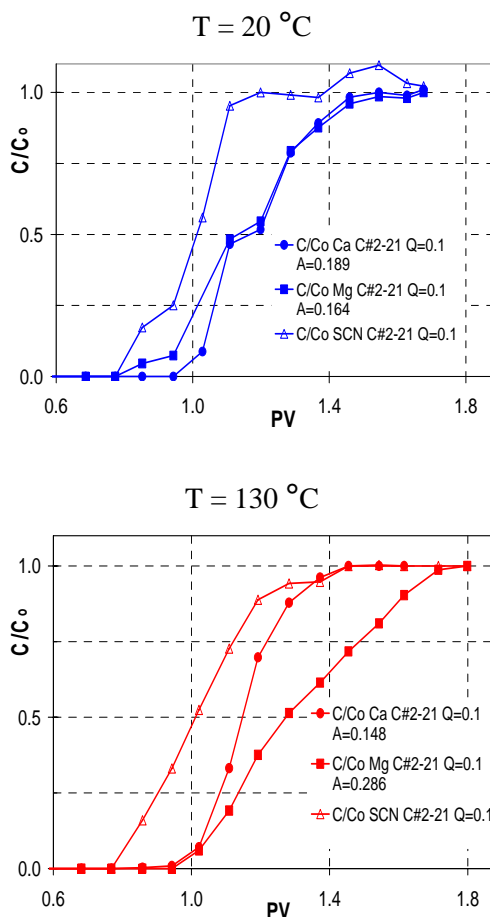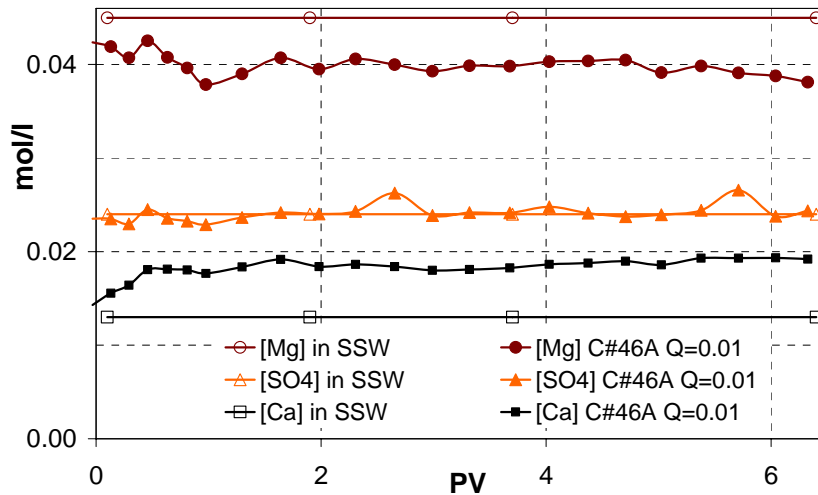
**Figure 5.20** *Changes in molar concentrations of $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$ when flooding SSW through the 46A limestone core at 130 °C. Flow rate: 1 PV/D ( 0.01 ml/min).*

## 5.4.2 Seawater induced wettability modification of limestone

Before core 46A was subjected to slow flooding with seawater in Figure 5.20, the chromatographic wettability test was used to determine the initial wetting state of the core, Figure 5.21. The core was flooded with SSW½M at room temperature, and the separation area between the tracer and $SO_4^{2-}$ curves, which is proportional to the water-wet area of the core, was determined to A = 0.107. The fact that the tracer curve passed through the coordinates (1.0, 0.5) indicated that the total pore volume of the core was connected and flooded by the injected fluid. After the core had been exposed to seawater at high temperature, 130 °C, the wetting state was again measured by the chromatographic wettability test. Figure 5.22 shows that the separation area between the curves had increased to A = 0.141. In other words, the core had become more water-wet, with a calculated increase of 32 %. The increase in water-wetness is also illustrated by the decrease in relative concentration of $Ca^{2+}$ because of increased adsorption of $Ca^{2+}$ at the water-wet surface sites.

**Figure 5.21** *Chromatographic wettability test on core 46A before exposure to SSW at high temperature. The core was flooded with SSW½M ([SCN⁻] = [SO₄²⁻] = 0.012 mol/l) at a rate of 0.1 ml/min.*



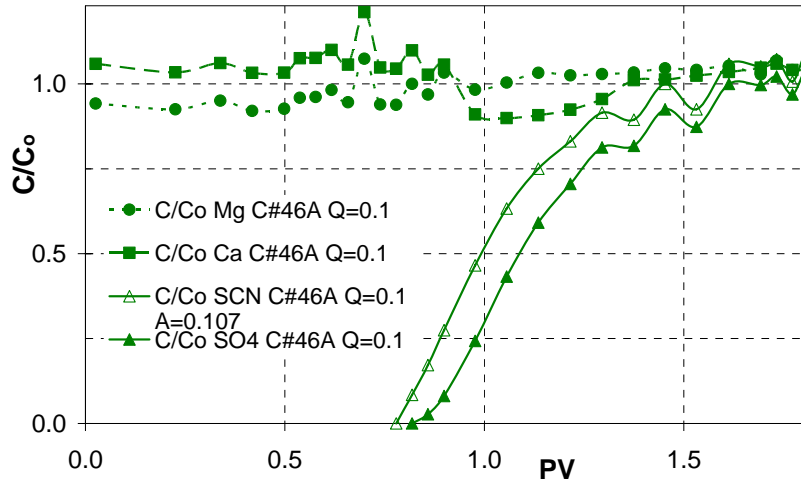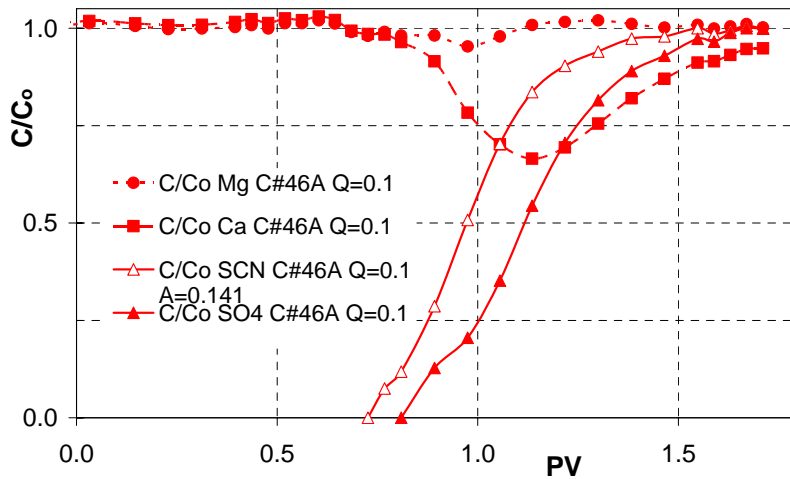**Figure 5.22** *Chromatographic wettability test on core 46A after exposure to SSW at high temperature. The core was flooded with SSW½M ([SCN⁻] = [SO₄²⁻] = 0.012 mol/l) at a rate of 0.1 ml/min.*

The interplay between the limestone surface and the potential determining ions $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ is illustrated in Figure 5.23. Core 2-21 was first flooded with 3 PV SSW-U at room temperature, then flooded with SSW½M, the salinity was kept constant and equal to SSW salinity. The concentrations of $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$ in the effluent were determined and are plotted in Figure 5.23.
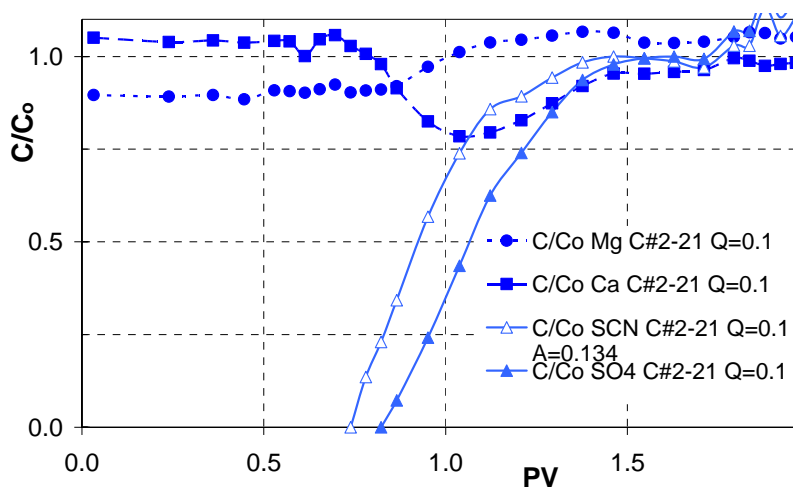


**Figure 5.23** *The interactions between surface active ions ($Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$) present in SSW and the carbonate surface, core 2-21. The core was flooded with SSW½M ($[SCN^-] = [SO_4^{2-}] = 0.012$ mol/l) at a rate of 0.1 ml/min*

At first, the concentration of $Ca^{2+}$ in the pore fluid was very close to the initial concentration, while the concentration of $Mg^{2+}$ decreased significantly compared to the initial condition. In both cases, the concentration remained constant until the breakthrough of $SO_4^{2-}$. At breakthrough of $SO_4^{2-}$, the concentration of $Ca^{2+}$ decreased drastically, while the concentration of $Mg^{2+}$ increased. Thus, the presence of $SO_4^{2-}$ in the pore fluid caused an immediate dynamic activity in the system. At 20 °C the affinities of $Ca^{2+}$ and $Mg^{2+}$, in the absence of $SO_4^{2-}$, towards the limestone surface were equal, but because $[Mg^{2+}] \sim 4[Ca^{2+}]$ in SSW, $Mg^{2+}$-ions are in excess, and thus dominate the adsorption onto the surface, even though being more strongly hydrated than $Ca^{2+}$. However, when $SO_4^{2-}$ is present, $SO_4^{2-}$ adsorbs onto the positively charged carbonate surface, thus lowering the positive charge density. $Ca^{2+}$ can then adsorb onto the surface due to less electrostatic repulsion (Strand et al., 2006a). In addition, $SO_4^{2-}$ forms an ion-pair with $Mg^{2+}$ in the aqueous phase

(Equation 5.2), which lowers the activity of $Mg^{2+}$ in solution, and $Mg^{2+}$ is then desorbed from the carbonate surface. The test in Figure 5.23 was performed at room temperature. As the temperature is increased, especially beyond 100 °C, the observed effects are likely to increase because of enhanced adsorption of $SO_4^{2-}$, and increased $Mg^{2+} \cdots SO_4^{2-}$ ion-pair formation (Carlberg and Matthews, 1973; Strand et al., 2006a).

All chemical interactions that are important for the wettability alteration of chalk by seawater, are also present in limestone, therefore, a strong possibility of using seawater as an EOR fluid also for limestone, exists.

### 5.4.3   Limestone reservoir core cleaning

Cleaning of reservoir carbonate cores is a never-ending discussion, and recently, a study demonstrated very clearly the importance of proper cleaning of reservoir limestone cores in order to obtain uniformly water-wet core samples that were needed to obtain reliable $P_c$-curves (Masalmeh and Jing, 2007).

Carboxylic material from the crude oil is strongly bonded to the carbonate surface, and must be removed by chemical reactions rather than by solvent cleaning only. Water-saturated toluene has been suggested as the best fluid to remove this material from the carbonate surface (Thomas et al., 1993). Water then acts as a strong nucleophile, removing some of the carboxylic material from the surface. Reservoir limestone core 20A, core properties in Table 4.1, was cleaned using water-saturated toluene and methanol, and afterwards the chromatographic wettability test was performed to determine the water-wet area inside the core. As the results suggest in Figure 5.24, there was no water-wet area inside the core after cleaning, as shown by no separation of the tracer curve and sulphate curve, A = 0.015. This method did not succeed in cleaning the core. However, based on the experimental results in this preliminary study, Figures 5.21 and 5.22, the best available method today to remove this strongly bonded organic material, is probably to flood the carbonate core with seawater at high temperature, about 130 °C. Because the relative concentrations of $Mg^{2+}$ and $Ca^{2+}$ are different in SSW and formation water, the core may undergo some changes at the surface by flooding with SSW, i.e. some $Ca^{2+}$ may be substituted by $Mg^{2+}$ in the surface lattice. Therefore, it is recommended that flooding with SSW is followed by flooding with hot distilled water or some other low salinity brine in order to dissolve the $MgCO_3$ formed at the surface (Korsnes et al., 2006a).
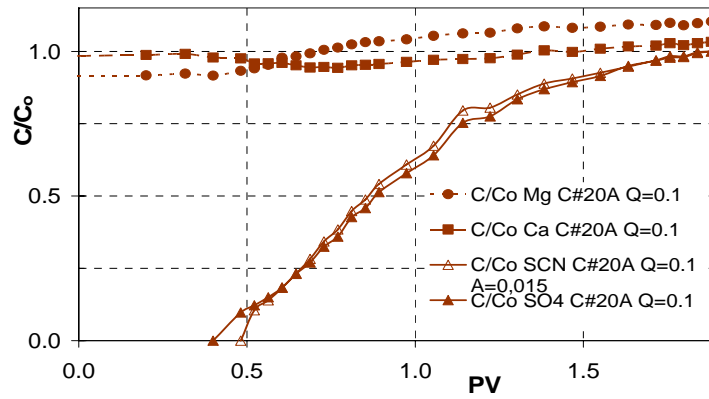
**Figure 5.24** *Chromatographic wettability test on core 20A after cleaning with toluene and methanol. The core was flooded with SSW½M ([SCN⁻] = [SO₄²⁻] = 0.012 mol/l) at a rate of 0.1 ml/min.*

# 6 Concluding remarks

The ability of seawater to enhance oil recovery from chalk, by wettability alteration of the surface, has been further explored in this study. Influences of base number in crude oil, and of diluting the seawater with produced water, on the wettability altering ability, have been looked at. Finally, the potential of using seawater as an EOR fluid in limestone was investigated.

## 6.1 Conclusions

The main conclusions drawn from this study were:

> ➢ Model bases should not be used to represent natural crude oil bases in wettability studies on chalk, because their wetting mechanisms might be totally different. The model base, benzyl amine, a small molecule but a rather strong base, increased adsorption of carboxylic material onto the chalk surface by co-adsorption and thus lowering the electrostatic repulsion between the adsorbed carboxylic material. The natural petroleum bases are large molecules that, due to steric hindrance, cannot co-adsorb on the surface, but instead form acid-base complexes in the oil, thereby preventing the carboxylic material from adsorbing.

> ➢ It was found that some of the outcrop chalk material had been contaminated with seawater and therefore contained initial sulphate. As a result of that, and by using the porous plate for $S_{wi}$ establishment, sulphate was increased in concentration in the initial water, preventing the carboxylic material in crude oil from adsorbing. In order to create reproducible wetting conditions, it is, prior to any wettability studies, recommended to pre-flush outcrop chalk cores with at least 4 PV distilled water in order to remove dissolvable sulphate salts that can affect the initial wetting conditions.

> ➢ Modelling of the compatibility of seawater and produced water indicated that precipitation of $CaSO_4$ in reservoirs >100 °C will take place, along with $SrSO_4$ and $BaSO_4$ due to some mixing of SSW with FW. Because the solubility of $CaSO_4$ and $SrSO_4$ decreases with temperature, precipitation occurs in the reservoir, rather than in the injector, where the temperature is lower. In

contrast, the solubility of $BaSO_4$ increases with temperature, thus $BaSO_4$ can be precipitated in the injector. However, because $S_{wi}$ in North Sea chalk reservoirs is 5-7 %, precipitation of $BaSO_4$ in the injector could be minimized by diluting 1 part PW with 8 parts SSW.

➢ The reservoir temperature is a very important parameter regarding scale potential. Ekofisk (130 °C) will experience far more sulphate stripping in the reservoir, by $CaSO_4$ formation and $SO_4^{2-}$ adsorption than Valhall (90 °C). Thus, considerable sulphate scale is to be expected at Valhall.

➢ The reservoir temperature is also crucial for the wettability alteration mechanism to be initiated. In the spontaneous imbibition experiments using mixtures of seawater and produced water as imbibing fluids, the oil recovery depended on temperature. Below 90 °C, the results showed no difference in recovery between imbibing fluid containing sulphate or not. However, at temperatures higher than 100 °C, there was a clear tendency of increased recovery using PW-SSW mixtures compared to pure PW, which did not contain sulphate. At 110 °C, viscous flooding of PW into the core that produced 30 % OOIP by spontaneous imbibition of PW, resulted in a recovery increase of 5-10 %, whereas viscous flooding with SSW was even more successful, resulting in 30 % OOIP recovery increase due to wettability alteration of the chalk surface.

➢ The effect of reservoir temperature on enhanced oil recovery by both spontaneous imbibition and forced displacement of seawater was investigated. At 100 °C hydrogen-bonds solvating $SO_4^{2-}$ and $Mg^{2+}$, which are important ions for the wettability alteration mechanism, break, thus increasing the reactivity of both ions. Thus, the results showed that at 90 °C there was no difference between spontaneously imbibing FW or SSW, meaning that no wettability alteration had taken place. By forced displacement, on the other hand, SSW was much more efficient than FW, and a wettability alteration was experienced by forcing SSW into the rock. At 110 °C both spontaneous imbibition and forced displacement by SSW was more efficient than FW, due to the wettability alteration catalysed by sulphate. In addition, forced displacement was more efficient compared to spontaneous imbibition.

➢ The results from the preliminary study on wettability alteration of limestone by seawater showed that the chromatographic wettability test that was developed for chalk, also worked for limestone. The test documented adsorption of sulphate, calcium and magnesium onto the limestone surface. In addition, by slowly flooding limestone cores with SSW at high temperature, there was evidence of substitution of $Ca^{2+}$ by $Mg^{2+}$ at the limestone surface.

➢ Measuring the water-wet area inside a limestone core before and after exposure to SSW at high temperature, 130 °C, showed that SSW flooding rendered the limestone core more water-wet than cleaning the core with the more traditional method using water-saturated toluene and methanol. Thus, a better way to clean a limestone reservoir core is to flood it with seawater at high temperature.

## 6.2 Future work

The experimental work, upon which this thesis is built, has given many interesting results that could be worth looking further into. Below, some thoughts on future work are presented:

➢ Oil properties: Acidic and basic material in the oil may be water-extractable (soluble in water) or non-extractable in water, thus the influence of different oils on chalk wetting may vary, and they may also respond differently to seawater injection.

➢ Sulphate stripping: Experimental quantification of sulphate stripping in chalk cores at various temperatures during seawater injection.

➢ Limestone: Preliminary results show promising results regarding seawater as an EOR fluid, hence a full study should be initiated, including core preparation, affinities of potential determining ions, wettability modification for EOR, also by use of surfactants, injected water optimization etc.

➢ Dolomite: Based on the results from limestone, it is probable that EOR can be achieved by seawater injection into dolomite reservoirs as well, thus a preliminary study is suggested.

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