Low Carbon Enhanced Oil Recovery Solution for Carbonates

by

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Md Ashraful Islam Khan

Summary

Oil production from mature fields causes significant CO_2 emissions, primarily linked to the management and processing of injected and produced water. As fields age, the demand for injected water increases, increasing both costs and emissions. Similarly, in the ageing field, water production increases with time that requires to process produced water which is a costly and emission-intensive process. This thesis addresses the challenge by optimizing injection water to enhance oil recovery in carbonates with reduced water injection, decreased water production and thereby reducing CO_2 emissions.

The fundamentals of carbonate reservoir, oil recovery from carbonates, forces affecting fluid flow, the main mechanisms for wettability alteration in carbonates along with potential determining ions and favorable conditions for facilitating wettability alteration were discussed to help better understand the result and discussion part of the thesis.

The study aimed to identify optimized injection water for wettability alteration, improving oil recovery and simultaneously reducing CO_2 emissions by minimizing water injection/production. Various low-carbon Enhanced Oil Recovery (EOR) solutions including, ion-modified brines, brines with additional salts, and carbonated water, were designed, and tested in outcrop and reservoir chalk cores at high temperatures. Different oil recovery tests were performed using different injection brines to find their effectiveness in improving oil recovery. This experimental thesis work also investigates the primary reasons behind increased oil recovery and proposes a guideline for selecting representative outcrop core material that represents reservoir cores.

Stevns Klint outcrop chalk core was found as a suitable analogue for North Sea chalk reservoirs for EOR and CCS studies. A 20 mM concentration of Ca^{2+}, Mg^{2+}, and SO_4^{2-} added brine was identified as the most effective ion-modified brine. Polsulphate salts, particularly added in produced water, demonstrated superior performance in enhancing oil recovery when additional salt is added to prepare injection brine. Carbonated water also exhibited promising EOR potential including carbon storage opportunities. The presence of positive capillary forces in cores was recognized as a crucial factor for oil mobilization in carbonates.

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Submitted to Fuel.

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Paper 4	**The Effect of Carbonated Produced Water for Enhanced Oil Recovery in Sandstones.** Alfred Obo, Mahmood Fani, Aleksandr Mamonov, Md Ashraful Islam Khan, Tina Puntervold, Skule Strand. *Presented at IOR+ 2023, The Hague, Netherlands, October 2023.*

Nomenclature

Φ	*Porosity*
Σ	*Interfacial tension*
σ_{ow}	*Interfacial tension between oil and water*
Θ	*Contact angle measured through the water phase*
$\Delta\rho$	*Difference in density between two phases*
ΔP_g	*Pressure difference over the oil-water surface due to gravity*
ΔP	*Pressure difference across capillary tube / Pressure drop*
M	*Fluid viscosity*
A	*Area where* F_C *is active*
AA	*Aalborg outcrop chalk*
A_{Ref}	*Reference area which indicates a completely water-wet state*
AN	*Acid Number*
ASTM	*American Society for Testing and Materials*
A_{Wett} / A_W	*The area between the thiocyanate/lithium and sulphate curve of a sample*
BET	*Brunauer Emmett Teller method to measure specific surface area*
BN	*Base number*
CCS	*Carbon capture and storage*
CCUS	*Carbon capture, utilization, and storage*
CFW	*carbonated formation water*
CoBR	*Crude oil, brine and rock*
CSW	*Carbonated seawater*
CW	*Carbonated water*
CWT	*Chromatographic Wettability Test*
DI	*De-ionized Water*
DW	*Distilled water*
E	*Displacement efficiency*
EDX/EDS	*Energy-Dispersive X-ray Spectroscopy*
E_D	*Microscopic displacement*
E_V	*Macroscopic displacement*
EOR	*Enhanced Oil Recovery*
F_C	*Capillary force*
g	*Gravity acceleration constant*
H	*Height of the column*
I_{AH}	*Amott-Harvey index*
I_{CW}	*Chromatographic wettability index*

IC	*Ion chromatography*
I_O	*Amott index for oil*
I_W	*Amott index for water*
I_{W-SI}^* /I_{WSI}	*Modified Amott water index*
ICP-MS	*Inductively Coupled Plasma-Mass-Spectrometry*
IFT	*Interfacial Tension mN/m*
IOR	*Improved Oil Recovery*
k	*Absolute permeability, mD*
kro	*Relative permeability of oil*
krw	*Relative permeability of water*
L	*Core length/ Length of capillary tube*
mD	*Millidarcy*
NCS	*Norwegian Continental Shelf*
NMR	*Nuclear magnetic resonance*
OOIP	*Original oil in place*
Pc	*Capillary pressure*
P_o	*Pressure in the oil phase*
POC	*Polar organic components*
P_w	*Pressure in the water phase*
PS	*Polysulphate*
PV/D	*Pore volume per day*
PW	*Produced water*
r	*Radius of cylindrical pore channel/ Radius of capillary tube*
SAIL	*Surface-Active Ionic Liquids*
SC	*Standard conditions*
SEM	*Scanning Electron Microscope*
SI	*Spontaneous imbibition*
SK	*Stevns Klint outcrop chalk*
Swr	*Residual water saturation*
Swi	*Initial water saturation*
S_{or}	*Residual oil saturation*
SI_C	*Oil recovery (%OOIP) by SI from the evaluated core*
SI_{WWC}	*Oil recovery (%OOIP) by SI from a strongly water-wet or reference core*
SmW	*Smart Water*
SW0T	*Seawater without sulphate and thiocyanate/lithium tracer*
SW1/2T, SW1T	*Seawater that contains sulphate and thiocyanate/lithium tracer*
TDS	*Total Dissolved Salt*
UR	*Ultimate oil recovery (%OOIP),*
V_{avg}	*Average flow velocity in capillary tube*
VF	*Viscous flooding*
WIUSBM	*USBM wettability index*

1. Introduction

The production of mature oil fields specially from carbonate reservoirs is a significant contributor to CO_2 emissions due to the circulation and handling of large volumes of produced gas and water (Masnadi & Brandt, 2017). The natural reservoir pressure often becomes insufficient for fluid production, necessitating the use of energy-intensive measures such as additional pumps, gas lift, downhole or surface lift pumps as well as water injection. These methods require substantial energy input, leading to increased carbon emissions (Farajzadeh, 2019).

To mitigate these emissions, one approach is to reduce the volumes of non-hydrocarbon fluids produced and this can be achieved through the application of low-carbon EOR methods by reducing water production, late water breakthrough and increasing oil recovery, all while saving energy in processing excess water.

The production of oil from these fields typically results in a high water cut, with more than 90% of the produced fluid being water (Masnadi & Brandt, 2017). Produced water (PW) is usually re-injected into the reservoir after some treatment. However, PW is not a good injection fluid for EOR in carbonates due to not having essential ions for wettability alteration and its high mobility in the reservoir (Puntervold & Austad, 2008). Controlling the mobility of the injected water by adding, e.g., polymers and improving its microscopic sweep efficiency, for instance, by adding surfactants could result in additional oil in the producing wells. Such an approach should also consider the additional energy required to produce the oil. Their breakthrough into the production stream can add to the energy burden of the production site. The separation and treatment of oil and water emulsions along with polymers and other chemicals are also energy-intensive processes (Farajzadeh, 2019; Farajzadeh et al., 2019).

Low-carbon EOR techniques aim to address these challenges by optimizing the injection of water-based fluids by just modifying ions in the injecting water or by adding water soluble cheap salts. Efficient water injection for EOR can prevent early water breakthrough, resulting in incremental oil production and reduced CO_2 intensity in produced oil. Starting EOR projects earlier in the field's lifecycle is also advantageous from a carbon emissions perspective.

In addition to water-based injection fluids, CO_2 EOR represents a mature technology with the potential to reduce net CO_2 emissions from both conventional and unconventional hydrocarbon reservoirs. Injected CO_2 can replace produced fluids and be permanently stored in the reservoir, effectively financing large-scale carbon capture and storage (CCS) efforts while reducing the carbon footprint of oil production (Azzolina et al., 2017).

In summary, low-carbon EOR methods, such as water-based injection fluids without chemicals, modified produced water reinjection and CO_2 EOR, offer promising strategies for reducing CO_2 emissions associated with mature oil fields. These techniques improve oil recovery, minimize water production, and enhance the energy efficiency of oil production, making them valuable techniques in the transition towards more sustainable and environmentally responsible oil industry.

1.1 Objective of the study

This study primarily aimed to develop a cost-effective, low-carbon EOR solution for high-temperature carbonate reservoirs. Due to the limited availability of preserved carbonate reservoir cores, it is important to use representative outcrop analogues for parametric studies to understand CoBR (Crude oil, brine, and rock) interactions, including fluid flow in porous media, and wettability for EOR studies. In this study, two most available outcrop chalk cores in Europe were analysed and compared with reservoir chalk cores to find the best analogue for parametric studies.

The best representative outcrop chalk core was used for oil recovery experiments to develop an inexpensive but efficient injection brine, a Smart Water with a composition that is more efficient than seawater (SW) in altering wettability in high temperature (130 °C) chalk and improve the oil recovery. The EOR potential of the most promising designed brine was thereafter tested on a North Sea reservoir chalk system consisting of two unused reservoir chalk cores, reservoir formation water (FW), and stock tank oil from the same chalk reservoir.

Moreover, it was investigated if PW can be improved as injection brine by adding Polysulphate (PS) salt. PS were also used as an additive to SW and distilled water (DW) to investigate its effectiveness in enhancing wettability by wettability alteration at high temperature in most representative chalk outcrop.

CO_2 injection together with water or carbonated water (CW) injection is one of the common low carbon EOR solutions as it has opportunities to store the CO_2 permanently in the reservoir. In this study, it was investigated if CW could induce EOR effects in representative chalk cores at high temperature and which mechanisms were working behind such effects if there were any EOR effect. The solubility of CO_2 in different brines and oil was studied by experimental and simulation work to understand the EOR mechanism and the potential of CO_2 storage in the reservoir.

Lastly, the study investigated the significance of capillary forces in the oil recovery process from representative heterogeneous, low-permeable chalk cores by comparing oil recoveries through spontaneous imbibition (SI) and low-rate viscous flooding (VF).

2. Theory

2.1 Carbonates

Carbonates, primarily formed through the sedimentation of calcareous organic material, are often referred to as biogenic rocks due to their organic origin. These rocks can be categorized into clastic, composed of fragmented sediment material, or non-clastic, mostly comprising intact sediments. A bioclastic rock is a rock type composed of fragmented or detrital organic material that hasn't undergone full chemical homogenization (Skinner et al., 1991). Geologists generally classify rocks with over 50% carbonate minerals as carbonate rocks (Mazzullo et al., 1992).

Carbonate minerals, with diverse ionic compositions and structures, include 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 primarily composed of calcite, dolomite, or a combination. Limestone contains more than 50% calcite, while dolomite comprises at least 50% dolomite mineral (Mazzullo et al., 1992). Dolomite ($CaMg(CO_3)_2$) consists of CO_3^{2-} layers interleaved with Ca^{2+} and Mg^{2+} layers. Dolomite forms gradually through "dolomitization," where Mg^{2+} ions substitute Ca^{2+} ions in $CaCO_3$ (calcite or aragonite), following the equation:

$$2\,CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+} \qquad \textbf{(2.1)}$$

Chalk, classified as a limestone, originates from the deposition of calcareous skeletal debris, primarily from unicellular planktonic algae coccolithophorid, with some foraminiferal material. Coccolithophorid algae consist of coccospheres (2-20 μm diameter) built from coccolithic ring structures (3-15 μm diameter), composed of calcite crystals in ring fragments or platelets (0.25-1 μm diameter). Chalk is finely grained and highly porous due to small pores between skeletal constituents but has low permeability owing to microscopic constituent sizes (Milter, 1996).

Remarkably, 40-60% of the world's total hydrocarbon production originates from carbonate rocks, including prominent fields like Saudi Arabia's Ghawar

Field and the South Pars/North Dome field in Iran and Qatar, both predominantly composed of carbonate rocks (Flügel, 2004).

Norwegian carbonate reservoirs, mainly in the North Sea on the Norwegian Continental Shelf (NCS), formed through tectonic events from the Devonian to Late Jurassic. Primarily composed of chalk deposits from Upper Cretaceous to Paleocene, with coccolitophorids sedimentation (Faleide et al., 2015). Ekofisk, a chalk reservoir, was discovered in 1969 and remains a major North Sea hydrocarbon resource, contributing about 10% of NCS's net oil equivalents (Kallesten et al., 2021). Despite Ekofisk's efficient SW injection for oil recovery since 1987, substantial resources remain in flooded zones, prompting to find a more efficient recovery method.

2.1.1 Importance of EOR in carbonates

Carbonate reservoirs pose unique challenges for oil recovery due to their geological characteristics. These reservoirs are often fractured, exhibit low permeability, and have low water-wettability. Consequently, they typically yield low oil recovery rates, often below 30% (Cuiec, 1984; L.E. Treiber & W.W. Owens, 1972). In a study of 161 carbonate rocks, Chilingar and Yen (1983) found that 15% were strongly oil-wet, 65% were oil-wet, 12% displayed intermediate wettability, and only 8% were water-wet.

In such reservoirs, secondary waterflooding is less effective because injected water primarily follows high-permeable fracture paths, displacing only a small fraction of the oil located in these fractures, which constitutes a small portion of the total oil in place (OOIP). To achieve substantial oil recovery, it's essential to displace oil from the low-permeability matrix through spontaneous imbibition of the injected fluid. However, the inherent oil-wet nature of carbonate rocks hampers spontaneous imbibition, as negative capillary pressures prevent water uptake into the matrix.

To boost recovery from carbonate reservoirs, altering the wettability of rock surfaces is crucial. This alteration aims to make the rock surface less oil-wet, thereby increasing capillary pressure and promoting spontaneous imbibition of water, which in turn displaces the trapped oil. This wettability modification can be achieved through various methods, including the use of Smart Water brines or other EOR techniques like surfactant injection or carbon dioxide (CO_2) flooding.

EOR techniques are of particular interest in carbonate reservoirs. EOR encompasses methods beyond primary and secondary recovery and can be initiated simultaneously with primary production and secondary processes. EOR includes practices like polymer and foam injections for mobility control, surfactants and alkaline agents for chemical flooding, hydrocarbon solvents and CO_2 for miscible flooding, and thermal methods like steam and in-situ combustion. It's essential to tailor EOR strategies to the unique characteristics of carbonate reservoirs to maximize oil recovery at the early age of reservoir’s production life (Mahani & Thyne, 2023).

2.2 Displacement forces

Oil displacement within a porous medium involves a complex interplay of forces, with capillary, gravity, and viscous forces playing key roles (Morrow, 1979). In oil production, two primary processes are at play: spontaneous imbibition and forced displacement. Spontaneous imbibition relies on gravity and capillary forces, while forced displacement processes are driven by viscous forces. For naturally fractured reservoirs, capillary forces are a dominant driving mechanism (Mazzullo et al., 1992).

In this context, overcoming capillary forces is essential for mobilizing oil within a porous system. In an ideal EOR process, the overall displacement efficiency (E) can be expressed as the product of microscopic (E_D) and macroscopic (E_V) displacement efficiencies (**Eq. 2.2**):

$$E = E_D \cdot E_V \qquad \textbf{(2.2)}$$

E_D indicates fluid mobilization at the pore scale, assessing how effectively the displacing fluid interacts with the oil and minerals. Meanwhile, E_V provides a volumetric interpretation of reservoir displacement and sweep efficiency. Sweep efficiency relates to how fluid moves through the system, specifically how displaced oil is transported to the producer (Green & Willhite, 1998).

Understanding and optimizing these displacement forces and efficiencies are critical in designing effective EOR strategies for oil recovery from porous reservoirs.

2.2.1 Capillary forces

Capillary forces within a petroleum reservoir arise from a complex interplay of factors, including surface and interfacial tensions (IFT), pore size, geometry, and the wetting properties of the system. Capillary pressure, the difference in pressure across the curved interface between immiscible fluids, results from the tension at the interface (Green & Willhite, 1998). It's defined as the pressure in the nonwetting phase minus the pressure in the wetting phase. Conventionally, it's expressed as the pressure in the oil phase minus the pressure in the water phase for a water/oil system. Capillary pressure can be positive or negative depending on which phase is the wetting one. Laplace's equation (**Eq. 2.3**) quantifies capillary pressure across a curved surface in terms of radii of curvature.

$$P_c = P_o - P_w = \sigma_{ow}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{F_c}{A} \tag{2.3}$$

where,

P_c	Capillary pressure
P_o	Pressure in the oil phase
P_w	Pressure in the water phase
σ_{ow}	IFT between oil and water
F_C	Capillary force
A	Area where F_C is active
R_1, R_2	Curvature Radii of interface between oil and water

For a capillary tube, capillary pressure can be described by equation (**Eq. 2.4**). Here, IFT, capillary size, and fluid wettability significantly influence capillary pressure.

$$P_C = \frac{2\sigma_{OW} cos\theta}{r} \tag{2.4}$$

Where,

θ	contact angle measured through the water phase
r	Radius of cylindrical pore channel

Capillary pressure's impact on fluid flow within porous media hinges on whether the reservoir is fractured. In fractured reservoirs, strong capillary forces drive spontaneous imbibition of water into the matrix, enhancing waterflood displacement efficiency. However, sandstone reservoirs, often unfractured, can suffer from high residual oil saturation (Sor) due to strong capillary forces during waterflooding, known as the "end effect" (Anderson, 1987). Reducing the oil-water IFT can alleviate this issue.

2.2.2 Gravity forces

Gravity forces play a crucial role in reservoir fluid flow, particularly when there's a significant density contrast between the displacing and displaced fluids, as well as when oil-water IFT is low. Gravity force, as described in equation (**Eq. 2.5**), is continually active in the presence of immiscible fluids. This force exerts upward pressure on the lighter fluid, leading to fluid segregation. In displacement scenarios, this can manifest as gravity override (e.g., CO_2 and solvent flooding) or gravity under-ride (e.g., waterflood), as noted by Green and Willhite (1998).

$$\Delta P_g = \Delta \rho g H \tag{2.5}$$

Where,

ΔP_g	Pressure difference over the oil-water surface due to gravity
$\Delta \rho$	Difference in density between two phases
g	Gravitational acceleration constant, equal to 9.8 m/s^2
H	Height of the column

2.2.3 Viscous forces

Viscous forces within a porous medium are characterized by the pressure drop resulting from fluid flow through the medium. Flow through a pore requires the viscous force to exceed the capillary forces. Considering the porous medium as a collection of parallel capillary tubes, the pressure drop for laminar flow within a single capillary tube can be calculated using the following equation (**Eq. 2.6**) (Green & Willhite, 1998).

$$\Delta P = \frac{8\mu L v_{avg}}{r^2\, g_c} \tag{2.6}$$

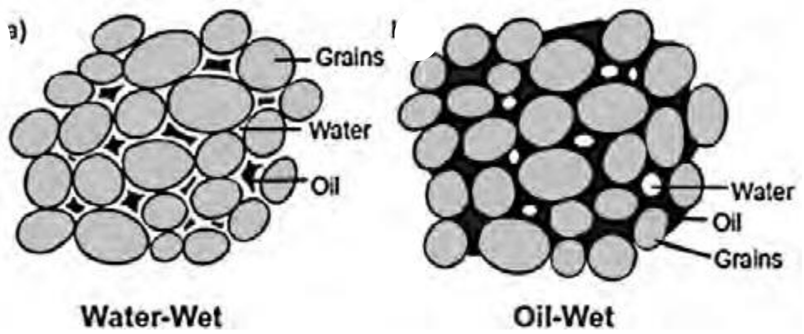
Where,

ΔP	Pressure difference across capillary tube
μ	Viscosity
L	Length of capillary tube
V_{avg}	Average flow velocity in capillary tube
r	Radius of capillary tube
g_c	Conversion factor

2.3 Wettability

Wettability in reservoir rocks profoundly influences their physical characteristics, including capillary pressure, relative permeability (kro and krw), and fluid distribution, making it a critical property (Anderson, 1986; Craig, 1971). Over millions of years, the interaction between water, oil, and rock establishes wettability conditions in a reservoir system. Wettability typically falls into four states: water-wet, oil-wet, mixed-wet, or fractional wettability (Donaldson & Alam, 2008).

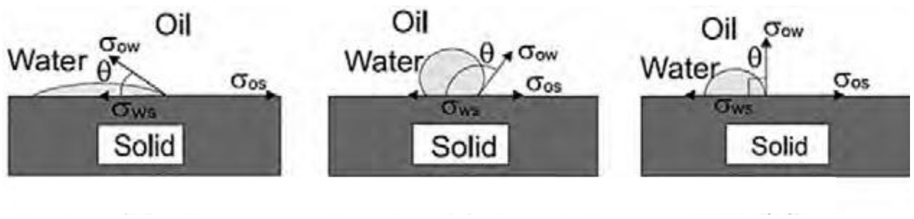
In a water-wet condition, water occupies smaller pores and forms a continuous phase throughout the porous matrix, while the non-wetting phase is present as disconnected droplets in larger pores (**Figure 2.1 (a)**).



(a) (b)

Figure 2.1: Wettability, (a) water-wet and (b) oil-wet conditions (Ahr, 2011).

Water-wet surfaces exhibit a contact angle (θ) of less than 90° (**Figure 2.2 (a)**).



(a) (b) (c)

Figure 2.2: A schematic of the different contact angles for; (a) water-wet condition where water spreads along the surface, (b) on such a surface oil beads up against the surface, indicating an oil-wet condition, (c) no preference for oil or water, figure taken from Dandekar (2013).

Conversely, in an oil-wet condition, oil occupies smaller pores as a continuous phase, while water exists in larger pores, forming a continuous phase at high water saturations (**Figure 2.1 (b)**). Oil-wet systems have contact angles (θ) greater than 90° (**Figure 2.2 (b)**).

Intermediate or neutral wettability occurs when neither oil nor water exhibits a preference, resulting in a contact angle θ of 90° (**Figure 2(c)**).

Strongly water-wet, strongly oil-wet, and intermediate wettability are considered homogeneous wettability, where the porous matrix uniformly favours water or oil (Craig, 1971; Radke et al., 1992). Mixed wettability reflects heterogeneous conditions with coexisting areas of both oil-wet and water-wet surfaces. Smaller rock pores are preferentially water-wet, while larger pores are oil-wet and filled with oil (Salathiel, 1973).

Fractional wettability represents heterogeneous conditions with distinct water-wet and oil-wet areas (Anderson, 1986). This variation can result from differences in mineral properties and crude oil characteristics (Brown & Fatt, 1956).

Wettability profoundly impacts reservoir behaviour, influencing fluid flow, and recovery processes. Understanding and controlling wettability is crucial in optimizing hydrocarbon recovery strategies.

2.3.1 Factors affecting wettability

Wettability plays a critical role in carbonate reservoirs, controlling key reservoir parameters like capillary pressure, oil and water relative permeability, and fluid distribution, which ultimately impact oil displacement efficiency. Several factors influence wettability, primarily driven by interactions among rock mineralogy, brine composition, and crude oil. Modifying these parameters can significantly alter the wetting state, underscoring the importance of understanding how each factor can affect system’s wettability.

2.3.1.1 Type of minerals

Formerly, it was widely assumed that all petroleum reservoirs exhibited water-wet characteristics. However, contact angle measurements have since revealed that most carbonate reservoirs tend to range from neutrally wet to oil-wet (Chilingar & Yen, 1983). Carbonate reservoirs, in general, lean more towards oil-wet characteristics compared to sandstone reservoirs (Treiber & Owens, 1972). Defining wettability in these reservoirs is challenging due to their complex mineral compositions, fractures, and rock heterogeneities (Abdullah et al., 2007). Carbonate surfaces, being composed of positively charged divalent ions like Ca^{2+} and Mg^{2+}, tend to carry a positive charge at basic conditions, allowing negatively charged organic acids to adsorb onto them (Anderson, 1986).

In systems favouring water-wetness, the early stages of water flooding typically yield higher recovery than those favouring oil-wetness. Intermediate wettability is often considered an optimal condition for improved oil recovery (Bobek et al., 1958). Altering wettability as an EOR technique necessitates achieving a mixed wettability state, which is influenced by the rock's chemical composition.

The presence of silica in chalk samples was found to promote a more water-wet condition compared to samples with lower silica content (Strand et al., 2007). This was attributed to negatively charged silica stabilizing the water film between the rock and oil-water interface, preventing direct oil contact with the surface. Additionally, observations indicate that Mg^{2+} can displace Ca^{2+} in chalk, leading to a more water-wet carbonate surface (Austad et al., 2009). Dolomitic carbonates, which have high Mg^{2+} concentrations, might exhibit a similar effect (Shariatpanahi et al., 2016).

The water-wetness of carbonates has been shown to increase in the presence of SO_4^{2-} (Puntervold et al., 2007a), and notably, tertiary low salinity EOR effects in carbonates can be achieved when anhydrite is present (Austad et al., 2012).

2.3.1.2 Oil composition

The composition of crude oil plays a pivotal role in defining wettability, with crucial consequences for reservoir behaviour (Buckley, 1996). Crude oil contains an array of surface-active components, including both acidic and basic groups, capable of complicated interactions with carbonate surfaces (Fathi et al., 2011a; Standnes & Austad, 2000b). Specifically, carboxylic acid groups (R-COOH), found in the heavier fractions of crude oil, can under alkaline conditions adsorb onto positively charged carbonate surfaces.

These interactions are influenced by several key factors, including the chemical composition of the crude oil, the nature of the rock, and the initial brine. For instance, asphaltenes, which constitute a significant portion of the heavy fractions of crude oil, are rich in polar elements like nitrogen, sulphur, and oxygen. The concentration of asphaltenes is dependent on the source of the crude oil, which further highlights the complexity of these interactions (Skauge et al., 1999).

Measuring the acid number (AN) and base number (BN) offers a quantifiable means of assessing the surface-active constituents within crude oil, with measurements typically expressed in mg KOH/g of oil (Fan & Buckley, 2007). Studies have demonstrated that increasing AN values correlate with a reduction in water-wetness in various contexts (Standnes & Austad, 2000b). Exposure of outcrop chalk material to different crude oils revealed diminished water-wetness with increasing AN, as evidenced by contact angle measurements. These findings were reinforced by another study, which found that higher AN values led to reduced wettability in chalk samples (Puntervold, 2008; Zhang & Austad, 2005).

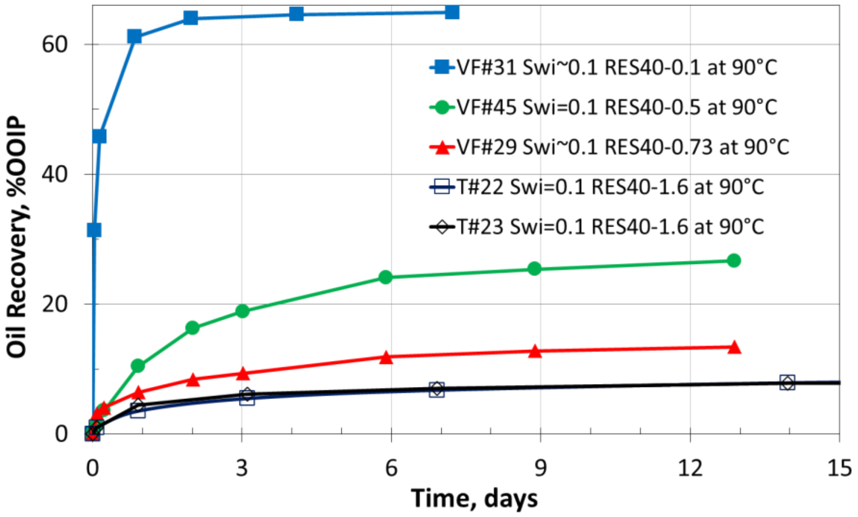


Figure 2.3: Spontaneous imbibition experiments characterizing the effect of increasing AN on chalk wettability. Experiments were performed at 90°C, and saturated with different crude oils with different AN (Puntervold, 2008).

Additionally, AN was observed to have an impact on water-wetness in reservoir limestone (Ravari, 2011). Furthermore, it has been revealed that certain surface-active components, specifically carboxylic acids, may become water-extractable in the presence of aqueous phases, further influencing wettability. When these water-extractable acids were introduced into a crude oil lacking polar elements, they significantly altered the wettability of chalk cores. Chalk saturated with crude oil containing water-extractable acids displayed reduced water-wetness compared to cores saturated with the original crude oil (Fathi et al., 2011a; S. J. Fathi et al., 2010).

It's worth noting that the influence of the BN on wettability is generally less pronounced. However, the type of basic material present can impact wettability dynamics. For instance, a strong model base was found to influence wettability by co-adsorbing with carboxylic acids onto the surface. This process mitigated electrostatic repulsion, enabling increased adsorption of carboxylic material and reducing water-wetness. Conversely, in natural petroleum-based oils containing larger basic molecules, an increase in water-wetness was observed with rising base numbers. This phenomenon was attributed to the formation of acid-base complexes that hindered the adsorption of carboxylic acids onto the surface, resulting in higher water-wetness (Puntervold et al., 2007b).

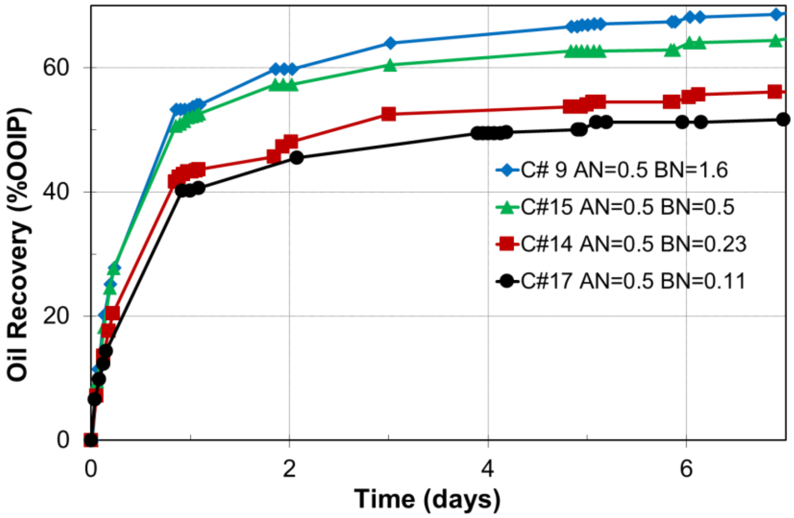


Figure 2.4: Spontaneous imbibition experiments characterizing the effect of increasing BN on chalk wettability. Experiments were performed at 70°C, and saturated with different crude oils with different BN (Puntervold et al., 2007b).

These findings collectively underscore the intricate interplay between crude oil composition and reservoir wettability, highlighting the need to consider these factors in understanding and optimizing reservoir behaviour.

2.3.1.3 Water saturation and brine composition

The composition of FW or connate water in a formation, often distinct from injected brine during water flooding, significantly influences wettability. In carbonate formations, connate water, rich in calcium, imparts a positive charge to the carbonate surface. It also contains moderate magnesium levels and minimal sulphate. Even small sulphate concentrations in FW have been observed to notably impact initial core wettability (Puntervold et al., 2007b). The presence of sulphate increases water-wetness in the system (Shariatpanahi et al., 2011). Presence of Mg^{2+} in the FW makes the core more water wet while presence of Ca^{2+} makes the core less water wet (**Figure 2.5**).

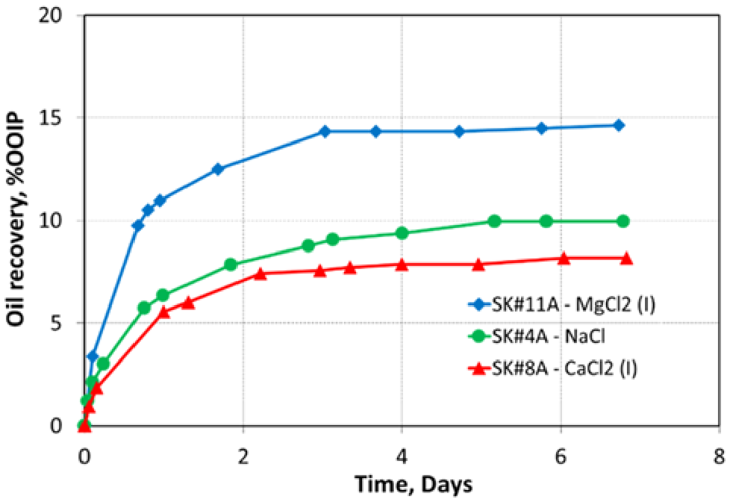


Figure 2.5: Oil recovery by spontaneous imbibition of FW into SK chalk cores at 25 °C with Swi = 0.10 using formation brines with the same salinity, 63000 ppm, but different types of cations: Pure NaCl brine, $MgCl_2$ with high Mg^{2+} concentration, and $CaCl_2$ with high Ca^{2+} concentration. Oil 1 with AN = 0.34 mgKOH/g was used (Shariatpanahi et al., 2016).

Pre-flooding a core with DW, as opposed to leaving it untreated, resulted in approximately 30% lower oil recovery by spontaneous imbibition. This underscores that sulphate, whether in the FW or rock, can significantly increase water-wetness (Puntervold et al., 2007a). Increasing initial water saturation enhances recovery via spontaneous imbibition and intensifies water-wetness. Improved water-wetness is attributed to greater initial water saturation, exposing more rock to crude oil for wettability alteration. Thin contouring water films may serve as potential sites for the adsorption of polar active components (Brady et al., 2015). Therefore, the stability of the water film between oil and rock plays a pivotal role in determining initial wettability (Ravari, 2011).

2.3.1.4 Temperature and pressure

The solubility of polar active components in crude oil increases with rising pressure and temperature (Anderson, 1986). At atmospheric conditions, cores tend to exhibit more oil-wet behaviour due to reduced solubility of wettability-altering components. Pressure changes during core material extraction can cause fluid expulsion from porous media, altering fluid spatial distribution. Consequently, light ends may be lost from the crude oil, favouring the deposition of asphaltenes, shifting wettability towards a less water-wet state (Anderson, 1986).

However, some studies, like Wang and Gupta's experiments, have shown that the pressure effect on wettability measurements is not highly sensitive (Wang & Gupta, 1995). The reactivity of polar components is also influenced by the system's mineralogy. In high-temperature carbonate reservoirs, decarboxylation processes may occur, lowering the acid number due to the presence of calcium carbonate, which acts as a catalyst (Zhang & Austad, 2005). Since carbonate surface wetting is sensitive to carboxylic material, these effects should be evaluated in terms of mineralogy.

Hjelmeland and Larrondo (1986) reported that increasing temperatures in a carbonate system reduced IFT, whereas increased pressure had a minimal effect. This temperature-related observation is consistent with other carbonate systems regarded as more water-wet (Hamouda & Rezaei Gomari, 2006). Rao's research suggested that quartz surfaces tend to become more oil-wet with rising temperature, while calcite surfaces in carbonates tend to become more water-wet (Rao, 1999). These findings underscore the complexity of wettability alterations in relation to pressure and temperature variations.

2.3.1.5 Core cleaning and restoration

The wettability of carbonate cores in laboratory experiments can be significantly influenced by the method used for core cleaning and restoration. Shariatpanahi et al. (2012) explored the impact of different core cleaning methods, introducing a "mild" cleaning approach using kerosene and heptane as non-aggressive agents. Cleaning method involving toluene/methanol demonstrated increased ultimate recovery compared to mild cleaning, suggesting that a more aggressive cleaning approach using toluene/methanol can shift the wettability towards a more water-wet state.

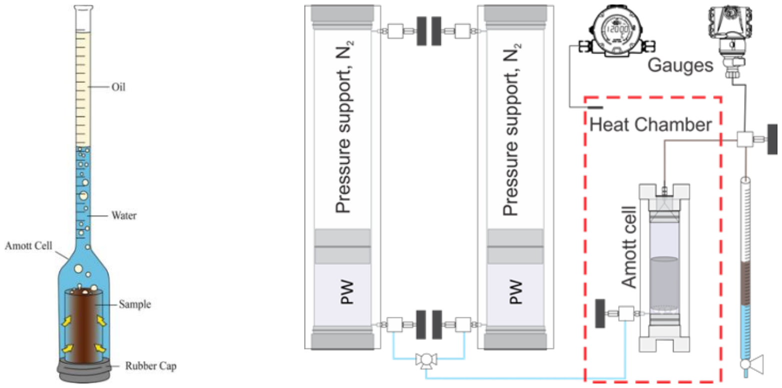
Additionally, Hopkins et al. (2017) observed that the adsorption of POC was somewhat proportional to the injected amount of crude oil into the rock. Increased crude oil exposure during core restoration led to a less water-wet state, indicating that the wettability of the core was influenced by the amount of crude oil injected, reducing water-wetness during the second restoration phase (Hopkins et al., 2017). Piñerez et al. (2020) recently showed that 1 PV oil is enough to mimic the wettability in each restoration. More oil exposer would make the chalk core less water wet.

2.3.2 Evaluation of wettability

2.3.2.1 Spontaneous imbibition

Spontaneous imbibition is an experimental method to assess the wettability of porous rock, primarily influenced by capillary forces, which depend on IFT and wettability. It provides insights into wettability based on imbibition rate and total fluid displacement. The setup, as depicted in **Figure 2.6 (a)**, involves an Amott cell containing a rock sample saturated with the displaced phase (oil) and an imbibing phase (water).

In a water-wet scenario, produced oil is collected in the upper part of the burette, while for a strongly oil-wet case, normally, no oil is produced. However, the Amott cell may face issues like leakage and water evaporation at temperatures exceeding 60°C. In such cases, a custom steel cell with brine pressure support at 10 bar, controlled by nitrogen gas to prevent evaporation (**Figure 2.6 (b)**), is typically employed. This alternative ensures reliable measurements under high-temperature conditions.



(a) (b)

Figure 2.6: Spontaneous imbibition apparatus, (a) Amott cell and (b) Steel cell for high temperature.

2.3.2.2 Chromatographic wettability test for carbonates

This wettability assessment method utilizes chromatography to separate sulphate ions (SO_4^{2-}) and thiocyanate (SCN^-)/lithium (Li^+) as tracers (Strand et al., 2006). The procedure involves initially flooding a carbonate core with brine without any tracer or sulphate. Subsequently, a brine with an equal molar concentration of SCN^-/Li^+ and SO_4^{2-} is injected into the core. The effluents are then analysed using an ion chromatography. Plotting ion concentrations against the injected pore volume allows the calculation of the area between the two curves. The wettability index, indicating the degree of wettability, can be determined using **Eq. 2.7**:

$$I_{CW} = \frac{\mathrm{A_{Wett}}}{\mathrm{A_{Ref}}} \tag{2.7}$$

Where,

I_{CW} = Wettability index, ranges from 0 (completely oil-wet) to 1 (completely water-wet).

A_{Wett} = Area calculated between the curves of the ionic concentration of sulphate and lithium/thiocyanate.

A_{Ref} = Reference area which indicates a completely water-wet state.

In summary, the calculated area A_{Wett} is directly proportional to the water-wet surface in the porous medium because both SCN^- and SO_4^{2-} contacted the same water-wet region (Strand et al., 2006).

Figure 2.7 provides an example of this method. When sulphate ions have ample pore surface available for adsorption, A_{Wett} increases, indicating strong water-wettability. Conversely, as sulphate adsorption decreases, the water-wetness level in the system diminishes.

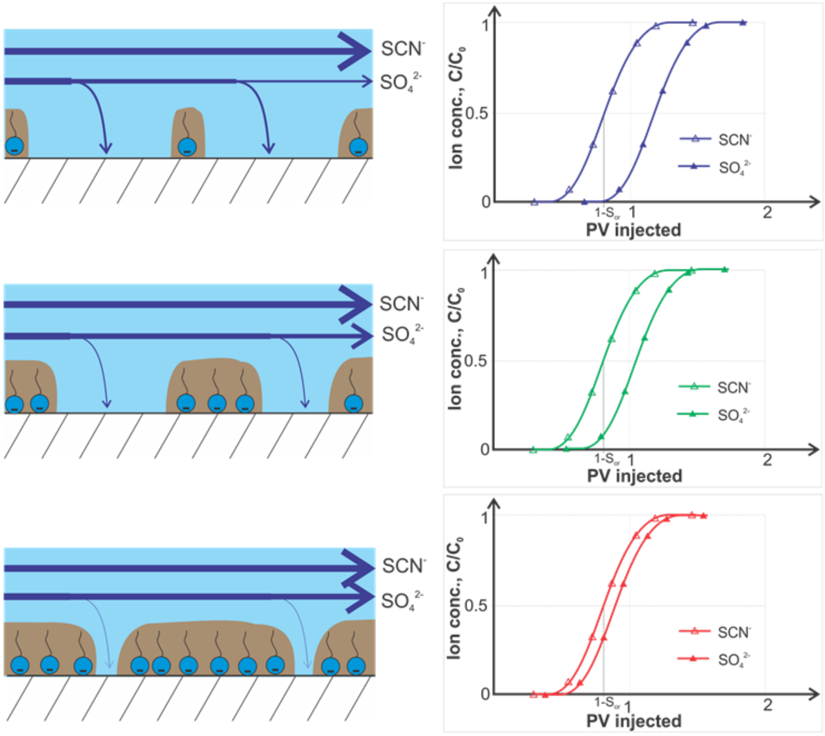
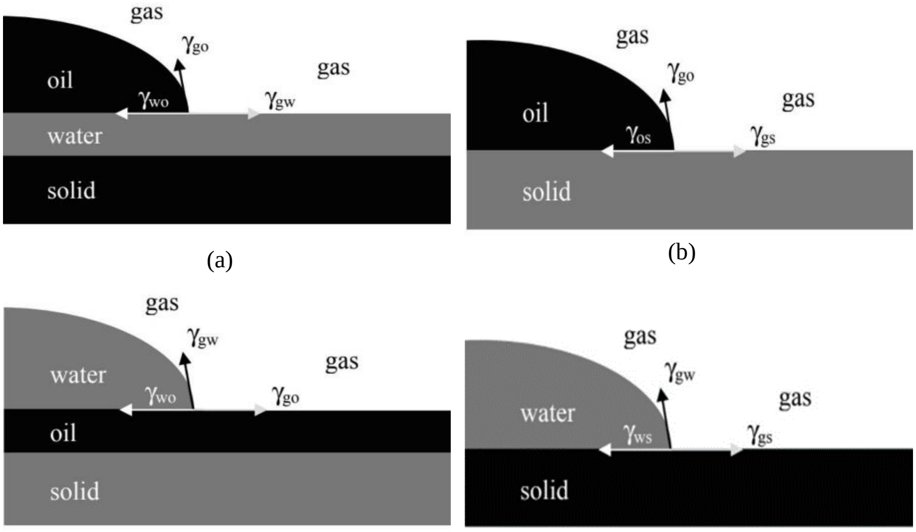


Figure 2.7: From top to bottom: completely water wet-state, completely oil-wet state and mixed wet state.

2.3.2.3 Contact angle

Contact angle measurements have become a widely employed technique in recent decades. This method entails placing a droplet of a specific fluid, such as water, onto a flat solid surface. This measurement cannot be performed in porous rock system. The solid surface is then submerged in a different fluid, often oil, than the initial wetting phase. The angle at which the water droplet maintains contact with the solid provides critical insights. This angle can vary from 0°, signifying extreme water-wettability, to 180°, indicating extreme oil-wettability. When the contact angle hovers around 90°, the wetting behaviour is considered neutral.

Figure 2.8 (a-d) serves as a visual representation of contact angle measurements. In **Figure 2.8 (a)**, a scenario of strong water-wettability is depicted, where the contact angle between water and the solid is virtually nonexistent, leading to the formation of a thin water film on the solid's surface. **Figure 2.8 (b)** illustrates a strong oil-wet condition, showcasing the presence of an oil film. In **Figure 2.8 (c)**, we observe a weakly water-wet situation with the formation of a water film, while **Figure 2.8 (d)** portrays a weakly oil-wet scenario without an oil film.



(a) (b)

(c) (d)

Figure 2.8: Contact angle measurements for (a) strongly water-wet with water film, (b) weakly water-wet with no water-film, (c) strongly oil-wet with oil film, and (d) weakly oil-wet with no oil-film (Donaldson & Alam, 2008).

2.3.2.4 Amott wettability index

The Amott wettability test assesses wettability via combined oil recovery tests, involving both spontaneous and forced imbibition methods. The fundamental theory is established on finding the imbibed fluid through spontaneous imbibition as the wetting phase, which displaces the non-wetting phase. The capillary pressure throughout the different imbibition phases is measured. This method consists of saturating a core with brine to achieve Sor, followed by a series of stages (see **Figure 2.9**) (Anderson 1986b, Morrow 1990).

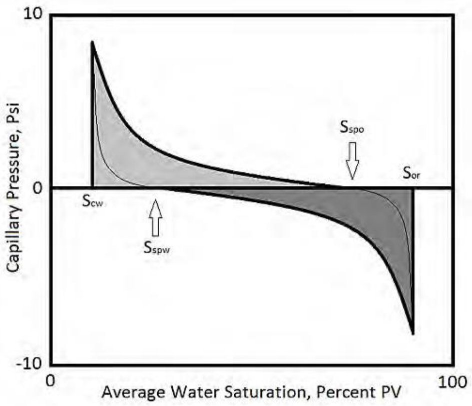


Figure 2.9: Cycle showing the capillary pressure against water saturation, each stage illustrates an imbibition test.

The Amott wettability index is quantified through two distinct indices: the Amott index for water (I_W) and the Amott index for oil (I_O) (Morrow 1990)

$$I_W = \frac{\Delta S_{ws}}{\Delta S_{wt}} \quad \textbf{(2.8)}$$

$$I_O = \frac{\Delta S_{os}}{\Delta S_{wt}} \quad \textbf{(2.9)}$$

When spontaneous imbibition leads to the recovery of a significant portion of the oil, the I_W approaches to 1. In contrast, if I_W approaches 0, it indicates that the core demonstrates less water-wettability, suggesting that water is less effective in displacing and recovering oil during the imbibition process (Morrow et al. 1994).

Additionally, the Amott-Harvey index, more commonly used than the Amott test, simplifies wettability assessment into a single value. The Amott-Harvey index (I_{AH}) is calculated as the difference between I_W and I_O (Anderson 1986b).

$$I_{AH} = I_w - I_o \quad \textbf{(2.10)}$$

I_{AH}'s value ranges from -1 to 1, with 1 indicating a strongly water-wet system and -1 indicating a strongly oil-wet system.

2.3.2.5 Other methods

Besides the above-stated approaches, various other techniques have been recommended for assessing the wettability. Some of them are based on the thermodynamic definition of wetting related to the physicochemical reaction caused by intermolecular forces of attraction (Jiang et al., 2020; Xie et al., 2015), IFT and displacement-pressure measurements, shape of relative permeability curves, shape of recovery curves, permeability and saturation measurements (based on saturation frequency distributions of samples as a function of their permeabilities), dye adsorption, flotation experiments (for unconsolidated rocks), x-ray photoelectron spectroscopy, (Anderson, 1987; Fatemi et al., 2012; Jahanbakhsh et al., 2016). Other than those, nuclear magnetic relaxation measurements (Newgord et al., 2019), use of well logs and capillary pressure curve are also used to measure wettability (Morrow, 1990).

2.4 Wettability alteration in carbonates for EOR

Wettability alteration in carbonates can be achieved by flooding chemicals such as surfactants, nanoparticles, alkalis or naturally occurring salts, modified brine (Smart Water), CW or different gases. Mostly used wettability modifier in carbonates are discussed below:

2.4.1 Surfactants

The modification of carbonate rocks wettability towards a more water-wet state for EOR using surfactants has been extensively studied by researchers. Surfactants, characterized by their amphiphilic nature, possess both hydrophilic and hydrophobic properties, making them highly surface-active. These surfactants can be broadly classified into anionic, cationic, zwitterionic, or non-ionic types based on their hydrophilic groups (Green & Willhite, 2018; Spinler & Baldwin, 2000).

Additionally, there is a growing interest in bio-based surfactants, derived from natural sources, owing to their environmental advantages (Singh et al., 2021; Singh et al., 2023). Researchers have conducted imbibition tests to evaluate the potential of various surfactant types in altering the wettability of oil-wet carbonate rocks (Chen & Mohanty, 2015; Standnes & Austad, 2000b; Wu et al., 2008). Cationic surfactants, particularly those from the quaternary ammonium and phosphonium families, have shown promise in expelling oil, primarily through the formation of ion-pairs via electrostatic interactions with adsorbed negative compounds from crude oil on rock surfaces (Standnes & Austad, 2000b). This mechanism, combined with hydrophobic interactions between alkyl chains, leads to desorption from the carbonate surface and subsequent wettability alteration towards a more water-wet state (Tafur et al., 2023).

Anionic surfactants, while generally less effective, exhibit some potential, with ethoxylated sulphonates showing relatively higher efficiency. These surfactants are thought to form a surfactant layer with hydrophobic chains oriented towards the carbonate surface, resulting in a double-layer water-wet surface (Jarrahian et al., 2012; Standnes & Austad, 2000b; Standnes & Austad, 2003).

Non-ionic surfactants, specifically ethoxylated alcohol types, have been found to be less effective than cationic surfactants, with their wettability alteration mechanism involving the formation of a bilayer structure (Standnes et al., 2002).

However, it's important to note that surfactant effectiveness is significantly affected by high temperatures, low pH environments, and salinity. It also has processing and disposal challenges in the downstream (Adibhatla & Mohanty, 2006; Strand et al., 2003).

2.4.2 Ionic liquid

Ionic liquids are a class of salts characterized by their unique properties, including low melting or glass transition temperatures below 100 °C. They are known for their exceptional thermal stability, high solvation capacity, and the ability to undergo functionalization. Ionic liquids can be engineered to withstand harsh environmental conditions (Bera & Belhaj, 2016; Bin Dahbag et al., 2015). Remarkably, they exhibit negligible vapor pressure, making them environmentally friendly and preventing atmospheric contamination, as highlighted by Nandwani et al. (2018).

Ionic liquids with extended alkyl chains, typically comprising more than six carbon atoms, possess surfactant properties and demonstrate self-aggregation into micelles when introduced into water. This unique characteristic allows them to reduce IFT, a critical factor in various applications (Cooper et al., 2004).

In recent years, researchers have explored the potential of these surfactant-like ionic liquids, often referred to as Surface-Active Ionic Liquids (SAILs), in EOR applications. Bera and Belhaj (2016) emphasized SAILs' ability to lower water-oil IFT and their robust performance under challenging conditions, such as high salinity and temperature. Furthermore, Somoza et al. (2022) conducted a comprehensive review of core-flooding experiments involving these salts, noting that most studies focused on sandstone reservoirs, despite the anticipated high adsorption of cationic surfactants in such formations. Nevertheless, these studies revealed additional oil recoveries ranging from 5% to 12% of the original oil in place (OOIP) (Bin Dahbag et al., 2015; Liu et al., 2019; Rodríguez-Palmeiro et al., 2017). Assessments conducted on carbonate cores reported even more promising oil recovery values, typically falling within the range of 8% to 20 %OOIP (Nabipour et al., 2017; Sakthivel, 2022; Somoza et al., 2022; Zabihi et al., 2020).

Despite these encouraging outcomes, achieving ultra-low IFT using pure SAILs remains a challenge. Consequently, researchers have explored blending cationic SAILs with traditional anionic surfactants to facilitate the formation of mixed micelles, often referred to as catanionic micelles. This approach enhances surface activity when in contact with the oil phase, as observed in core flooding tests comparing these blends with pure surfactants (Jia et al., 2017; Somoza et al., 2022).

Moreover, contact-angle measurements have indicated that certain SAILs possess the ability to alter wettability towards a more water-wet state (Cao et al., 2015; Nabipour et al., 2017; Sakthivel, 2022). Notably, a limited number of studies, conducted by Sakthivel and Elsayed (2021) and Manshad et al. (2017), have explored the potential of SAILs to modify wettability through imbibition tests in carbonate cores at elevated temperatures (80-100 °C). These experiments yielded impressive spontaneous imbibition values, leading to an extra oil recovery of up to 34%.

2.4.3 Smart Water

Smart Water is a technique used to modify the wettability of carbonate rocks towards a more water-wet condition, achieved by altering the ionic composition of the injection water (Fathi et al., 2010; Fathi et al., 2011b; Strand et al., 2006).

A notable Smart Water EOR effect has been observed in naturally fractured chalk fields in the North Sea through the injection of SW (Austad et al., 2008; Hermansen et al., 2000). This alteration in wettability is induced by specific ions found in SW, namely calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulphate (SO_4^{2-}). The catalyst for this process has been identified as SO_4^{2-} present in SW. Ca^{2+} also plays a significant role as it can co-adsorb onto the chalk surface, facilitating the wettability alteration process. Mg^{2+} become relevant at elevated temperatures, where they can replace Ca^{2+} on the chalk surface, making more calcium ions available in the bulk fluid, thereby positively impacting the EOR effect (Zhang et al., 2007). The influence of increased SO_4^{2-} and Ca^{2+} in imbibing brine can be observed in **Figures 2.10** and **Figures 2.11** respectively.

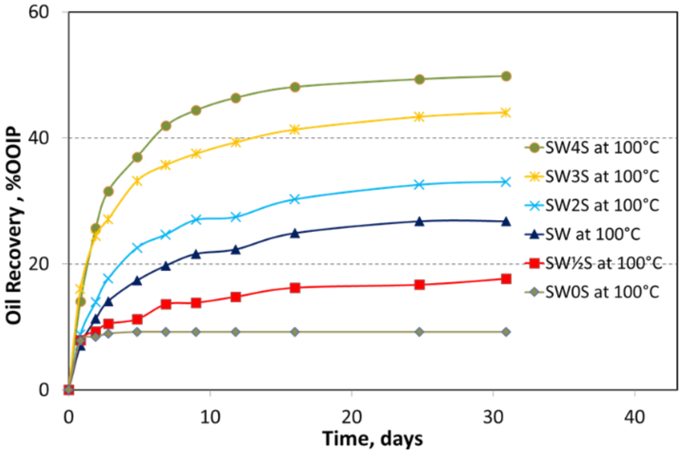


Figure 2.10: Spontaneous imbibition experiments on chalk at 100 °C displaying the EOR effect on Stevns Klint chalk cores by increasing sulphate concentration (Zhang et al., 2007).

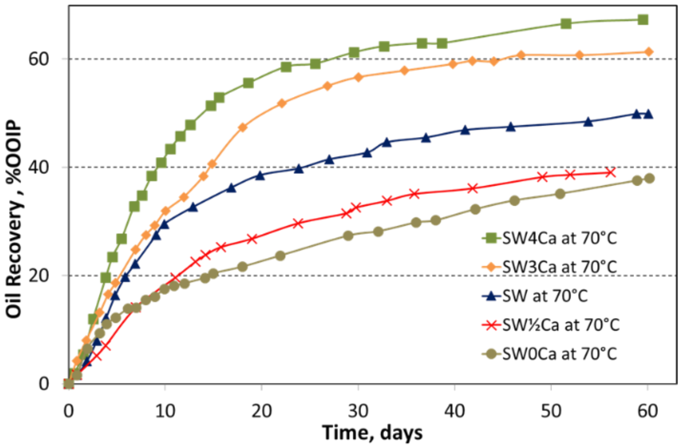


Figure 2.11: Spontaneous imbibition experiments on chalk at 70 °C on displaying the EOR effect by increasing calcium concentration (Zhang et al., 2007).

Modifying the Smart Water composition can enhance oil recovery in carbonate reservoirs more than SW. For instance, reducing the concentration of sodium chloride (NaCl) in SW or increasing the concentration of sulphate in the brine can increase oil recovery beyond the wettability alteration potential of SW (Fathi et al., 2011b; Puntervold et al., 2015), as illustrated in **Figure 2.12**.

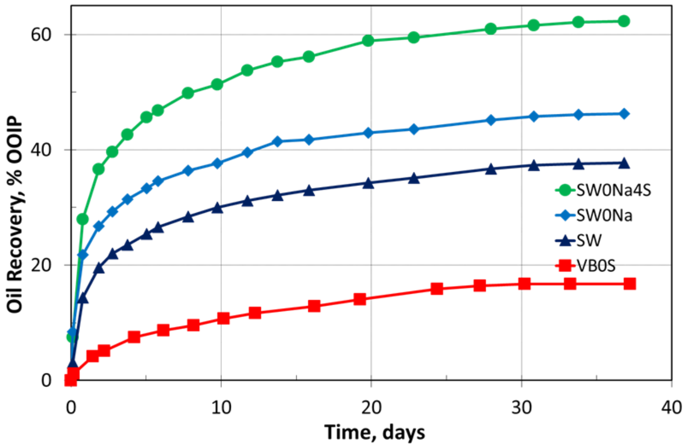


Figure 2.12: Spontaneous imbibition experiments on chalk, EOR effect at 90 °C on chalk cores by using VB (formation water), SW, and two modified SW brines; SW0NaCl and SW0NaCl-4SO4 (Fathi et al., 2011b).

The wettability alteration process in carbonates is temperature-dependent (Fathi et al., 2011b). It appears that improved oil recovery is more pronounced at higher temperatures. This effect is attributed to the increased reactivity of ions towards carbonate surfaces. As the temperature rises, the hydration number of ions in water decreases, allowing for more ion-ion interactions and increased chemical reactivity. Temperature effects can impact both the initial wetting state and the wettability alteration processes (Piñerez Torrijos et al., 2019a; Strand et al., 2008; Zavitsas, 2005).

In the Smart Water EOR mechanism for carbonates, the adsorption of SO_4^{2-} ions onto the rock surface reduces the positive surface charge, facilitating the co-adsorption of Ca^{2+}, which is the common ion in $CaCO_3$. This, in turn, leads to a reaction between Ca^{2+} and the adsorbed acidic components on the surface, primarily represented by dissociated carboxylic acids ($RCOO^-$) (Zhang, 2006). This reaction triggers the desorption of organic molecules, thereby changing wettability, as depicted in **Figure 2.13**.

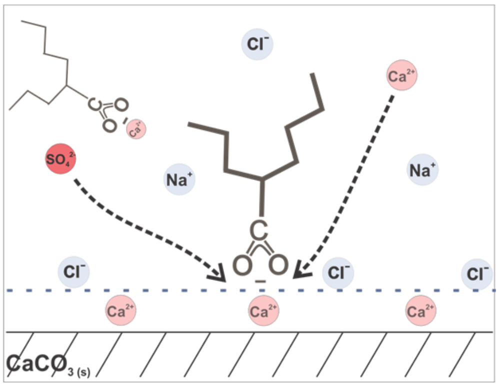


Figure 2.13: A schematic illustration of Smart Water mechanism in carbonates. The active ions are SO_4^{2-} and Ca^{2+}. At high temperature Mg^{2+} becomes more reactive influencing the Ca^{2+} concentration in solution (Zhang, 2006).

It's important to note that temperature also influences this process. At high temperatures, Mg^{2+} ions become more reactive due to dehydration. Experiments have shown that Mg^{2+} can interact with calcite surfaces, releasing more Ca^{2+} ions into the surrounding environment and accelerating the wettability alteration process (Zhang et al., 2007). Furthermore, at elevated temperatures, Mg^{2+} ions form complexes with SO_4^{2-} ions, reducing the precipitation of $CaSO_4$, which, in turn, lowers the concentration of Ca^{2+} and SO_4^{2-}, essential components in the wettability alteration process.

In a comparative study conducted by Zhang et al. (2007), several spontaneous imbibition tests at varying concentrations of SO_4^{2-}, Ca^{2+}, and Mg^{2+} were evaluated at increasing temperatures, starting at 70°C with gradual increments to 100 and 130°C. The study revealed that calcium's role is highly relevant but necessitates the presence of sulphate, as illustrated in **Figure 2.14**.

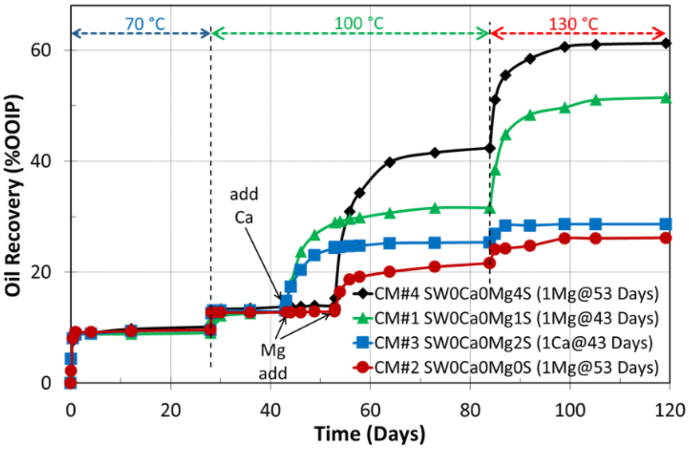


Figure 2.14: Spontaneous imbibition on chalk cores with SW at changing SO_4^{2-}, Ca^{2+} and Mg^{2+} concentrations and temperatures (Zhang et al., 2007).

2.4.4 Carbonated water

To achieve the ambitious goal of net-zero carbon emissions by 2050, the oil industry is actively seeking environmentally friendly methods to increase oil recovery. One promising solution is Carbon Capture, Utilization, and Storage (CCUS), where CO_2 is captured and utilized to enhance oil recovery while permanently storing CO_2 in the reservoir in the process.

Numerous experiments and field trials have confirmed that CO_2 injection can significantly boost oil recovery by reducing oil viscosity and improving sweep efficiency (Esene et al., 2019). However, direct CO_2 injection faces challenges such as gravity segregation, viscous fingering effects, and technical complexities in handling CO_2. To address these issues while retaining CO_2 storage potential, the concept of injecting CW has gained popularity (Riazi et al., 2009).

Several mechanisms were proposed in various literature for the enhanced oil recovery seen by CW injection (Bisweswar et al., 2020). The primary mechanism involves the mass transfer of CO_2 from the water phase to the oil phase, driven by the significantly higher solubility of CO_2 in oil compared to water (Abedini & Torabi, 2013; Dong et al., 2011; Green & Willhite, 1998). This process leads to oil swelling, a reduction in IFT between oil and rock, lower oil viscosity, reconnection of isolated oil droplets, enhanced relative permeability of oil, and improved oil mobilization, ultimately resulting in higher sweep efficiency (Riazi et al., 2009). Additionally, wettability alteration due to CO_2 mass transfer has been proposed, where CO_2 dissolution into the oil phase destabilizes polar organic components attached to rock surfaces, facilitating their movement. Changes in aqueous phase pH in CW further modify surface charges at water/oil and water/rock interfaces, leading to alterations in system wettability and increased oil recovery (Sohrabi et al., 2015).

Another mechanism contributing to oil recovery during CW injection is the evolution of solution gas from heavy oil due to CO_2 dissolution (Mosavat, 2014). Furthermore, the interaction between the rock and CW, resulting in rock dissolution and increased permeability by creating new pathways for oil mobilization, is believed to play a role in boosting oil recovery (Kono et al., 2014).

Numerous studies have reported significant additional oil recovery in carbonate reservoirs through the injection of CW, while also offering CO_2 storage opportunities (Esene et al., 2019). Early research conducted by the Oil Recovery Corporation in the 1940s found that injecting CW after conventional water flooding led to an additional 15% oil production (Adiputra et al., 2018). Studies by Lake et al. (1984) reported an extra 26% oil recovery in tertiary mode when CW was injected, particularly effective for light oil reservoirs. More recent extensive research conducted by the Heriot Watt Institute of Petroleum Engineering Center demonstrated increased oil recovery in both secondary and tertiary modes through core flooding and micro-model experiments (Sohrabi et al., 2015). Kilybay et al. (2016) conducted oil recovery experiments by flooding different Smart Waters and Carbonated Smart Water into carbonate reservoir core plugs, resulting in an additional oil recovery of approximately 14%. This was attributed to CO_2 mass transfer inducing viscosity reduction, local flow diversion, and trapped oil swelling. Evidence of carbonate dissolution and pore enlargement was observed through NMR (Nuclear Magnetic Resonance) porosity and ICP-MS (Inductively Coupled Plasma-Mass-Spectrometry) studies (Kilybay et al., 2016). Furthermore, sand pack flooding experiments conducted by Mosavat (2014) demonstrated the feasibility of CO_2 storage through CW injection. Numerical simulations and laboratory experiments by Kechut et al. (2011) estimated that approximately 47-51% of total injected CO_2 can be stored through injection.

3. Experimental

3.1 Material

3.1.1 Rock material

In this study, outcrop chalk cores from 2 separate quarries and reservoir chalk cores from 2 separate reservoir systems were used.

3.1.1.1 Reservoir cores

Reservoir chalk cores (SU2, WZ, RC1, and RC2) were obtained from two distinct reservoir systems located in the North Sea. SU2 and WZ cores were extracted from the same reservoir system, with SU2 originating from an oil zone located at a depth of 1384.5 meters below sea level, while WZ was taken from the aquifer zone below the oil-water contact at a depth of 1412.3 meters below sea level. RC1 and RC2 was drilled from an oil reservoir situated much deeper, at a depth of ~3100 meters below sea level. The cores were received in a consolidated and well-preserved state, with the presence of fluids observed during the cleaning process. Permeability, porosity, and pore volume measurements were conducted during core preparation.

3.1.1.2 Outcrop cores

There is limited access to outcrop chalk material in Europe. There are still two active chalk quarries in Denmark that belong to the same chalk deposition as the North Sea chalk reservoirs and from where the chalk samples were collected for this study.

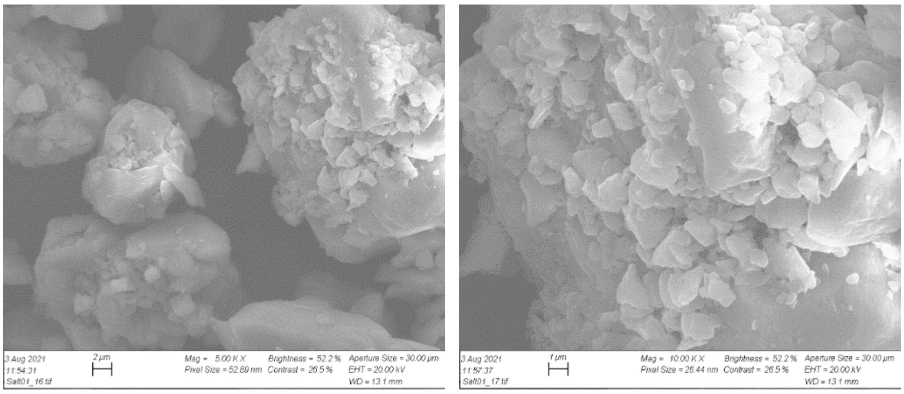
Outcrop Stevns Klint (SK) chalk sample was obtained from a quarry near Copenhagen, Denmark. This chalk sample is predominantly composed of over 98% $CaCO_3$ and has a low content of silicate impurities. The SK chalk is considered to be representative of chalk reservoirs found in the North Sea (Frykman, 2001).

Additionally, an Aalborg (AA) outcrop chalk core collected from the Rørdal quarry in Aalborg, Denmark was also utilized in this study. The outcrop cores were carefully prepared by drilling in the same direction from different blocks, followed by lathe shaving and saw cutting to achieve the desired cylindrical size for fitting into the Hassler core holder. The physical properties such as porosity, permeability and pore volume of the SK and AA outcrop chalk cores were measure during core preparation.

3.1.2 Polysulphate

Polysulphate (PS), also known as polyhalite, is a naturally occurring salt mined from a polyhalite rock layer 1200 m below the surface in the Boulby mine located near the North Yorkshire coast of the United Kingdom. The deposition of polyhalite happened 260 million years ago in the Permian period and believed to be the only source of PS worldwide. The deposition is estimated to be 1 billion tonnes and mined PS is easily available and mainly used as a fertiliser today (ICL, 2023).

The PS salt used in this study was provided by the ICL group. It had a slightly grey colour and was delivered in granulated to powder form. The diameter of the salt particles was predominantly in the range of 5 to 30 µm. High-resolution SEM images of the salt particles are shown in **Figure 3.1.**



(a) (b)

Figure 3.1: SEM images of a PS sample at (a) 5000X magnification and (b) 10000X magnification.

EDS analysis was performed to determine the elemental composition of a PS sample, and the atomic weight % (wt%) of anions and cations present are given in **Table 3.1**.

Table 3.1: Elementary composition of PS by atomic weight % of anions and cations.

Anions		Cations	
Element	Atomic wt%	Element	Atomic wt%
Sulfur, S	85.4	Sodium, Na	9.3
Chloride, Cl	14.6	Magnesium, Mg	21.9
		Calcium, Ca	36.9
		Potassium, K	25.5
		Silica, Si	3.3
		Aluminium, Al	3.2

The salt composition was found to be dominated by sulphate anions and calcium, potassium, and magnesium cations. The PS salt was used, as delivered and without further treatment, as an additive to different brines to prepare injection brines containing the important wettability modifying ions (Ca^{2+} and SO_4^{2-}) for carbonate rocks.

3.1.3 Brine

Synthetic brines were prepared in the laboratory by dissolving specific amounts of reagent-grade salts in DW. The brine solutions were mixed overnight and filtered through a 0.22 μm Millipore filter before use. In the establishment of the initial wettability in the outcrop chalk cores, a SO_4^{2-}-depleted FW based on Valhall chalk field composition (FW_A) was used, while reservoir FW (FW_B) was used in the reservoir chalk cores. It is worth mentioning that there was not a big difference in salinity between the two FW (FW_A and FW_B).

3 different Smart Water brines, SmW1, SmW2, and SmW3, were used in this study. SmW1 was made by adding 10 millimolar (mM) $CaSO_4$ salt to DW. SmW2 contained 20 mM $CaSO_4$ and 20 mM $MgCl_2$, while SmW3 contained 20 mM $CaSO_4$ and 40 mM $MgCl_2$, with the extra magnesium added to improve the solubility of $CaSO_4$ at elevated temperature.

All these above-mentioned brine compositions are given in **Table 3.2**.

Table 3.2: Brine compositions.

Ions	FW_A (mM)	FW_B (mM)	SmW1 (mM)	SmW2 (mM)	SmW3 (mM)
Na^+	997	1001	0	0	0
K^+	5	4.9	0	0	0
Ca^{2+}	29	89.6	10	20	20
Mg^{2+}	8	18.2	0	20	40
Cl^-	1066	1220.1	0	40	80
HCO_3^-	9	5.9	0	0	0
SO_4^{2-}	0	0	10	20	20
Sr^{2+}	0	5.2	0	0	0
Li^+	0	0	0	0	0
SCN^-	0	0	0	0	0
TDS (g/L)	62.83	71.14	1.4	4.63	6.5
Density (g/cm^3)	1.041	1.0485	0.999	1.0019	1.0035
Bulk -pH	7.3	6.67	7.06	7.16	7.25

The SW composition is based on the composition of the North Sea SW. Produced water (PW) composition is based on PW from a North Sea chalk reservoir. The PS-containing brines; DW-PS, SW-PS and PW-PS were made by mixing DW, SW and PW, respectively, with 5.00 g PS per litre solution. The solutions were mixed for 6 days with a magnetic stirrer before filtration through a 0.22 µm Millipore filter. After filtering, the insoluble particle residue was quantified by weight. It was found that more than 95 % of the PS dissolved in both DW and SW, while 81 % dissolved in PW, due to its higher salinity. Variations in the ion composition of the prepared brines were observed since PS is a naturally occurring salt. To minimize these variations, 20-litre stock solutions of DW-PS, SW-PS, and PW-PS were prepared and used throughout the experimental work.

The two brines SW0T and SW½T, where SW½T contains the non-adsorbing tracer SCN-/Li+ and adsorbing SO_4^{2-}, were used in surface reactivity tests described later. The ion compositions of the filtrated brines were analysed by ion chromatography (IC) and are given in **Table 3.3**.

Table 3.3: Compositions and properties of additional used brines.

Ions	SW (mM)	PW (mM)	DW-PS (mM)	SW-PS (mM)	PW-PS (mM)	SW0T (mM)	SW½T (mM)
K^+	10	5.0	17.4	28.2	20.5	10.0	22.0
Ca^{2+}	13	31	15.2	29.6	41.0	13.0	13.0
Mg^{2+}	45	8.0	5.8	47.9	15.3	45.0	45.0
Na^+	450	1027	6.3	466.2	1000	460.0	427.0
Li^+	-	-	-	-	-	-	12.0
Cl^-	525	1096	9.2	528.5	1072	583.0	583.0
HCO_3^-	2.0	13	-	-	-	2.0	2.0
SO_4^{2-}	24	1.0	31.5	55.9	30.8	-	12.0
SCN^-	-	-	-	-	-	-	12.0
pH	8.0	7.3	7.5	8.1	6.9	7.7	7.5
TDS (mg/L)	33390	65000	4885	38140	69060	33390	33390
Density (g/cm^3)	1.024	1.040	1.002	1.025	1.045	1.024	1.024

Carbonated seawater (CSW), carbonated formation water (CFW) and carbonated distilled water (CDW) were prepared by equilibrating excess CO_2 (g) with the respective brine in a pressure cylinder at 6-7 bar and 23 °C. The equilibrated carbonated brine was then moved to a separate cylinder at a higher pressure, so no gas cap was formed.

3.1.4 Solubility of CO_2 in brines

The solubility of CO_2 in brines at 60°C was measured in the pressure range from 10 to 200 bar. 150 ml of a specific brine (DW, SW, FW) was mixed with 150 ml of CO_2 (g) at 10 bar in a pressured cylinder. The 2-phase system with a CO_2 gas cap above the brine was then temperature equilibrated overnight at 60°C. At each pressure stage, the CO_2 – brine systems were mixed and allowed to equilibrate into 2 phases before a single flash of the equilibrated carbonated brine phase was performed. A small volume of the carbonated brine was flashed to standard conditions (SC). The pressure was maintained in the sample cylinder during the flash experiment. The mass of brine collected in the flash apparatus and liberated gas volume at SC was measured by a gasometer. The GOR as mg CO_2 per gram of brine was calculated based on the average of 3 flash experiments at each pressure stage. The pH of the carbonated brine was also measured in freshly taken samples after each flash experiment at SC.

3.1.5 Crude oil

Two different crude oils (Oil A and Oil B) were used in this study. The chemical and physical properties of the oils are listed in **Table 3.4**.

3.1.5.1 Oil A

Oil A is a laboratory-designed crude oil containing natural existing acidic and basic polar organic components (POC). The oil was made by mixing portions of a base stock tank oil with an acid number (AN) of 1.85 mg KOH/g and base number (BN) of 0.67 mg KOH/g with portions of the same stock tank oil depleted in POC by silica gel treatment, giving AN = BN ~ 0 mgKOH/g. The crude oil was centrifuged and filtered through a 5 µm Millipore filter prior to analyses and use. AN and BN were measured by potentiometric titration using modified versions of ASTM D664 and ASTM D2896 (ASTM International, 1988, 1989), developed by Fan and Buckley (2007). Oil A with AN = 0.5 mg KOH/g and BN = 0.3 mg KOH/g, was used in core experiments on the outcrop chalk. The uncertainty in the AN and BN analyses is ±0.02 mgKOH/g.

3.1.5.2 Oil B

Oil B is the stock tank oil from the chalk reservoir and was provided by the operator company. Oil B had a low asphaltenic content of 0.6 wt% and quantified AN = 0.1 mg KOH/g and BN = 2.6 mg KOH/g. Oil B was used in core experiments on the reservoir chalk.

Table 3.4: Crude oil properties.

Sample	AN (mg KOH/g)	BN (mg KOH/g)	Asphaltene content (wt%)	Density (g/cm^3)	Viscosity @23 °C (cP)	Viscosity @60 °C (cP)
Oil A	0.5	0.3	<1	0.81	2.5	1.8
Oil B	0.1	2.6	<1	0.81	43.1	11.6

There is a significant difference in the viscosities between Oil A and Oil B. However, Aslanidis et al. (2023) recently showed there is very low effect of oil viscosity in oil recovery in spontaneous imbibition tests. There is also a low effect of oil viscosity in oil recovery in viscous flooding test if the injection rate is low. Therefore, a low injection rate during viscous flooding using reservoir cores was maintained at 0.5 PV/D.

3.2 Method

3.2.1 Core preparation

Before oil recovery experiments were performed on the outcrop and reservoir cores, the cores were cleaned, and fluid saturations were established.

3.2.1.1 Core cleaning of outcrop chalk cores

The SK chalk quarry at Sigerslev in Denmark is located close to the sea and might contain precipitated sea salts, especially SO_4^{2-} salts, which may reduce the adsorption of polar organic components and thus impact the core wettability after exposure to crude oil (Puntervold et al., 2007b). The cores were therefore mounted in a Hassler core holder and flooded with a minimum of 5 PV of DW at room temperature (23 °C) to remove any easily dissolvable salts. The flooding of DW continued until no SO_4^{2-} was detected in the effluent. Pressure difference along the cores were measured during core cleaning to calculate the permeability of the outcrops.

3.2.1.2 Core cleaning of reservoir chalk cores

The reservoir chalk cores (RC1, RC2, and SU2), containing brine and reservoir oil, were mildly cleaned at room temperature using a Hassler core holder. The cores were flooded at a rate of 0.1 ml/min with ~10 PV of low aromatic kerosene until a clear effluent was observed. The kerosene was then displaced by flooding 5 PV n-heptane (hereafter referred to as heptane). In the end, the core was flooded with 5 PV DW to displace the initial brine and easily dissolvable salts. Pressure difference along the cores were measured during DW flooding to calculate the permeability of the reservoir cores.

3.2.1.3 Fluid restoration

Before oil recovery experiments, the cleaned cores went through a fluid restoration process, involving initial water and oil saturation. To compare the results among cores, it is important the reduce the number of variables affecting the experimental results. Both water and oil volumes introduced during fluid restoration could affect wettability and the fluid flow in the porous media.

After cleaning, the cores were dried at 90 °C to constant weight. Then, 10% initial water saturation (S_{wi}) with FW (FW_A for outcrops and FW_B for reservoir cores) was established by the desiccator technique described by Springer et al. (2003). The cores were saturated with 10 times diluted FW, and target $S_{wi} = 0.10 \pm 0.02$ was controlled by weight measurements during the water evaporation process taking place in the desiccator. When the target S_{wi} was reached, the cores were equilibrated in a closed container for at least 3 days to assure even ion distribution inside the core.

The core with the established $S_{wi} = 0.1$ was mounted in a Hassler core holder with a confining pressure of 20 bar at 50 °C. It was vacuumed for a few minutes until the vapor pressure of the water was reached. Then, the crude oil (Oil A for outcrop cores and Oil B for reservoir cores) was introduced from both sides of the core, pressurized to 5 bar, followed by consecutive flooding of 2 PV of crude oil from both ends to obtain as homogeneous oil saturation in the core as possible. The reservoir core, RC1 and RC2, were only flooded 1 PV of oil B to make it less oil wet.

After the fluid saturation process the core was wrapped with Teflon tape to avoid unrepresentative adsorption of polar organic components (POC) at the outer core surfaces. Finally, the core was placed in an aging cell surrounded by the respective crude oil and aged for 14 days at respective experimental temperature (90/110/130 °C) with a cell pressure of 10 bar to avoid boiling of fluids.

3.2.2 Oil recovery tests

The restored and aged cores were exposed to viscous flooding or/and spontaneous imbibition experiments to evaluate wettability and the presence of capillary forces in the cores, and the effect of brine injection and wettability alteration on oil recovery. Fluid flow in oil reservoirs is controlled by gravity, capillary, and viscous forces. In short time core experiment, the contribution from gravity forces is small, especially for low permeable cores. Spontaneous imbibition experiments represent the capillary forces while viscous flooding experiments represent contribution from viscous forces dictated by the pressure drop applied during the experiment.

3.2.2.1 Oil recovery by spontaneous imbibition

After removing the Teflon tape, the aged core was immersed in imbibing brine in a steel imbibition cell at respective experimental temperature (90/110/130 °C) and 10 bar pressure to avoid boiling of liquids. The cumulative oil production by spontaneous imbibition of water was collected and measured in a graded burette at time steps. The oil recovery was calculated as a percentage of oil originally in place (%OOIP) and presented versus time.

3.2.2.2 Oil recovery test by viscous flooding

Oil recovery by viscous flooding was performed on the restored cores. After reaching the oil recovery plateau for by spontaneous imbibition, the core was placed in a Hassler core holder at experimental temperature with 20 bar confining pressure and 10 bar back pressure. The injection rate was maintained at 0.5 PV/D for the reservoir cores. Aged outcrop cores were also used for viscous flooding directly after ageing at respective experimental temperature (90/110/130°C). The produced oil was collected in a graded burette and recorded against time. The pressure drop over the core was logged during the displacement test.

3.2.3 Capillary forces by spontaneous imbibition

To assess the presence and effectiveness of capillary forces, spontaneous imbibition experiments were conducted. The cores were fully saturated with heptane as the oil phase and placed in a glass Amott cell. The cores were then imbibed with DW at a temperature of 23°C. The process of imbibition allowed the water to spontaneously displace the oil from the porous medium. The oil recovery was measured and recorded over time. By monitoring the oil recovery during spontaneous imbibition, the efficiency of positive capillary forces in mobilizing oil from the heterogeneous pore systems of the cores could be directly evaluated. A simplified wettability index based only on spontaneous imbibition experiments was proposed by Piñerez Torrijos et al. (2019). The degree of water-wetness is quantified by a modified Amott water index ($I_{W_{SI}}$) using a very water-wet core as a reference, **Eq. 3.1**.

$$I_{w_{SI}} = \frac{(\%OOIP)_{core}}{(\%OOIP)_{ref}} = \frac{SI_C}{SI_{WWC}} \tag{3.1}$$

The oil recovery (%OOIP) by spontaneous imbibition from a strongly water-wet or reference core is termed, SI_{WWC}, and the SI_C is the oil recovery (%OOIP) by spontaneous imbibition from the evaluated core. The water wetness degree, $I_{w_{SI}}$ approaches 1 for a strongly water-wet core and 0 for a neutral-wet to oil-wet core (Piñerez Torrijos et al., 2019).

3.2.4 Surface reactivity

The surface reactivity of both outcrop and reservoir chalk cores was investigated using a chromatographic wettability test, which was developed by Strand et al. (2006) to assess the wettability and reactivity of specific ions, such as SO_4^{2-}, Ca^{2+}, and Mg^{2+}, with the carbonate surface. The tests were conducted in a Hassler core holder under ambient temperature, with a confining pressure of 20 bar and a back pressure of 10 bar. The cores were sequentially flooded separately at a constant rate of 0.2 ml/min with SW0T (without Li^+/SCN^- and SO_4^{2-}) followed by SW½T (with Li^+/SCN^- and SO_4^{2-}). The tracer used in the test had no affinity for the chalk surface and thus followed the displacement front. In contrast, SO_4^{2-} exhibited an affinity for the water-wet chalk surface and was eluted with a delay compared to the tracer. During the SW½T flooding, effluent samples were collected and analysed by ion chromatography (IC). The concentrations of either Li^+ or SCN^- and SO_4^{2-} ions were determined and plotted relative to the injected pore volumes (PV), the separation area (A_w) between the curves, representing the water-wet surface area, was calculated using the trapezoidal method.

3.2.5 Other analyses

3.2.5.1 Pore size distribution

Mercury capillary injection (MICP) measurements were conducted by Stratum Reservoir to assess the pore size distribution of both outcrop and reservoir chalk cores. MICP is a commonly used technique in reservoir characterization to determine the distribution of pore sizes and understand the rock's pore structure and connectivity. This information is crucial for understanding fluid flow and storage capacity within the rock, which is essential in evaluating the reservoir's potential for oil and gas recovery and EOR studies.

3.2.5.2 SEM & EDX analyses

To characterize the pore surfaces, grain sizes, and elemental composition of the rock material, Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) analyses were performed. The analyses were conducted using a Zeiss Supra Environmental Scanning Electron Microscope (ESEM) equipped with an EDX detector. SEM allows for high-resolution imaging of the rock sample, providing detailed information about the surface morphology, pore structures, and grain boundaries. EDX, on the other hand, is a technique that enables the identification and quantification of the elemental composition of the sample. By combining SEM imaging with EDX analysis, valuable insights into the microstructure and chemical composition of the rock material can be obtained, aiding in the characterization and understanding of its properties that are needed for EOR studies.

3.2.5.3 Specific surface area (BET)

Specific surface area of the minerals was determined using the Micromeritics TriStar II apparatus based on the Brunauer Emmett Teller (BET) method. This involves measuring the adsorption of nitrogen and gas on the sample's surface at a given pressure to calculate the surface area. The samples were prepared for measurement using VacPrep 061, which removes contaminants like water vapor and adsorbed gas from the surface and pores of the sample via vacuum and heat. To prevent fluidization of the samples, vacuum was slowly applied during the preparation process. The BET method is one of the most widely used techniques for determining surface area because of its accuracy and versatility. Proper sample preparation is critical to obtain accurate surface area measurements, as contaminants can interfere with gas adsorption and affect the results. Therefore, techniques such as vacuum and heat treatment are often used to ensure that the samples are clean and free of unwanted species (Micromeritics, 2023)

4. Result and Discussion

This thesis aims to provide improved insights to enhance the understanding of low-carbon EOR methods in carbonate formations. The identification of a representative outcrop chalk material was achieved through diverse laboratory experiments. Several low-carbon EOR solutions, including ion-modified water, brine with PS additive, and CW, were systematically evaluated for their efficacy in producing extra oil in carbonate reservoirs at high temperatures. The presented and discussed results contains key findings including the potential main reason for the extra oil recovery.

4.1 Selection of representative outcrop

The use of outcrop material is a common practice in parametric studies aimed at understanding various aspects of crude oil, brine, and rock (CoBR) interactions, such as fluid flow in porous media, wettability, and EOR investigations, primarily due to the limited availability of well-preserved reservoir cores. However, it's crucial to note that outcrop core can only effectively describe reservoir behavior when the properties closely resemble those of the actual reservoir rock.

This section is primarily focused on identifying representative outcrop chalk materials that can serve as analogues for North Sea chalk reservoirs. Many North Sea chalk reservoirs are maturing, with increasing water production, prompting the need for IOR/EOR solutions to reduce residual oil saturation. These mature chalk reservoirs, often situated near industrial areas in Western Europe, can also be used as potential candidates for CO_2 storage in CCS projects.

Two outcrop systems (SK and AA) were compared with reservoir chalk cores (SU2, WZ, and RC1) originating from two different North Sea reservoir systems. The best matched outcrop analogue would be used for further studies in the later sections of this research.

4.1.1 Rock properties

Petrophysical properties are essential for porous media classification. Porosity regulates the storage capacity, while permeability and pore size distribution control the fluid flow and the capacity to mobilize pore fluids. Sedimentary rocks function as capillary systems due to their abundant pore surfaces and small pore diameters. In such capillary systems, fluid within the pores becomes surface trapped. The mobilization of an oil phase in these systems requires substantial pressure differentials, and mobility is strongly influenced by wettability.

Fluid flow within porous media is governed by pore size distribution, where fractures and larger pores offer optimal pathways due to reduced surface friction. In contrast, smaller pores tend to hold a significant proportion of hydrocarbons. Consequently, the presence of heterogeneous pore size distributions highlights the role of capillary forces and spontaneous imbibition in enhancing the efficiency of oil displacement from rock matrices.

4.1.1.1 Porosity and permeability

Prior to core flooding experiments on both outcrop and reservoir cores underwent core cleaning and fluid restoration procedures. During these processes, porosity and absolute water permeability were measured and are presented in **Table 4.1**.

Table 4.1: Porosity and permeability of the reservoir and outcrop chalk cores.

Core data	Outcrop core		Reservoir core		
	SK	AA	SU2	WZ	RC1
Porosity φ (%)	48.8	47.0	38.6	28.9	39.1
Water permeability kw (mD)	3.0	3.1	3.5	0.4	4.5

Both outcrop cores, SK and AA, exhibit notably high porosity, close to 48%. Reservoir cores from the oil zone, SU2 and RC1, has porosity of ~39%, affirming robust fluid storage capabilities. Similarly, both the outcrops (SK and AA) and 2 reservoir cores (SU2 and RC1) showed similar permeabilities ranging from 3 to 4.5 mD. Increased compaction due to overburden of the reservoir chalk reduced its porosity but did not affect permeability. In contrast, the aquifer-sampled reservoir core has experienced a reduced porosity of 29%, significantly impacting the absolute water permeability of 0.4 mD, roughly one-tenth of the averaged permeability observed in outcrop and oil zone cores.

The presence of oil in the pore space substantially curtails brine-rock interactions, potentially affecting mineral dissolution and precipitation that influence porosity and permeability. The reduced permeability and porosity restrict the feasibility of employing water zone chalk for CO_2 storage.

4.1.1.2 Pore size distribution

Reservoir and outcrop chalks heterogeneity and pore size distributions were evaluated through mercury injection capillary pressure (MICP) measurements. **Figure 4.1 (a)** showcases the outcomes of this analysis across outcrop chalk cores (SK and AA) and **Figure 4.1 (b)** showcases reservoir chalk cores (WZ, SU2, and RC1) respectively.

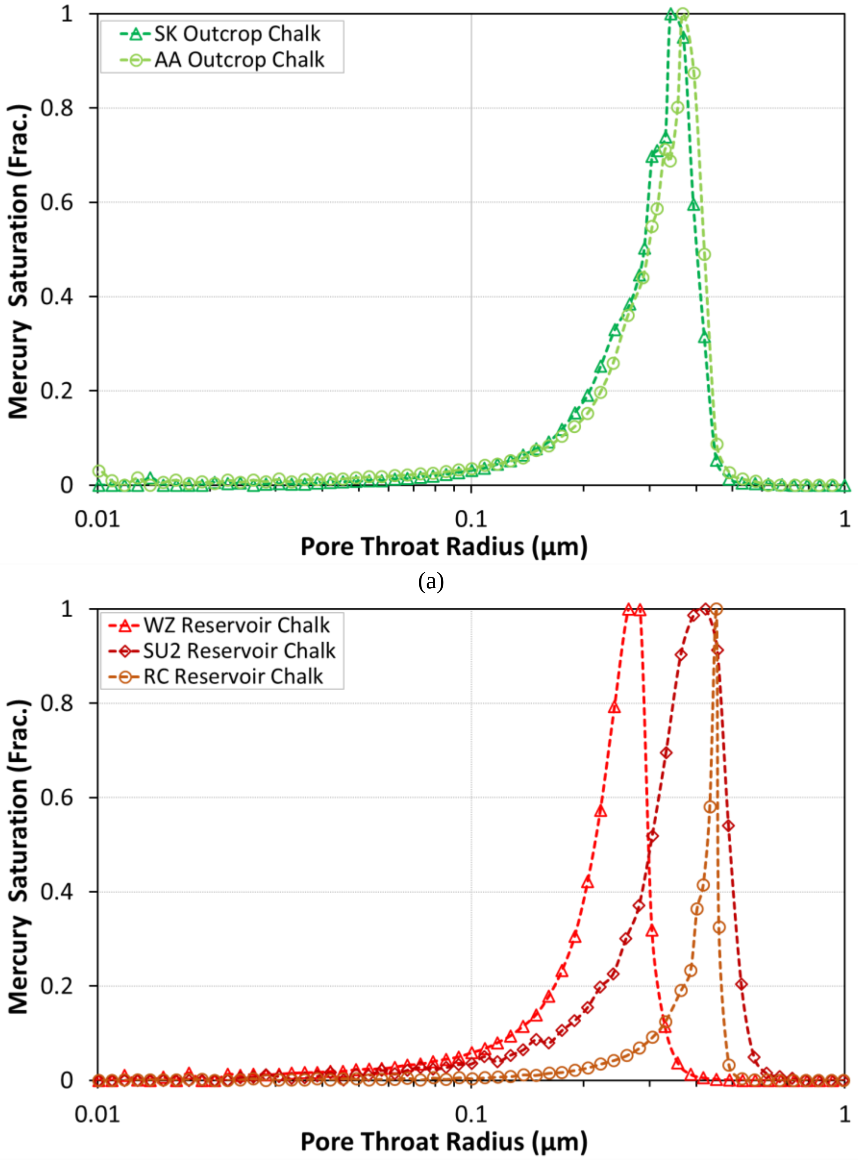
The results obtained from MICP validate the presence of extremely narrow pore throat radii in all chalk samples. **Table 4.2** provides an overview of the minimum, peak, and maximum throat radii.

Table 4.2: Pore size distribution in chalk, minimum, peak, and maximum detected values.

Chalk type	Pore throat radiuses (μm)			max/min
	Min	Peak	max	
Outcrop SK	0.011	0.34	0.73	66
Outcrop AA	0.010	0.37	0.62	62
Reservoir RC1	0.011	0.45	0.67	67
Reservoir SU2	0.220	0.42	0.78	61
Reservoir WZ	0.011	0.26	0.53	48

The minimum pore throat sizes were found to be greater than 0.01 μm, with a peak size close to 0.4 μm, and maximum pore throats measuring under 0.8 μm. This clearly classifies all chalk samples as heterogeneous, with the largest pore throat size being at least 48 times greater than the smallest.

It's worth highlighting that the WZ core, representing the reservoir water zone, demonstrates a different pore size distribution compared to the other samples. In the WZ core, both the peak and the maximum pore throat sizes are shifted to the left, which corresponds to the observed reductions in permeability and porosity.



(a)

(b)

Figure 4.1: Pore size distribution by MICP for (a) SK and AA outcrop chalk, (b) WZ, SU2, and RC1 reservoir chalk.

4.1.1.3 Pore surface area

Sedimentary rocks characterized by small pore diameters tend to exhibit a significant amount of pore surfaces. To assess the pore surface areas in both reservoir and outcrop chalks, BET-specific surface area measurements were conducted on representative rock samples. The results of these BET analyses are provided in **Table 4.3**.

Table 4.3: BET-specific surface area (m^2/g) measured on outcrop and reservoir chalk.

	Outcrop chalk		Reservoir chalk		
	SK	AA	SU2	WZ	RC1
BET, (m2/g)	2.0	3.9	1.2	2.0	1.7

The BET surface area of reservoir and outcrop SK chalk demonstrates significant similarity, ranging from 1.2 to 2 m^2 of mineral surfaces per gram of rock. This confirms that chalk with small pore diameters generate an extensive mineral pore surface area that can interact with pore fluids, confirming its classification as capillary system.

For AA outcrop chalk, the BET-specific surface area was 3.9 m^2/g, 95% higher than SK chalk, and 130% and 225% higher than the two oil zone reservoir chalk samples.

4.1.1.4 Mineral composition and grain sizes

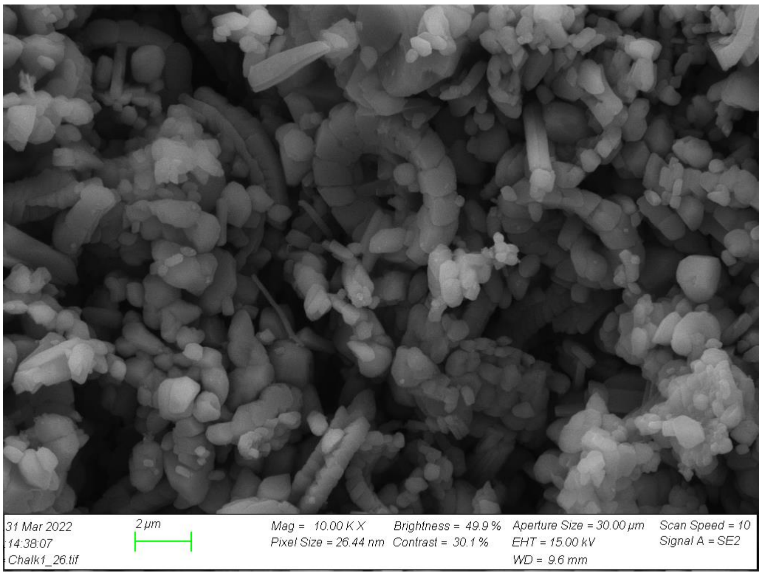
Mineral compositions of reservoir chalk (SU2, WZ, RC1) and outcrop chalk (SK, AA) were determined by SEM and EDX analysis on representative rock samples from chalk cores. **Table 4.4** outlines the EDX analysis from outcrop and reservoir chalk samples.

Table 4.4: Element (cation) composition in atomic weight % (At%) by EDX analyses of the outcrop and reservoir chalk.

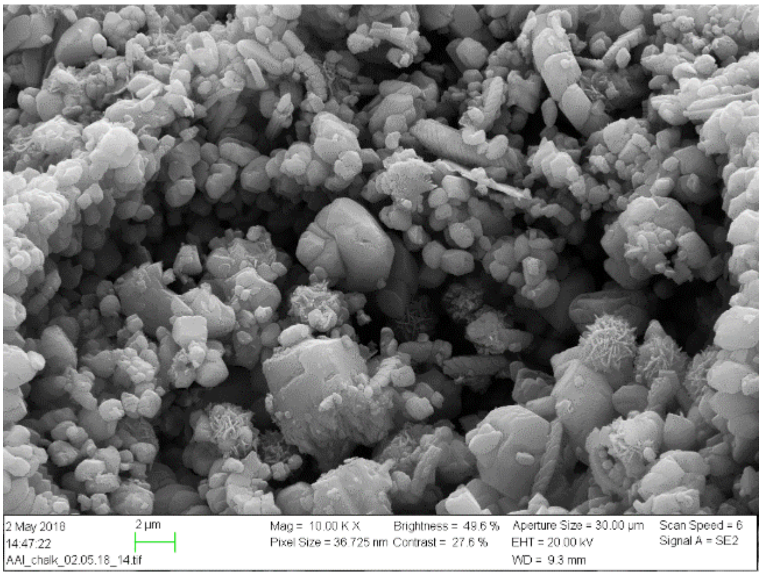
Element (Cation)	Outcrop Chalk		Reservoir Chalk		
	SK At%	AA At%	SU2 At%	WZ At%	RC1 At%
Calcium	98.5	88.9	>99.9	98.3	98.5
Magnesium	0.08	0.9	–	–	0.2
Aluminium	0.1	1.1	–	–	0.03
Silica	0.6	8.7	–	1.7	1.3
Potassium	0.2	0.5	–	–	0.0
Sulfur	0.4	–	–	–	0.03
Sodium	0.02	–	–	–	–

SK chalk prominently featured over 98 At% of calcium-bearing minerals, primarily $CaCO_3$. This consistent calcium concentration was observed in all analyzed reservoir chalk samples as well. In contrast, AA chalk contained 8 At% silica impurities, which decreased the calcium content to 89 At%. Other chalk samples contained less than 2 At% silica.

The mineral grain sizes and grain size distribution were also compared qualitatively among individual chalk samples using SEM images at a consistent magnification of 10000 (**Figure 4.2**). Intact coccolith rings were observed in all reservoir chalk samples signifying minimal physical degradation, chemical dissolution, or mineral precipitation that might alter grain shapes or prompt secondary minerals. Across the investigated chalk samples, the average size of individual chalk grains approached 1 μm. Low water saturation in the oil zone curbs mineral dissolution and reprecipitation, which could affect porosity and permeability. Comparatively, reservoir water zone sample WZ experienced significant reductions in both porosity and permeability, presented in **Table 4.1.**


31 Mar 2022
14:38:07
Chalk1_26.tif
2 µm
Mag = 10.00 K X
Pixel Size = 26.44 nm
Brightness = 49.9 %
Contrast = 30.1 %
Aperture Size = 30.00 µm
EHT = 15.00 kV
WD = 9.6 mm
Scan Speed = 10
Signal A = SE2

(a)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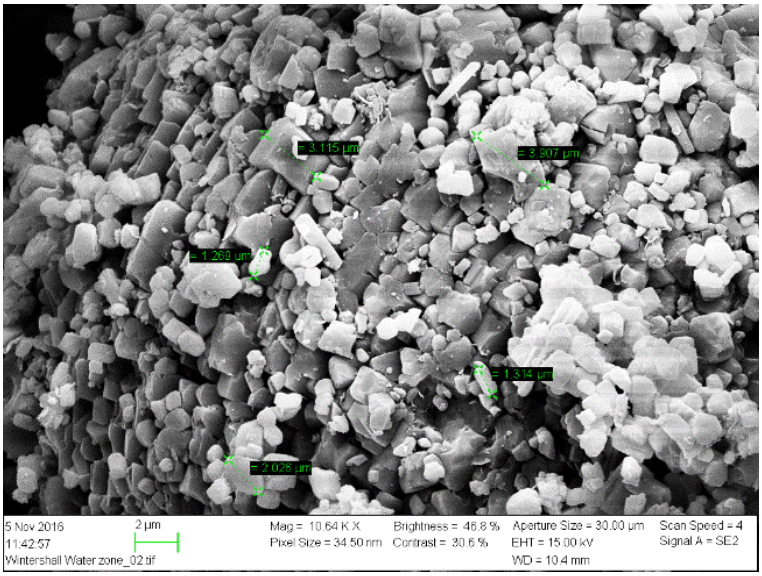
(b)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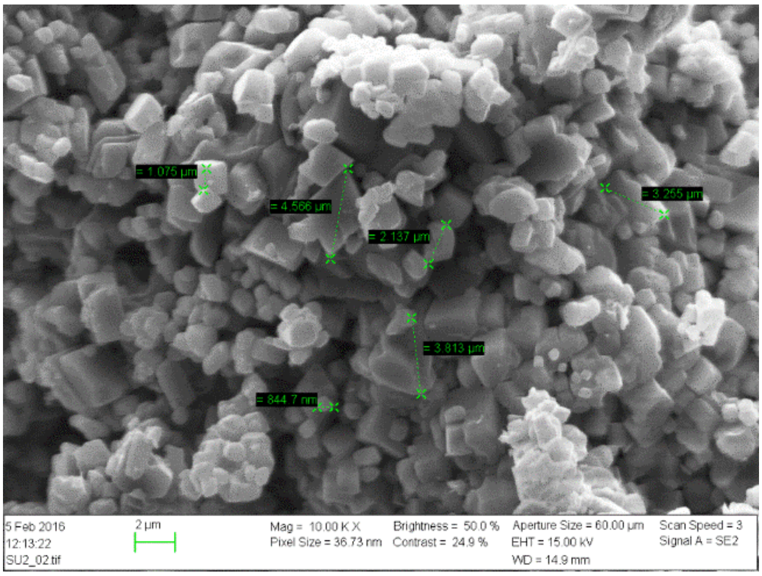
(c)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5 Feb 2016
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2 µm
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Brightness = 50.0 %
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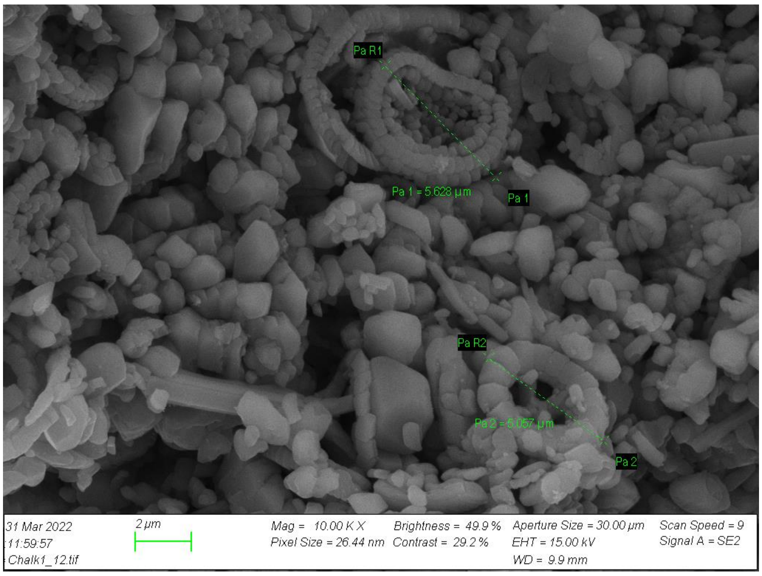
(d)



(e)

Figure 4.2: SEM pictures at 10 000 times magnification performed on (a) SK outcrop chalk, (b) AA outcrop chalk, (c) WZ reservoir chalk, (d) SU2 reservoir chalk, and (e) RC1 reservoir chalk.

In AA chalk, authigenically formed opal-CT lepispheres were observed in open cavities randomly distributed between chalk grains, as shown in **Figure 4.2 (b)**. This amorphous SiO_2 content explains the elevated silica levels in EDX analyses (Flörke et al., 1976). The presence of opal CT also explains the increased BET surface area, although this didn't affect AA chalk's porosity or permeability (**Table 4.3**).

Porous rock pH typically ranges from 5 to 9, behaving as buffered systems due to reactive mineral surfaces and carbonate species. Silicate minerals generally exhibit negative surface charges at pH above 3, while calcite surfaces become positively charged at pH below 9-10. Aalborg chalk's mixed mineralogy could significantly influence chemical adsorption or desorption, particularly when ample mineral surfaces interact with limited pore liquid. This encompasses ion exchange reactions and charged polar organic component adsorption present in crude oils, affecting mineral surface water-wetness (Piñerez Torrijos et al., 2020).

SK chalk shows stronger acidic POC adsorption on mineral surfaces, diminishing capillary forces (Mjos et al., 2018). Comparative studies by Konstantinopoulos et al. (2019) and Klewiah et al. (2019) reveal polar acidic component adsorption on AA chalk surfaces being lower than SK chalk, while polar basic components adsorption is notably higher due to negatively charged silicate surfaces. Crude oil exposure reduces Aalborg chalk's water-wetness. Silica's presence in these comparative studies significantly influences polar component adsorption and initial wetting, impacting capillary forces.

4.1.2 Wettability of outcrop and reservoir cores

Fluid flow in porous media is controlled by capillary, gravity, and viscous forces. Permeability drives viscous forces, while density difference between hydrocarbon and brine controls gravity forces. High specific surface area emphasizes capillary forces, as seen in chalk samples. Both outcrop SK chalk and reservoir chalk showed similar mineral composition, permeability, grain and pore sizes, and surface areas. Expectedly, outcrop chalk has slightly higher porosity due to different depositional environment. Notably, outcrop chalks lack crude oil exposure, while reservoir chalk from the water zone might have experienced oil migration affecting surface wettability affecting presence of capillary forces. Crude oil-invaded reservoir chalks, especially from the oil zone, exhibit altered capillary forces due to POC impacting mineral surfaces.

To assess the presence of capillary forces, spontaneous imbibition tests were conducted at 23°C using heptane-saturated cores and DW. Heptane has lack of POC that could alter mineral surface wettability. **Figure 4.3** illustrates heptane recovery from cores, revealing capillary-driven imbibition observations.

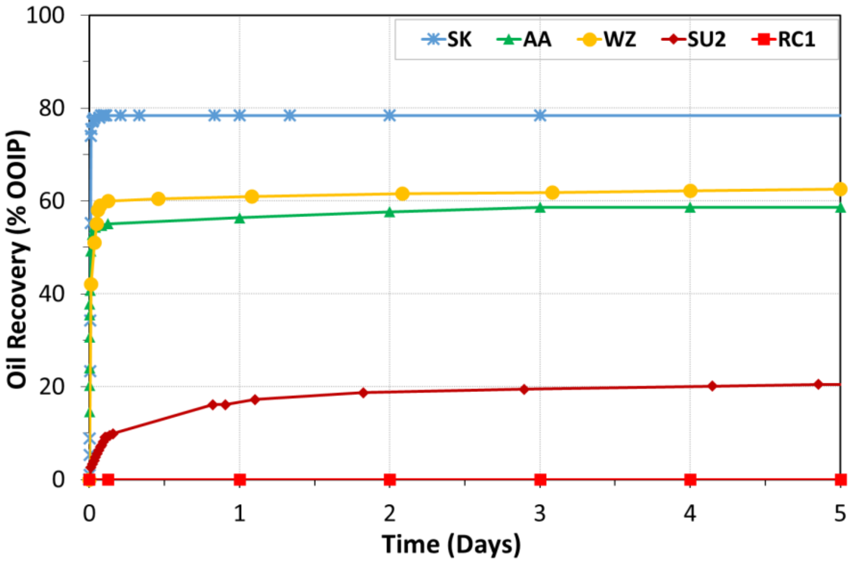


Figure 4.3: Recovery of heptane by DW imbibition at 23 °C from the 100 % heptane-saturated mildly cleaned SK and AA outcrop chalk cores; WZ, SU2, and RC1 reservoir chalk cores.

DW imbibition into outcrop SK core demonstrated rapid oil mobilization, recovering 75% of original oil in place (OOIP) in less than 30 minutes. A 78 %OOIP ultimate recovery in 2 hours confirmed strong positive capillary forces and very water-wet behavior. AA chalk core exhibited similar behavior, mobilizing 55 %OOIP within 2 hours, reaching a 59 %OOIP plateau in 3 days, confirming strong capillary forces.

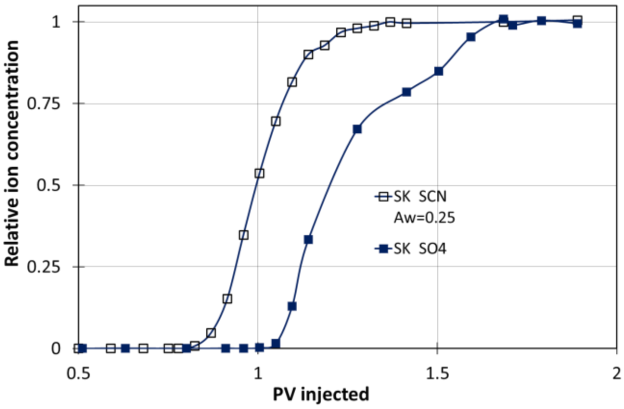
The reservoir core from the water zone, WZ, also displayed presence of capillary forces, despite a 10x permeability reduction. DW imbibition yielded 60 %OOIP in less than 3 hours, suggesting a strongly water-wet character. Even though the water zone is a part of the oil migration route during reservoir filling, WZ's mineral surfaces weren't exposed to POC in the reservoir crude oil. This indicates that the main migration routes were fractures and high permeable pathways.

The SU2 core from the oil zone, exhibited reduced capillary forces. In 2 hours, only 10 %OOIP was produced, with a 20 %OOIP ultimate recovery after 5 days, confirming a significant reduction in positive capillary forces. For core RC1 from a different chalk reservoir's oil zone, no positive capillary forces were observed. Immobile heptane during imbibition indicated the role of POC in crude oil-rock interaction, despite similar properties to SU2 core.

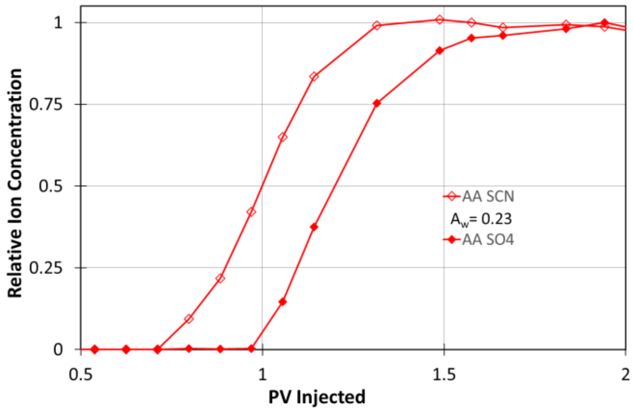
Spontaneous imbibition tests highlight the significance of crude oil type, exposure level, and mineral surface reactivity when choosing outcrop systems as reservoir analogues. Mineral surface reactivity and water-wetness influence potential mineral dissolution and precipitation, impacting rock integrity during CCS projects.

4.1.3 Surface reactivity

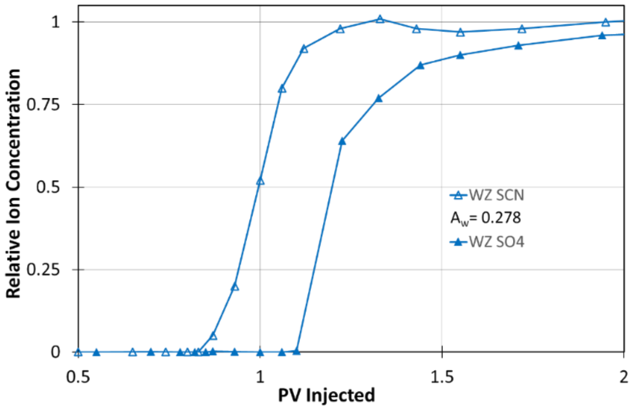
MICP and BET-specific surface analyses confirm the extensive pore surfaces in all chalks, influencing POC adsorption, water-wet mineral surfaces, capillary forces, mineral interactions, and rock integrity during oil production or CCS projects. Mineral surface reactivity in both outcrop and reservoir chalk was evaluated by the chromatographic surface reactivity test developed by Strand et al. (2006). **Figure 4.4** demonstrates water-wet mineral surface reactivity assessments for both outcrop and reservoir cores.



(a)


Relative Ion Concentration
1
0.75
0.5
0.25
0
0.5
1
1.5
2
PV Injected
AA SCN
A_w= 0.23
AA SO4

(b)


Relative Ion Concentration
1
0.75
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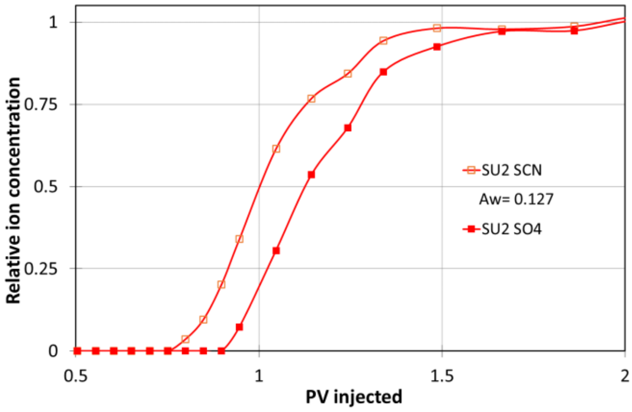
0.25
0
0.5
1
1.5
2
PV Injected
WZ SCN
A_w= 0.278
WZ SO4

(c)


Relative ion concentration
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0.75
0.5
0.25
0
0.5
1
1.5
2
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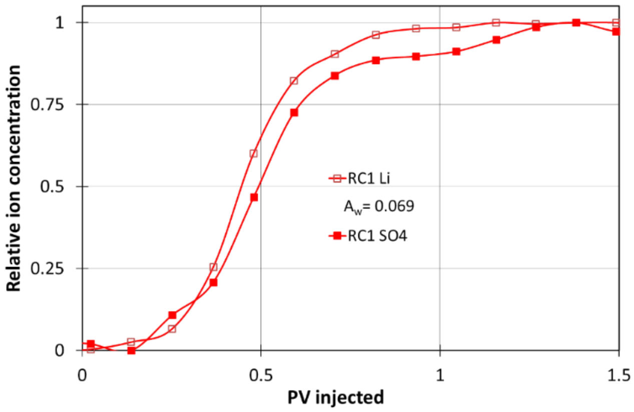
SU2 SCN
Aw= 0.127
SU2 SO4

(d)



(e)

Figure 4.4: Chromatographic separation between sulphate and lithium/thiocyanate ions in (a) SK outcrop chalk, (b) AA outcrop chalk, (c) WZ reservoir chalk, (d) SU2 reservoir chalk, and (e) RC1 reservoir chalk.

Ion interactions primarily occurs on water-wet mineral surfaces. SK and AA outcrop chalks exhibit calculated separation areas (A_W) of 0.25 and 0.23 respectively (**Figure 4.4 (a-b)**), typical for strongly water-wet chalks using SW0T/SW½T chromatographic brine at 23°C. Reservoir core WZ from the water zone has $A_W = 0.28$ (**Figure 4.4 (c)**), similar to the outcrops, signifying the presence of large amount of reactive water-wet mineral surfaces. Spontaneous imbibition showed in **Figure 4.3** confirms strong positive capillary forces and very water-wet behavior for the outcrop and water zone chalk.

For reservoir chalk sampled in the oil zone, notable reduction in separation areas between tracer and sulphate curves is observed. Core SU2 with only 20 %OOIP mobilized during spontaneous imbibition has $A_W = 0.127$ (**Figure 4.4 (d)**), indicating significantly less mineral surfaces available for ion interaction. Reduced water-wet surfaces (A_w) by ~50% compared to outcrop cores markedly reduces oil mobilization potential.

In the case of the RC1 core, where no positive capillary forces were identified by spontaneous imbibition, still a substantial presence of water-wet mineral surfaces was observed. Specifically, an Aw value of 0.069 indicates approximately 30% of the water-wet surface compared to the strongly water-wet water zone core (**Figure 4.4 (e)**).

The chromatographic surface reactivity findings validate that, there is a clear link between water wet surface area (A_w), and the presence of capillary forces. Despite reservoir cores exhibiting a neutral to oil-wet behavior, a considerable level of water wet mineral surfaces is still present and interaction between brine and rock can occur. This interaction has the potential to influence rock integrity in water flooding processes or in carbon capture and storage (CCS) projects that utilize depleted oil reservoirs for CO_2 storage.

4.1.4 Selection of outcrops as reservoir analogues

In reservoir engineering, porosity and permeability are fundamental petrophysical parameters for characterizing rock systems and simulating reservoir flow. Yet, this study underscores the importance of considering additional physical and chemical factors that influence porous rock properties. Pore size distribution, grain sizes, BET-specific surface area, and mineralogy were investigated alongside porosity and permeability in assessing rock analogues for chalk reservoirs. These properties impact capillary forces, wettability, and mineral-fluid interactions, crucial for maintaining well integrity, reservoir stability, wettability, and cap rock security during oil production and CCS projects.

The SK outcrop chalk emerged as a suitable analogue due to its similarity in petrophysical behaviour, mineral composition, and chemical surface reactivity to the assessed reservoir chalks.

Although AA outcrop chalk shares similar petrophysical qualities with reservoir chalks, its presence of SiO_2 minerals makes it unsuitable for wettability and mineral dissolution studies due to heightened availability of reactive surfaces, impacting rock integrity and EOR studies.

The core from water zone chalk reservoir exhibited mineral properties and water-wet behavior similar to outcrop samples. Yet, a drastic permeability reduction makes it unsuitable as a reservoir analogue. Considering the presented laboratory findings, the SK outcrop chalk emerges as a more fitting analogue for North Sea chalk reservoirs, therefore, will be used for parametric EOR studies as an analogue for the North Sea chalk reservoir core in this research.

4.2 EOR in carbonates by ion modified water

SW injection into the high temperature Ekofisk oil field have been a tremendous success. The mixed wet highly fractured low permeable chalk reservoir has responded very well to SW injection, reaching oil recovery above 50%. Laboratory studies have confirmed that SW behaves as a Smart Water to improve the sweep efficiency by increasing capillary forces and changing the wettability towards more water wet condition (Zhang et al., 2007). The goal of this section is to formulate an effective injection brine by modifying its ion composition, a Smart Water, surpassing the efficiency of regular SW at high-temperature (130 °C) chalk and improved oil recovery. Based on previous published work by the Smart Water EOR Group at the University of Stavanger (Zhang, 2006; Fathi et al., 2011b; Puntervold et al., 2015), three brines were created by adjusting salinity and concentrations of surface-active ions (Ca^{2+}, Mg^{2+}, and SO_4^{2-}) using common salts in DW. The EOR potentials of these brines were assessed through secondary and tertiary spontaneous imbibition and viscous flooding on equally restored SK outcrop chalk cores, comparing results with SW. The most promising brine design's EOR potential was further tested on a North Sea reservoir chalk system, involving two unused reservoir chalk cores, reservoir FW, and stock tank oil from the same chalk reservoir.

4.2.1 EOR potential in outcrop chalk

To evaluate the efficiency of the designed brines SmW1, SmW2, and SmW3, in mobilizing oil by spontaneous imbibition, SK outcrop chalk cores were used. SmW1 contained 10 millimolar (mM) $CaSO_4$, SmW2 contained 20 mM $CaSO_4$ and 20 mM $MgCl_2$, while SmW3 contained 20 mM $CaSO_4$ and 40 mM $MgCl_2$. The reason behind selecting these compositions was explained in **Paper IV**. The effectiveness of SmW1, SmW2, and SW was tested in tertiary mode after spontaneous imbibition with FW. All the cores were equally restored to mixed-wet conditions. Swi of 10% with FW_A was established in all cores before the cores were exposed to the same amount of Oil A in the fluid restoration and aging process. Physical properties of the cores were measured during core preparation and are presented in **Table 4.5**.

Table 4.5: Physical properties of the outcrop chalk cores.

Core data	Outcrop Stevns Klint cores						
	SK1	SK2	SK3	SK4	SK5	SK6	SK7
Length (cm)	7.21	7.02	7.22	7.27	6.71	7.05	6.86
Diameter (cm)	3.79	3.78	3.79	3.78	3.81	3.81	3.81
Bulk Volume, (ml)	81.34	78.78	81.45	81.58	76.53	80.46	78.38
PV (ml)	38.86	37.87	38.61	38.40	37.97	39.59	37.77
Porosity (φ) %	47.78	48.07	47.41	47.07	49.61	49.21	48.18
k (water) (mD)	4.1	4.0	3.6	3.9	–	3.2	–

4.2.1.1 *Spontaneous imbibition in secondary mode*

Spontaneous imbibition oil recovery tests in secondary mode were conducted at 130 °C and the efficiency of the designed brines; SmW1, SmW2, and SmW3, were compared against the performance of SW. The oil recovery results from these experiments are illustrated in **Figure 4.5**.

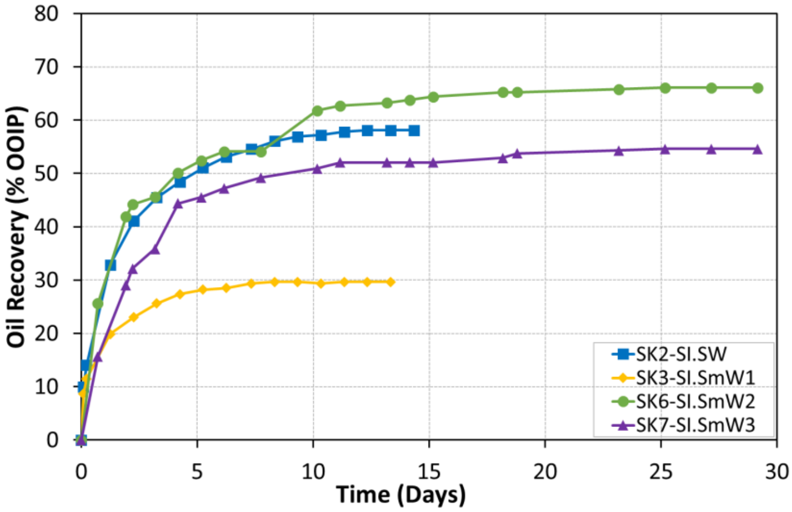


Figure 4.5: Oil recovery by SI at 130°C on equally restored outcrop SK chalk cores with S_{wi} = 10% FW_A and exposed to Oil A. The imbibing brines in secondary mode were SmW1 in core SK3, SmW2 in core SK6, SmW3 in core SK7, and SW in core SK2.

For SmW1, the ultimate recovery plateau reached 30 %OOIP within 9 days. For SmW2, both the speed of imbibition and the ultimate oil recovery significantly increased. After 9 days, the oil recovery reached 58 %OOIP and continued to rise to an ultimate recovery of 66 %OOIP after 25 days. This illustrates the strong influence on the ion composition of the designed brine on the capillary forces generated during spontaneous imbibition and the subsequent oil mobilization from heterogeneous pore structures. Notably, SmW1 contained 10 mM Ca^{2+} and SO_4^{2-} ions, while SmW2 contained 20 mM Ca^{2+} and SO_4^{2-} ions along with 20 mM Mg^{2+}. The increase in positive capillary forces and oil mobilization in SmW2 was attributed to the increase of Ca^{2+} and SO_4^{2-} ions by 10 mM.

In contrast, the oil recovery with SmW3, decreased to 55 %OOIP as the concentration of Mg^{2+} ions were increased from 20 to 40 mM. The speed and the ultimate recovery were significantly lower than that achieved with SmW2. The results emphasize the complex relationship between ion composition, capillary forces, and oil mobilization, highlighting the importance of brine formulation for optimizing oil recovery in reservoir systems.

The influence of SW as a wettability alteration fluid in chalk is well-recognized, particularly at elevated temperatures like 130 °C (Austad et al., 2005). In this context, using SW as a reference imbibing fluid produced an ultimate oil recovery of 58 %OOIP. While slightly surpassing SmW3, this result falls short of the recovery achieved with SmW2. These findings suggest a potential opportunity for optimizing the SW composition to enhance positive capillary forces and maximize oil mobilization, even at high temperature. The relatively low recovery observed with SmW1 aligns with prior experiences highlighting the importance of sufficient Ca^{2+} and SO_4^{2-}concentrations (Fathi et al., 2011b).

The results from the spontaneous imbibition experiments including initial wettability of SK cores using heptane (**Figure 4.3 (a)**) are summarized in **Table 4.6**. Based on the results, the modified Amott water index, $I_{w_{SI}}$, is calculated using **Eq. 3.1.**

Table 4.6: Summary of the SI tests in secondary mode in outcrop SK chalk.

Core	S_{wi} FW_A %	Oil	Imbibing brine	Temperature °C	Secondary SI %OOIP	Final $I_{w_{SI}}$
SK	0	C_7	DW	23	78	1.00
SK2	10	Oil A	SW	130	58	0.74
SK3	10	Oil A	SmW1	130	30	0.38
SK6	10	Oil A	SmW2	130	66	0.85
SK7	10	Oil A	SmW3	130	55	0.71

By using $I_{w_{SI}}$, the results obtained from the spontaneous imbibition experiments could be used to estimate the level of water wetness in the particular cores after spontaneous imbibition. The most water-wet core was obtained using SmW2 as imbibing brine, with an index of $I_{w_{SI}} = 0.85$, followed by SW with $I_{w_{SI}} = 0.74$ and SmW3 with $I_{w_{SI}} = 0.71$. The lowest index of $I_{w_{SI}} = 0.38$ was observed for SmW1.

4.2.1.2 Spontaneous imbibition in tertiary mode

The effectiveness of SmW1, SmW2, and SW was also tested in tertiary mode after spontaneous imbibition of FW$_{A}$. The results are presented in **Figure 4.6** and summarized in **Table 4.7**.

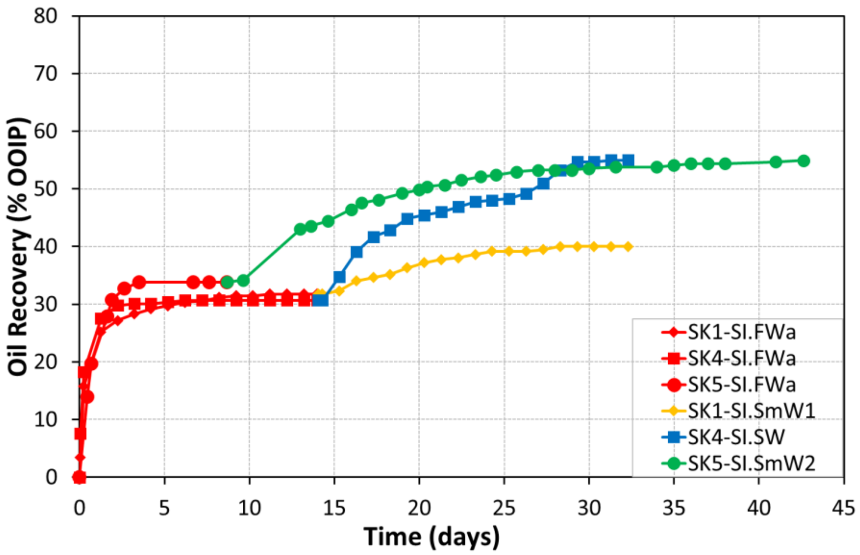


Figure 4.6: Oil recovery by SI at 130 °C on equally restored outcrop SK chalk cores with S$_{wi}$ = 10% FW$_{A}$ and exposed to Oil A. FW$_{A}$ was used as imbibing brine in secondary mode in all three cores, followed by tertiary imbibition of SmW1 in core SK1, SmW2 in core SK5, and SW in core SK4.

Oil recovery by FW$_{A}$ imbibition was in the range of 31-34 %OOIP for all three cores, confirming very good experimental reproducibility between the restored cores. This gives the cores an initial modified Amott water index, $I_{w_{SI}}$, of 0.40–0.44, summarized in **Table 4.7**.

Table 4.7: Summary of the SI tests in tertiary mode in outcrop SK chalk.

Core	S_{Wi} (%FW_A)	Oil	Temp. (°C)	Secondary SI brine	Secondary SI %OOIP	Initial $I_{w_{SI}}$	Tertiary SI brine	Ultimate (Extra) oil recovery %OOIP	Final $I_{w_{SI}}$	$\Delta(I_{w_{SI}})$
SK0	0	C_7	23	DW	78	1.00	–	–	–	–
SK1	10	Oil A	130	FW_A	32	0.41	SmW1	40 (8)	0.51	0.10
SK5	10	Oil A	130	FW_A	34	0.44	SmW2	55 (21)	0.71	0.27
SK4	10	Oil A	130	FW_A	31	0.40	SW	55 (24)	0.71	0.31

After reaching the oil production plateau using FW_A in secondary mode, the imbibing brines were changed to SmW1, SmW2, or SW. SmW1 displayed a modest extra oil mobilization of 8 %OOIP, whereas SmW2 and SW yielded significantly higher additional oil recoveries of 21% and 24 %OOIP, respectively. Notably, SmW1's reduced content of Ca^{2+} and SO_4^{2-} reduced its efficiency as a wettability modifier, aligning with prior research that demonstrated improved oil recovery from outcrop SK chalk through elevated concentrations of Ca^{2+} and SO_4^{2-} (Zhang & Austad, 2006; Zhang et al., 2006, 2007).

Comparing the ultimate oil recoveries by spontaneous imbibition with SmW2 and SW in tertiary mode, both brines exhibited identical ultimate recoveries of 55 %OOIP. This implies comparable oil displacement efficiency despite SmW2's notably lower salinity (7 times less) than SW. However, examining SmW2 and SW imbibition in both secondary and tertiary modes revealed enhanced efficiency in secondary mode. SmW2 in secondary mode achieved an ultimate recovery of 66 %OOIP compared to 55 %OOIP in tertiary mode. Similarly, SW in secondary mode resulted in an ultimate recovery plateau of 58 %OOIP, whereas tertiary mode's ultimate recovery was 55 %OOIP. These findings align with prior observations in Smart Water EOR for sandstones, where Smart Water proved notably more effective in secondary mode compared to tertiary mode (Aghaeifar et al., 2018). Increased water saturation leads to a reduced contribution from capillary forces.

The spontaneous imbibition outcomes on outcrop SK chalk emphasizes the potential to enhance waterflooding performance beyond SW injection by designing Smart Water brines with modified chemical compositions.

4.2.2 EOR potential in reservoir chalk

Evaluation of SW and modified Smart Water (SmW2) for EOR potential was conducted on reservoir chalk cores, although the limited number of available reservoir cores restricted the scope of experimentation. Two reservoir chalk cores (RC1 and RC2), obtained from the reservoir oil zone, were subjected to a sequential process. Initially, the cores underwent mild cleaning with kerosene and heptane to remove crude oil while maintaining most of the POC adsorbed onto the mineral surfaces. Subsequently, a 5 PV DW flooding was performed to remove initial brine and easily dissolvable salts. Physical properties of the cores were measured during core restoration and given in **Table 4.8**.

Table 4.8: Physical properties of the reservoir chalk cores.

	Reservoir cores	
Core data	RC1	RC2
Length (cm)	5.68	5.94
Diameter (cm)	3.77	3.77
Bulk Volume, (ml)	63.57	66.43
PV (ml)	24.85	25.74
Porosity (φ) %	39.10	38.80
k (water) (mD)	4.50	4.40

Spontaneous imbibition experiments, carried out at 23°C on 100% heptane-saturated RC1 core **(Figure 4.3 (e))**, revealed that the mildly cleaned core lacked positive capillary forces, indicating an initial wettability from neutral to oil-wet. Similar behaviour was also confirmed for core RC2 which is reported in **Paper IV.**

Both reservoir cores went through a fluid restoration process with an initial water saturation (Swi) of 10% with FW (FW_B), followed by 1 PV Oil B injection. To prevent over-exposure to crude oil and to maintain representative reservoir wettability during fluid restoration, the core was only exposed to 1 PV of oil. This approach aligns with recently published methodologies for ensuring reproducible and representative core wettabilities in laboratory studies, both in carbonate (Piñerez et al., 2020) and sandstone (Aslanidis et al., 2022) cores.

After core restoration, both reservoir cores, RC1 and RC2, underwent spontaneous imbibition at 130 °C using FW (FW_B) as imbibing brine to assess the presence of positive capillary forces. The results of these spontaneous imbibition experiments are shown in **Figure 4.7**.

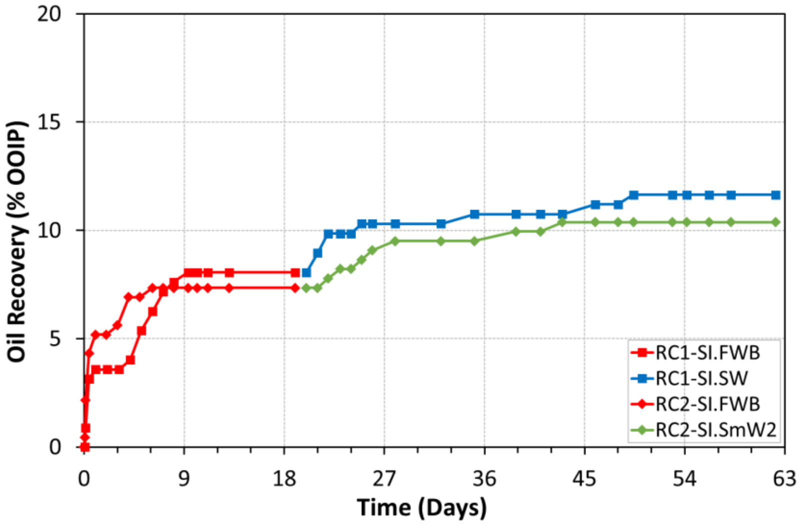


Figure 4.7: Oil recovery at 130°C by SI of reservoir cores equally restored with S_{wi} = 10% of FW_B and exposed to 1 PV Oil B. FW_B was used as initial and imbibing brine in secondary mode, followed by tertiary imbibition of SW in core RC1 and SmW2 in core RC2.

The initial rapid oil mobilization of around 4-5 %OOIP observed with FW_B is attributed to thermal fluid expansion at elevated temperatures. The oil recovery gradually reached to plateaus of 8 %OOIP after 9 days for core RC1 and 7 %OOIP after 6 days for RC2, can be attributed to modest positive capillary forces. The restored reservoir chalk cores displayed weak positive capillary forces, indicated by a modified Amott water index of $I_{w_{SI}} \approx 0$, and a neutral initial core wettability. In contrast, the restored outcrop SK chalk cores exhibited significantly stronger positive capillary forces (see **Table 4.7**).

After 19 days, the imbibition brines were switched to SW for RC1 and SmW2 for RC2. Subsequently, a gradual increase in oil mobilization was observed in both cores, reaching the ultimate oil recovery plateaus of approximately 11 %OOIP for both cores after 50 and 45 days, respectively. The additional oil mobilization achieved with SW and SmW2 in tertiary mode signifies a wettability alteration process leading to increased capillary forces.

Following the spontaneous imbibition tests, both cores were placed into Hassler core holders for viscous for water injection, with a confining pressure of 20 bar and a back-pressure of 10 bar. The flooding experiments were conducted at the reservoir temperature of 130°C, at a rate of 0.5 PV/D. RC1 was flooded with SW, while RC2 was flooded with SmW2. Throughout the experiments, oil recovery and pressure drop were continuously monitored and recorded over time. The outcomes of these viscous flooding experiments are graphically represented in **Figure 4.8**.

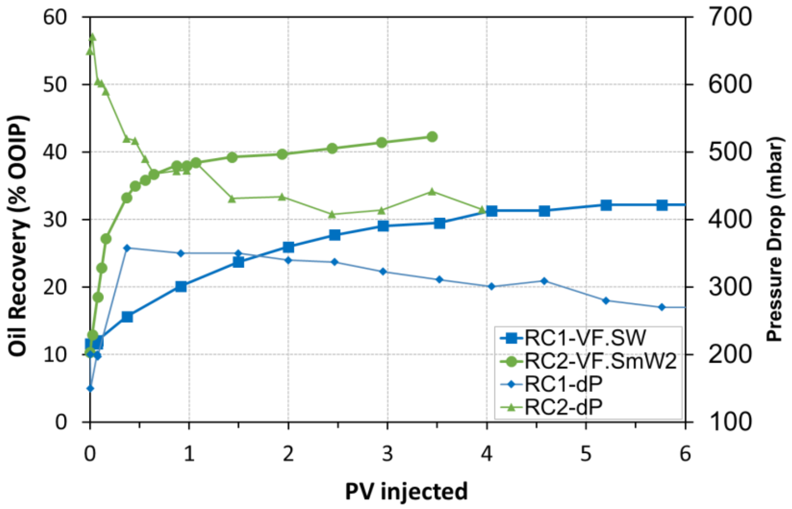


Figure 4.8: Oil recovery by VF at 130 °C on core RC1 and RC2 already imbibed with FW_B and SW or SmW2, respectively. The injection rate was 0.5 PV/D using SW in RC1 and SmW2 in RC2.

During the SW injection into core RC1, the oil recovery increased from 11 %OOIP after spontaneous imbibition to an ultimate oil recovery of 32 %OOIP after 5 PV of injection, resulting in an additional oil production of 21 %OOIP, as illustrated in **Figure 4.8**. For core RC2, the impact of SmW2 injection on production was even more significant. The recovery increased from 11 %OOIP after spontaneous imbibition to 43 %OOIP after 4 PV of injection, surpassing the recovery achieved with SW injection by 11 %OOIP.

In terms of pressure drop profiles, SW injection into core RC1 showed an initial increase from 200 mbar to 360 mbar after 0.3 PV, followed by a gradual decline to 270 mbar after 6 PV, as shown in **Figure 4.8**. In contrast, the pressure drop profile for core RC2 exhibited a different behavior. The pressure drop decreased from an initial 670 mbar to 415 mbar after 4 PV. The reason for this considerable difference in pressure drop profiles is complex and could be related to the heterogeneous nature of pore systems in the cores, potentially influencing fluid distributions.

It's important to note that the pressure drops observed during these experiments, exceeding 270 mbar for cores with a length of 7 cm, are higher than expected in the main reservoir region between injection and production wells. The distinct variation in pressure drop profiles underscores that pressure drop alone doesn't necessarily correlate directly with oil mobilization. In heterogeneous pore systems, positive capillary forces likely play a crucial role in the process, as highlighted in previous studies (Aslanidis et al., 2021).

The comparison between SW and SmW2 injection is quite evident, showcasing the superior efficiency of SmW2 as an injection brine. Equally important is the improved displacement efficiency achieved through SmW2 injection, marked by a notably reduced water production. After injecting 1 PV SmW2 injection, the oil recovery had reached 38 %OOIP, while SW injection had only yielded 20 %OOIP. The summarized results from the spontaneous imbibition and viscous flooding experiments conducted on the reservoir cores, including the initial wettability established with heptane, are presented in **Table 4.9**.

Table 4.9: Summary of the SI and VF experiments of reservoir chalk.

Spontaneous imbibition (SI) (%OOIP)						Viscous flooding (VF) (%OOIP)		
Core	C7	FWB	SW	SmW2	Total	SW	SmW2	Extra oil after SI
RC1	0	8.1	+2.7	–	10.8	32.0	–	+21.2
RC2	0	7.3	–	+3.1	10.4	–	43.6	+33.2

4.2.3 Improved sweep by wettability alteration

The significant enhancement in oil mobilization efficiency seen during the injection of SmW2 into the reservoir chalk cores can be reasonably attributed to its ion composition, which appears helpful to induce wettability alteration towards more water wet conditions and create stronger positive capillary forces leading to faster imbibition rates and improved oil mobilization. This aligns well with the observations from spontaneous imbibition experiments performed on slightly water-wet outcrop SK chalk (as shown in **Figure 4.5** and **Figure 4.6**). In the case of viscous flooding experiments conducted on heterogeneous reservoir chalk cores characterized by low water wetness, the increased displacement efficiency is not attributable to changes in mobility ratio or relative permeabilities. Instead, it is a consequence of increased positive capillary forces improving the mobilization of oil in the displacement front, consequently expanding the mobile oil bank and reducing the water production.

This mechanism is illustrated in **Figure 4.9**. Positive capillary forces induced by SmW2 encourage fluid movement into smaller or unexposed pores that were previously not swept, achieved through spontaneous imbibition. This action enhances the sweep efficiency. As illustrated in **Figure 4.9 (a)**, water is drawn into the rock matrix from the higher-permeability pore network in the porous medium characterized as slightly water-wet conditions. In contrast, **Figure 4.9 (b)** illustrates the increased positive capillary forces and spontaneous imbibition of water resulting from wettability alteration toward more water-wet conditions. This situation promotes a more stable waterfront, increased oil mobilization, and consequently improved sweep efficiency.

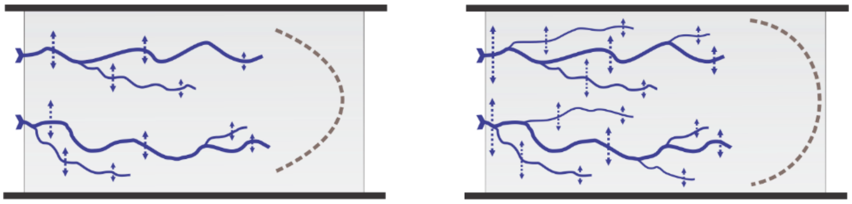

(a) (b)

Figure 4.9: Oil mobilization and displacement efficiency in heterogenous core systems as an effect of increased positive capillary forces, at (a) slightly water-wet conditions and at (b) water-wet conditions. The stippled arrows represent the positive capillary forces.

The results obtained from both spontaneous imbibition and viscous flooding experiments provide convincing evidence that the designed SmW2 brine is not only highly effective for outcrop SK chalk cores, which possess significant positive capillary forces, but also holds promise as the most efficient injection brine for reservoir chalk cores possessing significantly weaker positive capillary forces. The ultimate oil recovery achieved from the heterogeneous reservoir chalk cores was notably lower compared to that from the restored outcrop SK chalk cores. This clearly underscores the fact that the reservoir chalk cores initially possessed weaker positive capillary forces upon arrival at the laboratory in comparison to the outcrop SK chalk cores.

However, it is challenging to definitively determine whether the restored wettability conditions in the reservoir chalk cores accurately reflect the actual wettability of the chalk reservoir. The condition of the reservoir cores upon arrival seemed inadequate, as they were not properly preserved in wax and had been stored under laboratory conditions for an extended period. Such poor preservation could potentially result in exposure to air and subsequent evaporation of lighter fluid components, both of which could conceivably impact the wettability of the cores.

The recent study by Mokhtari et al. (2023) on reservoir chalk highlighted a difference in the behavior of reservoir chalk compared to SK outcrop chalk regarding the role of SO_4^{2-} in wettability alteration. From multiple restorations on the same reservoir chalk core, it was claimed that SO_4^{2-} was not an important ion in the wettability alteration process in reservoir chalk. It's important to note that the effectiveness of sulphate in wettability alteration in chalk tends to be limited at temperatures below 90 °C (Puntervold et al., 2007a; Strand et al., 2008). Therefore, the results obtained by Mokhtari et al. (2023) align with prior observations on SK outcrop chalk when experiments were conducted at 70 °C.

Webb et al. (2005) also confirmed the efficiency of SW as an EOR fluid in reservoir chalk. Numerous experimental studies have been conducted on mixed-wet reservoir limestone, which shares similarities with chalk containing $CaCO_3$, showing the undeniable benefit of sulphate at temperatures of 90 °C and above (Austad et al., 2015; Awolayo et al., 2016; Shariatpanahi et al., 2012). The present study's results also demonstrate similarities in rock properties between outcrop SK chalk and the used reservoir chalk: both SW and SmW2, containing SO_4^{2-}, outperformed FW, that does not contain SO_4^{2-}, as EOR injection fluids. However, drawing universal conclusions about all chalk reservoirs requires more research, considering factors such as chalk composition, presence of silica or clay, which influence wettability, crude oil component adsorption, and CoBR interactions during waterflooding (Puntervold et al., 2021; Strand et al., 2007). Furthermore, the presence of $CaSO_4$ in carbonate or chalk reservoirs can release Ca^{2+} and SO_4^{2-} ions into injection brines, potentially making even diluted SW or FW (initially with low or no SO_4^{2-}) efficient EOR fluids in chalk (Austad et al., 2015; Austad et al., 2012). Based on these, more evidence is required before claiming that SO_4^{2-} is not important for wettability alteration in reservoir chalk. The sweep efficiency associated with wettability alteration is a complex process involving complex interactions between crude oil, formation brine, injection brine, and rock—each comprising multicomponent phases.

4.3 EOR in carbonates by Polysulphate additive

Making ion modified water for carbonate field applications poses a challenge. Attempts to enhance injection water quality involve employing reverse osmosis alongside nanofiltration and adding additional chemicals (Nair, 2019). However, these methods are energy-intensive and require large investments, increasing both capital and operational expenditures (Yousef & Ayirala, 2014). Therefore, there is a demand for cost-effective Smart Water production to reduce the financial burden on both operational and capital expenses in oil production activities.

PS is a low cost and easily soluble mineral that could be added to water or brine to create a Smart Water composition containing the divalent ions, Ca^{2+}, Mg^{2+}, and SO_4^{2-}, to induce chemical wettability alteration in chalk. The properties of PS mineral are presented in the experimental section. To evaluate if PS could be used as EOR additive in fresh water/distilled water, SW, or produced water (PW), a series of experiments were performed on equally restored SK chalk. 5 g of PS was mixed to DW, SW, and PW to prepare DW-PS, SW-PS, and PW-PS respectively.

4.3.1 Oil recovery test by spontaneous imbibition

Twelve SK chalk cores were used in to evaluate PS brine (DW-PS, SW-PS, and PW-PS) for oil recovery and compare with oil recovery by FW_A and PW at 90°C and 110°C by spontaneous imbibition tests. Petrophysical properties of the cores were measured during core preparation and presented in **Table 4.10**.

Table 4.10: Petrophysical properties of the outcrop SK chalk cores.

Core	Length cm	Diameter cm	Pore volume ml	Porosity %	Permeability mD
SK11	7.1	3.8	38.6	48.8	4.1
SK12	7.1	3.8	39.1	48.6	4.7
SK13	7.1	3.8	39.1	48.8	3.8
SK14	7.2	3.8	40.1	49.2	3.8
SK15	7.0	3.8	41.3	49.3	4.1
SK16	6.9	3.8	38.6	49.2	4.7
SK17	7.1	3.8	37.9	47.4	3.8
SK18	7.0	3.8	40.0	50.2	3.8
SK19	7.3	3.8	39.9	48.0	3.5
SK20	7.0	3.8	39.3	50.1	3.4
SK21	7.0	3.8	39.0	49.0	3.3
SK22	7.2	3.8	38.5	48.5	3.5

All the cores were equally restored to mixed-wet conditions. Swi of 10 % was established in all cores before the cores were exposed to 5 PV of Oil A. The cores were aged separately in the same oil at 90 °C for 2 weeks before performing spontaneous imbibition.

At 90 °C, when PW and FW_A were used as imbibing brines, only modest oil recoveries of 12% and 22 %OOIP were observed for SK21 and SK11 respectively. Since these brines lack SO_4^{2-} ions (**Table 3.3**), which act as catalysts for wettability alteration at the chalk surface, a highly water-wet behavior wasn't anticipated. It's noteworthy that the composition of PW was based on the FW_A composition from the same North Sea chalk reservoir (Puntervold & Austad, 2008). The low SO_4^{2-} concentration in PW is likely derived from SW used as the injected brine in the field or from dissolved rock minerals. However, this concentration is expected to be insufficient to induce significant wettability alteration. The results of SI at 90 °C is presented in **Figure 4.10**.

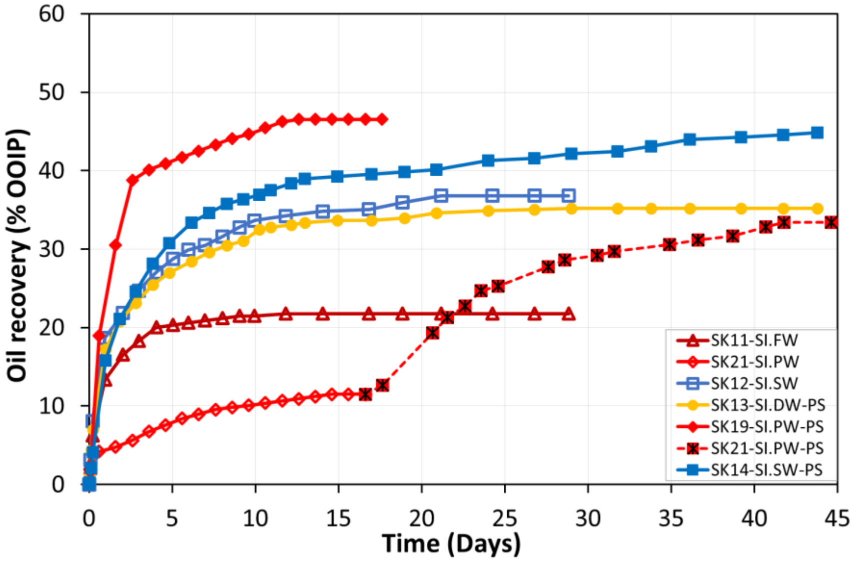


Figure 4.10: Oil recovery tests at 90 °C by SI. All cores were equally restored with S_{wi} = 10% FW_A and exposed to Oil A. The cores were imbibed using FW_A, PW, SW, DW-PS, SW-PS, or PW-PS in secondary mode. SK21 was imbibed by PW-PS in tertiary mode after PW imbibition.

Utilizing SW as the imbibing brine at 90 °C in core SK12, a notable enhancement in both imbibition speed and ultimate oil recovery were observed. About 37 %OOIP was mobilized after 21 days compared to the 12 and 22 %OOIP for PW and FW_A, respectively. This suggests that SW generated stronger positive capillary forces, effectively doubling the amount of mobilized oil. The addition of PS to SW in core SK14 further improved the recovery, reaching an ultimate oil recovery of 45 %OOIP.

By introducing PS to DW in core SK13, the ultimate recovery plateau reached 35 %OOIP after 28 days, similar to the results obtained with SW. However, the most rapid imbibition and highest ultimate recovery at 90 °C were achieved using PW-PS in core SK20, reaching an ultimate oil recovery of 47 %OOIP within just 14 days—8 %OOIP higher than the recovery achieved with SW-PS at the same time.

In case of core SK21, when oil recovery plateau was reached, the imbibition brines were changed from PW to PW-PS to see the effect of PS in PW. The oil-brine-rock system responded with a gradual and significant increase in oil mobilization from both cores confirming increased positive capillary forces causing continuing spontaneous water imbibition. A new recovery plateau at 34 %OOIP was reached after a total of 42 days, corresponding to an additional recovery of 22 %OOIP by PW-PS imbibition proving the efficiency of PW-PS even in tertiary mode.

At 110 °C (**Figure 4.11**), the results of oil recovery by spontaneous imbibition using FW_A, PW, SW, SW-PS, DW-PS, and PW-PS followed similar patterns as those observed at 90 °C. The lowest oil recoveries, at 31 %OOIP after 5 days, were obtained with FW_A and PW in cores SK22 and SK15, respectively. These baseline oil production results confirmed slightly water-wet conditions, with the low concentration of SO_4^{2-} in PW insufficient to induce significant positive capillary forces.

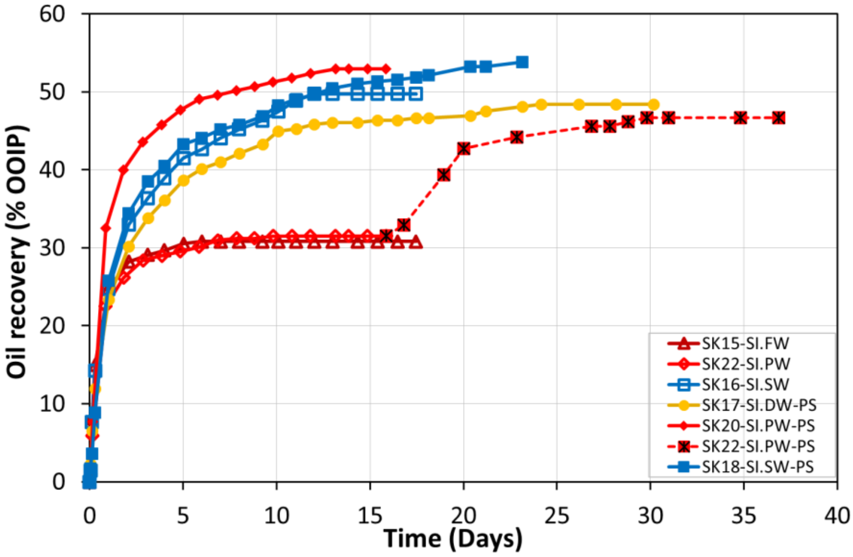


Figure 4.11: Oil recovery tests by SI at 110 °C. All cores were equally restored with S_{wi} = 10% FW_A and exposed to Oil A. The cores were imbibed using FW_A, PW, SW, DW-PS, SW-PS, or PW-PS in secondary mode. SK22 was imbibed by PW-PS in tertiary mode after PW imbibition.

When SW was employed as the imbibition brine in core SK16, the oil recovery increased to 50 %OOIP, indicating a notable rise in capillary forces that mobilized an additional 19 %OOIP of crude oil. The addition of PS to DW in core SK17 resulted in a brine with Smart Water properties similar to SW, leading to an oil recovery and production of 49 %OOIP after 24 days, 18 %OOIP more than that achieved with FW_A imbibition.

The highest oil recoveries were observed with SW-PS and PW-PS as imbibing brines in cores SK18 and SK20, respectively. Utilizing SW-PS as the imbibition brine led to an ultimate oil recovery of 54 %OOIP after 23 days, 4 %OOIP higher than that achieved with SW imbibition. The most effective Smart Water brine was PW-PS, reaching an ultimate recovery plateau of 53 %OOIP after just 14 days. This recovery plateau was notably 22 %OOIP higher than that achieved with PW imbibition. The main difference between SW and PW is the concentration of SO_4^{2-}, Ca^{2+}, and Mg^{2+}.

In case of core SK22, when oil recovery reached a plateau, the imbibition brines were changed from PW to PW-PS to see the effect of PS in PW. In line with the experiment at 90 °C, a gradual and significant increase in oil mobilization confirming increased positive capillary forces. A new recovery plateau at 47 %OOIP was reached, corresponding to an additional recovery of 15 %OOIP proving the efficiency of PW-PS even in tertiary mode.

The ultimate oil recovery results from **Figure 4.10** and **Figure 4.11** are systemized in **Table 4.11**.

Table 4.11: Summary of ultimate oil recoveries, UR (%OOIP), by SI at 90 and 110 °C.

Imbibing fluid	FWA	PW	SW	SW-PS	DW-PS	PW-PS
UR (%OOIP) at 90 °C	22	12	37	45	35	47
UR (%OOIP) at 110 °C	31	33	50	54	48	53
Temperature effect (Δ%OOIP)	9	21	13	9	13	6

Comparing the results obtained at both 90 and 110 °C, it becomes evident that PW-PS emerged as the most efficient imbibition brine, slightly surpassing the efficiency of SW-PS. This enhanced performance can be attributed to the addition of 5 g/L of PS salt, which notably increased the concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions in DW, SW, and PW brines. For a comprehensive comparison of the chemical compositions of all these brines, refer to **Table 4.12**.

Table 4.12: Comparison of brine compositions.

Ions (mM)	SW	FWA	PW	DW-PS	SW-PS	PW-PS
Ca^{2+}	13	29	31	15.2	29.6	41.0
Mg^{2+}	45	8.0	8.0	5.8	47.9	15.3
SO_4^{2-}	24	–	1.0	31.5	55.9	30.8
SO_4^{2-}/ Ca^{2+} ratio	1.8	0.00	0.032	2.07	1.89	0.751
SO_4^{2-}/ Mg^{2+} ratio	0.53	0.00	0.13	5.4	1.17	2.01
pH	8.0	7.3	7.3	7.5	8.1	6.9
TDS (mg/L=ppm)	33390	62800	65000	4885	38140	69060
Density (g/cm3)	1.024	1.040	1.040	1.002	1.025	1.045

The imbibition results depicted in **Figure 4.10** and **Figure 4.11** reveal that no direct correlation between the ultimate oil recovery and the pH of the imbibition brines could be established. Despite pH values ranging from 6.9 to 8.1 in all brines, no discernible trend emerged. Furthermore, no consistent relationship existed between ultimate oil recovery and salinity. Notably, the highest and lowest ultimate oil recoveries were achieved through the imbibition of high saline PW-PS and PW respectively. A similar observation holds true for density, as no systematic effects of density on the results were evident.

The observed effects on EOR are more accurately attributed to the specific compositions of the brines, particularly the concentrations of divalent ions. The presence of both Ca^{2+} and SO_4^{2-} ions is crucial for facilitating efficient wettability alteration, a principle that aligns with the Smart Water model proposed by Zhang et al. (2007). Brines such as FW_A and PW, which lacked sulphate ions, exhibited with least brine imbibition into the chalk, resulting in the lowest oil recoveries at both temperatures.

A key factor to consider is the SO_4^{2-}/Ca^{2+} ratio, which ideally approaches 2, as observed in SW, DW-PS, and SW-PS brines. Comparing the compositions of the two most effective spontaneous imbibition brines, PW-PS and SW-PS, reveals that PW-PS boasts a significantly higher salinity than SW-PS, with a Ca^{2+} concentration of 41 mM, considerably surpassing the 30 mM present in SW-PS. PW-PS exhibits a Mg^{2+} concentration three times lower and almost half the SO_4^{2-} concentration compared to SW-PS. Impressively, the composition of PW-PS yields a balanced SO_4^{2-}/Ca^{2+} ratio of 0.75, further demonstrating its effectiveness. Furthermore, the highest SO_4^{2-}/Mg^{2+} ratio of 2 is achieved in PW-PS, signifying the presence of two SO_4^{2-} ions for every Mg^{2+}

ion. It's worth noting that Mg^{2+} and SO_4^{2-} ions are known to form ion pairs in aqueous solutions, as outlined in the following reaction equation:

$$\mathrm{Mg^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow [Mg \cdots SO_4]\,(aq)} \qquad \textbf{(4.1)}$$

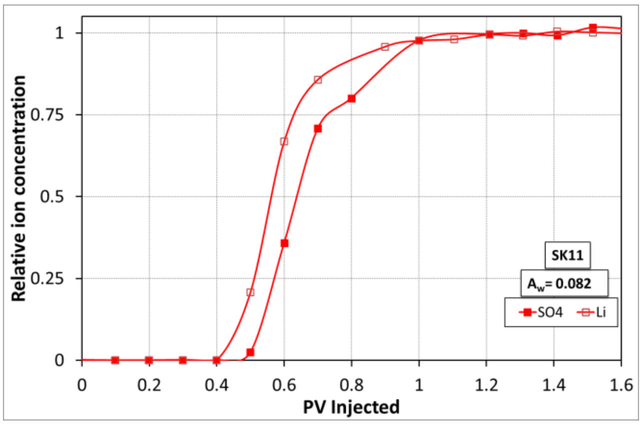
Indeed, the SO_4^{2-}/Mg^{2+} ratio plays a crucial role in the wettability alteration process by influencing the availability of free SO_4^{2-} ions capable of participating in the imbibition-driven wettability alteration. A lower SO_4^{2-}/Mg^{2+} ratio could lead to fewer free SO_4^{2-} ions being accessible to engage in the wettability alteration process through imbibition in SW-PS compared to PW-PS. This difference in the SO_4^{2-}/Mg^{2+} ratio might explain the experienced differences in imbibition rates between SW-PS and PW-PS that have been observed.

A similar phenomenon, where the SO_4^{2-}/Mg^{2+} ratio affected oil recovery through spontaneous imbibition, was also demonstrated in **section 4.2**. In that section, the Mg^{2+} concentration in a modified injection water was elevated to prevent the precipitation of $CaSO_4$. However, this alteration inadvertently led to reduced oil recovery efficiency compared to that achieved using a modified brine with a lower Mg^{2+} concentration. This underscores the delicate balance of ion concentrations and ratios that impact the complex interplay of fluid-rock interactions during imbibition processes in chalk reservoirs.

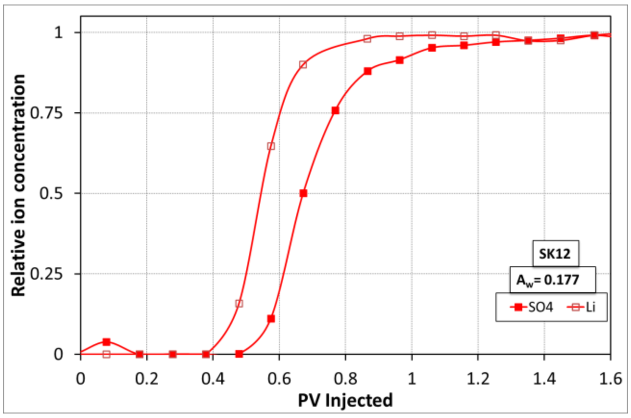
In summary, the findings from the oil recovery experiments through spontaneous imbibition indicate that the introduction of PS salts to various make-up brines, within the salinity range of approximately 5000 to 70000 ppm, can lead to EOR through wettability alteration.

4.3.2 Fraction of water-wet surface area

To verify the modification of rock surface wettability achieved by the Smart Water brines in this study using PS as an EOR additive, a series of CWT tests were conducted to quantify the fraction of water-wet surface area within the cores. After the spontaneous imbibition tests at both 90 °C and 110 °C, the CWT tests were performed at room temperature using the SW0T and SW½T brines. Effluent samples were collected and subjected to analysis, and the separation between the elution curves of Li^+ and SO_4^{2-} was plotted for all cores imbibed at 90 °C (**Figure 4.12**) and 110 °C (**Figure 4.13**).


Relative ion concentration
1
0.75
0.5
0.25
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
PV Injected
SK11
A_w= 0.082
SO4
Li

(a)


Relative ion concentration
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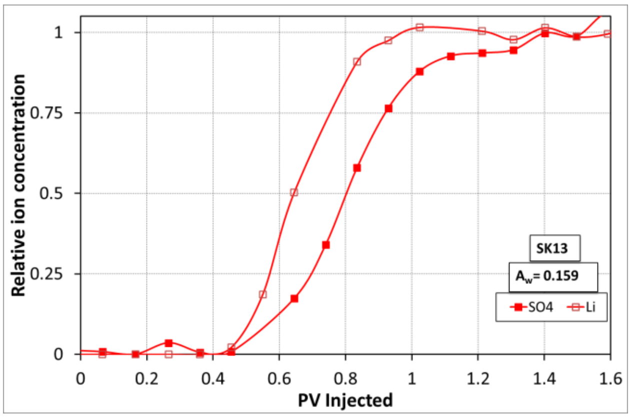
0.25
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
PV Injected
SK12
A_w= 0.177
SO4
Li

(b)


Relative ion concentration
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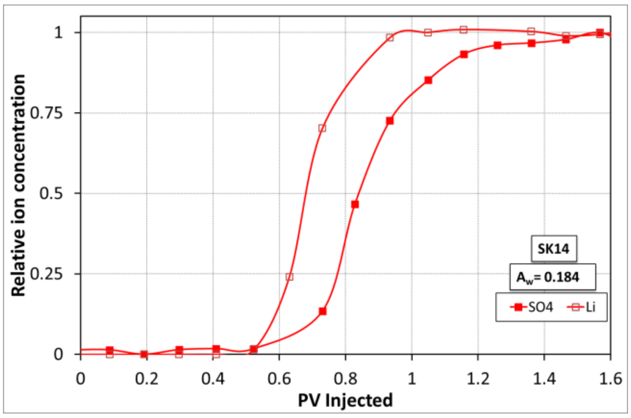
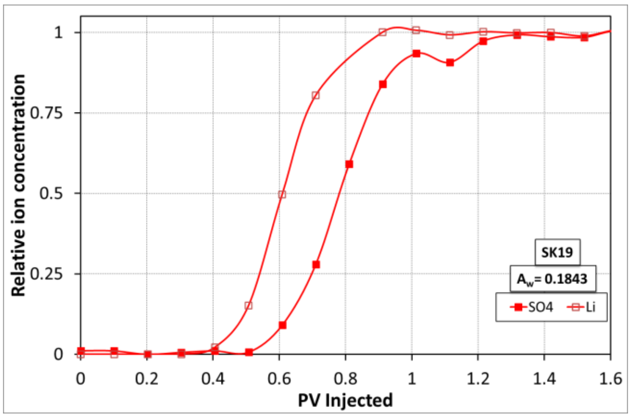
0.75
0.5
0.25
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
PV Injected
SK13
A_w= 0.159
SO4
Li

(c)

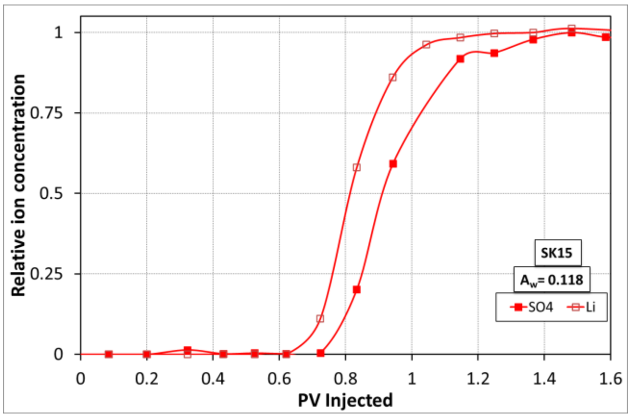


(d)

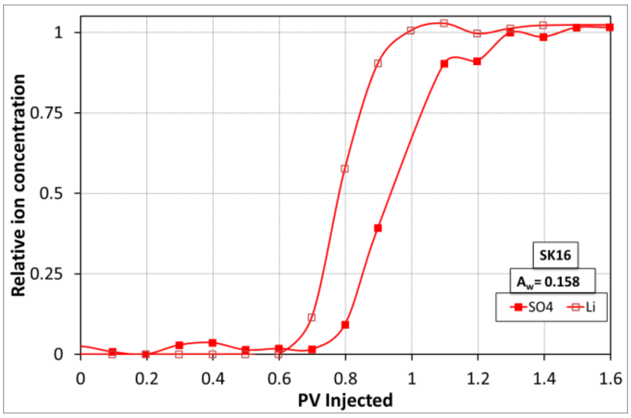


(e)

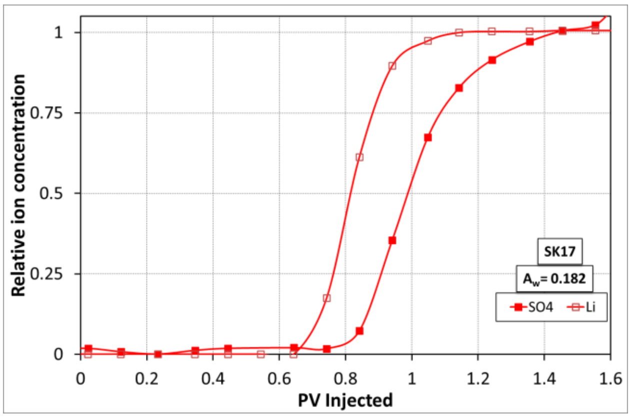
Figure 4.12: Chromatographic separation after the SI tests at 90 °C using (a) FW_A, (b) SW, (c) DW-PS, (d) SW-PS and (e) PW-PS as imbibition fluids.


Relative ion concentration
0
0.25
0.5
0.75
1
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
PV Injected
SK15
A$_w$= 0.118
SO4
Li

(a)


Relative ion concentration
0
0.25
0.5
0.75
1
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
PV Injected
SK16
A$_w$= 0.158
SO4
Li

(b)


Relative ion concentration
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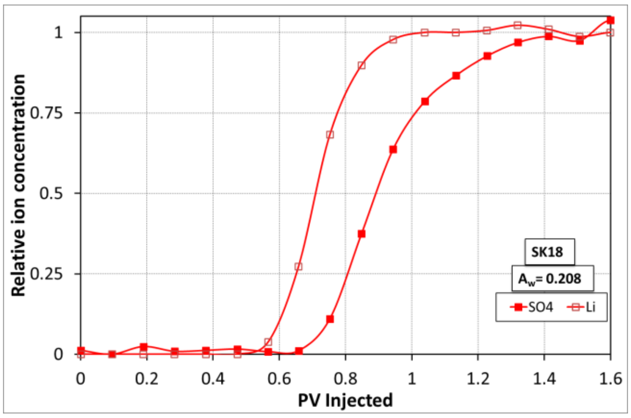
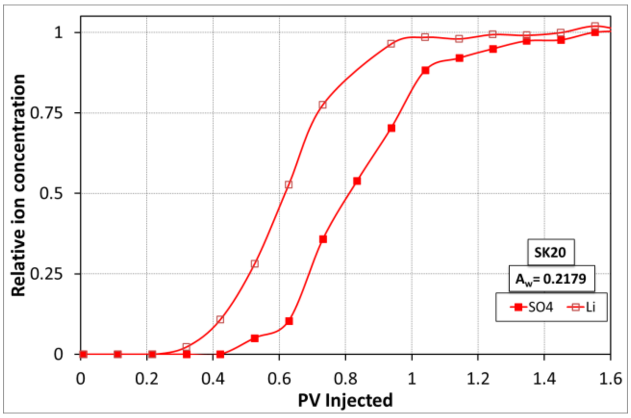
0.25
0.5
0.75
1
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
PV Injected
SK17
A$_w$= 0.182
SO4
Li

(c)



(d)



(e)

Figure 4.13: Chromatographic separation after the SI tests at 110 °C using (a) FW_A, (b) SW, (c) DW-PS, (d) SW-PS and (e) PW-PS as imbibition fluids.

The results from the CWTs are summarized in **Table 4.13**. A typical chromatographic separation area for a completely water wet Stevns Klint chalk core at ambient temperature is $A_w = 0.25$ using SW0T and SW1/2T brines (See **Paper V**). Using this number, the chromatographic wettability indices, I_{CW}, have been calculated based on **Eq. 2.7**, and are given in **Table 4.13**.

Table 4.13: Adsorption area, A_w, and calculated wettability index, I_{cw}, for SK cores at 90 °C and 110 °C.

	T = 90 °C			T = 110 °C		
Imbibition brine	Core #	A_w	I_{cw}	Core #	A_w	I_{cw}
FW_A	SK11	0.082	0.323	SK15	0.118	0.465
SW	SK12	0.177	0.697	SK16	0.158	0.622
DW-PS	SK13	0.159	0.626	SK17	0.182	0.717
SW-PS	SK14	0.184	0.724	SK18	0.208	0.819
PW-PS	SK19	0.184	0.724	SK20	0.218	0.858

Keep in mind that I_{CW} equals 0 for a completely oil-wet chalk core and 1 for a completely water-wet chalk core. The lowest I_{CW} values were recorded with FW_A, resulting in $I_{CW} = 0.323$ at 90 °C and $I_{CW} = 0.465$ at 110 °C. These findings indicate a substantial reduction in the water-wet surface area (A_W) compared to a SK chalk core not exposed to crude oil with POC. FW_A imbibition does not promote chemical-induced wettability alteration due to unfavorable brine composition.

For the two cores spontaneously imbibed with SW, SK12 and SK16, a notable increase in the water-wet area, corresponding to elevated wettability indices of $I_{CW} = 0.70$ at 90 °C and $I_{CW} = 0.62$ at 110 °C, were observed. This confirms wettability alteration towards a more water-wet state. After DW-PS imbibition, the wettability indices obtained were $I_{CW} = 0.63$ at 90 °C and $I_{CW} = 0.72$ at 110 °C, closely resembling the values observed for SW. This confirms that DW-PS has a similar potential to alter core wettability as SW.

SW-PS brine imbibition yielded significantly higher oil recovery compared to SW and DW-PS brines. Additionally, it resulted in substantially larger wettability indices, measuring $I_{CW} = 0.72$ at 90 °C and $I_{CW} = 0.82$ at 110 °C. The highest wettability indices were recorded for PW-PS brine, with $I_{CW} = 0.72$ at 90 °C and $I_{CW} = 0.86$ at 110 °C. This particular brine also induced the most positive capillary forces and delivered the highest oil recovery results during spontaneous imbibition at both 90°C and 110°C.

4.3.3 Benefits of PW-PS injection

Water injection has been a common practice in oil reservoirs for maintaining pressure and enhancing displacement efficiency. Typically, the choice of injected water source depends on factors like availability, implementation costs, and displacement effectiveness. As reservoirs mature, oil production decreases while produced water (PW) volumes increase. Currently, PW is either disposed to in the sea or reinjected into the reservoir. However, with growing environmental concerns and stricter regulations, the cost of treating PW before disposal is rising. Future regulations may necessitate PW reinjection after pretreatment to meet water quality standards and ensure injectivity.

The findings in this study suggest that PS can be added with PW to function as a Smart Water solution in carbonate reservoirs. This addition of PS is not expected to significantly escalate the cost of PW treatment before reinjection. Moreover, it has the potential to enhance the displacement efficiency of the injected brine. **Table 4.14** provides a summary of the EOR effects of SW, a standard injection brine, and PW-PS (a potential Smart Water) in comparison to the results obtained with FW_A and PW, two other potential injection brines.

Table 4.14: Summary of secondary ultimate oil recoveries (UR) and the water-wet area (A_w) at 90 °C and 110 °C.

	FWA	PW	SW	PW-PS	% increase SW	% increase PW-PS
UR, SI at 90 °C (%OOIP)	22	12	37	47	118*	176*
UR, SI at 110 °C, (%OOIP)	31	33	50	53	56*	66*
A_w at 90 °C	0.082	–	0.177	0.184	115**	124**
A_w at 110 °C	0.118	–	0.158	0.218	34**	85**

* Base line from the average of FW_A and PW SI recoveries

** Base line from FW_A CWT

Both SW and PW-PS exhibited substantial enhancements in positive capillary forces and oil mobilization compared to FW_A and PW. This led to a notable increase in water-wet surfaces in the cores. In comparison to baseline recoveries, SW achieved a remarkable 118% and 56% increase in oil mobilization at 90 °C and 110 °C, respectively, along with a corresponding rise of 115% and 34% in water-wet surfaces. When PW-PS was employed as the imbibing brine it outperformed SW, achieving a significant boost in ultimate oil recoveries by 176% and 66%, along with increases of 124% and 85% in water-wet surfaces at 90 and 110°C, respectively.

These experimental findings illustrate the beneficial impact of PS as a Smart Water additive to the injection brine for mixed-wet chalk reservoirs. Elevated concentrations of divalent ions such as Ca^{2+}, Mg^{2+}, and SO_4^{2-} promoted increased positive capillary forces and oil mobilization, resulting in higher water-wet mineral surfaces. Previous studies have also indicated that SW and modified SW can function as Smart Water solutions in reservoir limestones (Austad et al., 2015; Kilybay et al., 2016), underscoring the potential advantages of using PS minerals as additives for PW reinjection also in limestone reservoirs.

4.4 EOR in carbonate by carbonated water

Several researchers have suggested CW as a promising EOR fluid. Beyond enhancing oil production, the use of CW as an injection fluid offers the potential to reduce greenhouse gas, specifically CO_2, in the atmosphere by CO_2 storage in the reservoir. The primary suggested mechanism driving increased oil recovery through CW injection is believed to be oil swelling and reduction of oil viscosity, facilitated by the transfer of CO_2 from the aqueous phase to the oil phase. Additionally, wettability alteration has been considered as a plausible mechanism. This section aims to assess various types of CW for their potential in achieving higher oil recovery.

4.4.1 Solubility of CO_2

Understanding CO_2 solubility in brines at increasing pressure and temperature conditions is crucial for discussing the mechanism of CW in EOR and also for understanding the capacity of CO_2 storage in aquifer. A series of flash experiments were conducted at 60°C, spanning a wide range of pressures, to measure the solubility of CO_2 in various brines, including FW_A, SW, and DW. The results of the flash experiments, as shown in **Figure 4.14**, reveal important insights into CO_2 solubility behavior.

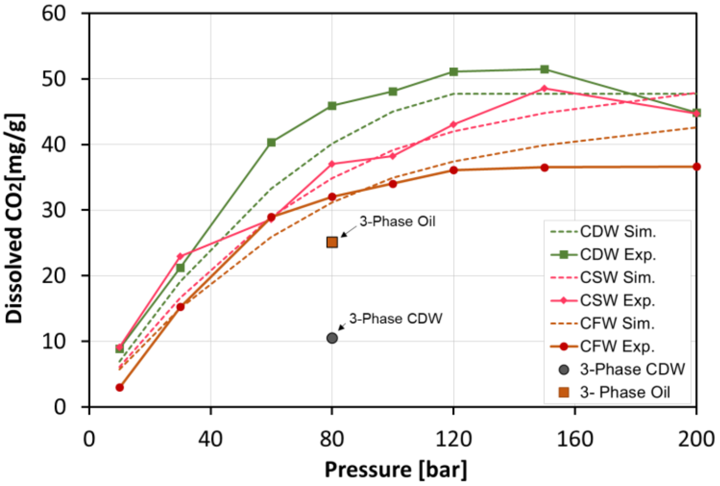


Figure 4.14: Solubility of CO_2 in FW_A, SW, and DW against pressure at 60°C. Continuous lines are representing experimental data and dotted lines are representing the simulated data. 2 single points are representing the solubility of CO_2 in the water phase and the oil phase when both phases are present.

It is evident that as pressure increases, the solubility of CO_2 gradually rises. However, beyond the 100 bar threshold, there is a notable plateau in solubility. An interesting observation appears when both temperature and pressure exceed 31°C and 73 bar, respectively, as CO_2 transforms into a supercritical fluid. Remarkably, this phase transition does not substantially affect the solubility of CO_2 within the brine phase. Additionally, CO_2 solubility is linked to brine salinity. Specifically, the highest solubility is recorded in DW water, with a reducing trend as brine salinity increases. Nevertheless, even in the brine with the highest salinity (62830 ppm), the solubility of CO_2 differs by no more than 40% from that observed in FW_A and DW at elevated pressure stages beyond the critical CO_2 pressure.

Importantly, CO_2 solubility in brines remains relatively low, with maximal values of 50 mg/g observed in DW water. Notably, at the injection pressure of 10 bar used for flooding experiments, CO_2 solubility remains consistently below 10 mg/g across all brines examined.

To validate the experimental findings, simulations were performed by using PHREEQC software to estimate CO_2 solubility in DW, SW, and FW_A. Encouragingly, the simulated results closely align with the experimental data, confirming the reliability and utility of PHREEQC for estimating CO_2 solubility in diverse brines. These results are also consistent with earlier research conducted by Duan et al. (2006) and Spycher and Pruess (2004).

The main mechanism behind extra oil recovery using CW is believed to be the mass transfer of CO_2 from the water phase to the oil phase, increasing the volume and reducing the viscosity of oil phase. To evaluate the amount of CO_2 transferred from the water phase to the oil phase, equal volumes of CDW and crude oil were mixed, equilibrated, and oil and water phase were flashed to SC. The result, **Figure 4.14**, confirms that two third of the CO_2 from CDW could dissolve into the oil phase. Given that CO_2 solubility is significantly higher in oil than in water, 3-phase flash experiment at 80 bar and 60°C clearly proves this phenomenon of mass transfer. The experiment demonstrates the potential for EOR through CW, in line with prior studies (Abedini & Torabi, 2013; Dong et al., 2011; Green & Willhite, 1998). However, it's crucial to acknowledge that the quantity of CO_2 transferred to the oil phase remains limited, suggesting that alternative mechanisms, rather than swelling and viscosity reduction of the oil phase, may be the primary drivers for EOR.

Furthermore, the pH of different CW in different equilibrating pressures were examined (**Figure 4.15**).

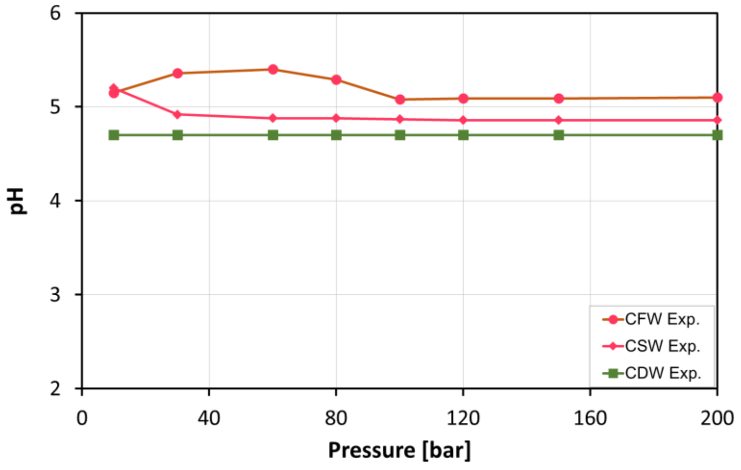


Figure 4.15: The experimental (Exp.) pH of different carbonated brines at different pressure and constant temperature (60°C). pH was measured at ambient conditions.

Across all brines and pressures, pH values consistently fell within the range of 4.7 to 5.2, with only slight variations observed. It is worth mentioning that the measurements were done in SC and most of the dissolved CO_2 were released from the CW. Yet, the pH of the CW at SC was low.

Carbonic acid (H_2CO_3) is formed by dissolving CO_2 into different brine which is a weak acid (**Eq. 4.2**). Carbonic acid is then rapidly separated into carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) (**Eq. 4.3** and **4.4**) which provide hydrogen ions that give lower pH values (~5).

$$CO_2\ (aq) + H_2O \rightleftharpoons H_2CO_3 \qquad \textbf{(4.2)}$$

$$H_2CO_3 \rightleftharpoons H^+ +\ HCO_3^- \qquad \textbf{(4.3)}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad \textbf{(4.4)}$$

Simulation results of pH using PHREEQC confirm the low pH trend (**Figure 4.16**).

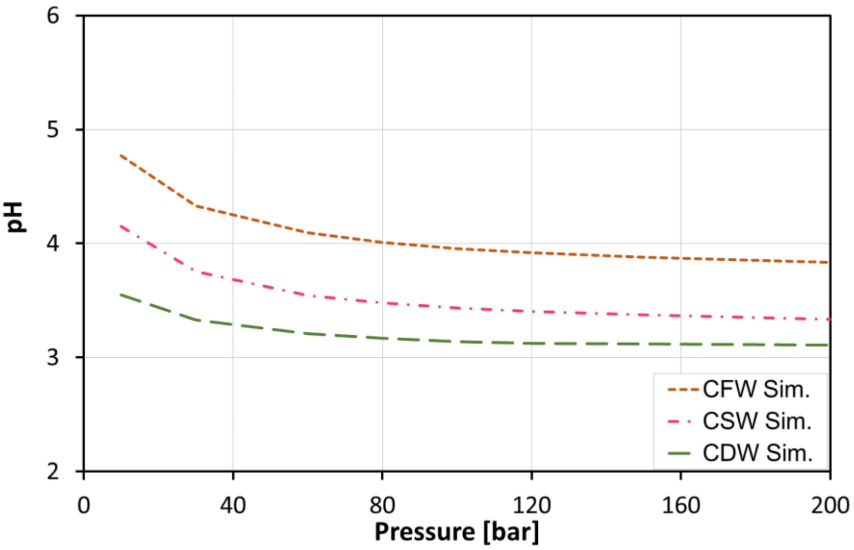


Figure 4.16: Simulated (Sim.) pH of different carbonated brines at different pressure and constant temperature (60°C).

Simulated pH of different carbonated brines at higher pressure were lower than the experimented pH. The main reason for this anomaly is that the experimented pH was measured in room condition.

4.4.2 Oil recovery by viscous flooding

To evaluate the effectiveness of CW as an EOR fluid, equally restored SK chalk cores were used in a series of core flooding experiments. The petrophysical properties of the cores were measured during core restoration process and provided in **Table 4.15**.

Table 4.15: Physical properties of the SK cores.

Core #	Pore volume (mL)	Porosity (%)	Water permeability k_w (mD)
SK23	40.9	49.5	3.8
SK24	36.3	45.4	4.1
SK25	38.3	47.2	3.8

All cores were restored with S_{wi}=10% FW_A and Oil A. The cores were flooded at 130°C maintaining 20 bar confining pressure and 10 bar back pressure. The injection rate was constant at 1 PV/D in all experiments. At the end, the injection rate was increased four times (4PV/D) to evaluate any end effects. 4 different injection brines were used, FW (FW_A), SW, CFW, and CSW. The carbonated brines were equilibrated with CO_2 gas at 6-7 bar, before the carbonated brine phase was transferred to a separate cylinder. The amount of CO_2 dissolved in the carbonated brines used for injection was then close to 5 mg CO_2/g of brine.

In the first flooding experiment on core SK25, FW_A was injected in secondary mode at a rate of 1 PV/D. An ultimate oil recovery plateau of 68 %OOIP was reached after 2 PV was injected, **Figure 4.17**. The pressure drop (ΔP) gradually increased and reached the maximum value of 450 mbar after 0.5 PV before gradually dropped and stabilized at 150 mbar.

The first produced water was observed after 0.5 PV was injected (60 %OOIP). The produced water pH was close to 6.5, slightly lower than the bulk FW_A pH of 7.3. The pH in produced water samples was measured and compared with %OOIP in **Paper VI**.

After 3.5 PV, the injection brine was switched to CFW. During the next 5 days (5 PV), 5% extra oil was mobilized. The ΔP immediately increased from 150 mbar to 800 mbar which could not be explained by a change in the viscosity of CFW. With 4 times increase in ΔP it is difficult to pinpoint if the extra oil mobilized is a result of the CFW or increased viscous forces.

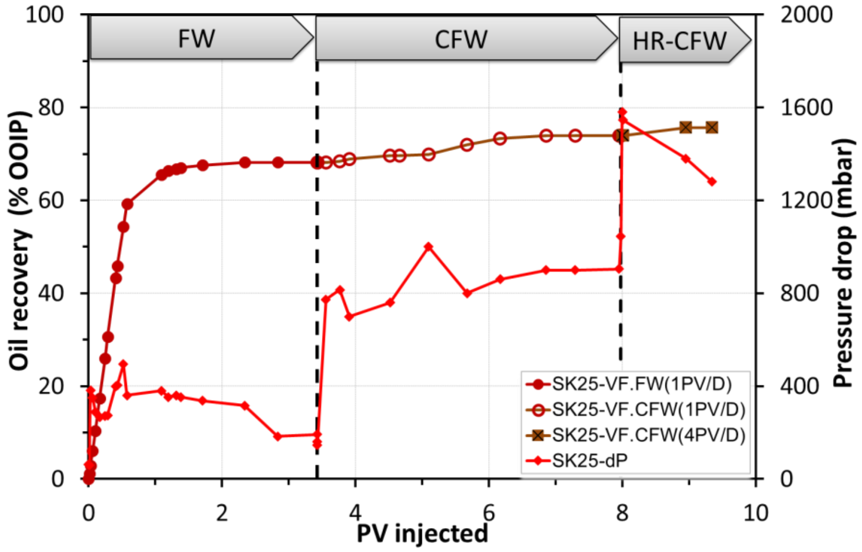


Figure 4.17: Oil recovery tests by VF of core SK25 at 130°C. The core was restored with S_{wi} = 10% FW_A and exposed to Oil A. The flooding sequence was FW_A-CFW at a flooding rate of 1 PV/D. Oil recovery (%OOIP) and average ΔP (mbar) was plotted against the PV injected. At the end, the injection rate was increased 4 times to 4 PV/D (High rate, HR).

During CFW injection the pH in produced water samples went down below 6, confirming the presence of CFW which have a bulk pH of 5.2.

Since the chalk cores used in this experiment are mainly composed of calcite minerals, $CaCO_3$ dissolution could happen in presence of water, and $CaCO_3$ breaks into Ca^{2+} and CO_3^{2-} ions. CO_3^{2-} that take up a proton (H^+) from water and becomes HCO_3^- leaving OH^- behind. On the other hand, CO_2 dissolved in water will form a weak carbonic acid, H_2CO_3 which turns to H^+ and HCO_3^-. The weak carbonic acid system is buffered in the porous media. This chemical process is illustrated simply in **Figure 4.18**. The chemical equilibrium depicted in the figure does not change too much regardless of which brine (FW_A, SW, or DW) is being used.

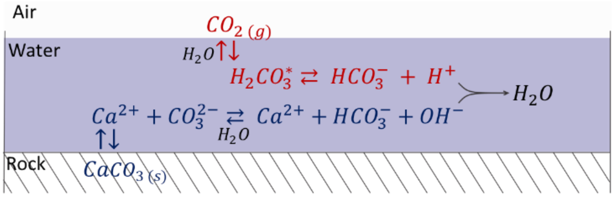


Figure 4.18: Simple illustration of chemical processes happening inside the core in presence of both $CaCO_3$ (s) and CO_2.

Therefore, the carbonate is working as a buffer to the injected CFW and increases its pH. Nevertheless, a change in pH can change the reactivity of the polar organic components (POC) towards the positively charged calcite rock surface as seen in the equations below.

$$\mathbf{R-COOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{R-COO^-} + \mathrm{H_3O^+} \tag{4.5}$$

$$\mathrm{R_3N\!:} + \mathrm{H_2O} \rightleftharpoons \mathbf{R_3NH^+} + \mathrm{OH^-} \tag{4.6}$$

Negative charged POC (R-COO$^-$) has the strongest affinity towards the positively charged calcite surface (Standnes & Austad, 2000a). A reduction in pH could theoretically reduce the amount of R-COO$^-$ species and affect wettability, but the pK_a values for naphthenic acids described in **Eq. 4.5** are typically below 4.5 (Standal et al., 1999) and will not significantly change the amount of non-protonated carboxylic acids.

However, the pressure difference during CFW was four times higher than during FW$_A$ injection. If viscous forces are important in the oil mobilization this could also cause higher oil recovery.

Many researchers have claimed that when CW is injected into the carbonate reservoir, the acidic nature increases the dissolution of carbonate minerals which could promote an increase in porosity and permeability (Bowker & Shuler, 1989; Grigg & Svec, 2006; Shiraki & Dunn, 2000; Wellman et al., 2003). These changes in petrophysical properties help to increase oil recovery by creating a new flow path. $CaCO_3$ and $MgCO_3$ are carbonate minerals that can easily react with CW. FW$_A$ has a high concentration of both Ca^{2+} and Mg^{2+} ions which will limit the dissolution of carbonates even though the pH is somewhat reduced, as illustrated in **Figure 4.18**. If there was a new flow path created during the oil recovery experiment in **Figure 4.17**, the pressure drop should have been reduced.

After the oil production reached its plateau during CFW injection, the injection rate was increased from 1 PV/D to 4 PV/D to observe the effect of viscous forces and any end effects. A marginal extra oil mobilization of 1.5 %OOIP. The pH of the produced water was somewhat lower than at 1 PV/day, which could be explained by that the injection fluid has less time to interact with the minerals.

In the second oil recovery experiment on core SK-24, CSW was flooded in secondary mode followed by SW in tertiary mode. Injection of CSW gave an ultimate oil recovery of 79 %OOIP which was reached after 2.5 PV injected, **Figure 4.19**.

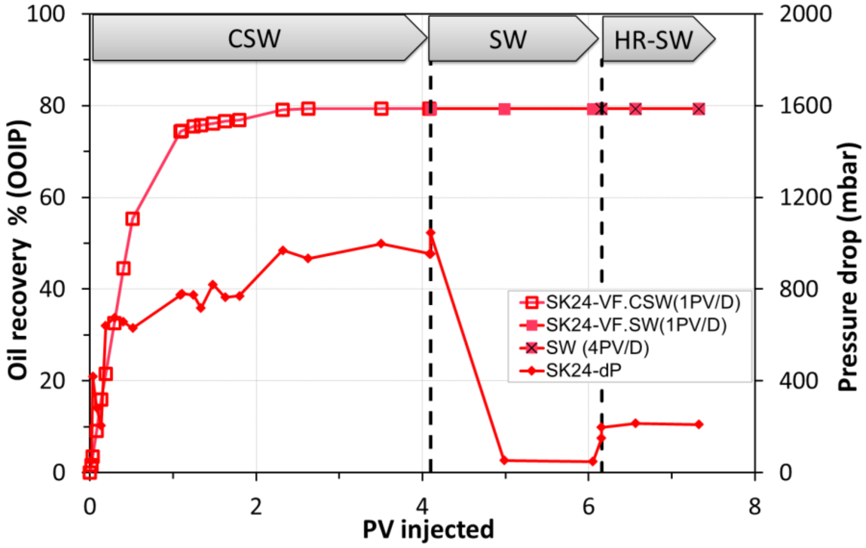


Figure 4.19: Oil recovery tests by VF of core SK24 at 130°C with a back pressure of 10 bar. The core was restored with S_{wi} = 10% FW_A and exposed to Oil A. The flooding sequence was CSW-SW at a rate of 1 PV/D. Oil recovery (%OOIP) and ΔP (mbar) was plotted against the PV injected. At the end, the injection rate was increased 4 times to 4 PV/D.

The ΔP was gradually increased during the whole CSW injection of 4 PV, even though water breakthrough took place after 0.5 PV injected. As previously discussed, the solubility of CO_2 reduces at higher temperatures and free CO_2 gas may promote the increase in ΔP.

After switching to SW, no extra oil mobilization was observed, but a significant decline in ΔP developed. This clearly indicates that free CO_2 liberated during CSW injection is taken up by SW and a new 2-phase flow system of Oil A and brine reestablished a more normal ΔP of 80 mbar. The results clearly indicate that CO_2 liberated from the brine phase trapped in the pore system is not easily diffusing into the residual oil but is being taken up in SW when that is passing through.

Increasing the injection rate 4 times did not mobilize any extra oil, but the ΔP increased to 200 mbar confirming typical pressure drop performance for a 2-phase fluid system in a heterogenous core.

Comparing the recovery results from FW_A-CFW injection (**Figure 4.17**), and CSW- SW injection (**Figure 4.19**), the CSW is significantly more efficient than FW_A in secondary mode. It is known that SW behaves as a Smart Water and is able to change wettability and improve the sweep by inducing more positive capillary forces (Austad et al., 2005; Puntervold et al., 2015). To be able to evaluate if the significant improvement in the oil recovery during CSW injection is a result of wettability alteration by the ions present in the SW, or if the CO_2 present in the aqueous phase also contributes to the extra mobilized oil, a third core flooding experiment was performed on core SK-23 by injecting SW followed by CSW.

SW injection in secondary mode gave an ultimate oil recovery of 74 %OOIP after 2 PV injected. The water breakthrough was observed after 0.5 PV injected when 65 %OOIP was recovered. The experimental result is presented in **Figure 4.20**.

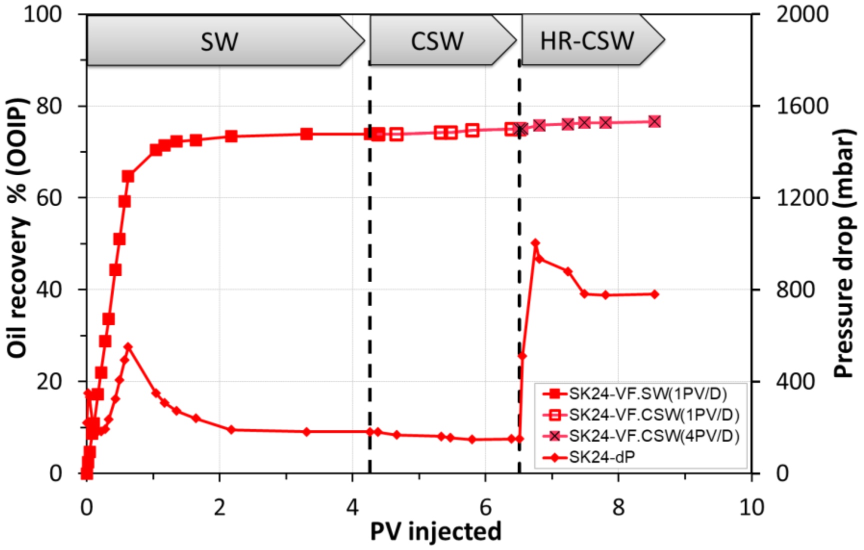


Figure 4.20: Oil recovery tests by VF of SK23 core at 130°C with a back pressure of 10 bar. The core was restored with S_{wi} = 10% FW_A and exposed to Oil A. The flooding sequence was SW-CSW at a rate of 1 PV/D. Oil recovery (%OOIP) and ΔP (mbar) was plotted against the PV injected. At the end, the injection rate was increased 4 times to 4 PV/D.

The ΔP profile is more normal and follows the same trend as observed during secondary FW_A injection when no gas phase is present, **Figure 4.17**. The highest ΔP of 500 mbar was observed after 0.6 PV, gradually declining to 170 mbar when the oil recovery plateau was reached. The PW pH was almost constant and were around 6.5 during the SW injection.

After 4 PV, the injection brine was changed to CSW. During the next 3 PV, a slight increase of 1 %OOIP extra oil was observed, indicating a tiny effect of the CO_2 present, supported by a slight decline in the PW pH towards 6. The ΔP during CSW injection indicated no free gas phase developing, and a low and stable ΔP of 150 mbar was observed, peaking at 1000 mbar during high-rate injection, before stabilizing again at 800 mbar. The significant increase in injection rate and ΔP had only a minor effect on oil mobilization, improving the recovery by only 2 %OOIP.

The overall recovery results confirm that by changing the chemistry of the injection brines, significant changes in ultimate oil recoveries could be observed. SW behaves as a Smart Water in mixed wet chalk, and the SW injection improved the ultimate oil recovery of 74 %OOIP compared to baseline oil recovery using FW_A giving 6 8%OOIP. By adding CO_2 to the brine phase, a slightly more acidic environment was created. CSW in secondary mode gave an ultimate oil recovery of 79 %OOIP which is significantly above SW recovery. Tertiary injection of CFW after FW_A and CSW after SW injection indicates smaller EOR effects.

The experimental results clearly demonstrate that the amount of CO_2 that could be dissolved in the brine phase is very limited. A significant amount of the CO_2 will still remain in the brine phase after equilibrium with the crude oil. The classical explanation linked to swelling and viscosity reduction of the oil phase is not likely the main mechanism for the extra oil mobilized during CW injection.

To evaluate the EOR mechanism of carbonated brines, we need to understand what could happen at the mineral surfaces linked to mineral dissolution processes and/or wettability alteration which could improve the sweep efficiency in water displacement processes in the presence of CO_2. It is clearly observed, a slightly pH reduction during CW injection (**See Paper VII**) due to mineral dissolution and/or wettability alteration, described in **Figure 4.18**.

4.4.3 Effect of carbonated water on mineralogy

The impact of CW on calcite mineral dissolution is shown in **Figure 4.18**. To evaluate the influence of exposure to carbonate water on mineral composition and pore surface minerals, SEM and EDX analyses were conducted. Following the core flooding experiments using carbonated brines, rock samples were extracted from the flooded cores, dried, and subjected to SEM and EDX analyses investigate any mineralogical or visual alterations on the mineral surfaces. SEM photos from core SK25, SK23, and SK24 are presented in **Figure 4.21, 4.22, and 4.23**, respectively.

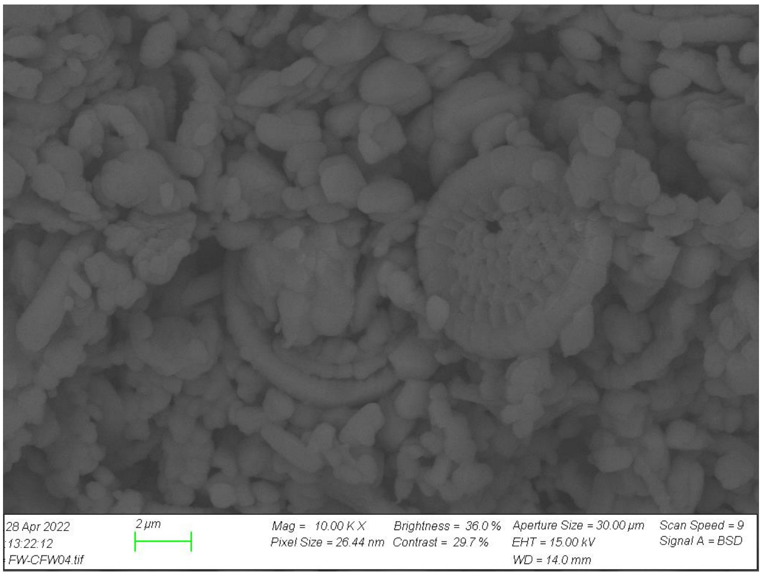


Figure 4.21: SEM photo of chalk sample from core SK25 after the oil recovery test by brine flooding (FW$_{A}$-CFW-HR CFW).

Figure 4.22: SEM photo of chalk sample from core SK23 after the oil recovery test by brine flooding (SW-CSW-HR CSW)

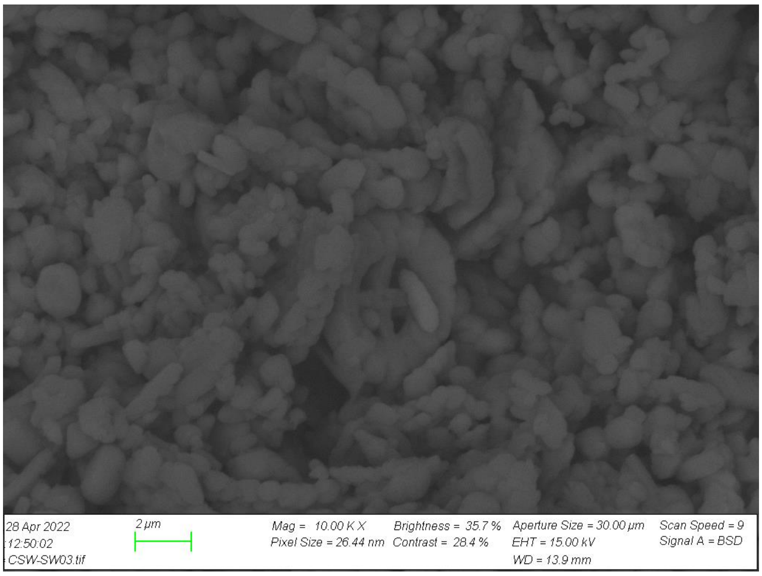


Figure 4.23: SEM photo of chalk sample from core SK24 after the oil recovery test by brine flooding (CSW-SW-HR SW)

Comparing with not flooded virgin SK core sample in **Figure 4.2 (a**), no observable changes in the mineral surfaces of the flooded rock samples following exposure to carbonated brine. The coccolith rings remained intact, the grain sizes and shapes of the rock fragments remained consistent. Furthermore, EDX analysis did not indicate any significant alterations in the elemental composition after exposure to carbonated brine.

A limited volume of carbonated brine, as used in the experiments, does not substantially affect the mineral surfaces, especially considering that there are approximately 2 square meters of mineral surfaces in one gram of Chalk. Simultaneously, the dissolution of calcite in brines with high Ca^{2+} concentration, such as FW_A and SW, is expected to be low due to the common ion effect.

It's worth noting that Kono et al. (2014) observed significant dissolution of carbonate minerals in their SEM study. They reported smaller and smoother grains after exposure to CW and observed a significant increase in Ca^{2+} concentration in the effluent brine. However, their core experiments involved injecting a considerably larger total pore volume of fluid, although injection rates were not reported. It appears that high injection volumes and rates can indeed lead to carbonate dissolution. Additionally, Riazi (2011) found evidence of corrosion in sandstone due to exposure to carbonated brine over an extended period at 2000 psi and 38°C, which was a static exposure test rather than a flooding experiment.

In contrast, our experiments involved flooding SK cores with only about 4 PV, which is more representative of conditions in the main reservoir area. Such exposure levels with several pore volumes of carbonated brine are more indicative of near-wellbore effects for injection wells.

4.5 Positive capillary forces: the key for optimized oil recovery

The flow of oil and water in porous rock systems is regulated by a combination of viscous, gravity, and capillary forces (Dake, 1983). Numerical models that rely on Darcy's law typically emphasize viscous forces when describing fluid flow in reservoirs, often overlooking the direct contribution of capillary forces in oil recovery experiments.

In order to illustrate the significance of capillary forces in the processes of oil mobilization, a series of oil recovery experiments was conducted using low-permeability, heterogeneous Stevns Klint outcrop chalk cores. The petrophysical characteristics of the cores were assessed during their preparation and are detailed in **Table 4.16**.

Table 4.16: Petrophysical properties of the outcrop SK chalk cores.

Core #	Porosity (%)	Water Permeability kw (mD)	Pore Volume (mL)
SK31	49.1	4.2	38.2
SK32	49.2	3.8	38.6
SK33	48.4	4.1	38.6
SK34	48.6	4.7	39.1
SK35	47.3	3.8	38.2
SK36	49.5	3.9	40.9
SK37	48.5	4.8	38.6
SK38	48.6	4.2	39.8
SK39	47.8	4.1	38.9
SK40	48.1	4.0	37.8

All Stevns Klint (SK) cores were uniformly restored to mixed-wet conditions. A water saturation (Swi) of 10% was uniformly established in all cores using FW_A prior to subjecting them to the same quantity of Oil A during the fluid restoration process. This process was followed by aging the cores to ensure consistent oil recovery results. Oil recovery experiments involving a combination of spontaneous imbibition and viscous flooding were performed to confirm the presence of capillary forces particularly in the context of static and dynamic wettability alteration processes using Smart Water.

4.5.1 Oil recovery by capillary and viscous forces

Core SK37 underwent to spontaneous imbibition using FW_A, which is the same brine that represented the initial water saturation of 10%. FW_A will not facilitate any chemically induced wettability alteration during the imbibition process. Once the oil recovery plateau was reached during spontaneous imbibition, the core was subsequently subjected to flooding with FW_A at a rate of 1 PV per day until the ultimate recovery plateau was achieved. The results of the oil recovery experiments for Core SK37 are depicted in **Figure 4.24**.

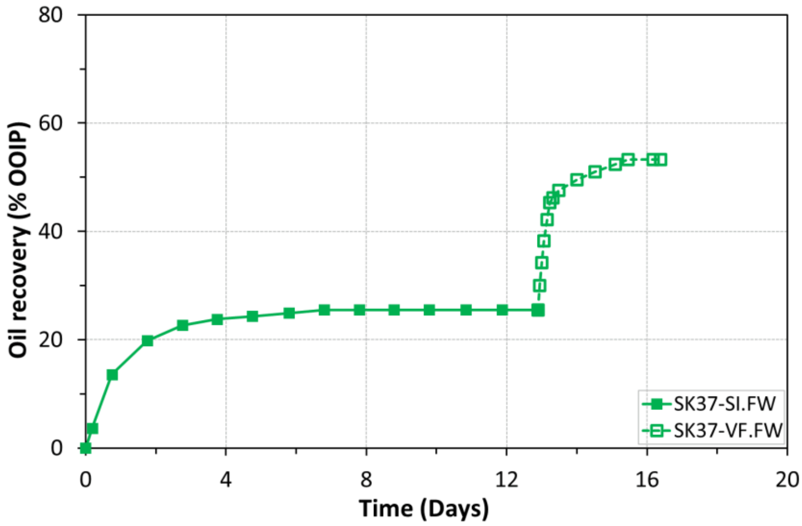


Figure 4.24: Oil recovery test on core SK37 at 90°C. The SK chalk core was restored with Swi=0.1 with FW_A and Oil A. The core was Spontaneously Imbibed with FW_A, followed by viscous flooding with FW_A at a rate of 1 PV/D.

Core SK37 reached an oil recovery plateau of 25 %OOIP after 8 days, confirming presence of positive capillary forces. The restored core wettability could be described as mixed - slightly water wet.

After 13 days, core SK37 was viscous flooded with FW_A at an injection rate of 1 PV/day. After 3 PV, a new ultimate oil recovery plateau of 53 %OOIP was reached, representing the effect of applied viscous forces which will force FW_A mainly through larger pores combined with oil mobilization by spontaneous imbibition of brine into smaller and less accessible pores in the heterogenous pore network.

To investigate the effect of capillary forces on the oil mobilization during viscous flooding experiments, a parallel experiment was performed on core SK38. Spontaneous imbibition with FW_A gave an ultimate oil recovery of 23 %OOIP after 9 days, **Figure 4.25**, confirming reproducible behavior in the core restoration process. By injecting SW instead of FW_A at the same injection rate of 1 PV/day, the ultimate oil recovery plateau reached 64 %OOIP after 5 days, confirming that a significant amount of extra oil was mobilized compared to FW_A even though the viscous forces applied were the same.

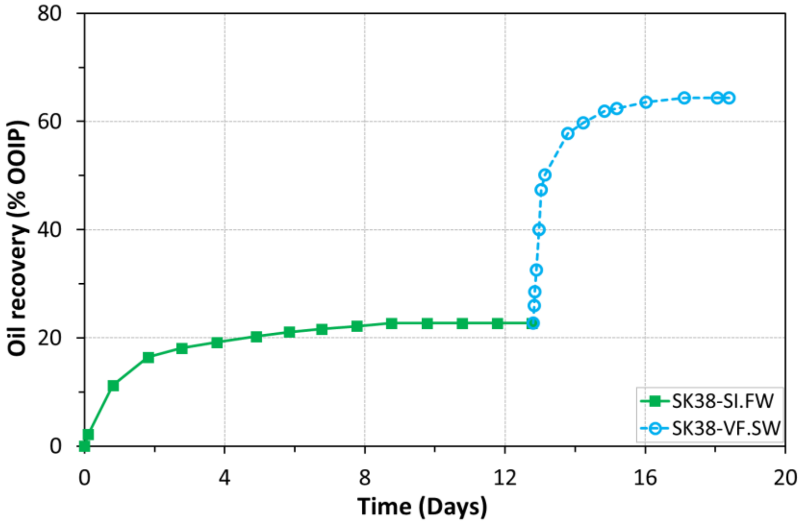


Figure 4.25: Oil recovery test on core SK38 at 90°C. The SK chalk core was restored with Swi=0.1 with FW_A and Oil A. The core was spontaneously imbibed with FW_A, followed by viscous flooding with SW at a rate of 1 PV/D.

To be able to explain this increased displacement efficiency using SW, a new series of spontaneous imbibition experiments were performed comparing the capillary forces available during spontaneous imbibition with FW_A and SW. Core SK31 and SK32 went through the same core restoration process as for SK37 and SK38. Both cores were spontaneously imbibed at 90 °C, SK31 with FW_A and SK32 with SW, **Figure 4.26**. Core SK31 reached an ultimate oil recovery of 22 %OOIP after 11 days, confirming initial restored conditions in line with SK37 and SK38. When SW was used as imbibing brine in secondary mode for core SK32, a significant increase in both speed of imbibition and ultimate oil recovery was observed, reaching 37 %OOIP after 21 days. The extra oil mobilization could only be explained by increased positive capillary forces, facilitated by a chemically induced wettability alteration, in line with the general understanding of Smart Water EOR processes, and specific to SW as a Smart Water in chalk as observed during viscous flooding of Core SK38 in **Figure 4.25**.

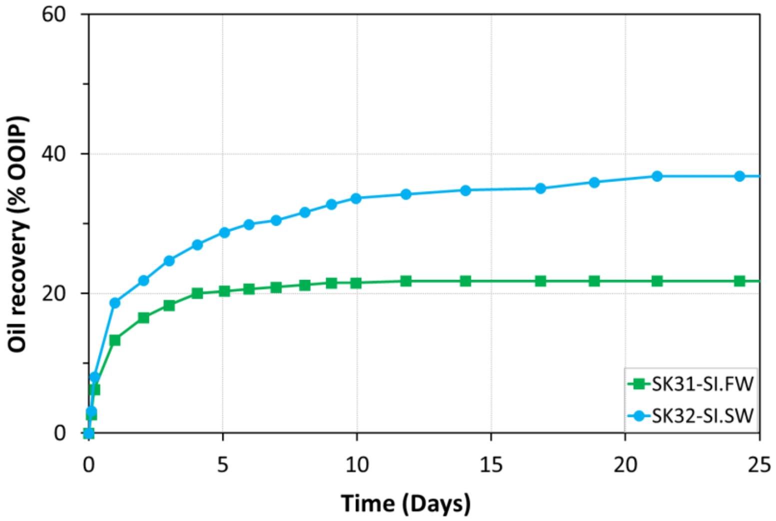


Figure 4.26: Oil recovery test on core SK31 and SK32 at 90°C. Both SK chalk core have been restored with S_{wi}=0.1 with FW_A and Oil A (AN of 0.58 mg KOH/g, BN of 0.30 mg KOH/g). Core SK31 was imbibed with FW_A and SK32 with SW.

Table 4.17 provides a summary of the experimental results from the mixed wet chalk cores at 90 °C.

Table 4.17: Experimental results from mixed wet SK cores at 90 °C.

	SK31	SK32	SK37	SK38
S_{wi}, %	10	10	10	10
SI FW_A, %OOIP	22		25	23
SI SW, %OOIP		37		
VF FW_A, %OOIP			53	
VF SW, %OOIP				64
$I_{w_{SI\,FW_A}}$	0.29		0.33	0.31
$I_{w_{SI\,SW}}$		0.49		

The results from spontaneous imbibition test confirm a dramatic reduction in capillary forces and oil mobilization when the cores were exposed to Oil A instead of heptane. The restored core wettability could be expressed by Amott water index ($I_{w_{SI}}$) showed in **Eq. 3.1** calculated for all spontaneous imbibition experiments performed by using 75 %OOIP as the reference for a very water wet core (Khan et al., 2023).

The Amott Water index gives an average initial $I_{w_{SI_{FW_A}}} = 0.31$ for the restored SK cores using Oil A. By introducing SW as an imbibing brine, the final Amott Water index for core SK32 increased to $I_{w_{SI_{SW}}} = 0.49$. This relatively small change in water index towards more water wet conditions has a significant effect on capillary forces. During SW injection into core SK38 the increased positive capillary forces mobilized 11 %OOIP or actually 21 % extra oil compared to the FW_A flooding of core SK37.

All the experiments presented have been performed at 90 °C. To evaluate how temperature affect capillary forces during core restoration and recovery potentials, a new series of experiments have been performed. All cores were prepared following the same core restoration procedure as described previously.

Cores SK33 and SK34 were spontaneously imbibed at 110 °C, where FW_A was used as the imbibing brine for core SK33 and SW for core SK34. The results are given in **Figure 4.27**.

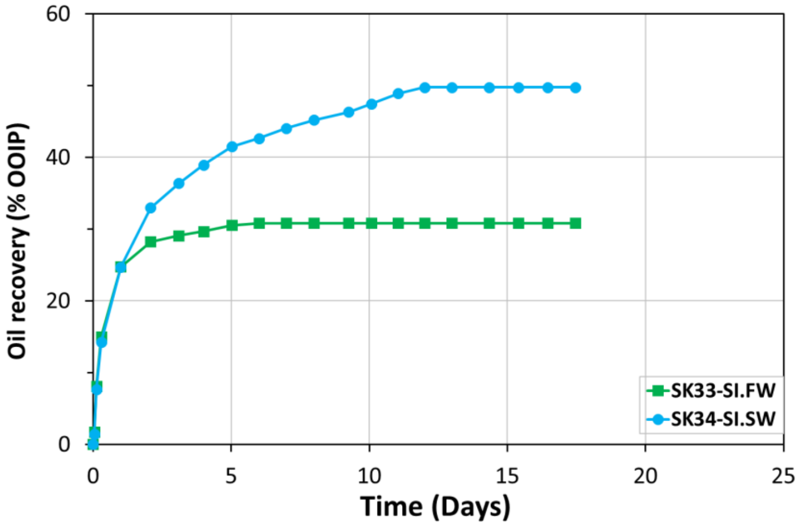


Figure 4.27: Oil recovery test on core SK33 and SK34 at 110°C. Both SK chalk cores have been restored with S_{wi}=0.1 (FW_A) and Oil A. Core SK33 was imbibed with FW_A and SK34 with SW.

In **Figure 4.28**, the spontaneous imbibition is performed at 130 °C, where core SK39 is exposed to FW_A and SW for core SK40.

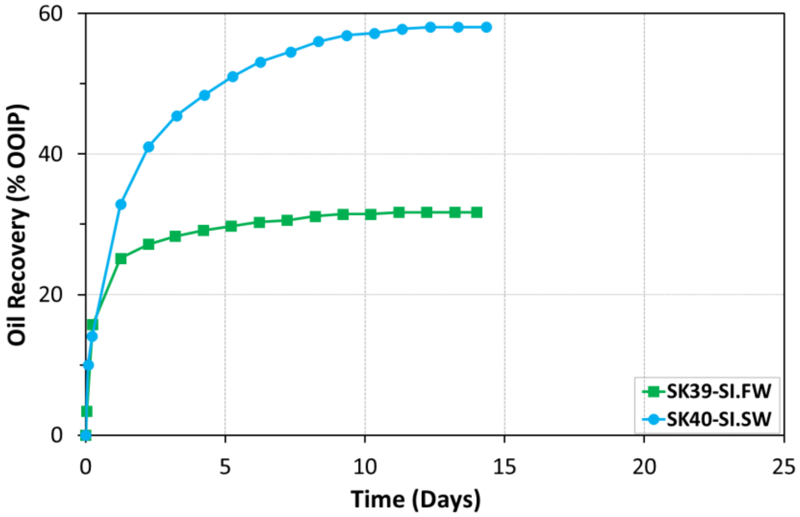


Figure 4.28: Oil recovery test on core SK39 and SK40 at 130°C. Both SK chalk cores were equally restored with S_{wi}=0.1 (FW_A) and Oil A. Core SK39 was imbibed with FW_A and SK40 with SW.

As the temperature increases, the oil recovery and capillary forces increases during FW_A imbibition. At 90 °C, the recovery was 22 %OOIP, while increasing to 31 %OOIP for SK33 at 110°C, and further to 32 %OOIP for SK39 at 130°C.

By using SW as an imbibing brine, increased speed of imbibition and ultimate oil recoveries were observed as the temperature increased. The ultimate oil recovery reached 37 %OOIP at 90 °C, 50 %OOIP at 110°C, and 58 %OOIP at 130 °C. This represents a significant increase in capillary forces compared to FW_A and demonstrates the reported Smart Water EOR effects for SW with increasing temperature (Puntervold et al., 2007a).

To verify if increased capillary forces present will also influence the ultimate oil recovery during viscous flooding experiments, two core flooding experiments were performed at 130 °C to assess the oil recovery potential of FW_A and SW brine in the secondary mode. By employing a rather low injection rate, the capillary forces were permitted to contribute to the oil mobilization process, **Figure 4.29**.

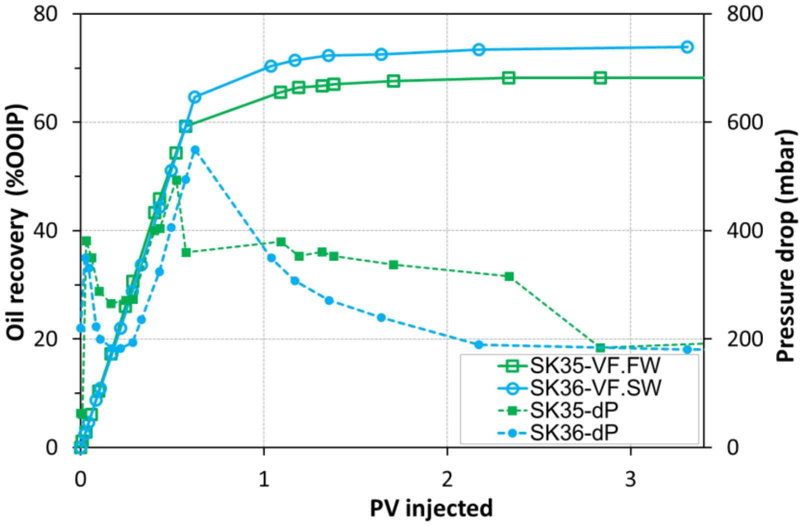


Figure 4.29: Oil recovery test on SK chalk core SK35 and SK36 at 130°C. Both cores were equally restored with S_{wi}=0.1 (FW_A) and Oil A. The cores were viscous flooded at an injection rate of 1 PV/day, core SK35 with FW_A and core SK36 with SW. Oil recovery (%OOIP) and pressure drop (mbar) were plotted against PV injected.

A piston-like fluid displacement was observed on both cores. The first produced water for core SK35 exposed to FW_A was observed after 60 %OOIP and 0.57 PV injected. For core SK36 exposed to SW, the numbers are 64 %OOIP and 0.62 PV. Increased positive capillary forces during SW injection significantly improved the displacement efficiency, giving an ultimate oil recovery plateau of 74 %OOIP after 2 PV injected, compared to 68 %OOIP for FW_A.

The pressure drop observations showed similar trends for both FW_A and SW injection, confirming that that the additional oil recovery with SW should be attributed to stronger positive capillary forces. It is important to highlight that an injection rate of 1 PV/day into a core with a length of 70 mm represents 0.2 ft/day which is quite low for core experiments. Still, pressure drop of more than 500 mbar after 0.6 PV injected was observed, stabilizing at 200 mbar at Sor.

A core typically represents the properties of a matrix block in a reservoir. If the pressure drop at S_{or} is scaled up using a linear tube flow model, a matrix block with a length of 1 m will see a pressure drop of 2.8 bar. On the reservoir scale with well distances of 300 meter from injector to producer, the pressure drop will then be above 850 bar (12 000psi) which is unrealistic in nature. This excludes matrix flow in low permeable reservoirs, and the pathways for viscous water through the oil-bearing zones are fractures, high permeable zones and/or the largest matrix pores. The reservoir matrixes normally hold more than 90% of the reserves and mobilization of the matrix oil is then completely dependent on the presence of positive capillary forces and the access to water from the pathways. In Smart Water EOR the aim is to improve the capillary forces and mobilize even more oil. The same water pathways will also control the main flux of oil from the matrix to the producers.

The same phenomena have also been reported from low permeable reservoir sandstone cores. Aghaeifar et al. (2019) highlighted the importance of capillary forces in oil mobilization processes by Smart Water injection. Low Salinity (LS) brine improved the positive capillary forces compared to FW, SW, and modified SW brines, and improved the displacement efficiency giving significantly higher ultimate oil recoveries in low-rate core flooding experiments. The findings highlighted the importance of including capillary forces in fluid flow models for porous systems. The contribution from capillary forces have also to be accounted for in reservoir simulators to give reliable estimates of oil production on reservoir scale, and to improve reservoir management decisions (Aghaeifar et al., 2018).

5. Conclusion

Representative outcrop chalks were investigated to find the best analogue to reservoir chalk for laboratory studies. Cost-effective and low-carbon EOR solutions for high-temperature carbonate reservoirs have been examined on the representative chalk outcrop and compared with reservoir chalk cores in this work. The significance of capillary forces in the oil recovery process was also studied. The main conclusions drawn from this study were:

- The SK outcrop chalk exhibited similar petrophysical properties, mineralogical composition, and chemical surface reactivity to studied North Sea reservoir chalk cores, that made it a good analogue for the reservoir chalks. This suitability can be extended to investigations of brine-rock interactions, studies involving mixed wettability conditions within the certain CoBR system, and studies of wettability alteration for EOR.
- Experiments performed on slightly water-wet outcrop SK chalk cores and neutral to oil-wet reservoir chalk confirmed that a Smart Water brine could be designed to be both inexpensive and more efficient than SW at a high temperature of 130 °C for carbonate reservoir. The optimal brine composition was found to be 20mM of Ca^{2+}, Mg^{2+}, and SO_4^{2-} ion concentrations each.
- Polsulphate can be added to the injected brines (SW, PW, DW) to increase their effectiveness to enhance oil recovery by wettability alteration and by creating positive capillary forces in carbonates at high temperature.
- When comparing produced water with added PS (PW-PS) with other brines such as FW, produced water (PW), PS added DW (DW-PS), and PS added seawater (SW-PS), PW-PS was found to be the most efficient Smart Water brine. PW-PS can solve industry's PW handling and disposal problem as well as increase oil recovery.
- Oil recoveries were slightly increased in chalk at high temperature both in secondary and tertiary mode by CW. CW injection can be one of the low carbon EOR solutions as it has opportunities to store the CO_2 permanently in the reservoir. The solubility of CO_2 in FW and oil proves that there is a good potential of CO_2 storage in the residual fluid.

No changes on the carbonate pore surfaces were observed after flooding with carbonated brines suggest carbonate reservoir can hold CO_2 without effecting its minerals significantly.

- Presence of positive capillary forces in the cores found to be very important for oil mobilization. Only small improvements in capillary forces have a significant effect on oil mobilization and ultimate oil recoveries during brine injection, both in cores at constant capillary forces, and in cores with dynamic increase of positive capillary forces facilitated by Smart Water. The effect of capillary forces needs to be accounted for when oil recovery processes from core experiments should be explained and mathematically modelled. This study proves the necessity of including capillary forces during upscaling of laboratory results to reservoir scale, to estimate oil production in reservoir simulators, and to improve reservoir management decisions.

5.1 Future work

Oil remains a fundamental energy source for modern civilization and is anticipated to retain its significance for decades to come. Therefore, research related to oil production with low carbon footprint and energy efficient industry should be continued along with search for cheap renewable energy solutions.

This thesis identifies SK outcrop chalk core as a representative alternative to the North Sea reservoir chalk, justifying further tests to assess its comparability with chalk cores from the Middle East, where most of the giant carbonate reservoirs were found.

Various low-carbon EOR solutions, such as ion-modified water, brine with PS additive, and CW, were systematically assessed for their effectiveness in increasing oil production in high-temperature carbonate reservoirs. The best-performing ion-modified water should be experimented in different carbonate systems. The amount of PS to prepare Smart Water brine can be optimized and more experiments on different core system are needed to confirm this promising phenomenon.

CW exhibited good oil recovery potential and CO_2 storage capacity compared to other brines. CW injection should be carried out in reservoir cores to confirm its effectiveness and CO_2 storage capacity should be quantified.

This experimental work proves that it is possible to design a more efficient injection brine than SW. These efficient brines should be tested in pilots and field trials. These brines hold the potential to significantly reduce the carbon footprint associated with oil production, aligning with the petroleum industry's target of achieving net-zero carbon goal.

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List of papers

I	**Polysulphate: A New Enhanced Oil Recovery Additive to Maximize the Oil Recovery From Carbonate Reservoirs at High Temperature.** Md Ashraful Islam Khan, Ivan Dario Piñerez Torrijos, Saja Hussam Aldeen, Tina Puntervold, Skule Strand. *SPE Reservoir Evaluation & Engineering, 2022,* 26 (03): 873–887. *Also presented at the ADIPEC, Abu Dhabi, UAE, October 2022. Paper Number: SPE-211443-MS.*
II	**Is Smart Water Flooding Smarter Than Seawater Flooding in a Fractured Chalk Reservoir?** Tina Puntervold, Md Ashraful Islam Khan, Iván Darío Piñerez Torrijos, Skule Strand. *Paper presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, USA, October 2022. Paper Number: SPE-210042-MS.*
III	**Comparing Outcrop Analogues with North Sea Reservoir Chalk for Laboratory Studies.** Md Ashraful Islam Khan, Skule Strand, Tina Puntervold, Aleksandr Mamonov. *Submitted to Petroleum Geosciences.* *Also presented at IOR+ 2023, The Hague, Netherlands, October 2023.*
IV	**Comparing Inexpensive, Customized Brine Compositions for Enhanced Oil Recovery in High Temperature Outcrop and Reservoir Chalk.** Md Ashraful Islam Khan, Ivan Dario Pinerez Torrijos, Abdullah Numan Tahmiscioğlu, Hidayat Ullah, Tina Puntervold, Skule Strand. *Submitted to Fuel.*
V	**Reinjection of Produced Water with Polysulphate Additive for Enhanced Oil Recovery.** Md Ashraful Islam Khan, Iván Darío Piñerez Torrijos, Meng Zhang, Skule Strand, Tina Puntervold. *Submitted to Energy and Fuel.*
VI	**Carbonated Smart Water Injection for Optimized Oil Recovery in Chalk at High Temperature.** Md Ashraful Islam Khan, Sander Haaland Kleiberg, Ivan Dario Pinerez Torrijos, Tina Puntervold, Skule Strand. *Peer reviewed paper presented in the 35th International Symposium of the Society of Core Analysts, August 2022, Austin, Texas, USA.*
VII	**Positive Capillary Forces: The Key for Optimized Oil Recovery in Low-Permeable Cores.** Md Ashraful Islam Khan, Skule Strand, Tina Puntervold, Aleksandr Mamonov. *Peer reviewed paper presented in the 36th International Symposium of the Society of Core Analysts, October 2023, Abu Dhabi, UAE.*

I	**Polysulphate: A New Enhanced Oil Recovery Additive to Maximize the Oil Recovery From Carbonate Reservoirs at High Temperature.** Md Ashraful Islam Khan, Ivan Dario Piñerez Torrijos, Saja Hussam Aldeen, Tina Puntervold, Skule Strand. *SPE Reservoir Evaluation & Engineering, 2022,* 26 (03): 873–887. *Also presented at the ADIPEC, Abu Dhabi, UAE, October 2022. Paper Number: SPE-211443-MS.*	Paper I

Polysulphate: A New Enhanced Oil Recovery Additive to Maximize the Oil Recovery From Carbonate Reservoirs at High Temperature

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Summary

Seawater (SW) injection is an enhanced oil recovery (EOR) success in the North Sea carbonate reservoirs due to wettability alteration toward a more water-wet state. This process is triggered by the difference in composition between injection and formation water (FW). "Smartwater" with optimized ionic composition can easily be made under laboratory conditions to improve oil recovery beyond that of SW. However, in the field, its preparation may require specific water treatment processes, e.g., desalination, nanofiltration, or addition of specific salts. In this work, a naturally occurring salt called Polysulphate (PS) is investigated as an additive to produce smartwater.

Outcrop chalk from Stevns Klint (SK), consisting of 98% biogenic $CaCO_3$, was used to investigate the potential and efficiency of the PS brines to alter wettability in chalk. The solubility of PS in SW and deionized water, and brine stability at high temperatures were measured. Energy dispersive X-ray and ion chromatography were used to determine the composition of the PS salt and EOR solutions, and to evaluate the sulphate adsorption on the chalk surface, a catalyst for the wettability alteration process. Spontaneous imbibition (SI), for evaluating wettability alteration of PS brines into mixed-wet chalk was performed at 90 and 110°C and compared against the recovery performance of FW and SW.

The solubility tests showed that the salt was easily soluble in both deionized water and SW with less than 5% solid residue. The deionized PS brine contained sulphate and calcium ion concentrations of 31.5 and 15.2 mM, respectively, and total salinity was 4.9 g/L. This brine composition is very promising for triggering wettability alteration in chalk. The SW PS brine contained 29.6 mM calcium ions and 55.9 mM sulphate ions, and a total salinity of 38.1 g/L. Compared with ordinary SW, this brine has the potential for improved wettability alteration in chalk due to increased sulphate content.

Ion chromatography revealed that the sulphate adsorbed when PS brines were flooded through the core, which is an indication that wettability alteration can take place during brine injection. The reactivity was also enhanced by increasing the temperature from 25 to 90°C. Finally, the oil recovery tests by SI showed that PS brines were capable of inducing wettability alteration, improving oil recovery beyond that obtained by FW imbibition. The difference in oil recovery between ordinary SW and SW PS imbibition was smaller due to the already favorable composition of SW.

PS brines showed a significant potential for wettability alteration in carbonates and are validated as a potential EOR additive for easy and on-site preparation of smartwater brines for carbonate oil reservoirs. PS salt, added to the EOR solution, provides the essential ions for the wettability alteration process, but further optimization is needed to characterize the optimal mixing ratios, ion compositions, and temperature ranges at which EOR effects can be achieved.

Introduction

Carbonate reservoirs account for approximately 50% of the world's hydrocarbon reserves, with more than 60% of the oil and 40% of the gas reserves (Bjørlykke 2015; Schlumberger 2022). Despite holding large reserves, the oil recovered from these reservoirs is usually lower than 30% of original oil in place (OOIP), thereby making the EOR potential from carbonates very attractive and high (Austad et al. 2008b; Høgnesen et al. 2005).

Carbonate reservoirs are known for being a challenging environment for oil production. The difficulties met by reservoir and production engineers are low matrix permeabilities combined with natural fractures, and unfavorable wettability as their wettability usually falls within the neutral to oil-wet range (Lucia et al. 2003), which limits capillary forces and reduces the potential for water imbibition into the rock matrices during water injection. All these conditions can lead to water fingering, early water breakthrough, and low oil recovery rates.

Wettability in carbonates is highly influenced by the presence of polar organic components (POCs) in crude oil, where the acidic components are more important than the basic components. The POCs are quantified with the acid number (AN) and base number (BN). Standnes and Austad (2000) observed a reduction in water-wetness when initially, very water-wet carbonate cores were exposed to crude oils with increasing AN. The impact of AN on carbonate wettability has been confirmed by other researchers (Hopkins et al. 2016a, 2016b, 2017; Mjos et al. 2018; Puntervold et al. 2007b; Zhang and Austad 2005). It is also important to note that the brine pH in carbonates is buffered to slightly alkaline conditions. Therefore, the species driving the wettability of the rock surfaces are dissociated carboxylic acids and nonprotonated bases.

The initial wetting of a carbonate reservoir is established when negatively charged carboxylates adsorb onto positively charged carbonate pore surfaces. This will happen during the oil migration into the reservoir. Reservoir temperature can affect the crude oil chemical composition due to decarboxylation processes that take place at high temperatures. These processes decrease the AN of the crude oil

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(Shimoyama and Johns 1972). Therefore, a higher water-wetness observed in a carbonate reservoir can be correlated to crude oils with low AN or high reservoir temperature (Rao 1999).

A water-based EOR method that can contribute with a wettability alteration toward more water-wet state is very important in heterogenous reservoirs. Increased capillary forces will promote SI of brine from fractures into the matrix and mobilize trapped oil. Delayed water breakthrough by taking benefit of reservoir heterogeneity is highly valuable in the pursuit for increased oil production from carbonate reservoirs. Smartwater is a method that meets all these requirements, and it is only prepared by changing the ionic composition of the injection water (Fathi et al. 2010, 2011; Strand et al. 2006a, 2006b).

Different authors proposed different mechanisms explaining the smartwater EOR effect seen in carbonate cores depending on minerals, oil properties, and brine compositions (Bartels et al. 2019; Hao et al. 2019; Liu and Wang 2020; Tetteh et al. 2020). The smartwater EOR effect can be divided into rock/fluid interaction (mainly wettability alteration) and fluid/fluid interaction effects. Several mechanisms related to fluid/fluid interactions have been proposed for injection brine-induced EOR: Formation of water-in-oil microdispersions/microemulsions (Sohrabi et al. 2017), osmosis (Fredriksen et al. 2018; Sandengen et al. 2016), and reduction of interfacial tension. Sohrabi et al. (2017) noticed the formation of water-in-oil microemulsions due to the presence of surface-active agents in crude oil. The authors proposed that these microdispersions/microemulsions would improve the oil recovery by making the carbonate rocks more water-wet and also by swelling the oil phase, which will reconnect the isolated oil droplets in the pore space resulting in improved sweep efficiency. However, the oil swelling effect in microdispersion formation was observed only in glass micromodels, not in real porous rock. Therefore, according to Tetteh and Barati (2018), these observations might not directly influence EOR processes in actual reservoir cores. Alhammadi et al. (2017) experienced higher oil recovery by injecting low-salinity (LS) water in carbonate reservoir cores from the Middle East and linked it to microdispersion formation. Tetteh and Barati (2018) also observed microdispersions in the produced samples of waterflooding in Indiana Limestone. While Sohrabi et al. (2017) and Tetteh and Barati (2018) referred to the formation of these microdispersions as due to the presence of surface-active agents of crude oil; Sandengen et al. (2016) proposed that they were formed due to osmotic movement caused by the salinity difference of LS injection brine and high-salinity formation brine. These brines are separated by crude oil acting as a semipermeable membrane, resulting in the movement of water ions from the LS brine to the oil. This forms emulsification and water-in-oil microdispersions, resulting in oil swelling that leads to fluid displacement. Sandengen et al. (2016) claimed that the osmosis mechanism could be the reason for the formation of the water-in-oil microdispersions observed by Sohrabi et al. (2017) in the glass micromodel visualization experiments. However, the rock mineralogy was not considered while investigating the osmosis mechanism for EOR, and only single salt brines were used during experiments, while most of the formation brines are a combination of several salts.

McGuire et al. (2005) proposed that decrease in interfacial tension between the brine and oil could improve the capillary number and enhance oil recovery in LS brine injection in sandstone, which might be relevant for carbonate as well. Nevertheless, many researchers did not see any significant EOR effect in the case of lower interfacial tension between oil and brine (Mahani et al. 2015; Tetteh and Barati 2018; Yousef et al. 2011).

Proposed mechanisms related to rock/fluid interactions or wettability alteration processes have been classified mainly as either electrostatic interactions or mineral dissolution. Wettability alteration associated with the electrostatic interaction between the rock surface, oil, and brine, is inspired by the Derjaguin-Landau-Verwey-Overbeek theory, which can be further classified into different mechanisms: Electrostatic bond linkages, multivalent ion exchange and electrical double layer expansion, and surface charge variation. Tetteh et al. (2020) pointed out that these mechanisms are similar to the mechanism of the chemically induced wettability alteration process proposed by Zhang et al. (2007), but in the mechanism, the specific ion properties are of utmost importance. This mechanism will be discussed later in this introduction. Mineral dissolution during water flooding has been proposed as mechanisms for the higher oil recovery by smartwater injection, e.g., dissolution of calcite ($CaCO_3$) (Chandrasekhar et al. 2018; den Ouden et al. 2015) and anhydrite ($CaSO_4$) (Austad et al. 2015; Chandrasekhar et al. 2018). In the latter case, dissolution of anhydrite provided the most important ions (Ca^{2+} and SO_4^{2-}) for chemically induced wettability alteration originally proposed by Zhang et al. (2007) to the injection brine. The proposed recovery mechanism by Zhang et al. (2007) has been verified in several parametric studies, showing that the presence of both Ca^{2+} and SO_4^{2-} facilitates wettability alteration toward more water-wet conditions and significantly improves the oil mobilization from heterogeneous pore systems. By modifying the SW composition, more efficient smartwater compositions can be made. Studies have shown that smartwater can be made by increasing the concentration of Ca^{2+} and SO_4^{2-} in SW or by lowering the salinity while maintaining the Ca^{2+} and SO_4^{2-} concentration of SW.

The wettability alteration is induced by the specific ions present in SW, calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulphate, (SO_4^{2-}). The catalyst for this process was identified to be the sulphate present in SW (Austad et al. 2008b; Zhang et al. 2007), and calcium appeared to be also an important ion that is able to coadsorb on the chalk surface to facilitate the process of wettability alteration. Magnesium ions seemed to be relevant at high temperatures, where it can be exchanged with calcium ions from the chalk surface, making more calcium ions available in the bulk fluid to subsequently impacting positively on the EOR effect (Korsnes et al. 2006). The effect of increased sulphate and calcium concentration on the imbibing brine can be observed in **Fig. 1**.

Further modification of SW composition can boost the oil recovery factor in carbonates. For instance, reducing concentration of NaCl in SW or increasing concentration of the catalyst (sulphate) in the brine (Fathi et al. 2011) is a way to increase oil recovery beyond the wettability alteration potential of SW (**Fig. 2**).

The wettability alteration process in carbonates is also temperature-dependent (Fathi et al. 2011), and it appears that the potential for improved oil recovery is enhanced at higher temperatures. The reason behind this effect is connected to the increased reactivity of ions toward carbonate surfaces at higher temperatures. As the temperature increases, the hydration number of the ions present in water decreases. This change is translated into fewer water molecules surrounding them, allowing more interactions between ions and increasing chemical reactivity (Zavitsas 2005). The temperature effects could impact both the established initial wettability and the wettability alteration processes (Piñerez Torrijos et al. 2019; Strand et al. 2008; Zavitsas 2005).

In a comparative study performed by Zhang et al. (2007), oil recovery by SI tests, using brines with varying SO_4^{2-}, Ca^{2+}, and Mg^{2+} concentrations, was evaluated at increasing temperatures from 70 to 100°C and 130°C. It was found that the role of calcium was highly relevant, but that it required the presence of sulphate for being efficient in the wettability alteration process (**Fig. 3**). Note that the four imbibition brines containing varying amounts of sulphate did not produce any oil, above that expected by thermal expansion, until the addition of divalent cations, as indicated in the figure.

The mechanism behind improved oil recovery using smartwater or LS water is still a debate. Smartwater can be LS brine or high-salinity SW as long as its composition can result in higher oil recovery by changing the wettability (Puntervold et al. 2015). A well-known smartwater EOR effect has been observed in natural fractured chalk fields in the North Sea by injecting SW (Austad et al. 2008a; Hermansen et al. 2000). However, Seyyedi et al. (2018) found no extra oil recovery by injecting SW in North Sea quartz-containing reservoir chalk cores from the Ekofisk Formation. In that case, LS water was found to be more effective than SW, and the authors claimed that the presence of a high amount of quartz affects the oil recovery behavior. In a recent study of the initial wettability in three different

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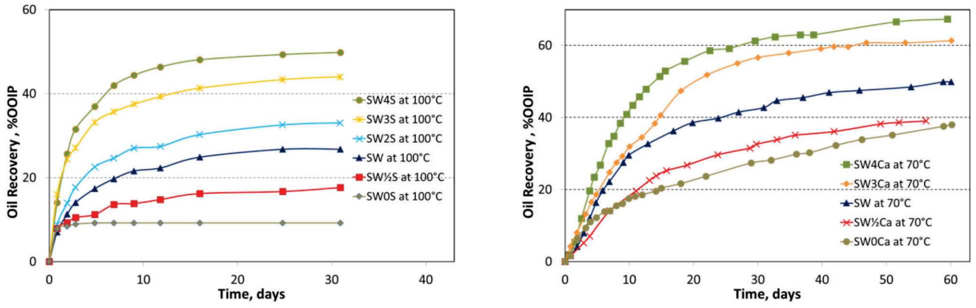

(a) (b)

Fig. 1—SI experiments on chalk. (a) Tests at 100°C displaying the EOR effect on SK chalk cores by increasing sulphate concentration. (b) EOR effect at 70°C in chalk cores by increasing calcium concentration (Zhang and Austad 2006).

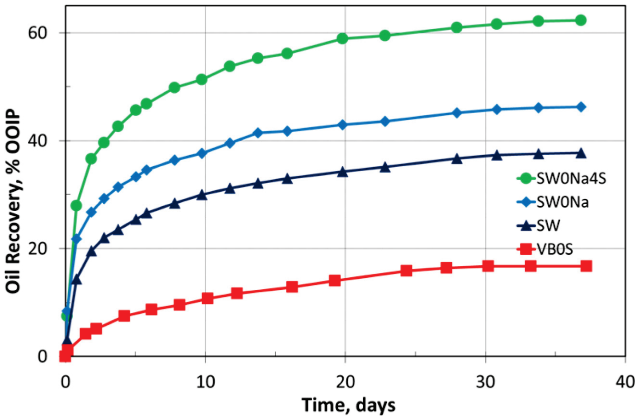

Fig. 2—SI experiments on chalk, EOR effect at 90°C on chalk cores by using VB0S (FW), SW, and two modified SW brines; SW0NaCl and SW0NaCl-4SO4 (Fathi et al. 2011).

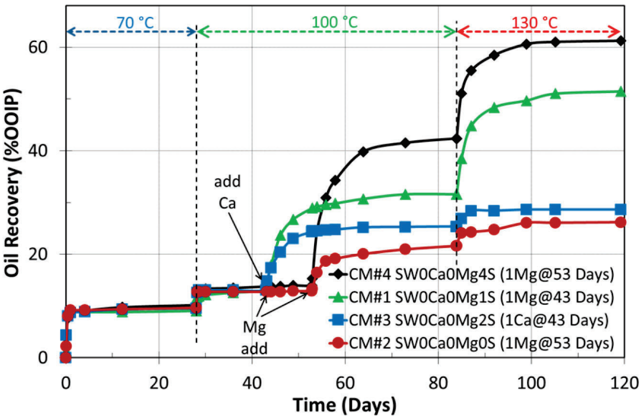

Fig. 3—SI on chalk cores with SW at changing SO_4^{2-}, Ca^{2+}, and Mg^{2+} concentrations and temperatures (Zhang et al. 2007).

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outcrop cores, pure calcite, sandstone, and silica-containing calcite, it was found that the silica content in the calcite had a significant effect on the generation of initial wettability in the cores (Puntervold et al. 2021). It is not unlikely that presence of noncarbonate minerals in carbonate rock can influence the smartwater EOR effect and the composition of the smartwater. Other studies have shown that even dolomite [$CaMg(CO_3)_2$] or dolomitic cores respond differently to SW or modified SW injection compared with chalk/limestone (Puntervold et al. 2018; Romanuka et al. 2012; Shariatpanahi et al. 2016).

Puntervold et al. (2022) recently found that a tailor-made LS brine, containing 20 mM Ca^{2+}, Mg^{2+}, and SO_4^{2-} at a salinity of ~5,000 ppm, was a more efficient imbibition fluid in North Sea reservoir chalk than was SW. This smartwater brine contained all the essential ions to induce wettability alteration, according to the mechanism proposed by Zhang et al. (2007), while at the same time having a reduced salinity, which improves the access of the wettability alteration ions to the chalk surface (Fathi et al. 2011; Puntervold et al. 2015).

Preparation of smartwater for carbonate field applications is a challenge. Efforts have been made to improve SW by using reverse osmosis in combination with nanofiltration. Nevertheless, these methods are highly energy intensive and represent a large investment because they increase capital expenditure and operation expenditure (Ayirala and Yousef 2014). Thereby, there is a need for production of smartwater at low cost that can reduce their impact in operation expenditure and capital expenditure during oil production activities.

Studies by Nair and coworkers at the University of Stavanger used nanofiltration of SW attempting to create a retentate (water containing ions not passing through the membrane) rich in divalent ions and a permeate (water containing ions passing through the membrane) free of divalent ions. The obtained two solutions could be used as main stock (makeup water) for the preparation of smartwater brines (Ravindran 2019). The process required a pressure of 9–18 bar, forcing the SW stream to go through the semipermeable membrane as illustrated in **Fig. 4**.

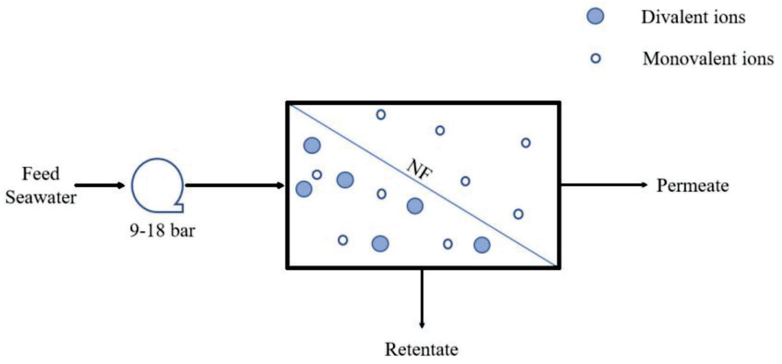

Fig. 4—Schematic of a nanofiltration process with SW as main feed (Ravindran 2019).

The results from the work showed that nanofiltration using SW as main feed was not effective for producing a smartwater enriched in divalent ions and reduced (monovalent ions) salinity. Ion rejection (ions not passing through the membrane) at different pressures quantified by Ravindran (2019) is displayed in **Fig. 5**.

The rejection of monovalent Na^+ and Cl^- ions was 15–35%, which means that most of these ions passed through the membrane to the permeate, but that a significant amount was present in the retentate. The rejection of calcium increased from 55 to 70% when the pressure increased from 9 to 18 bar. Even though the concentration of monovalent and divalent ions in the permeate could be changed, typically only 5–20% of the feed is allocated to the permeate, resulting in retentates with ion concentrations close to SW.

Preparation of smartwater is a challenge both technically and economically. The best performing smartwater (SW0Na4S) brine described in **Fig. 2** precipitates at higher temperature, approximately above 110°C and can thus only be used at temperatures up to approximately 110°C. Moreover, it requires additional chemicals to increase sulphate concentration and expensive filtration processes (such as reverse osmosis, nanofiltration, etc.) to reduce NaCl in the brine. Preparing LS brine also requires expensive filtration, which requires additional energy. Therefore, there is a need for identifying an optimized injection brine that contains the essential ions to induce wettability alteration and is also cheap and easy to prepare.

In this work, PS salts [$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$] as an EOR additive are evaluated. PS is added to water/brine for preparing smartwater, having a composition containing the essential ions, Ca^{2+} and SO_4^{2-}, for inducing chemical wettability alteration in chalk. Dissolution of PS in water/brines should provide the potential to determining ions needed for the wettability alteration process in carbonates, and the solution must be stable at high temperature. The performance of PS as an additive will be evaluated based on dissolution tests, chemical surface reactivity tests, and SI tests on restored mixed-wet chalk cores.

Experimental Work

Materials. ***Rock Samples.*** Outcrop chalk collected from the SK quarry, near Copenhagen, Denmark, was used in these experiments, and it is known to be a good analog for North Sea chalk oil reservoirs (Frykman 2001). SK chalk consists of 98% pure $CaCO_3$ of biogenic origin, mainly coccoliths and fragments of coccoliths which is the building units of this material. Characteristic permeability is between 1 and 10 md, and porosity is relatively high (45–50%). The pore size distribution is presented in **Fig. 6**, and pore sizes typically range from 0.1 to 1 µm.

Under the scanning electron microscope (SEM), it is possible to see the porous media structure in detail. Coccolithic rings and their fragments as well as the heterogeneity of the chalk surface are clearly visualized in **Fig. 7**.

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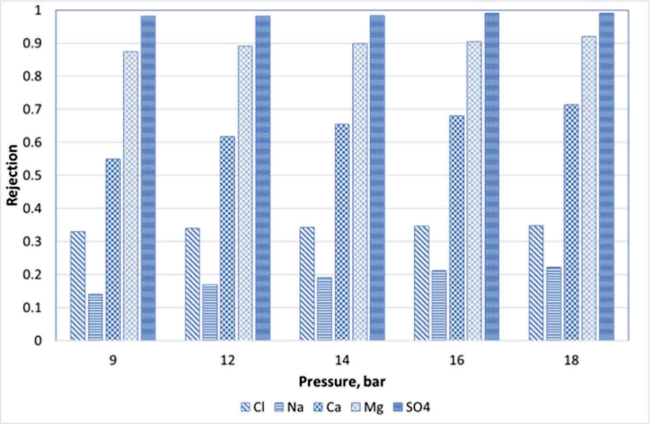

Fig. 5—Ion rejection at different pressures using nano-SW membranes (Ravindran 2019).

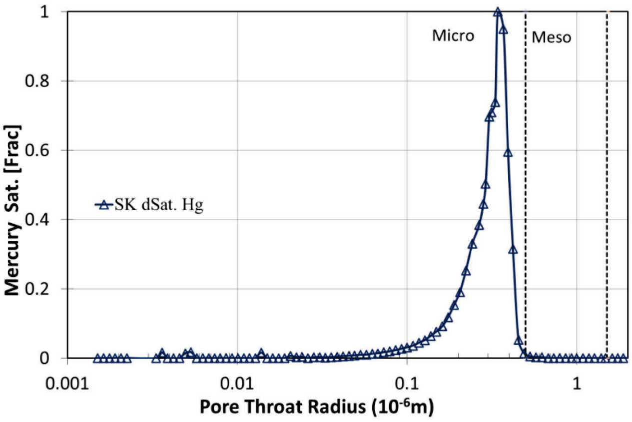

Fig. 6—Pore size distribution for SK chalk determined by mercury injection capillary pressure.

All cores were drilled from the same chalk block in the same direction and cut and shaped to the desired diameter of 3.8 cm and the desired length of 7 cm. All cores were inspected visually, and no fractures and distinct heterogeneities were observed. The properties of the cores used in this work are given in **Table 1**.

The physical properties of the cores were similar to previously published data (Fathi et al. 2010; Hopkins et al. 2016a, 2016b; Zhang et al. 2007).

PS Salt. The PS salt provided by ICL Group is also known as polyhalite. The salt is mined from a polyhalite rock layer of the Boulby mine, UK. The rock layer is located 1000 m below the North Sea near the North Yorkshire coast in the UK. The deposition of this polyhalite rock layer occurred 260 million years ago in the Permian period (**Fig. 8**), and only from this source, it is estimated that there are one billion tonnes of PS, making the cost of using PS low (ICL 2022).

The salt was slightly gray in color and was observed to be in range from granulated to powder form. The salt grains had different particle sizes well spread within the samples analyzed. The predominant particle diameter was in the range of 5–30 µm.

No further purification of the raw salt was performed. High-resolution SEM images were taken of the PS salt mineral, and energy dispersive X-ray was used to analyze its composition. The SEM images of PS salts at 5,000 and 10,000 times magnification are shown in **Fig. 9**.

Elemental analysis detecting both cations and anions was carried out for the PS sample. The results are presented below in **Table 2**. The sample composition is dominated by calcium, potassium, and magnesium cations. On the anion side, sulphate was the main component detected in the sample.

Crude Oil. A low asphaltenic dead oil with an AN of 2.90 mg KOH/g and a BN of 0.95 mg KOH/g was used as source. The dead oil was diluted with 40 wt% heptane, centrifuged, and filtrated through a 5-µm millipore filter. The prepared base crude oil was named RES40, and the AN and BN were measured to 2.18 and 0.66 mg KOH/g, respectively. The AN and BN of the oil samples were analyzed by potentiometric titration following the procedure by Fan and Buckley (2007). No asphaltenic precipitation was observed during filtration or in the storage phase. A batch of the RES40 oil was treated with silica gel to remove the surface active POC, providing an oil with

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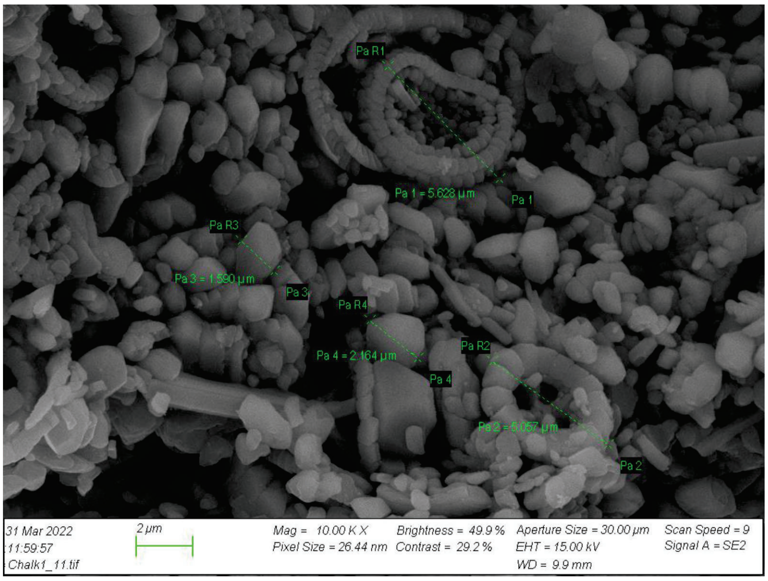

Fig. 7—SEM image of uncleaned SK outcrop chalk at 10,000X magnification.

Core		SK1	SK2	SK3	SK4	SK5	SK6	SK7	SK8	SK9
Length	(cm)	7.1	7.1	7.1	7.2	7.0	6.9	7.1	7.0	7.0
Diameter	(cm)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Pore volume	(mL)	38.6	39.1	39.1	40.1	41.3	38.6	37.9	40.0	37.9
Porosity	(%)	48.6	48.6	48.8	49.2	49.3	49.2	47.4	50.2	47.2
Permeability	(md)	4.1	4.7	3.8	3.8	4.1	4.7	3.8	3.8	4.0
BET (Brunauer, Emmett, and Teller) surface area	(m^2/g)					2.0				
Used in experiment		SIFW at 90°C	SISW at 90°C	SIDW-PS at 90°C	SISW-PS at 90°C	SIFW at 110°C	SISW at 110°C	SIDW-PS at 110°C	SISW-PS at 110°C	CWT at 25 and 90°C

Table 1—Physical properties of the SK cores.

AN = 0.0 mg KOH/g, named RES40-0 oil. Then, the diluted oil, RES40, and the silica-treated oil, RES40-0, were mixed in the proportion of 1:4 to obtain a crude oil (Oil A) with AN ~0.5 mg KOH/g. The reason for preparing a crude oil with AN ~0.5 mg KOH/g was to prepare slightly water-wet/mixed-wet chalk cores as the initial wettability depends on the AN of the crude oil (Standnes and Austad 2000). The final properties of Oil A were measured to AN = 0.58 mg KOH/g and BN = 0.30 mg KOH/g, with density and viscosity determined to be 0.81 g/cm^3 and 2.4 cp. The properties of the three oils are reported in **Table 3**.

Brines. SW and FW used in these experiments were made by mixing distilled water (DW) with reagent-grade salts. The SW composition is based on the SW composition from the North Sea. The FW composition is based on an FW from a North Sea chalk reservoir (Valhall formation brine without sulphate - VBOS). SW and FW were mixed overnight by magnetic rotation and filtered through a 0.22-µm millipore filter. The PS brines, DW-PS, and SW-PS were made by mixing DW and SW with 5.00 g PS per liter solution, respectively. The solutions were mixed for 6 days with a magnetic stirrer before filtration through a 0.22-µm millipore filter. Very similar amounts of PS salt were dissolved independently of the aqueous solution used, i.e., SW or DW. Thus, the solubility of the salt in different brines is high, and more than 95% of the PS added was dissolved. The ion compositions of the filtrated brines were analyzed by ion chromatography. The brine composition of DW-PS and SW-PS after 6 days of mixing is given in **Table 4**. The filters along with insoluble particles from the salts were dried, and the residue was quantified by weight and analyzed with SEM and energy dispersive X-ray. Small variations in ion composition of the prepared brines were observed from one batch to another as the PS is a naturally occurring salt, taken from a mine. To minimize variations in the concentrations, stock solutions of 20 L for both DW-PS and SW-PS were prepared and used throughout this experimental work.

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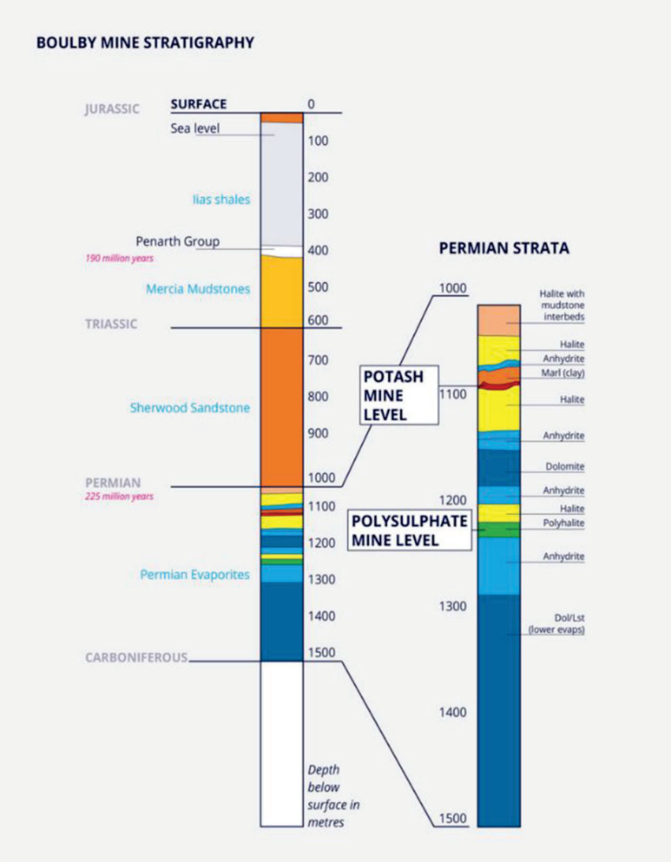

Fig. 8—Stratigraphy of the Boulby mine where PS is found in the Permian strata 1200 m below the surface level (ICL 2022).

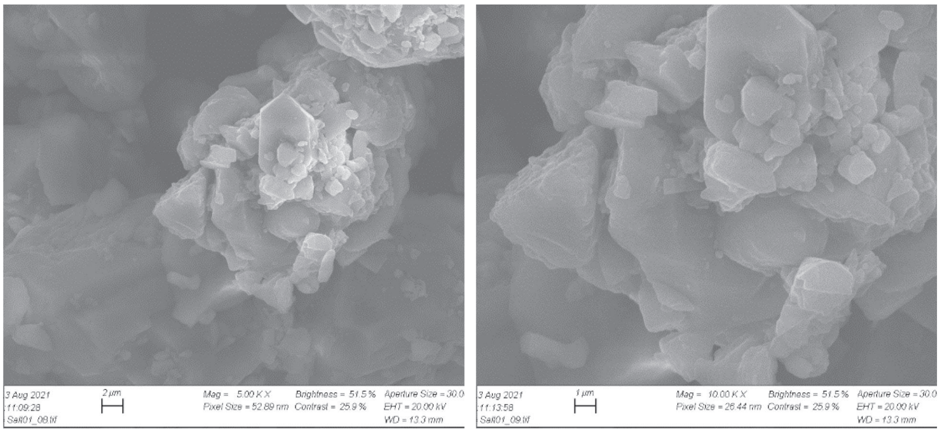

Fig. 9—SEM images of a PS sample at (left) 5,000X magnification and (right) 10,000X magnification.

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Cations		Anions	
Element	Atomic Weight %	Element	Atomic Weight %
Sodium	9.3	Sulfur	85.4
Magnesium	21.9	Chloride	14.6
Aluminum	3.2		
Silica	3.3		
Potassium	25.5		
Calcium	36.9		

Table 2—Elementary composition by atomic weight % of cations and anions in PS.

Oil	AN (mg KOH/g)	BN (mg KOH/g)	$\rho_{20°C}$ (g/cm^3)	$\mu_{20°C}$ (mPa·s)
RES40	2.18	0.66	0.81	2.4
RES40-0	0.0	0.05	0.81	2.1
Oil A	0.58	0.30	0.81	2.4

Table 3—Oil properties.

Ion (mM)/ Properties	SW	FW	DW-PS	SW-PS	DW0T	DW1T
[Na^+]	450.1	997.0	6.3	466.2	6.3	6.3
[K^+]	10.1	5.0	17.4	28.2	17.4	17.4
[Li^+]	-	-	-	-	-	24.0
[Ca^{2+}]	13.0	29.0	15.2	29.6	15.2	15.2
[Mg^{2+}]	44.5	8.0	5.8	47.9	5.8	5.8
[Cl^-]	525.1	1066.0	9.2	528.5	65.7	33.2
[HCO_3^-]	2.0	9.0	-	-	-	-
[SO_4^{2-}]	24.0	0.0	31.5	55.9	-	31.5
TDS (g/L)	33.38	62.83	4.9	38.14	-	-
Density (g/cm^3)	1.02	1.04	1.0	1.02	1.0	1.0
Bulk pH	7.8	7.3	7.5	8.1	7.8	7.8

Table 4—Properties of brines.

DW0T and DW1T brines were used for the surface reactivity tests. DW1T was actually DW-PS mixed with 1.0 g/L of LiCl that worked as a tracer, and DW0T was prepared with reagent-grade salts to have similar composition as DW-PS but depleted in SO_4^{2-}. All brine compositions are listed in **Table 4**.

Surface Reactivity. The surface reactivity of chalk cores in the presence of DW-PS was studied at different temperatures (25 and 90°C) using the chromatographic wettability test developed for evaluating the wettability and the reactivity of potential determining ions such as sulphate, calcium, and magnesium with the carbonate surface (Strand et al. 2006a, 2006b). The test is performed using a coreflooding setup. First, the core was conditioned by flooding 5–6 pore volumes (PV) with DW0T, a brine having similar concentration of ions as DW-PS but depleted in sulphate. Then the core was flooded with DW1T (DW-PS brine with a small amount of Li^+ ions as tracer). The tracer has no affinity for the chalk surface and therefore follows the displacement front. On the other hand, sulphate has affinity for the water-wet chalk surface and is thus eluted with a delay compared with the tracer. IC analysis of the effluents during the coreflooding will determine the tracer and sulphate concentrations. The relative amount of water-wet area or the reactivity of sulphate toward water-wet chalk minerals will be determined by the delay in sulphate elution compared with the elution of the tracer.

Core Restoration. ***Initial Water Saturation (S_{wi}).*** All cores were initially cleaned by flooding 5 PV of DW at room temperature to remove easily dissolvable salts, especially sulphate salts (Puntervold et al. 2007a). The cores were then dried at 90°C to a constant weight. The initial FW saturation (S_{wi}) of 10% was established using the desiccator technique, then the core was stored in a sealed container for 3 days to allow an even ion distribution within (Springer et al. 2003).

Oil Exposure and Aging. The cores with S_{wi} = 10% were vacuumed before saturation with Oil A. One PV of Oil A was flooded initially from both sides to saturate the core followed by 1.5 PV crude oil flooded in both directions at 50°C. A total of 4 PV was flooded to saturate the cores. Finally, the cores were wrapped in Teflon^{TM} tape to avoid unrepresentative adsorption of POC on the outer surface, and then the cores were aged in the same oil for 2 weeks at 90°C to achieve a homogeneous core wetting.

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Oil Recovery by SI. SI experiments were performed on the restored cores to evaluate the initial core wettability and the performance of different brines as EOR fluids. The imbibition experiments were performed at 90 and 110°C at a backpressure of 10 bar using FW, SW, DW-PS, and SW-PS as the imbibing brines. The volume of oil produced was calculated as %OOIP vs. time. The experimental setup is depicted in the following **Fig. 10**.

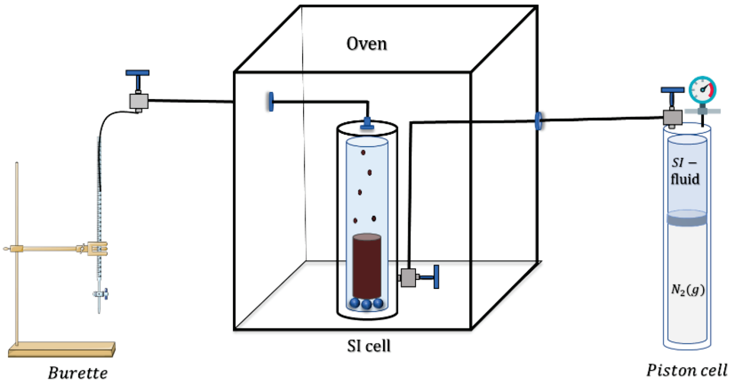

Fig. 10—Schematic of the setup used for the SI experiment.

Results and Discussion

Dissolution of PS Salts in DW and SW. The ion composition after dissolving 5.00 g of PS in 1 L of DW showed a sulphate concentration of 31.5 mM, slightly higher than the concentration of sulphate in SW, 24 mM (**Table 4**). The calcium concentration was 15.2 mM and magnesium 5.8 mM. In comparison with SW, the largest difference was observed for the magnesium which is 44.5 mM in SW. The PS salt also contains a significant amount of potassium which when dissolved in DW gave a concentration of 14.4 mM. The total salinity of DW-PS was 4,885 ppm, with a rather low concentration of sodium, 6.3 mM, and chloride, 9.2 mM. The insoluble part of the PS after filtration was 0.115 g, which means that the solid residue represents only 2.3% of the total PS salt added to DW.

After dissolving 5.00 g PS salt in 1 L of SW, the concentration of sulphate in SW-PS was 55.9 mM (**Table 4**). This represents an increase of 31.9 mM compared with SW, 24.0 mM. Calcium concentration was 29.6 mM, which represents an increase of 16.6 mM compared with the concentration of calcium in SW, 13.0 mM. Magnesium concentration was 47.9 mM, confirming an increase of 3.4 mM after PS exposure. Potassium concentration increased from 10.1 mM in SW to 28.2 mM in SW-PS, which represents an increase of 18.1 mM. The total salinity of the SW-PS brine was 38,140 ppm, which is an increase of 4,760 ppm compared with the salinity of SW. The solid residue after filtration was only 0.200 g, which represents only 4.0% of the PS added to SW.

It appears that in both brines, DW-PS and SW-PS, the concentrations of the determining ions calcium, sulphate, and magnesium are sufficient to trigger smartwater EOR effects. However, the concentrations of these ions are larger in the SW-PS solution, due to the original presence of these ions in SW.

It was observed that almost similar amounts of PS salt were dissolved independently of the aqueous solution used, i.e., SW or DW. More than a 95% of the salt was dissolved in the mixing processes. This might be due to the elementary composition of the salt (**Table 2**).

Residue Analyses. After filtration with the 0.22-µm millipore filter, the residue was dried and analyzed by SEM and energy dispersive X-ray. The SEM images of the residue from the dissolution of PS in DW and SW are presented in **Fig. 11**.

The particle sizes of the residue range from 0.2 up to 30 µm. Different grain shapes were observed under the microscope. Irregular grains were the most common, but also elongated crystals appeared to be a part of the residue in both samples. However, more small particles appeared present in the SW residue, and the particle surfaces also appeared more worn in the presence of SW.

Elemental analysis of the residues was carried out on both samples, and the results are given in **Table 5**.

The insoluble residue was dominated by calcium, sodium, and magnesium cations. On the anion side, sulphate was the main component detected. The DW residue was richer in calcium and sulfur than the SW residue. On the other hand, the SW residue contained more silica and aluminum. These results suggest that the dissolution in SW may have been more effective.

Surface Reactivity. The chromatographic surface reactivity test was performed at both 23 and 90°C using a 100% water saturated SK chalk core SK9. The chromatographic separation between the lithium tracer and sulphate is presented in **Fig. 12**.

The delayed elution of sulphate ions confirms that the sulphate ions gained from PS interact with the chalk surface, and the sulphate reactivity increases with increasing temperature. The first lithium tracer is observed in the effluent after 0.8 PV injected and reaches injection concentration after 1.4 PV. The increase in sulphate concentration is significantly delayed, especially for the test performed at 90°C. At 23°C, the injection concentration of sulphate was reached after 2.0 PV, while after 2.2 PV at 90°C. The separation area (A_w) between lithium tracer and sulphate was quantified by the trapezoidal method and increased from 0.18 at 23°C to 0.35 at 90°C, confirming that the sulphate adsorbs on the $CaCO_3$ surface, and that the adsorption is temperature-dependent. The increased reactivity of the sulphate ions at high temperatures could be explained by dehydration, breaking the hydrogen bond structures between water molecules surrounding the sulphate ion in solution. The results from the surface reactivity test are summarized in **Table 6**.

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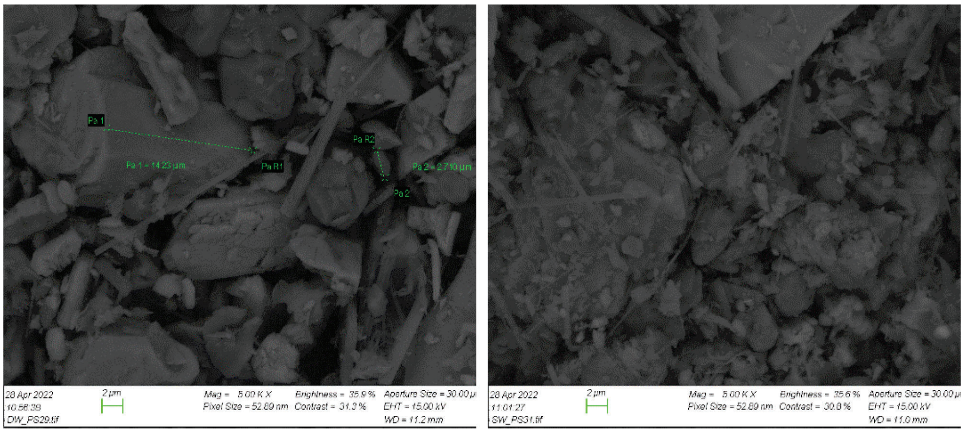

Fig. 11—SEM images at a magnification of 5,000X of PS residue after filtration with 0.22-µm millipore filter. (Left) DW residue and (right) SW residue.

	DW Residue	SW Residue
Element	Atomic Weight %	Atomic Weight %
Sodium	7.0	9.3
Magnesium	11.8	37.5
Aluminum	0.4	1.9
Silica	4.3	14.5
Potassium	0.5	1.5
Calcium	42.4	23.9
Sulfur	33.6	11.4

Table 5—Cation analyses for DW and SW residues after filtration.

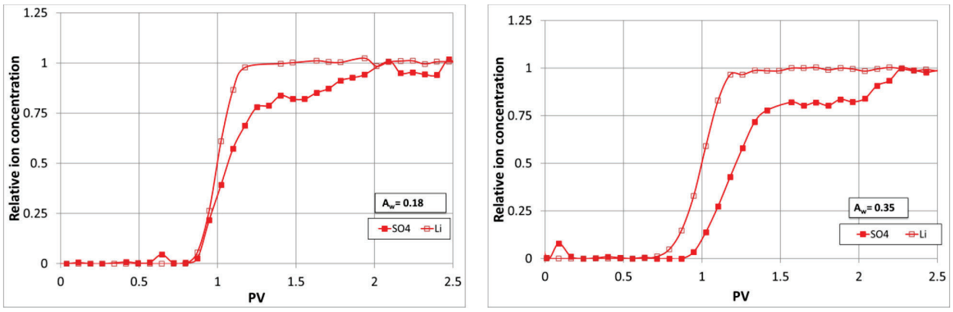

Fig. 12—Chromatographic separation between sulphate and lithium ions in SK outcrop chalk core SK9 (left) at 23°C and (right) at 90°C, flooding DW0T followed by DW1T at an injection rate of 0.2 mL/min.

Temperature	23°C	90°C
Chromatographic separation observed	Yes	Yes
Area of chromatographic separation, A_w	0.18	0.35

Table 6—Data from the surface reactivity tests.

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In summary, a chromatographic separation between sulphate and lithium reveals the potential of the DW-PS as a possible wettability modifier in carbonates. Thus, increased wettability alteration and increased oil mobilization when this brine is used as smartwater (Strand et al. 2006b) can be expected. The increased chromatographic separation at higher temperatures confirms higher reactivity at elevated temperatures, which increases the EOR potential at high reservoir temperatures.

Effect of PS on Oil Recovery. ***PS at 90°C.*** Four equally restored cores were used in this study at 90°C. SI tests were performed to evaluate the restored core wettability and oil mobilization potential by using different imbibition brines. Core SK1 was exposed to FW as the imbibing brine. FW will not facilitate any chemical-induced wettability alteration as long as FW is used as the initial brine. The oil production during SI with FW will give the wettability and baseline oil production from the restored core. Core SK2 was imbibed with SW as imbibing brine. SW is known to behave as a smartwater for mixed-wet cores and is commonly used as injection brines for pressure support for offshore reservoirs. The other two imbibing brines tested were DW-PS and SW-PS. These brines are used to evaluate the effect of PS to improve the oil mobilization by wettability alteration. Core SK3 was imbibed with DW-PS while core SK4 was imbibed with SW-PS. The oil recovery results at 90°C are presented in **Fig. 13**.

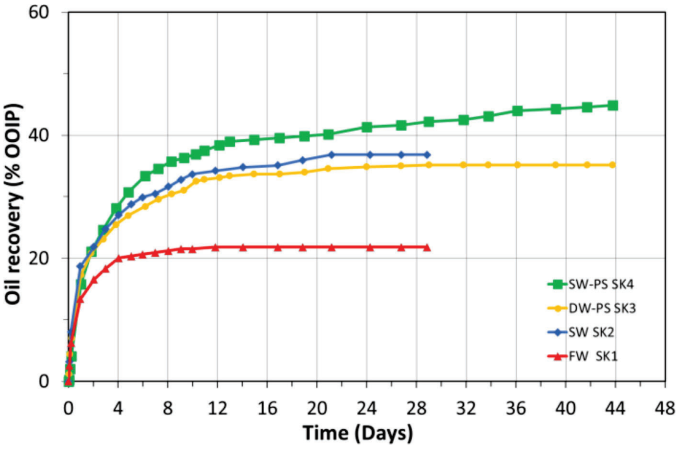

Fig. 13—Oil recovery tests at 90°C by SI of equally restored cores with S_{wi} = 10% and exposed to Oil A. Core SK1 was exposed to FW as the imbibing brine, SK2 to SW, SK3 to DW-PS, and SK4 to SW-PS.

The production plateau for core SK1 reached the ultimate recovery plateau of 22 %OOIP after 12 days using FW as the imbibing brine. The moderate imbibition of FW confirms that the restored SK chalk cores behave slightly water-wet.

SI as an oil recovery method is a practical way of quantifying the wettability of porous systems as both the imbibition rate and ultimate recovery give relevant information that describes the core's wettability (Anderson 1986). A core can be considered to be water-wet, to some degree, if water can imbibe into the oil saturated core. Previously, Puntervold et al. (2021) showed that a similarly prepared SK chalk core, but saturated with oil having no POCs, imbibed FW to 75 %OOIP. This was considered to be the oil recovered from a strongly water-wet core as there were no POCs in the oil. In contrast, an oil-wet core should not imbibe water and an example of a reservoir core of intermediate to oil-wet condition is described by Puntervold et al. (2022) where there was no oil produced by SI of FW.

The restored core SK2 was imbibed with SW. Both the speed of imbibition and the ultimate oil recovery plateau of 37 %OOIP after 21 days is a substantial improvement compared with FW. This confirms that SW induces a wettability alteration in the chalk core during the test, resulting in a significantly more water-wet state (Austad et al. 2008b; Fathi et al. 2010). Wettability alteration also took place with the imbibing brines containing PS. Core SK3 imbibed with DW-PS reached an ultimate production plateau of 35 %OOIP after 28 days, which is very close to the ultimate oil recovery obtained for SW. When using SW-PS as imbibing brine, the ultimate recovery and speed of imbibition of core SK4 were the highest seen. An ultimate oil recovery of 45 %OOIP was reached after 44 days, providing an extra 8 %OOIP compared with SW. These results show that SW as displacement fluid can be improved by the addition of PS salts before injection. PS can also be added to fresh surface and aquifer water to be as efficient as SW in wettability alteration of chalk. Addition of PS to the injection water increases the concentrations of SO_4^{2-} and Ca^{2+} ions needed to induce an efficient wettability alteration, as suggested in the model proposed by Zhang et al. (2007).

PS at 110°C. SI of the restored core SK5 with FW as imbibing brine provides the baseline of oil production and wettability at 110°C, because no chemical-induced wettability alteration will take place when FW is used both as initial brine during core restoration and as the imbibition brine. SW was used as the imbibing brine on core SK6 as a reference for a smartwater. To evaluate the effect of PS as a smartwater additive, DW-PS and SW-PS brines were used as imbibing brines in core SK7 and core SK8, respectively. The results from the SI oil recovery tests at 110°C are given in **Fig. 14**.

The oil recovery results follow the same trend as that observed at 90°C, with the lowest oil recovery with FW and highest oil recovery with SW-PS brine. The recovery plateau with FW on core SK5 reached a recovery plateau of 31 %OOIP after 5 days. Without wettability alteration, the baseline oil production with FW confirms slightly water-wet conditions in core SK5, in-line with the experiment performed on core SK1 at 90°C. When SW was used as the imbibing brine in core SK6, the oil recovery increased from 31 %OOIP with FW to 50 %OOIP with SW, which is an increase of 19 %OOIP, confirming a change in core wettability giving both increased speed of imbibition and significant higher oil mobilization. For the imbibing brines with PS, the recovery plateau with DW-PS on core SK7 was 49% after 24 days, while SW-PS gave the highest ultimate oil recovery of 54 %OOIP after 23 days on core SK8, when the experiment ceased out due to scaling in the inlet line. By adding PS to freshwater, DW-PS, a brine with smartwater properties equal to SW was made. 18 %OOIP

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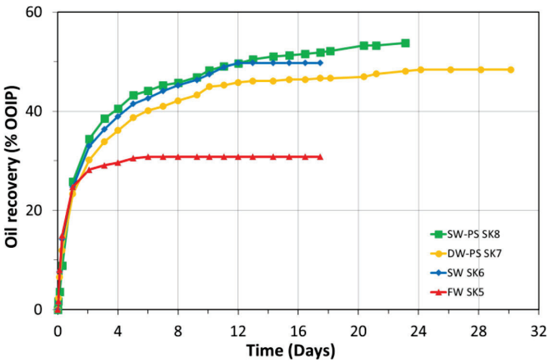

Fig. 14—Oil recovery by SI at 110°C in secondary mode in similarly restored outcrop cores using FW (core SK5), SW (core SK6), DW-PS (core SK7), and SW-PS (core SK8) as imbibition brines.

extra oil compared with that by FW imbibition was mobilized from core SK7 using DW-PS as the imbibing brine. PS added to SW significantly increased both the Ca^{2+} (29.6 mM) and SO_4^{2-} concentrations (55.9 mM) in the SW-PS brine, resulting in the most efficient smartwater brine, mobilizing 23 %OOIP extra oil, which is 4 %OOIP more than that achieved with SW.

Temperature Effect. It was observed that the speed of imbibition significantly increased when the temperature increased from 90 to 110°C, which also gave a significant increase in the ultimate oil recovery. The chemical reactivity of sulphate and calcium ions present in the smartwater brines increases with increasing temperature, which results in a significant increase in the ultimate oil mobilization from heterogeneous pore systems. Increased ion reactivity was observed with increasing temperature during the surface reactivity tests performed with the PS brine DW-PS (**Fig. 12**), clearly indicating that temperature will influence the recovery potential for PS brines. These results are in-line with previous reported findings (Strand et al. 2006a). Higher oil recovery at higher temperature can also be connected to the surface reactivity shown in **Fig. 12**. The surface reactivity tests showed that the sulphate from the PS salts reacted with the carbonate minerals, and that this process was increased at higher temperatures. Thus, the oil recovery was higher at 110°C. The ultimate oil recovery results shown in the SI tests at 90 and 110°C (**Figs. 13 and 14**) are systemized in **Table 7**.

Imbibition Fluid	OOIP % T = 90°C	Δ OOIP % Relative to FW T = 90°C	OOIP % T = 110°C	Δ OOIP % Relative to FW T = 110°C
FW	22	-	31	-
SW	37	15	50	19
DW-PS	35	13	48	17
SW-PS	45	23	54	23

Table 7—Summary of oil recovery.

Significant higher oil mobilization was observed at 110°C for brines capable of inducing wettability alteration, i.e., SW, DW-PS, and SW-PS. For SW the ΔOOIP % relative to FW increased from 15% OOIP at 90°C to 19 %OOIP at 110°C, and for DW-PS ΔOOIP % increased from 13 %OOIP at 90°C to 17 %OOIP at 110°C (**Table 7**). For SW-PS, the ΔOOIP % of 23 %OOIP at 90°C did not increase when the temperature increased to 110°C, most likely due to $CaSO_4$ precipitation, which will reduce the effective concentration of Ca^{2+} and SO_4^{2-} needed for the wettability alteration.

Is PS an Alternative Additive for Smartwater Preparation? From the experimental results at 90 and 110°C, it is possible to conclude that the brines prepared with the PS salt are validated as wettability modifiers; and hence, that PS salt could be used to produce smartwater giving significant EOR effects.

The mechanistic understanding of how PS contributes to the smartwater EOR mechanism for carbonates is believed to agree with the previously proposed mechanism by Zhang et al. (2007). Here, the adsorption of SO_4^{2-} ions, now provided by the PS salts, on the rock surface will reduce the positive surface charge facilitating a coadsorption of Ca^{2+}, which is a common ion to $CaCO_3$. Then, a reaction between Ca^{2+} and the adsorbed acidic components on the surface, which are largely represented by dissociated carboxylic acids ($RCOO^-$), takes place, triggering the desorption of the organic molecule, in turn changing the wettability as illustrated in **Fig. 15**.

It is important to point out that also temperature will influence this process. Mg^{2+} ions at high temperature become more reactive due to dehydration. Experiments have confirmed that Mg^{2+} can interact with the calcite surfaces and release more Ca^{2+} ions into the surrounding environment, speeding up the process of wettability alteration (Zhang et al. 2007). The influence of Mg^{2+} ions on the wettability alteration process at high temperature was observed in **Fig. 3**. At high temperatures, the Mg^{2+} ions will complex with SO_4^{2-} ions reducing or preventing anhydrite ($CaSO_4$) precipitation, which will lower the active concentration of Ca^{2+} and SO_4^{2-} ions that are needed in the wettability alteration process.

Injection brines containing PS outperformed FW as injection brine. At 90°C, the oil mobilization was improved by 61% with DW-PS and by 105% with SW-PS. Furthermore, no salt precipitation or scaling was observed in the injection or production lines during the SI tests at 90°C. Thus, the best performing brine in this set of experiments was the SW-PS brine. At 110°C, the increment in oil mobilization

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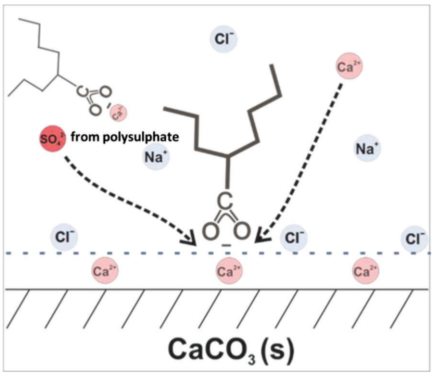

Fig. 15—A modified schematic illustration of the smartwater wettability alteration mechanism in carbonates involving PS salts. The active ions are SO_4^{2-} and Ca^{2+}. After Zhang et al. (2007).

relative to FW was 57% for DW-PS and 74% for SW-PS. Increased temperature and high concentration of Ca^{2+} and SO_4^{2-} in the injection brines could result in $CaSO_4$ precipitation, as observed in the injection line after 23 days for core SK8. Referring to the composition of SW-PS, it is only $CaSO_4$ that can precipitate at higher temperature. $CaSO_4$ precipitation is the most common precipitation problem in the oil industry and is a function of temperature and salinity (Carlberg 1973). Puntervold et al. (2009) showed $CaSO_4$ precipitates at higher temperature using simulation and experiments. $CaSO_4$ precipitation could explain the similar performance of SW-PS at 110 and 90°C.

The potential to use PS as an additive exists, and yes, it can be an implementable EOR alternative. If PS should be used as a smartwater additive for a given carbonate reservoir system, the amount of PS added needs to be optimized based on reservoir temperature, bottomhole temperature in injection wells, and the ion composition of the makeup water.

It is important to note that the oil recovery observed with DW-PS was very similar to that observed with SW. This opens the possibility of using PS salt in onshore carbonate fields where access to SW as smartwater is limited. The results with SW-PS showed that increased sulphate and calcium concentrations can lead to higher recoveries. Thus, it would be important to maximize the ion content, while at the same time staying below their $CaCO_4$ precipitation threshold. Field implementation will require laboratory testing to identify those precipitation thresholds for specific brines prepared with different water sources.

Another benefit of using the PS salt is linked to improvement of current water management strategies. For example, PS salts can be applied to minimize the use of expensive filtration systems, i.e., reverse osmosis or nanofiltration when specific water compositions are required. In case of field operation, most injection waters are pretreated for solid removal before injection. Typically, sand filter, membrane filter, or gravity separation is used for solid removal depending on space and weight limitations of the platform, especially offshore. These filtering processes are cheap and already installed on the platform, thus no extra capital expenditure should be expected related to the treatment of PS brines.

Conclusion

A study for evaluating the potential of PS brines as a new additive for smartwater processes in carbonates has been carried out. The study combined chemical characterization and wettability studies by chromatographic and SI tests. The rock material used was SK outcrop chalk, which is commonly used for parametric studies and wettability studies in carbonates. SI tests were performed at 90 and 110°C, using FW, SW, DW-PS, and SW-PS as imbibing brines, with the latter two containing the PS salt. The conclusions derived from this work are presented below.

- The chromatographic wettability tests suggested that there was potential for wettability alteration by using a PS-based brine.
- The chromatographic separation area increased from 0.18 to 0.35 by increasing the temperature from 25 to 90°C, confirming an increased reactivity of sulphate as the temperature was elevated.
- The PS salt was easily dissolved in SW and DW. The solubility of the PS salt in different brines appeared to be rather high, with more than a 95% of the salts used being fully dissolved at a concentration of 5 g/L.
- During the SI tests, FW recovered 22 and 31 %OOIP at 90 and 110°C, respectively. These results set the lowest oil production baseline since no wettability alteration was induced in these tests.
- Wettability alteration was confirmed by using DW-PS and SW-PS as they recovered more oil than that observed with FW. At 90°C, the improvement in oil production with DW-PS was 61% and for SW-PS 105% relative to FW. At 110°C, the incremental oil for DW-PS in relation to FW was 57%, and for SW-PS it was 74%.
- Precipitation was observed at 110°C with the SW-PS brine, occurring in the inlet line of the SI cell. However, the ultimate oil recovery with SW-PS brine was the highest observed, 54 %OOIP.
- The performance of DW-PS at both 110 and 90°C was very similar to that observed with SW, providing an opportunity to obtain an injection brine with wettability alteration efficiency similar to SW for onshore fields where there is limited or restricted access to SW.

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II	**Is Smart Water Flooding Smarter Than Seawater Flooding in a Fractured Chalk Reservoir?** Tina Puntervold, Md Ashraful Islam Khan, Iván Darío Piñerez Torrijos, Skule Strand. *Paper presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, USA, October 2022. Paper Number: SPE-210042-MS.*	Paper II

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III

Comparing Outcrop Analogues with North Sea Reservoir Chalk for Laboratory Studies.
Md Ashraful Islam Khan, Skule Strand, Tina Puntervold, Aleksandr Mamonov.
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Paper III

Comparing Outcrop Analogues with North Sea Reservoir Chalk for Laboratory Studies

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Abstract

Chalk has been an important reservoir rock in the North Sea for the last 50 years. However, the reservoirs are maturing, which increases the relevance of affordable improved oil recovery (IOR) solutions. Due to the limited availability and high cost of obtaining reservoir core material, the use of representative outcrop samples is essential for parametric studies on reservoir wettability, capillary forces, relative permeability, oil recovery, and enhanced oil recovery (EOR) studies. Representative core material is also needed for upcoming Carbon Capture and Storage (CCS) studies involving reservoir rock integrity and storage potential of CO_2 in depleted reservoirs.

In this study, both the physical and the chemical properties of easily available outcrop chalk from Stevns Klint (SK) and Aalborg (AA) were compared with preserved core material from two North Sea chalk reservoirs.

SK chalk showed very similar chemical and physical behavior as both reservoir chalks. Even though the important physical properties of AA Chalk were comparable, the mineralogy and amount of reactive pore surfaces exclude it as a proper analogue to reservoir chalk. Using reservoir core sampled in the water zone is also not recommended due to a significant reduction in porosity and permeability compared to cores from the oil zone.

Background of The Study

Carbonate reservoirs hold a significant portion of the world's proven oil reserves, including the chalk reservoirs in the North Sea region. The carbonate reservoirs are undergoing maturity, highlighting the growing importance of cost-effective enhanced oil recovery (EOR) solutions (Puntervold et al., 2022). However, obtaining reservoir core material for EOR studies can present challenges and incur costs. As a result, the use of representative outcrop samples becomes crucial for parametric studies focused on rock wettability and its influence on oil recovery potential and selections of optimized EOR strategies.

Crude oil, brine, and rock (CoBR) interaction plays crucial roles in dictating reservoir properties and oil recovery potential. The presence of polar organic components, asphaltenes, and resins in crude oil impact the wettability of the reservoir, thereby affecting oil recovery. The reactivity of different minerals and their interactions with formation brine and injection brine also significantly impact oil recovery studies in both sandstone (Khan et al., 2021; Mamonov et al., 2018) and carbonate (Korsnes et al., 2006). Pore heterogeneity, pore size distribution, and the presence of fractures within the rock also play important roles in determining oil recovery.

Furthermore, salinity, ion composition, and the reactivity of ions in the formation and injection brines are vital considerations in oil recovery studies. The chemical reactivity between crude oil, brine, and rock is also influenced by temperature. Understanding the properties of CoBR phases that control reservoir wettability and impact wettability alteration processes is essential for optimizing oil recovery strategies (Fathi et al., 2011; Fathi et al., 2010; Shariatpanahi et al., 2016; Standnes & Austad, 2000).

A summary of the CoBR properties that dictate reservoir properties and their impact on oil recovery is presented in **Figure 1.** This figure provides an overview of the interplay between various factors influencing oil recovery in carbonate reservoirs, highlighting the complexity and multi-dimensional nature of the process.

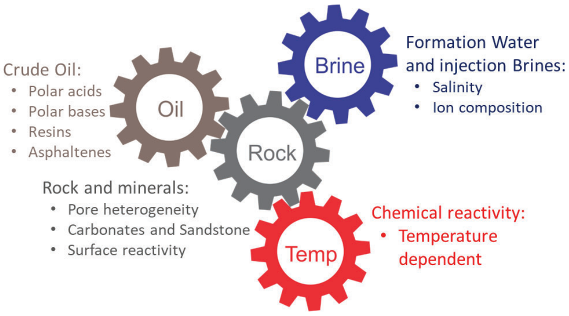


Figure 1 *CoBR properties that dictate the reservoir properties and oil recovery potential.*

Due to the limited availability and high cost of obtaining reservoir chalk core material, it is crucial to analyze representative chalk outcrop samples that can serve as substitutes for reservoir cores. Stevns Klint (SK) chalk has been extensively studied, providing a comprehensive understanding of COBR interactions. Various experiments have been conducted on SK chalk, investigating its initial wetting properties, capillary forces, relative permeability, as well as oil recovery and enhanced oil recovery (EOR) potential (Hopkins et al., 2017; Khan, Strand, et al., 2023; Mjos et al., 2018; Puntervold et al., 2015; Skule Strand et al., 2006; Skule. Strand et al., 2006). Parametric studies using SK chalk have explored EOR strategies employing different injection brines, such as sulphate-rich polysulphate brine (Khan et al., 2022), carbonated water (Khan et al., 2023), modified produced water (Khan, Torrijos, Zhang, et al., 2023), brine with ionic liquid (Tafur et al., 2023), and ion-modified injection water (Khan et al., 2023).

However, Aalborg chalk has not received the same level of extensive study. This work aims to establish a better understanding of the behaviour of Aalborg chalk by comparing it to two different reservoir systems and the SK outcrop. The screening methodology proposed in this paper can also be employed to identify suitable outcrop materials that serve as good analogues for limestone reservoirs as well.

Experimental Section

Rock Material

In this study, 2 outcrop and 3 reservoir chalk cores from 2 separate reservoir systems were used.

Reservoir core

Reservoir chalk cores (SU2, WZ, and RC1) were obtained from two distinct reservoir systems located in the North Sea. SU2 and WZ cores were extracted from the same reservoir system, with SU2 originating from an oil zone located at a depth of 1384.5 meters below sea level, while WZ was taken from the aquifer zone below the oil-water contact at a depth of 1412.3 meters below sea level. RC1 was drilled from an oil reservoir situated much deeper, at a depth of 3920 meters below sea level. The cores were received in a consolidated and well-preserved state, with the presence of fluids observed during the cleaning process. Permeability and porosity measurements were conducted during core cleaning and fluid restoration. The physical properties of the reservoir cores are presented in **Table 1**.

Outcrop Chalks

There is limited access to outcrop chalk material in Europe. There are still two active chalk quarries in Denmark that belong to the same chalk deposition as the North Sea Chalk reservoirs.

Outcrop Stevns Klint (SK) chalk was sampled in the Sigerslev quarry near Copenhagen. This chalk is predominantly composed of $CaCO_3$ with very low content of silicate impurities and are used for painting and paper production. The SK chalk is considered to be representative of chalk reservoirs found in the North Sea (Frykman, 2001).

Additionally, Aalborg (AA) outcrop chalk collected from the Rørdal quarry in Aalborg, was also utilized in this study. The chalk is mainly used for Cement production and have a higher silicate content compared to SK chalk.

The outcrop cores were carefully prepared by drilling in the same direction from different blocks, followed by lathe shaving and saw cutting to achieve the desired cylindrical size for fitting into the Hassler core holder. **Table 1** provides detailed information on the physical properties of the SK and AA outcrop chalk cores.

***Table 1**. Physical properties of the reservoir and outcrop chalk cores.*

Core data	Reservoir core			Outcrop core	
	SU2	WZ	RC1	SK	AA
Length (cm)	6.34	6.3	5.68	7.00	6.43
Diameter (cm)	3.76	3.77	3.77	3.79	3.79
Bulk Volume (ml)	70.40	70.33	63.57	79.45	72.57
PV (ml)	27.14	20.34	24.85	38.80	34.09

Brines

In the laboratory, synthetic brines were prepared by dissolving precise amounts of reagent-grade salts in distilled water (DW). These brine solutions were thoroughly mixed overnight and then filtered through a 0.22 µm Millipore filter prior to their use. The composition of the Formation Water (FW) was based on the formation water extracted from Valhall chalk field from the North Sea, but with a reduced sulphate content. On the other hand, the composition of Seawater (SW) was based on seawater obtained from the North Sea. Two types of brines, SW0T and SW½T, were used in surface reactivity tests. SW½T was basically SW containing the non-adsorbing tracer (SCN^-/Li^+) as well as the adsorbing sulphate, while SW0T was the same SW without any tracer and sulphate. Detailed compositions of all the brines can be found in **Table 2**.

Surface reactivity test

The surface reactivity of both outcrop and reservoir chalk cores was investigated using a chromatographic wettability test, which was developed by Strand et al. (2006) to assess the wettability and reactivity of specific ions, such as sulphate, calcium, and magnesium, with the carbonate surface. The tests were conducted in a Hassler core holder under ambient temperature, with a confining pressure of 20 bar and a back pressure of 10 bar. The cores were sequentially flooded separately at a constant rate of 0.2 ml/min with SW0T (without Li^+/SCN^- and SO_4^{2-}) followed by SW½T (with Li^+/SCN^- and SO_4^{2-}). During the SW½T flooding, effluent samples were collected and analysed. The concentrations of either Li^+ or SCN^- and SO_4^{2-} ions were determined and plotted relative to the injected pore volumes (PV). The tracer used in the test had no affinity for the chalk surface and thus followed the displacement front. In contrast, sulphate exhibited an affinity for the water-wet chalk surface and was eluted with a delay compared to the tracer. By performing ion chromatography (IC) analysis on the effluent samples, the concentrations of the tracer and sulphate were determined. The delay in sulphate elution, compared to the tracer, provided information on the relative amount of water-wet area or the reactivity of sulphate towards water-wet chalk minerals.

***Table 2.** Brine compositions.*

Ions	FW (mM)	SW (mM)	SW0T (mM)	SW½T (mM)
Na^+	997	450.1	460	427
K^+	5	10.1	10	22
Ca^{2+}	29	13	13	13

Mg^{2+}	8	44.5	45	45
Cl^-	1066	525.1	583	583
HCO_3^-	9	2	2	2
SO_4^{2-}	0	24	0	12
Sr^{2+}	0	0	0	0
Li^+	0	0	0	12
SCN^-	0	0	0	12
TDS (g/L)	62.83	33.39	33.39	33.39
Density (g/cm^3)	1.041	1.0226	1.024	1.024
Bulk -pH	7.3	7.11	7.7	7.5

Pore size distribution

Mercury capillary injection (MICP) measurements were conducted by Stratum Reservoir to assess the pore size distribution of both outcrop and reservoir chalk cores. MICP is a commonly used technique in reservoir characterization to determine the distribution of pore sizes and understand the rock's pore structure and connectivity. This information is crucial for understanding fluid flow and storage capacity within the rock, which is essential in evaluating the reservoir's potential for oil and gas recovery and EOR studies.

SEM & EDX analyses

To characterize the pore surfaces, grain sizes, and elemental composition of the rock material, Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) analyses were performed. The analyses were conducted using a Zeiss Supra Environmental Scanning Electron Microscope (ESEM) equipped with an EDX detector. SEM allows for high-resolution imaging of the rock sample, providing detailed information about the surface morphology, pore structures, and grain boundaries. EDX, on the other hand, is a technique that enables the identification and quantification of the elemental composition of the sample. By combining SEM imaging with EDX analysis, valuable insights into the microstructure and chemical composition of the rock material can be obtained, aiding in the characterization and understanding of its properties that are needed for EOR studies.

Evaluation of capillary forces by spontaneous imbibition (SI)

To assess the presence and effectiveness of capillary forces, spontaneous imbibition (SI) experiments were conducted. The cores were fully saturated with heptane as the oil phase and placed in a glass Amott cell. The cores were then imbibed with distilled water (DW) at a temperature of 23°C. The process of imbibition allowed the water to spontaneously displace the oil from the porous medium. The oil recovery was measured and recorded over time. By monitoring the oil recovery during SI, the efficiency of positive capillary forces in mobilizing oil from the heterogeneous pore systems of the cores could be directly evaluated.

Result and discussion

Due to the limited availability of preserved reservoir cores, the use of outcrop material is common in parametric studies for understanding CoBR interactions, including fluid flow in porous media, wettability, and EOR studies. Outcrop results could only be used to describe reservoir behaviour when properties are similar to the reservoir rock.

In this study, we have been focusing on outcrop chalk as analogue to North Sea chalk reservoirs. Most of the North Sea chalk reservoirs are maturing with increasing water production and there is a need for IOR/EOR solutions for lowering the residual oil saturation. Most of these mature chalk reservoirs are located close to industrial areas in West Europe and are also being evaluated as candidates for CO_2 storage in CCS projects.

Rock Properties

The petrophysical properties are important parameters for classifying porous media. The porosity dictates the storage capacity of the rock. The permeability and pore size distribution dictate the fluid flow and the ability to mobilize the pore fluids.

Porosity and permeability

In front of the experiments performed on outcrop and reservoir cores, the cores have gone through core cleaning and fluid restoration processes in the lab. During these operations, porosity and absolute water permeability of the cores have been measured and are reported in **Table 3**.

***Table 3**. Porosity and permeability of the reservoir and outcrop chalk cores.*

Core data	Reservoir core			Outcrop core	
	SU2	WZ	RC1	SK	AA
Porosity φ (%)	38.6	28.9	39.1	48.8	47.0
Water permeability k_w (mD)	3.5	0.4	4.5	3.0	3.1

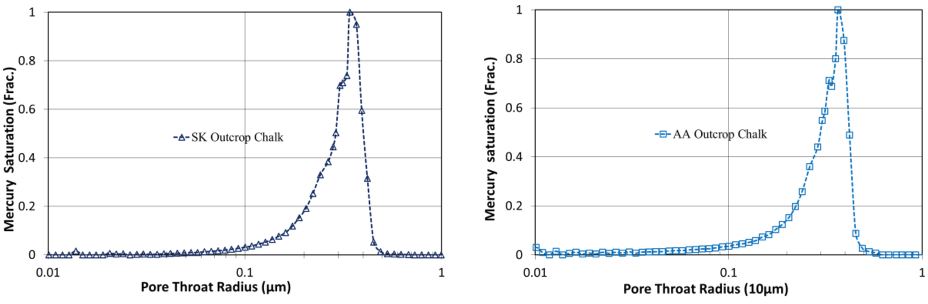
Both outcrop cores, SK and AA, have very high porosity, close to 48%. The porosity is still high for the reservoir cores sampled in the oil zone, SU2, and RC1, close to 38%, confirming high fluid storage capacities in both reservoir and outcrop cores. For the reservoir core sampled below the oil zone, from an aquifer, a significant reduction in the porosity to 29% is observed. A reduced porosity significantly affects the absolute water permeability of 0.4 mD which is close to 10 times lower than the average measured permeability of outcrop and oil zone cores.

The presence of oil in the pore space significantly reduces brine rock interactions where mineral dissolution and precipitation reaction could affect both porosity and permeability of the rock systems. Reduced permeability and porosity will limit the use of water zone chalk as a location for CO_2 storage.

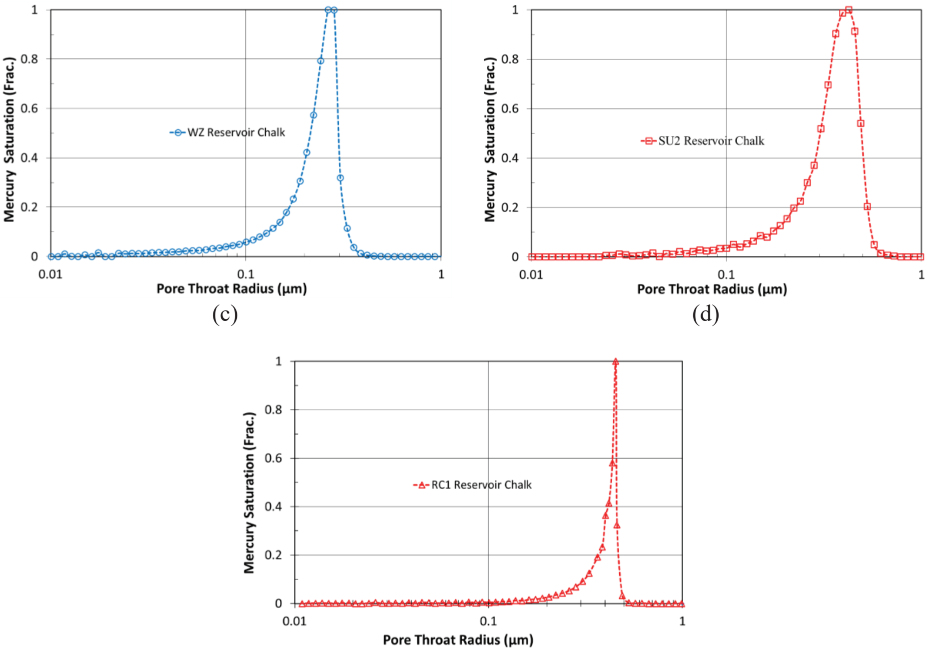
Pore size distribution

Sedimentary rocks are capillary systems due to the presence of large amounts of pore surfaces and small pore diameters. The pore size distribution dictates the fluid flow in the porous media. The fractures and largest pores have the lowest surface friction and are the preferred pathways for fluid flow. Conversely, a significant portion of hydrocarbons tends to reside in smaller pores. As a result, the presence of a heterogeneous pore size distribution underscores the significance of capillary forces and the spontaneous imbibition of water in enhancing the displacement efficiency of oil from the rock matrix.

To evaluate the heterogeneity of reservoir and outcrop chalks, pore size distributions were determined by mercury injection capillary pressure (MICP) measurements. **Figure 2** illustrates the results obtained from this analysis on the outcrop chalk cores (SK and AA) as well as the reservoir chalk cores (WZ, SU2, and RC1).



(a) (b)



(c)

(d)

(e)

Figure 2 *Pore size distribution by MICP for (a) SK outcrop chalk, (b) AA outcrop chalk, (c) WZ reservoir chalk, (d) SU2 reservoir chalk, and (e) RC1 reservoir chalk.*

The MICP results confirm very small pore throat radiuses for all the chalk samples. The minimum, peak, and maximum throat radii are summarized in **Table 4**.

Table 4*. Pore size distribution in chalk, Minimum, Peak, and maximum detected values.*

Chalk type	Pore throat radiuses (µm)			max/min
	Min	Peak	max	
Outcrop SK	0.011	0.34	0.73	66
Outcrop AA	0.010	0.37	0.62	62
Reservoir RC1	0.011	0.45	0.67	67
Reservoir SU2	0.220	0.42	0.78	61
Reservoir WZ	0.011	0.26	0.53	48

The minimum pore throats are larger than 0.01 µm, peaking close to 0.4 µm with maximum pore throats less than 0.8 µm. This confirms that all chalks should be classified as heterogeneous, with the largest pore throat at least 48 times larger than the smallest.

The only chalk sample with significantly different in pore size distribution is the reservoir water zone sample, core WZ. Compared to other samples, the peak and maximum values for WZ core are shifted to the left confirming the reduced permeability and porosity results.

Pore surface area

Sedimentary rocks with small pore diameters should also give a rock system with large amounts of pore surfaces. In these capillary systems, pore fluids are surface trapped. Large pressure drops are needed to mobilize an oil phase, and mobility becomes wettability dependant.

To evaluate the amounts of pore surfaces in the reservoir and outcrop chalk, BET-specific surface area measurements were performed on representative rock samples. The results from the BET analyses are presented in **Table 5**.

Table 5. *BET-specific surface area (m^2/g) measured on outcrop and reservoir chalk.*

	Outcrop chalk		Reservoir chalk		
	SK	AA	SU2	WZ	RC1
BET, (m^2/g)	2.0	3.9	1.2	2.0	1.7

The BET surface area of the reservoir and outcrop SK chalk is quite similar with values from 1.2 to 2 m^2 of mineral surfaces in only 1 gram of rock, confirming that porous media with small pore diameters will have a huge amount of mineral pore surfaces interacting with the pore fluids and should be regarded as capillary systems.

A significantly higher BET-specific surface area was observed for the outcrop AA chalk with a value of 3.9 m^2/g of rock. This is 95% higher than observed for the SK chalk, and 130% and 225% above the surface area for two reservoir chalk samples taken in the oil zone. Further rock analyses are performed using SEM and EDX analyses which could explain the variation in pore surfaces observed.

Mineral composition and grain sizes

The mineral composition of reservoir chalk (SU2, WZ, RC1) and outcrop chalk (SK, AA) was determined using SEM and EDX analysis of representative rock samples taken from the chalk cores. **Table 6** presents the results of the EDX analysis for outcrop and reservoir chalk samples.

The outcrop Stevns Klint (SK) had more than 98At% calcium bearing minerals, mainly $CaCO_3$. The same amount of calcium was also confirmed in all reservoir chalk samples analysed. On the other hand, Aalborg (AA) chalk with a very high surface area had 8At% silica impurities, reducing the calcium content to 89At%. All the other chalk samples contained less than 2At% silica.

Table 6 *Element (cation) composition in atomic weight % (At%) by EDX analyses of the outcrop and reservoir chalk.*

	Outcrop Chalk		Reservoir Chalk		
Element (Cation)	SK At%	AA At%	SU2 At%	WZ At%	RC1 At%
Calcium	98.5	88.9	>99.9	98.3	98.5
Magnesium	0.08	0.9	-	-	0.2
Aluminum	0.1	1.1	-	-	0.03
Silica	0.6	8.7	-	1.7	1.3
Potassium	0.2	0.5	-	-	0.0
Sulfur	0.4	-	-	-	0.03
Sodium	0.02	-	-	-	-

The mineral grain sizes and grain size distribution could be qualitatively compared between the individual chalk samples from SEM pictures taken at the same magnification as seen in **Figure 3**.

Intact coccolith rings were observed in all reservoir chalk samples and in outcrop SK chalk, indicating minimal physical degradation, chemical dissolution, or mineral precipitation that could alter the grain shapes and form secondary minerals. The average size of the individual chalk grains was close to 1 µm in all investigated chalk samples.

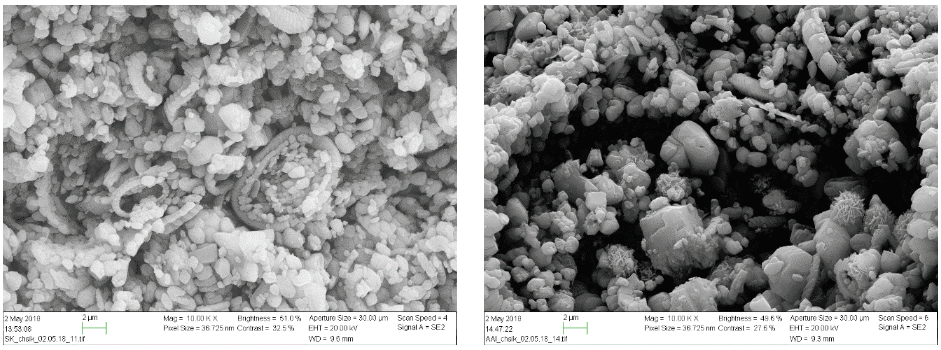
The potential of mineral dissolution is also controlled by the amount of water present in the pore space and the amounts of mineral surfaces available for interaction with the water phase. Less water wet mineral surfaces as we expect in the oil zone will also reduce the potential for mineral dissolution. The reservoir chalks from the oil zone are very similar to SK outcrop chalk regarding mineral composition and average grain sizes. In the oil zone, the water saturation is low which will reduce the potential of mineral dissolution and reprecipitation which could affect porosity and permeability.

The reservoir water zone sample WZ had a significant reduction in both porosity and permeability compared to the oil zone samples as seen in **Table 3**, even though this is not clearly seen from the grain size distribution but observed by the pore size distribution. The same reduction is not observed in the outcrop samples. The outcrops have not been exposed to higher salinity brines and higher temperatures which would also affect mineral dissolution and precipitation reactions.

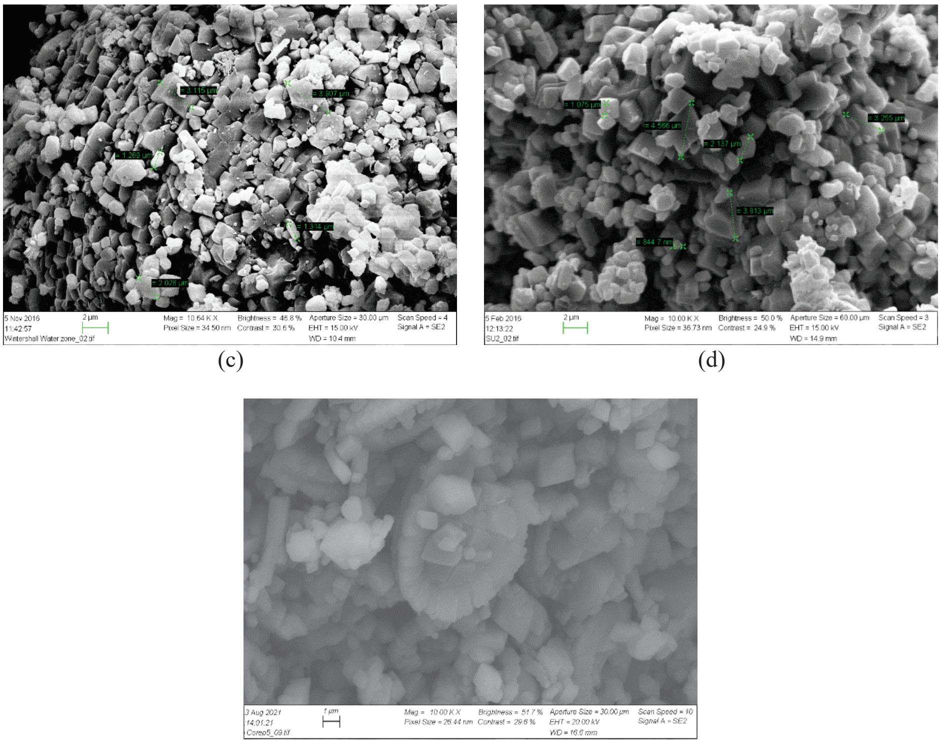
In the AA chalk, we observe authigenic formed opal-CT lepispheres in open cavities randomly distributed between the chalk grains, **Figure 3b**. This amorphous SiO_2 explains the high silica content in EDX analyses (Flörke et al., 1976). The presence of Opal CT could also explain the increased BET surface area of AA chalk compared to other samples, which, on the other hand, did not affect the porosity or permeability of AA chalk, **Table 3**.

In general silicate minerals have a negative surface charge at pH above 3. On the other hand, calcite surfaces are positively charged at pH below 9 – 10. Typical pH for porous rocks is in the range of 5 to 9 /and behaves as buffered systems due to the presence of reactive mineral surfaces and carbonate species as buffers. The mixed mineralogy observed in Aalborg chalk could significantly influence chemical adsorption or desorption processes, especially when huge amounts of mineral surfaces interact with a limited amount of pore liquid. Examples of this could be ion exchange reactions and adsorption of charged polar organic components present in crude oils reducing the water wetness of the mineral surfaces (Piñerez Torrijos et al., 2020).

In SK chalk, the acidic POC adsorbs more strongly to the mineral surfaces and reduces the presence of capillary forces (Mjos et al., 2018). In the work by Konstantinopoulos et al. (2019) and Klewiah et al., (2019), we saw polar acidic component adsorption on Aalborg chalk surfaces was less than Stevns Klint chalk, while polar basic components adsorption was notably higher due to negatively charged silicate surfaces. Crude oil exposure reduced Aalborg chalk's water wetness. In these comparative studies of Aalborg and Stevns Klint chalk, it was observed that the presence of silica plays a significant role in influencing the adsorption of polar components and the initial wetting process, thereby impacting capillary forces.



(a) (b)



(c) (d)

(e)

Figure 3 *SEM pictures at 10 000 times magnification performed on (a) SK outcrop chalk, (b) AA outcrop chalk, (c) WZ reservoir chalk, (d) SU2 reservoir chalk, and (e) RC1 reservoir chalk.*

Wettability of outcrop and reservoir cores

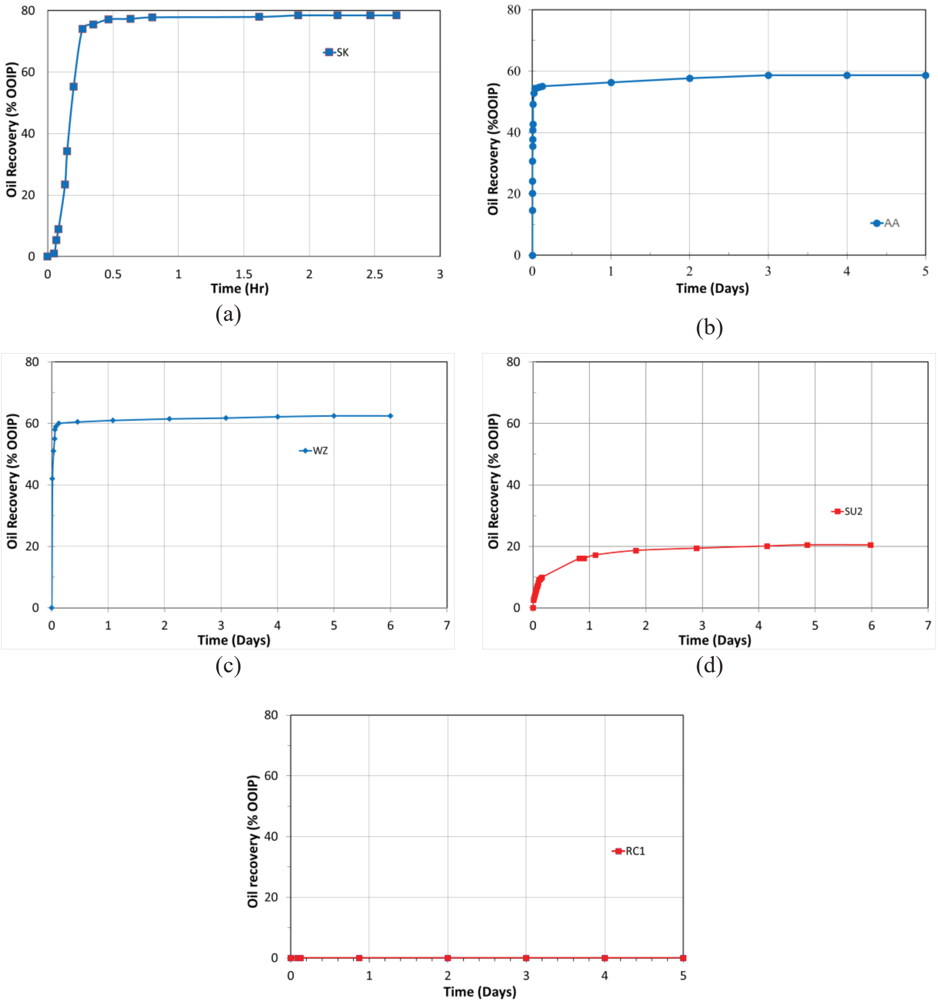
The fluid flow in porous media is dictated by capillary forces, gravity forces, and viscous forces. Permeability is the main petrophysical parameter dictating viscous forces, while the density difference between the hydrocarbon and brine phases controls gravity forces in a reservoir system. Capillary forces are dictated by the surface wettability and become more dominant in rock systems with high specific surface area as was observed in all chalk samples.

Both the outcrop SK chalk and reservoir chalk exhibited similar mineral compositions, permeabilities, grain sizes, pore size distributions, and specific surface areas. As expected, the porosity of the outcrop chalks that have not been exposed to the same temperatures and pressures are slightly higher than the reservoir chalks.

It is important to note that the outcrop chalks had never been exposed to crude oils. Furthermore, the reservoir chalk from the water zone might have experienced oil flow as a part of the migration route during the oil filling of the reservoir which could influence the wettability characteristics and capillary forces. Reservoir chalks from the oil zone have been invaded by crude oil containing polar organic components (POC). The presence of POC on the mineral surfaces can impact wettability and capillary forces within the rock.

To assess the presence of capillary forces in both the outcrop and reservoir chalk, spontaneous imbibition (SI) tests were conducted at 23 °C using 100% heptane-saturated cores with distilled water

(DW) as the imbibing fluid. The heptane does not contain any POC that could interact with charged mineral surfaces and modify the surface wettability. The results of the heptane recovery from the cores are presented in **Figure 4**, providing insights into the capillary-driven imbibition process.



(a) (b)

(c) (d)

(e)

Figure 4 *Recovery of heptane by DW imbibition at 23 °C from the 100 % heptane-saturated mildly cleaned (a) SK outcrop chalk, (b) AA outcrop chalk, (c) WZ reservoir chalk, (d) SU2 reservoir chalk, and (e) RC1 reservoir chalk cores.*

The imbibition of distilled water (DW) into the outcrop SK core led to rapid oil mobilization. 75% of the original oil in place (OOIP) was produced in less than 30 minutes. The ultimate oil recovery plateau of 78 %OOIP was reached after only 2 hours, confirming the presence of strong positive capillary forces and a very water wet behaviour.

Similarly, a strongly water-wet behaviour was also observed for the AA chalk core. Within less than 2 hours, 55 %OOIP was mobilized, and the ultimate oil recovery plateau of 59% OOIP was achieved after 3 days confirming the presence of strong positive capillary forces.

The reservoir core sampled in the water zone, WZ, showed the same strongly water wet behaviour as observed for the outcrop cores. Even a 10 times reduction in permeability had minor effects on the oil mobilization. Spontaneous imbibition using DW resulted in 60 %OOIP in less than 3 hours, emphasizing the presence of strong water-wet behaviour. Most likely water zone sample was in the migration route during the crude oil filling of the reservoir. Still, the mineral surfaces have not been exposed to POC present in the reservoir crude oil, excluding matrix flow and the main migration routes are natural fractures and high permeable pathways. For the SU2 core sampled in the oil zone in the same well, a significant reduction in capillary forces was observed. After 2 hours only 10 %OOIP was produced reaching an ultimate oil recovery of 20 %OOIP after 5 days. The results confirm that the mineral surfaces in chalk are reactive towards species present in the crude oil and there is a significant reduction in positive capillary forces.

The reservoir core RC1 sampled in the oil zone in a different chalk reservoir showed a significant different behaviour. No positive capillary forces were observed. The heptane in the pores was immobile during imbibition, confirming that even though the rock properties were very similar to the SU2 core, the amount and type of polar organic components in the crude would dictate the Crude Oil interaction towards the reactive chalk surfaces.

The spontaneous imbibition experiments confirm that the type of crude oil, amount of crude oil exposure, and reactivity of mineral surfaces are also important properties to consider when outcrop systems are selected as analogue for reservoir systems. The reactivity of the mineral surfaces and the amount of water-wet mineral surfaces are also important factors for evaluating the potential of mineral dissolution and precipitation reactions affecting the rock integrity during CCS projects.

Surface reactivity

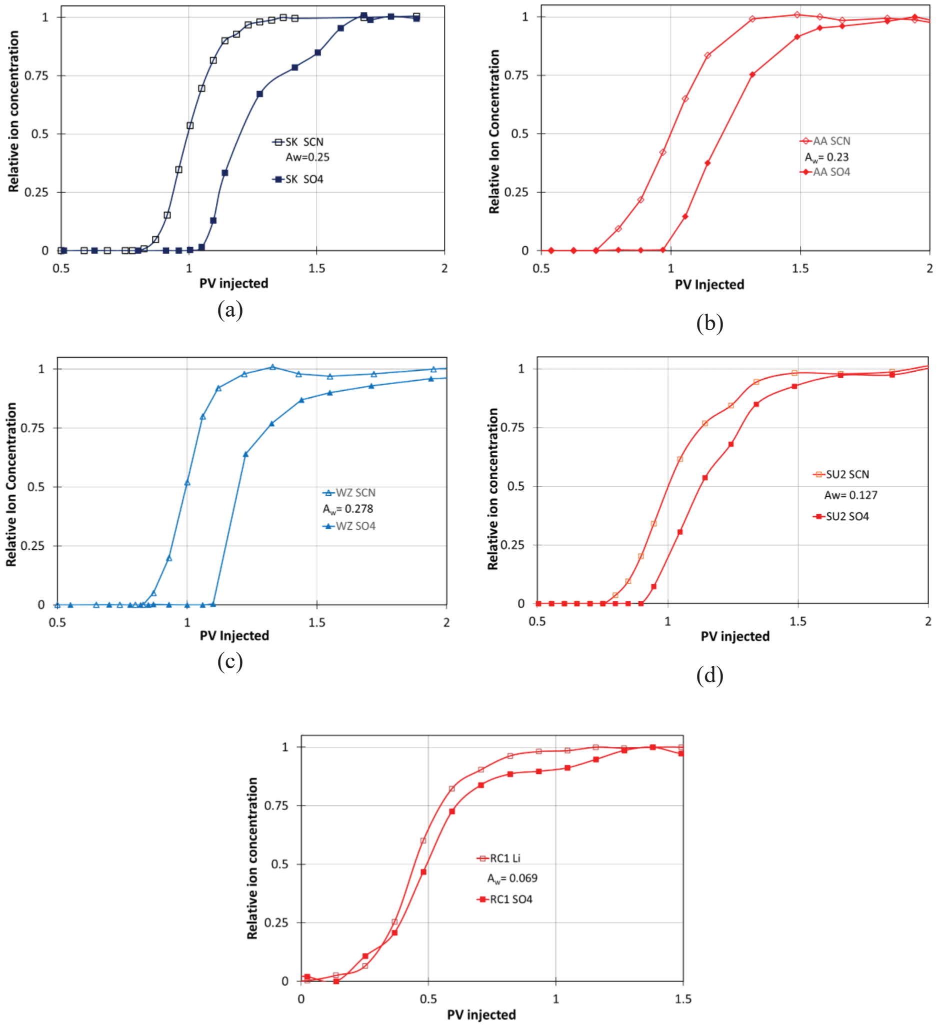
The MICP and BET-specific surface analyses confirm that all chalks have very small pores/pore throats giving a huge amount of pore surfaces that could interact with the pore fluids, affecting adsorption of POC, the amount of water wet mineral surfaces, capillary forces, mineral dissolution/precipitation reactions, or rock integrity during reservoir production or in CCS projects.

The reactivity of mineral surfaces in both the outcrop and reservoir chalk was examined using the surface reactivity test described by Strand et al. (2006). This is a chromatographic tracer test performed on cores and has been used for chalk, limestone, or dolomites to verify rock wettability, wettability alteration, or to detect surface active ions toward water wet mineral surfaces. Thiocyanate (SCN^-) or Lithium (Li^+) ions are used as non-reactive tracers to follow the displacement front. In **Figure 5**, both outcrop and reservoir cores have been tested to evaluate the amount of water wet mineral surfaces.

The ion interaction will only take place towards water wet-mineral surfaces, and we observed for the SK and AA outcrop chalk that the calculated separation area between the tracer and sulphate curve, Aw, is 0.25 and 0.23 respectively. This represents typical separation values for strongly water wet chalk cores when using the SW0T/SW½T chromatographic brine system at 23°C.

The reservoir core WZ sampled in the water zone has a water wet surface area Aw = 0.28 which is very close to the outcrops, confirming significant amount of reactive water wet mineral surfaces available. The spontaneous imbibition experiment in **Figure 4** also confirms the presence of strong positive capillary forces and a very water wet behaviour.

For the 2 reservoir chalk cores sampled in the oil zone, a significant reduction in the separation area between the tracer and sulphate curves is observed. For core SU2, where only 20 %OOIP was mobilized during spontaneous imbibition, the separation area Aw = 0.127, confirming significantly reduced amount of available mineral surfaces for sulphate interaction. The reduction in water wet surfaces to ~50 % compared to the outcrop cores is significantly reducing the oil mobilization potential.



(a)

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Figure 5 *Chromatographic separation between sulphate and lithium/thiocyanate ions in (a) SK outcrop chalk, (b) AA outcrop chalk, (c) WZ reservoir chalk, (d) SU2 reservoir chalk, and (e) RC1 reservoir chalk.*

For the RC1 core where no positive capillary forces were detected, a significant amount of water wet mineral surfaces was observed, where A_w = 0.069 represents ~30% of the water wet surface area measured in the strongly water wet outcrop cores.

The chromatographic surface reactivity results confirm that even though reservoir cores behave neutral to oil-wet, still a lot of brine-rock interaction could take place affecting the rock integrity in water flooding projects or in CCS projects using depleted oil reservoirs for CO_2 storage.

The shape of the tracer curves in figure 5 (a-d) describe the displacement efficiency when SW0T containing pores are displaced by the SW½T brine. All the four 100% SW0T saturated cores have nice S-shaped tracer curves. The first tracer breakthrough was observed after 0.7 – 0.8 PV injected and reaching 100% tracer concentration after 1.3 – 1.4 PV. All cores confirm equal displacement efficiencies on core scale, in line with the MICP results in figure 2. For core RC1 (Figure 2e) we also observed a high brine displacement efficiency during the surface reactivity test, but the results are not direct comparable. Core RC1 had the least amount of water wet surface area, and the test was performed at S_{or} of 45% which could affect the results.

Selection of outcrops as reservoir analogues and concluding remarks

In reservoir engineering, porosity and permeability are the 2 main petrophysical parameters used to describe rock systems. These are also the only parameters included in the simulators for describing flow in reservoir systems. It was observed in this comparison study between outcrops and reservoir chalks that other physical and chemical parameters could also have a significant effect on the porous rock properties and should also be accounted both in parametric studies to increase general competence on rock properties together with reservoir specific investigations in front of hydrocarbons production, or when depleted reservoirs or aquifers are evaluated as candidates in CCS projects.

In this comparison study, pore size distribution, grain sizes, BET-specific surface area, and mineralogy were also included in the rock analogue evaluation. Mineral composition and chemical reactivity of mineral surfaces could have a significant effect when pore fluids are introduced. The CoBR interaction has a direct impact on capillary forces and wettability, which in turn governs the amount of mineral surfaces accessible for dissolution and precipitation. This influence has a crucial role in maintaining well integrity, ensuring reservoir stability, and safeguarding the cap rock both during operational phases and long-term storage.

In this research, the SK outcrop chalk exhibited similar petrophysical properties, mineralogical composition, and chemical surface reactivity, that made it a highly suitable analogue for the reservoir chalks assessed. This suitability can be extended to investigations of brine-rock interactions, studies involving mixed wettability conditions within the certain CoBR system, and studies of wettability alteration for enhanced oil recovery (EOR).

The AA outcrop chalk displayed petrophysical properties very similar of those found in the reservoir chalks. However, it proved unsuitable as a reservoir analogue due to the presence of SiO_2 minerals, which led to a substantial increase in the availability of reactive mineral surfaces. This mixed mineralogy makes it unsuitable for wettability studies as well as mineral dissolution studies linked to rock integrity and wettability alteration studies for enhanced oil recovery (EOR).

Additionally, a reservoir core from the water zone was evaluated as a potential analogue to a core from the oil zone of the reservoir. The mineral properties were similar to the oil zone core and the core behaved very water wet as the outcrop cores. However, a tenfold reduction in permeability also makes it unsuitable as a reservoir analogue. As a result, SK outcrop chalk is a better analogue for the North Sea chalk reservoirs based on the laboratory studies presented in this work.

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IV

Comparing Inexpensive, Customized Brine Compositions for Enhanced Oil Recovery in High Temperature Outcrop and Reservoir Chalk.

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Submitted to Fuel.

Paper IV

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Abstract

The effectiveness of seawater as a wettability modifier in chalk and limestone can be significantly improved by depleting NaCl from the seawater, and/or adding extra sulfate (SO_4^{2-}) that together with the divalent calcium and magnesium cations (Ca^{2+}, Mg^{2+}) will desorb negatively charged oil molecules from positively charged rock surfaces.

Customized brine compositions were designed, aiming to be inexpensive to manufacture, stable with respect to solid precipitation and acting as Smart Water by enhancing oil mobilization by wettability alteration in chalk compared to that by seawater. Different brine compositions were tested in which the Ca^{2+}, Mg^{2+}, and SO_4^{2-} content was varied while keeping the salinity low. The compositions were chosen such that the brines could be made from adding cheap and readily available salts to fresh water.

Few enhanced oil recovery studies using Smart Water have been performed on reservoir chalk samples due to reservoir rock sample scarcity. Therefore, parametric studies were first performed on slightly water-wet Stevns Klint outcrop chalk cores. The most promising brine composition from the parametric study was tested and compared against seawater injection in restored reservoir chalk cores originating from the Norwegian Continental Shelf (NCS). The chemical and physical properties of the outcrop and reservoir chalk material were compared, and it was found that the Stevns Klint outcrop chalk was a very good analogue to the reservoir chalk used in this study. Oil recovery tests by spontaneous imbibition and viscous flooding were performed in both outcrop and reservoir chalk cores. The SmW2 brine, containing 20 mM $CaSO_4$ and 20 mM $MgCl_2$, was the most effective oil recovery brine in the outcrop chalk at 130 °C, surpassing the spontaneous imbibition performance of seawater in secondary mode. The same brine was also found to be the best performing brine in the reservoir chalk cores. These oil recovery experiments suggest that it is possible to prepare optimized Smart Water brines that do not precipitate at high temperature but are able to mobilize extra oil through wettability alteration by creating positive capillary forces and improving reservoir sweep.

Introduction

Injection of seawater (SW) in low permeable chalk reservoirs at high temperatures (T_{res} >100 °C) in the North Sea has been a tremendous success giving significantly higher oil recoveries than expected for mixed-wet highly fractured reservoirs [1-4]. The field observations have been confirmed in laboratory experiments, with oil recoveries of 50 – 60 %OOIP by spontaneous imbibition (SI) with SW at 130 °C in restored slightly water-wet outcrop Stevns Klint (SK) chalk cores [5, 6]. The estimated recovery from the

Ekofisk chalk reservoir at the same temperature is 50 – 55 %OOIP after SW flooding [7]. The main reason for the high oil recovery from this naturally fractured, low permeable reservoir is believed to be the ability of SW to change the wettability towards more water-wet conditions by a symbiotic interaction between the active ions, calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulfate (SO_4^{2-}) [5]. SO_4^{2-} is the catalyst and needs to be present for the wettability alteration process to take place [8]. Wettability alteration to more water-wet conditions improves spontaneous imbibition of water, mobilizing and producing additional oil. Fluid flow in porous media is controlled by gravity, capillary, and viscous forces. The combination of these forces will dictate the ultimate recovery, both in laboratory core experiments and in the production of oil reservoirs. SI experiments performed on cores in laboratory describe the contribution from capillary forces present in on the restored cores. The fluid properties and their interaction with the mineral surfaces during core restoration dictates the availability of positive capillary forces after core restoration [9].

Research on improving water-based enhanced oil recovery (EOR) methods have been ongoing for several decades. Smart Water injection, low-salinity waterflooding (LSWF) and ion-modified waterflooding (MWF) (similar to Smart Water injection) have been shown, in numerous laboratory studies and a few field pilots in different carbonate reservoirs other than Ekofisk and Valhall at the Norwegian continental shelf (NCS), to be potential and economic EOR solutions comparable to other chemical EOR techniques [10-13]. According to Shiran and Skauge [14], LSWF involves lowering the salinity and total dissolved solids (TDS) of the injected water by diluting with SW or fresh water. In contrast, MWF refers to the appropriate optimization of the ionic composition of injection water to achieve the favorable attributes of the crude oil – brine – rock (COBR) system and improve the microscopic displacement efficiency. The base water in MWF can be SW, produced water, or water from other economically available sources [15]. Al-Shalabi and Sepehrnoori [16] have summarized details of different core flooding studies in a table and tried to classify them in terms of rock material, temperature, pressure, salinity of injection water and formation water, and oil properties. What they found is that the improvement of oil recovery by modified water composition in both sandstone and carbonate rocks is case dependent. Early work by Zhang and Austad [5] showed that SO_4^{2-}, Ca^{2+}, and Mg^{2+} had synergetic effects on oil recovery from chalk, which was later also demonstrated in limestone [17]. Chandrasekhar and Mohanty [18] found that modified SW containing Mg^{2+} and SO_4^{2-} could change aged oil-wet calcite plates to more water-wet conditions. Awolayo et al. [19] and Puntervold et al. [20] demonstrated that the optimum ion-modified brine for additional recovery in the carbonate rocks and conditions studied contained four times the SO_4^{2-} concentration in SW.

At lower temperatures (T_{res} <100 °C), SW injection is less effective because the reactivity of SO_4^{2-}, Ca^{2+}, and Mg^{2+} ions toward the calcite surface is reduced [21]. Increased oil mobilization at a lower temperature can be achieved by spiking SW with extra Ca^{2+} [5] or SO_4^{2-} [22]. Increased oil recovery can also be achieved by depleting NaCl from SW, giving a reduction in the salinity from 33 000 ppm to 10 000 ppm, while maintaining the divalent ion concentrations [20]. The reason for the increased oil recovery at reduced salinity in this case, is explained by improved access to the positively charged mineral surface for the surface-active ions, Ca^{2+}, Mg^{2+}, and SO_4^{2-} responsible for the wettability alteration. At lower concentrations of non-reactive Na^+ and Cl^- ions the movement of the divalent ions through the ionic double layer is facilitated and desorption of the negatively charged acidic polar organic components from the calcite surface takes place at a larger extent [20, 23, 24]. The highest oil mobilization efficiency at temperatures below 100 °C was observed by combining reduced SW salinity with increased SO_4^{2-} [20, 23]. However, SW depleted in NaCl and spiked with SO_4^{2-} was not found more effective at higher temperatures (130 °C) because anhydrite ($CaSO_4$) precipitation lowers the concentration of active Ca^{2+} and SO_4^{2-} ions in solution [5], thus limiting the wettability alteration potential.

An optimized Smart Water brine that is more effective than SW at high temperature (130 °C) should not precipitate $CaSO_4$ in the injection well, wellbore or further into reservoir pores. It should have sufficient concentration of SO_4^{2-} ions that can take part in ion exchange reactions on the calcite surface for promoting wettability alteration. The SO_4^{2-} concentration can be achieved by dissolving gypsum ($CaSO_4{\cdot}2H_2O$), which is abundantly available in nature, in fresh water, resulting also in an equal concentration of Ca^{2+} ions in the brine. Experiments have confirmed that more than 20 mM gypsum is easily soluble in water at ambient conditions, but the solubility will decrease with increasing temperature [25]. The solubility of gypsum can be significantly increased even at higher temperatures by adding chloride salts such as NaCl or $MgCl_2$ to the solution [26]. The solubility of gypsum has also been reported to increase at higher pressures [27]. In high-temperature reservoirs, the reservoir pressure could then reduce the potential of anhydrite precipitation in the pore space. At the same time, the bottom hole temperature in an injection well will be significantly lower than that in the reservoir itself, which reduces the potential of anhydrite precipitation in the near wellbore zone. Therefore, the designed Smart Water could have a SO_4^{2-} concentration close to supersaturation at reservoir conditions.

Nanofiltration is being used as part of the SW treatment for SO_4^{2-} removal before injection to reduce the scaling potential in high temperature reservoirs [28]. The possibility of using nanofiltration of SW for producing Smart Water with low salinity and high concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} was previously investigated by Nair and coworkers [29]. In that work, five commercially available membranes were tested. It was found that the SO_4^{2-} concentration in the retentate was high at all tested pressures, but that a significant loss of Ca^{2+} and Mg^{2+} was observed. Additionally, the salinity of the retentate was not significantly reduced, due to accompanying monovalent ions ensuring charge balance in the permeate. It was concluded that Smart Water could not be obtained by nanofiltration of SW with the membranes tested.

Reverse osmosis (RO) is a well-known water treatment process to produce fresh water from SW and could be used for producing Smart Water. Gypsum and anhydrite are mineral deposits used as low-cost industry chemicals and could be used as the source for SO_4^{2-} and Ca^{2+} ions, while Mg^{2+} could be provided from $MgCl_2$ salts.

The objective of this work was to develop an inexpensive but efficient injection brine, a Smart Water with a composition that is more efficient than SW in altering wettability in high temperature (130 °C) chalk and improving the oil recovery. Three brines with tailored salinity and concentration of surface-active ions, Ca^{2+}, Mg^{2+}, and SO_4^{2-}, were made by dissolving cheap and readily available salts in distilled water. The EOR-potential of these brines were tested in both secondary and tertiary spontaneous imbibition (SI) and viscous flooding (VF) on equally restored SK outcrop chalk cores. The results were compared against the oil recovery obtained by SW, a known efficient Smart Water in chalk at high temperatures [30]. The EOR potential of the most promising designed brine was thereafter tested on a North Sea reservoir chalk system consisting of two unused reservoir chalk cores, reservoir formation water (FW), and stock tank oil from the same chalk reservoir.

Experimental

Materials

Rock material

In this study, eight outcrop and two reservoir chalk cores were used.

Outcrop chalk

The outcrop Stevns Klint (SK) chalk, collected from a quarry near Copenhagen, Denmark, consists of more than 98% $CaCO_3$, with low content of silicate impurities. The SK chalk is considered a good representative of North Sea chalk reservoirs [31, 32]. This outcrop has in previous laboratory studies shown similar physical properties and reproducibility in parametric studies [9, 20, 33]. Studies using SK chalk have explored EOR strategies employing different injection brines, such as sulphate-rich polysulphate brine [34], carbonated water [35], brine with ionic liquid [36] for chalk and produced rational reproducible results. The eight outcrop cores were drilled in the same direction from different blocks, shaved in a lathe, and cut with a saw to a diameter of 3.8 cm and a length of about 7 cm. The SK cores had a water permeability between 2-4 mD and porosity between 45-50%. The physical properties of the SK cores can be found in **Table 1**.

Reservoir chalk

The two reservoir cores (RC1 and RC2) used in this study had been preserved by wrapping in plastic film and aluminum foil after a drilling campaign carried out in the 1980s. At arrival, there was no wax film protecting the cores, however, the cores were consolidated and still contained fluids, observed during core cleaning. The reservoir cores were cut to obtain similar cylindrical dimensions, before core cleaning.

During the core cleaning and fluid restoration process, the water permeability and porosity of the reservoir cores were measured. The physical properties of the reservoir cores are reported in **Table 1** together with those of the outcrop SK cores.

Table 1. Physical properties of the reservoir and outcrop chalk cores.

	Reservoir cores (RC)		Outcrop Stevns Klint cores							
Core data	RC1	RC2	SK0	SK1	SK2	SK3	SK4	SK5	SK6	SK7
Length (cm)	5.68	5.94	7.00	7.21	7.02	7.22	7.27	6.71	7.05	6.86
Diameter (cm)	3.77	3.77	3.79	3.79	3.78	3.79	3.78	3.81	3.81	3.81
Bulk Volume, (ml)	63.57	66.43	79.45	81.34	78.78	81.45	81.58	76.53	80.46	78.38
PV (ml)	24.85	25.74	38.8	38.86	37.87	38.61	38.40	37.97	39.59	37.77
Porosity (ϕ) %	39.10	38.80	48.80	47.78	48.07	47.41	47.07	49.61	49.21	48.18
K (water) (mD)	4.50	4.40	2.0	4.1	4.0	3.6	3.9	-	3.2	-

Pore size distribution

Mercury injection capillary pressure (MICP) measurements were performed by Stratum Reservoir to evaluate the pore size distribution of both outcrop and reservoir chalk.

SEM & EDX analyses

Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) analyses were carried out using a Zeiss Supra Environmental Scanning Electron Microscope (ESEM) with EDX detector to characterize the rock material pore surfaces, grain sizes, and elementary composition.

Brines

Synthetic brines were prepared in the laboratory by dissolving specific amounts of reagent-grade salts in distilled water (DW). The brine solutions were mixed overnight and filtered through a 0.22 µm Millipore filter before use. In the establishment of the initial wettability in the outcrop chalk cores, a SO_4^{2-}-depleted formation water (FW) based on Valhall chalk field composition (FW_A) was used, while reservoir formation water (FW_B) was used in the reservoir chalk cores. It is worth mentioning that there was not a big difference in salinity between the two formation waters (FW_A and FW_B).

SW is currently being injected into the North Sea chalk reservoirs, and is, in this study, used to compare against the oil recovery efficiencies of three potential Smart Water compositions. The possibility of making Smart Water from RO water and added minerals was proposed with the following three brines, SmW1, SmW2, and SmW3. SmW1 was made by adding 10 millimolar (mM) $CaSO_4$ salt to DW. SmW2 contained 20 mM $CaSO_4$ and 20 mM $MgCl_2$, while SmW3 contained 20 mM $CaSO_4$ and 40 mM $MgCl_2$, with the extra magnesium added to improve the solubility of $CaSO_4$ at elevated temperature.

The two brines SW0T and SW½T, where SW½T contains the non-adsorbing tracer SCN^-/Li^+ and adsorbing SO_4^{2-}, were used in surface reactivity tests described later.

All brine compositions are given in **Table 2**.

Table 2. Brine compositions.

Ions	FW_A (mM)	FW_B (mM)	SW (mM)	SmW1 (mM)	SmW2 (mM)	SmW3 (mM)	SW0T (mM)	SW½T (mM)
Na^+	997	1001	450.1	0	0	0	460	427
K^+	5	4.9	10.1	0	0	0	10	22
Ca^{2+}	29	89.6	13	10	20	20	13	13
Mg^{2+}	8	18.2	44.5	0	20	40	45	45
Cl^-	1066	1220.1	525.1	0	40	80	583	583
HCO_3^-	9	5.9	2	0	0	0	2	2
SO_4^{2-}	0	0	24	10	20	20	0	12
Sr^{2+}	0	5.2	0	0	0	0	0	0
Li^+	0	0	0	0	0	0	0	12
SCN^-	0	0	0	0	0	0	0	12
TDS (g/L)	62.83	71.14	33.39	1.4	4.63	6.5	33.39	33.39
Ionic strength (mole/L)	1.11	1.34	0.66	0.04	0.1	0.2	0.64	0.65
Density (g/cm^3)	1.041	1.0485	1.0226	0.999	1.0019	1.0035	1.024	1.024
Bulk -pH	7.3	6.67	7.11	7.06	7.16	7.25	7.7	7.5

Crude oil

Two different crude oils (Oil A and Oil B) were used in this study. The chemical and physical properties of the oils are listed in **Table 3**.

Oil A

Oil A is a laboratory-designed crude oil containing natural existing acidic and basic polar organic components (POC). The oil was made by mixing portions of a base stock tank oil with an acid number (AN) of 1.85 mg KOH/g and base number [37] of 0.67 mg KOH/g with portions of the same stock tank oil depleted in POC by silica gel treatment, giving AN = BN ~ 0 mgKOH/g. The crude oil was centrifuged and filtered through a 5 µm Millipore filter prior to analyses and use. AN and BN were measured by potentiometric titration using modified versions of ASTM D664 and ASTM D2896 [38, 39], developed by

Fan and Buckley [40]. Oil A with AN = 0.53 mg KOH/g and BN = 0.31 mg KOH/g, was used in core experiments on the outcrop chalk. The uncertainty in the AN and BN analyses is ±0.02 mgKOH/g.

Oil B

Oil B is the stock tank oil from the chalk reservoir and was provided by the operator company. Oil B had a low asphaltenic content of 0.6 Wt % and quantified AN = 0.11 mg KOH/g and BN = 2.64 mg KOH/g. Oil B was used in core experiments on the reservoir chalk.

Table 3. Crude oil properties.

Sample	AN (mg KOH/g)	BN (mg KOH/g)	Asphaltene (wt%)	Density (g/cm^3)	Viscosity @23 °C (cP)	Viscosity @60 °C (cP)
Oil A	0.53	0.31	<1	0.81	2.5	1.8
Oil B	0.11	2.64	<1	0.81	43.1	11.6

There is a significant difference in the viscosities between Oil A and Oil B. However, Aslanidis et al. [41] recently showed there is very low effect of oil viscosity in oil recovery in spontaneous imbibition tests. There is also a low effect of oil viscosity in oil recovery in viscous flooding test if the injection rate is low. Therefore, a low injection rate during viscous flooding using reservoir cores was maintained at 0.5 PV/D.

Methods

Core preparation

Before oil recovery experiments were performed on the outcrop and reservoir cores, the cores were cleaned, and fluid saturations were established. The core preparation procedure is described in detail by Torrijos et al. [42].

Cleaning of outcrop chalk cores

The SK chalk quarry at Sigerslev in Denmark is located at sea level close to the sea and might contain precipitated sea salts, especially SO_4^{2-} salts, which may reduce the adsorption of polar organic components and thus impact the core wettability after exposure to crude oil [43]. All SK cores were initially cleaned in a Hassler core holder by flooded with distilled water (DW) at room temperature (23 °C) to remove any easily dissolvable salts. The flooding of DW continued until no SO_4^{2-} was detected in the effluent, a minimum of 5 PV.

Cleaning of reservoir chalk cores

The reservoir chalk cores (RC), containing brine and reservoir oil, were mildly cleaned at room temperature using a Hassler core holder. The cores were flooded at a rate of 0.1 ml/min with 10 PV of low aromatic kerosene until a clear effluent was observed. The kerosene was then displaced by 5 PV n-heptane (hereafter referred to as heptane). In the end, the core was flooded with 5 PV DW to displace the initial brine and easily dissolvable salts. During DW flooding effluent samples were collected, and the concentrations of cations and anions were analyzed. Each core was thereafter dried at 90 °C to constant weight, prior to fluid restoration.

Fluid restoration

Before oil recovery experiments, the cleaned cores went through a fluid restoration process, establishing the initial water and oil saturations. To compare the results between core experiments, it is important to reduce the number of variables affecting the experimental results. Both water and oil volumes introduced during fluid restoration could affect the core wettability and the fluid flow in the porous media.

After cleaning, the cores were dried at 90 °C to constant weight. A 10 % initial water saturation (S_{wi}) with FW was established by the desiccator technique described by Springer et al. [44]. The main reason for selecting low initial water saturation is because most of the chalk fields that have been producing in the North Sea have low initial water saturation. For Example, Ekofisk field has initial water saturation down to 2% in some part [45]. The cores were saturated with 10 times diluted FW, and target $S_{wi} = 0.10 \pm 0.02$ was controlled by weight measurements during the water evaporation process taking place in the desiccator. When the target S_{wi} was reached, the cores were equilibrated in a closed container for at least 3 days to assure even ion distribution inside the core.

The oil saturation of the core was performed in a Hassler core holder with a confining pressure of 20 bar at 50 °C. Heating the core during oil saturation helped the oil to flow easier. The core with $S_{wi} = 0.1$ was vacuumed to take out air from injection lines and pores. The vapor pressure of the water are reached after a few minutes. Then, the oil was introduced from both sides of the core, pressurized to 5 bar, and followed by consecutive flooding of 2 PV of crude oil from both ends to obtain as homogeneous oil saturation in the core as possible. Total 5 PV of Oil A was injected to saturate the outcrop core while only 1 PV of oil B was used to saturate reservoir core. The core was exposed to less than 1 PV of Oil B to avoid over-exposure of crude oil and an unrepresentative reservoir wettability during the fluid restoration process, in line with the recently published methodology for obtaining reproducible and representative core wettabilities in laboratory studies in both carbonate [46] and sandstone [47] cores.

After fluid saturations, the core was wrapped with Teflon tape to avoid unrepresentative adsorption of polar organic components (POC) at the outer core surfaces during aging. Finally, the core aging was performed in an aging cell surrounded by the respective crude oil for 14 days at 130 °C at 10 bar to avoid boiling of fluids.

Oil recovery tests

The restored and aged cores were exposed to viscous flooding (VF) or spontaneous imbibition (SI) experiments to evaluate wettability and the presence of capillary forces in the cores, and the effect of brine injection and wettability alteration on oil recovery. Fluid flow in oil reservoirs is controlled by gravity, capillary, and viscous forces. In short time core experiment, the contribution from gravity forces is small, especially for low permeable cores. SI experiments represent the capillary forces while VF experiments represent contribution from viscous forces dictated by the pressure drop applied during the experiment.

Oil recovery by spontaneous imbibition (SI)

After removing the Teflon tape, the aged core was immersed in imbibing brine in a steel imbibition cell at 130 °C and 10 bar pressure to avoid boiling of liquids. The cumulative oil production by spontaneous imbibition of water was collected and measured in a graded burette at time steps. The oil recovery was calculated as a percentage of oil originally in place (%OOIP) and presented versus time.

Oil recovery by viscous flooding (VF)

Oil recovery by viscous flooding was performed on the restored reservoir cores. After reaching the oil recovery plateau by SI, the core was placed in a Hassler core holder at 130 °C with 20 bar confining pressure and 10 bar back pressure. The injection rate was 0.5 PV/D. The produced oil was collected in a graded burette and recorded against time. The pressure drop over the core was logged during the displacement test.

Wettability determination by spontaneous imbibition (SI)

The presence of capillary forces and the core wettability were evaluated by SI. The cores were 100% saturated with heptane as the oil phase and imbibed with DW in a glass Amott cell at 23°C. Heptane recovery was measured and logged against time. SI is a practical way of quantifying the wettability of porous systems [48]. Both the imbibition rate and ultimate recovery give relevant information that describes the core wettability. SI experiments can be executed at both laboratory temperature in Amott glass cells or more representatively, at reservoir temperature in pressurized cells.

A simplified wettability index based only on SI experiments was proposed by Piñerez Torrijos et al. [49]. The degree of water-wetness is quantified by a modified Amott water index (I_{W-SI}^{*}) using a very water-wet core as a reference, **Eq. 1**.

$$I_{W-SI}^{*} = \frac{SI_C}{SI_{WWC}} \qquad (1)$$

The oil recovery (%OOIP) by SI from a strongly water-wet or reference core is termed, SI_{WWC}, and the SI_C is the oil recovery (%OOIP) by SI from the evaluated core. The water wetness degree, I_{W-SI}^{*}, approaches 1 for a strongly water-wet core and 0 for a neutral-wet to oil-wet core [49].

Surface reactivity test

To determine the water-wet fraction of pore mineral surfaces in the core, and their reactivity toward ions present in brines, surface reactivity tests were performed on both outcrop and reservoir chalk. This method was developed by Strand et al. [50] and is based on a chromatographic separation between adsorbing SO_4^{2-} at the water-wet sites on a carbonate surface and non-adsorbing tracers, like lithium (Li^+) or thiocyanate (SCN^-). The test was performed in a Hassler core holder at ambient temperature, with 20 bar confining pressure and 10 bar back pressure. The core was successively flooded at a constant rate of 0.2 ml/min with SW0T (without Li^+ and SO_4^{2-}), followed by SW½T (with Li^+ and SO_4^{2-}). Effluent samples were collected and analyzed during the SW½T flood. The relative ion concentrations of Li^+ and SO_4^{2-} were plotted against PV injected, and the separation area (A_w) between the curves, representing the water-wet surface area, was calculated using the trapezoidal method. The non-adsorbing tracer profile describes the pore heterogeneity of the core; an S-shaped profile with narrow width indicates a more homogeneous porous medium, while a tilted S-shaped profile indicates a more heterogeneous porous medium.

For the outcrop chalk the surface reactivity test was performed at ambient temperature on a 100% water saturated core before its exposure to any crude oil that could reduce the water wetness of the core. The injection rate of SW0T and SW½T was 0.2 ml/min. Effluent samples were collected, and ion concentrations were analyzed for further processing.

For the reservoir chalk the surface reactivity test was performed after completion of the SI and VF experiments. The core was flooded with SW0T to reach residual oil saturation, (S_{or}), followed by SW½T. The injection rate of SW0T and SW½T was 0.2 ml/min. Effluent samples were collected, and ion concentrations were analyzed for further processing.

Other analyses

The ion concentrations in the effluent samples were analyzed using an ICS-5000+ Ion Chromatograph, delivered by Dionex. The ion concentrations were determined using the external standard method, showing a reproducibility of ± 3%.

Fluid viscosity and density were measured using an Anton Paar Rheometer (MCR 302) and an Anton Paar Densitymeter (DMA-450), respectively.

Specific surface area of the minerals was determined using the Micromeritics TriStar II apparatus based on the Brunauer Emmett Teller (BET) method. This involves measuring the adsorption of nitrogen and gas on the sample's surface at a given pressure to calculate the surface area. The samples were prepared for measurement using VacPrep 061, which removes contaminants like water vapor and adsorbed gas from the surface and pores of the sample via vacuum and heat. To prevent fluidization of the samples, vacuum was slowly applied during the preparation process. The BET method is one of the most widely used techniques for determining surface area because of its accuracy and versatility. Proper sample preparation is critical to obtain accurate surface area measurements, as contaminants can interfere with gas adsorption and affect the results. Therefore, techniques such as vacuum and heat treatment are often used to ensure that the samples are clean and free of unwanted species [51].

The overview of all the tests performed on different cores including the oil and water type used, type of experiment and test temperature are summarized in **Table 4**.

Table 4. Detailed summery of performed experiments on different cores.

Core#	S_{wi} - Brine	Oil	Temp. °C	Oil recovery tests			Other tests performed
				Secondary SI brine	Tertiary SI brine	Secondary VF brine	
RC 1	10% - FW_B	Oil B	130	FW_B	SW	SW	Surface reactivity test
	0	C7	23	DW	-	-	
RC 2	10% - FW_B	Oil B	130	FW_B	SmW2	SmW2	Surface reactivity test
	0	C7	23	DW	-		
SK0	0	C_7	23	DW	-	-	Surface reactivity test
SK 1	10% - FW_A	Oil A	130	FW_A	FW_A	SmW1	
SK 2	10% - FW_A	Oil A	130	FW_A	SW	-	
SK 3	10% - FW_A	Oil A	130	FW_A	SmW1	-	
SK 4	10% - FW_A	Oil A	130	FW_A	FW_A	SW	
SK 5	10% - FW_A	Oil A	130	FW_A	FW_A	SmW2	
SK 6	10% - FW_A	Oil A	130	FW_A	SmW2	-	
SK 7	10% - FW_A	Oil A	130	FW_A	SmW3	-	

Results and discussion

It is known that Seawater (SW) behaves as a wettability alteration and compaction fluid in chalk [30]. Laboratory tests [20], pilot tests [52], and field evaluations [53] confirm that improved oil recovery can be achieved by both SW injection and SI imbibition in chalk. Injection of SW is, due to its abundance, relatively inexpensive and easy to implement, while producing Smart Water by e.g., desalination with selective removal or addition of ions can be space-demanding, coming with an extra cost for the additional water treatment if not already included in the field development plan. Hence, there is a need for developing Smart Water compositions that are both successful in the wettability alteration process as well as being inexpensive and easy to manufacture. Three potential Smart Water brines with customized salinity and concentrations of the surface-active ions Ca^{2+}, Mg^{2+}, and SO_4^{2-} were designed, and SI experiments were performed on SK outcrop chalk to test their EOR-potential in comparison to that by SW. The most promising brine composition was thereafter tested on two restored reservoir chalk cores at 130 °C to investigate if the observations from the outcrop chalk could be verified in the reservoir chalk, and if the SK outcrop chalk represented an analogue to the reservoir chalk.

Comparing outcrop and reservoir chalk properties

Chalk is an important reservoir rock on the NCS and there are four main hydrocarbon-bearing formations; Tor, Ekofisk, Hod, and Hugin [54]. From a geochemical point of view, chalk is regarded as a limestone, consisting of biogenic calcium carbonate, ($CaCO_3$). Coccolithophores are single-celled phytoplankton that produces small $CaCO_3$ shells, and the coccolithophores deposit typically at water depths from 100 – 400 meters [31, 55].

The Stevns Klint outcrop chalk used was collected from a quarry nearby the coast of Denmark, thus, over geological time, it has been exposed to e.g., weathering, rainwater washing, and SW influx. In a previous study, it was found that because of this exposure the outcrop chalk contained some anhydrite ($CaSO_4$), which had to be removed prior to laboratory work due to its influence on wettability establishment and consequently wettability alteration investigations [43].

The reservoir rock has not undergone the same weathering and water washing effects but was instead invaded by the migrating crude oil millions of years ago, preventing extensive water-rock chemical interactions. Even though the pressure and temperature of different chalk reservoirs are high in the North Sea, the porosity is very high, 45-50%, and the reservoir rock thus contains significant hydrocarbon volumes.

Mineralogy, pore and grain sizes, surface area, in addition to surface reactivity of the reservoir and outcrop chalk were compared before initial wettability and the oil recovery potential was investigated in both.

Mineralogy

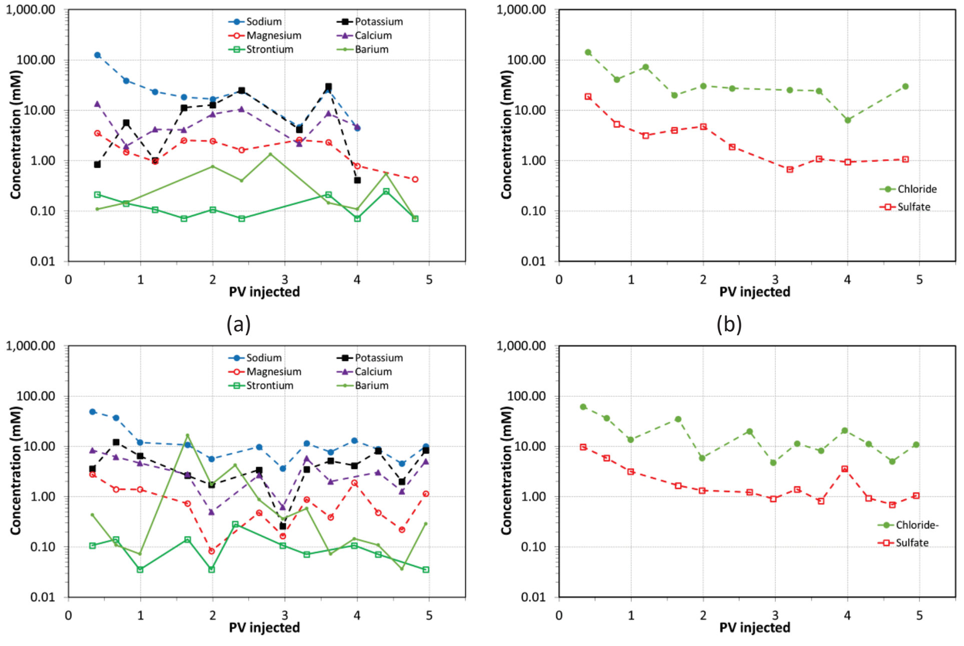
The mineral composition of the reservoir and SK outcrop chalk was determined by SEM and EDX analyses of small rock samples. In **Table 5** the results from the EDX analyses of the reservoir cores, RC1 and RC2, are reported.

Table 5. Cation composition in atomic weight % (At%) by EDX analyses of the reservoir chalk.

Cation	Reservoir Chalk	
	RC1 At%	RC2 At%
Ca	98.48	95.21
Mg	0.18	1.39
Al	0.03	0.57
Si	1.28	2.75
K	0.00	0.00
S	0.03	0.08

Minor differences in the composition of the two reservoir cores were observed. The reservoir chalk consists of >95 At% calcium (Ca), <3 At% silicon (Si), and <1.4 At% magnesium [56]. Only traces of sulfur (S) were observed, which could be linked to the presence of anhydrite ($CaSO_4$) or SO_4^{2-} anions.

After mild core cleaning of the reservoir cores with kerosene/heptane, they were flooded with DW to detect presence of formation water and dissolvable salts in the pores. Cation and anion concentrations in the effluent samples from RC1 and RC2, measured by ion chromatography, are presented in **Figure 1.**



(a) (b)

(c) (d)

Figure 1. Chemical analysis of the effluent during DW flooding of the reservoir cores, (a) RC1, cations and (b) RC1, anions; (c) RC2, cations and (d) RC2, anions.

The relative ion concentrations of FW_B (**Table 2**) were reproduced in the effluents during DW flooding, with the highest concentrations of Na^+ and Cl^- ions, and with a concentration of Ca^{2+} larger than that of Mg^{2+}. The ion concentrations diverting from the FW_B composition were K^+ and SO_4^{2-}. The presence of an increased amount of K^+ could be linked to KCl from drilling fluid contamination, but information about drilling mud composition was not available. The eluted low Ca^{2+} concentration in the effluent from both RC1 and RC2 testifies to low $CaCO_3$ mineral dissolution during DW flooding. The concentrations of Ba^{2+} and Sr^{2+}, known scaling ions when in contact with SO_4^{2-} ions from the injected SW or Smart Water, were found to be very low. Therefore, the possibility of a scaling problem in the production facilities is very low.

Moving to the anions, the SO_4^{2-} concentration was found to decrease from 20 mM and stabilized at 1 mM after 3 PV injected. The low concentration in the effluent confirmed that the amount of SO_4^{2-}bearing minerals accessible from the pores was limited. These effluent analysis results are in line with the EDX analyses results in **Table 5**, showing only traces of SO_4^{2-} in the reservoir chalk. The presence of SO_4^{2-} in the initial brine is important because it can affect the adsorption of POC during fluid restoration and the established core wettability [43, 57]. The presence of a significant amount of SO_4^{2-} bearing minerals in carbonate rocks could also contribute with Ca^{2+} and SO_4^{2-} ions to the injection water during waterflooding, the two ions needed for the Smart Water EOR effects in carbonates. Low salinity EOR effects was reported by Yousef et al. [58] and a chemical explanation of the observed effect was given by Austad et al. [59, 60] based on the reservoir limestone containing a relatively large amount of $CaSO_4$, releasing Ca^{2+} and SO_4^{2-} ions to the injected water, facilitating the wettability alteration process. Similar low salinity EOR effects were previously not observed in SK chalk free from anhydrite minerals [23, 24].

EDX analyses were additionally performed on the SK chalk before initial core cleaning with 5 PV DW, and the SK chalk cation composition is given in **Table 6**.

Table 6. Cation composition as atomic weight % (At%) of SK outcrop chalk.

Cation	Ca	Mg	Al	K	Si	Na	S
At%	98.54	0.08	0.13	0.22	0.57	0.02	0.44

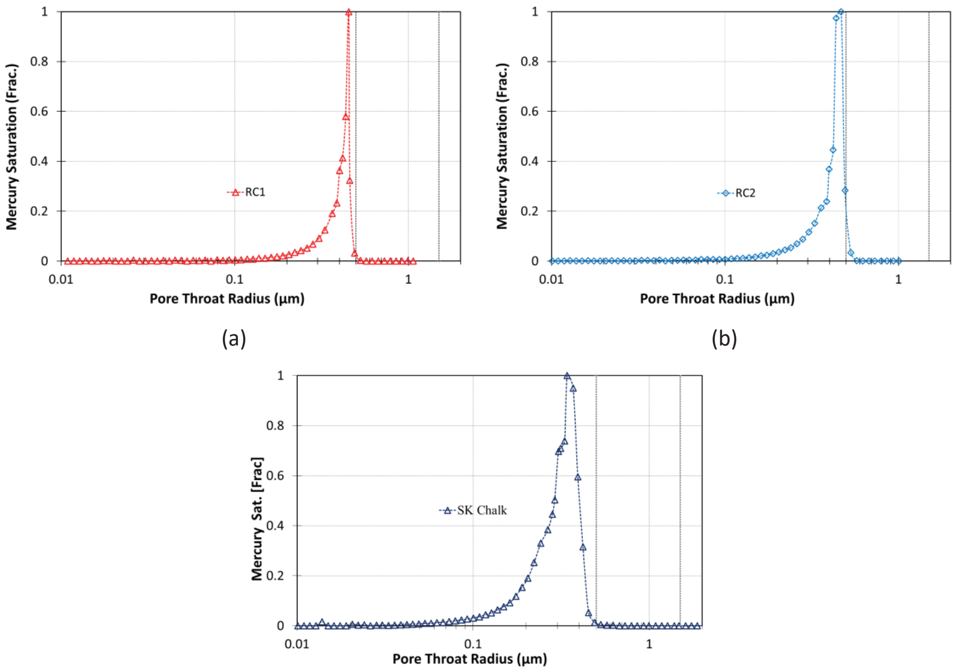
SK outcrop chalk consisted of >98 At% Ca^{2+}. Dissolvable ions such as Na^+, K^+, and SO_4^{2-} were detected, but their concentration would be reduced after 5 PV DW exposure. Puntervold et al. [43] previously showed that these easily dissolvable ions can be removed by flooding 5 PV DW to reduce their influence on the initial wettability establishment.

By comparing cationic compositions of the reservoir and SK chalk it was concluded that the two chalks were very similar in mineralogy. Both chalks consisted of a majority of $CaCO_3$, with low silicate impurities, albeit slightly larger in the reservoir chalk than in the SK chalk, and with negligible amounts of SO_4^{2-}-bearing minerals, which could influence initial wettability and the wettability alteration process during water injection.

Pore size distribution

Sedimentary rocks are capillary systems, and the pore size distribution influences the location of fluids and their flow in porous media. Large pores easily permit fluid flow during e.g. waterflooding of oil reservoirs, however they also lead to early water breakthrough and poor sweep efficiency. Often a large proportion of the hydrocarbons are residing in smaller pores into which capillary forces can limit fluid flow depending on the rock wettability. Hence, heterogeneous pore size distribution emphasizes the importance of capillary forces and spontaneous imbibition of water for improved oil displacement from the rock matrix.

Pore size distributions in both reservoir chalk cores, RC1 and RC2, and the SK outcrop chalk were evaluated by determining the pore throat radii by MICP, **Figure 2**.



(a)

(b)

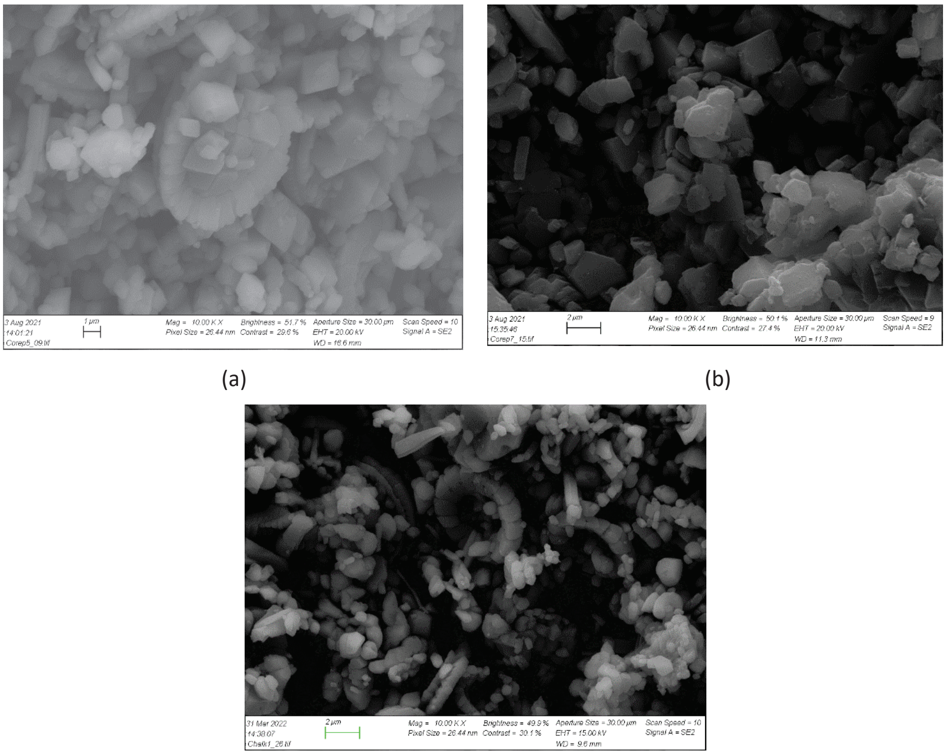
(c)

Figure 2. Pore size distribution by MICP for (a) RC1 and (b) RC2, and (c) outcrop SK chalk.

By comparing the results from the reservoir and outcrop SK chalk it was concluded that the reservoir and outcrop chalk have similar pore size distribution, with the maximum pore throat radius of 800 nm, peaking at 300 – 500 nm, and the smallest larger than 20 nm.

Grain sizes

Both reservoir and outcrop chalk had a low degree of consolidation. Grain sizes and their distribution could qualitatively be determined from the SEM pictures presented in **Figure 3**.



(a) (b)

(c)

Figure 3. SEM pictures at 10 000 times magnification of (a) RC1, (b) RC2, and (c) SK chalk.

Intact coccolith rings were observed in both reservoir and outcrop SK chalk. The individual grains seemed to not have been exposed to physical degradation, chemical dissolution, or precipitation reactions affecting their shape. Average chalk grain sizes were qualitatively estimated by image analysis to be close to 1000 nm in both reservoir and outcrop SK chalk.

Pore surface area

To evaluate available pore surfaces in the reservoir and outcrop chalk, BET specific surface area measurements were performed. The pore surfaces are important in the establishment of initial wettability by crude oil component adsorption. They are also important for the COBR-interactions responsible for the wettability alteration taking place by Smart Water flooding, causing enhanced oil recovery. The BET surface area results are presented in **Table 7**.

Table 7. BET specific surface area (m^2/g) of reservoir and SK outcrop chalk.

	Reservoir chalk		SK outcrop chalk	
	RC1	RC2	SK0	SK4
BET, (m^2/g)	1.68	1.71	1.96	2.01

The results revealed that the BET surface area was very similar in the reservoir and outcrop chalk, albeit slightly lower in the reservoir chalk. These results coincided with the slightly lower average porosity of 39.0 % determined in the reservoir chalk versus 48.3 % in the outcrop chalk (**Table 1**). The BET analysis results confirmed that the small grains contribute to a large surface area that is available for COBR-interactions during waterflooding.

Surface reactivity

The reactivity of the mineral surfaces in the outcrop SK chalk was tested by performing a surface reactivity test, the principles of which were described in detail in Strand et al. [50]. In brief, the tracer curve describes the displacement efficiency in waterflooding, and the SO_4^{2-} curve reveals if SO_4^{2-}-ions have affinity to the chalk surface, its adsorption onto the rock surface causing a delay in eluting from the core compared to the non-adsorbing tracer (SCN^- or Li^+). It is important to note that SO_4^{2-}-ions will only adsorb to the water-wet sites on the surface, and the test can thus reveal information about the core wettability. Affinity of SO_4^{2-} to the rock surface is a good indication if SW or SW-based Smart Water will be efficient EOR-fluids at high temperature (>70 °C) [61, 62]. The surface reactivity effluent analysis gave the ion profiles shown in **Figure 4**.

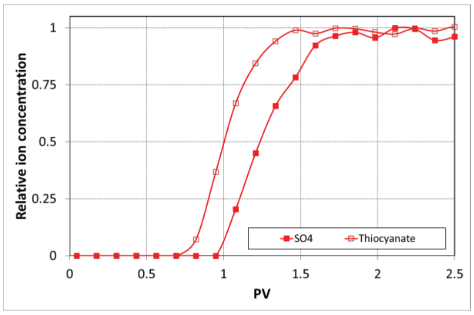
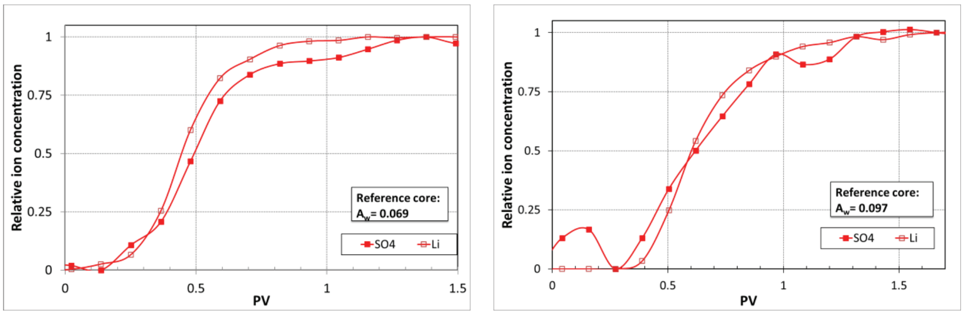


Figure 4. Surface reactivity test performed on outcrop chalk core SK0 by measuring effluent ion concentrations of the adsorbing SO_4^{2-} and the non-adsorbing tracer (SCN^-). The chromatographic separation area was quantified to be A_W= 0.249.

The delayed SO_4^{2-} curve showed that SO_4^{2-} ions interacted with the slightly water-wet outcrop chalk surface, reaching equilibrium concentration when all water-wet adsorption sites were occupied. The separation area, A_w, between the adsorbing SO_4^{2-} and the non-adsorbing SCN^- can be quantified and is proportional to the fraction of water-wet rock surface. In previous work by Hopkins et al. [63], a strongly water-wet SK chalk core should have an A_W close to 0.25 when flooding the SW0T/SW½T brines at 23°C. The calculated separation area measured for SK0 was A_W = 0.249, indicating a strongly water-wet behavior.

Despite not having a strongly water-wet reference reservoir chalk core, the surface reactivity test can provide information about ion interactions toward the water-wet pore surfaces, dissolvable SO_4^{2-}, and core heterogeneity. Note that for the reservoir chalk cores the surface reactivity tests were performed after the oil recovery tests presented later in this paper. The reasoning was that it was more important to get information about initial wettability and the presence of capillary forces in the preserved reservoir chalk material, hence these experiments were prioritized. An effect from this prioritization might be that the surface reactivity test suggests a slightly increased affinity of SO_4^{2-} for the chalk surface because of wettability alteration effects during the oil recovery tests. Nevertheless, analysis of the surface reactivity test effluents from the reservoir chalk cores RC1 and RC2 gave the effluent ion profiles shown in **Figure 5**.



(a) (b)

Figure 5. Surface reactivity test at 23°C on reservoir cores using SW0T/SW½T brines on (a) RC1 and (b) RC2. A_W is the chromatographic separation area between the non-adsorbing tracer (Li^+) and the adsorbing SO_4^{2-}.

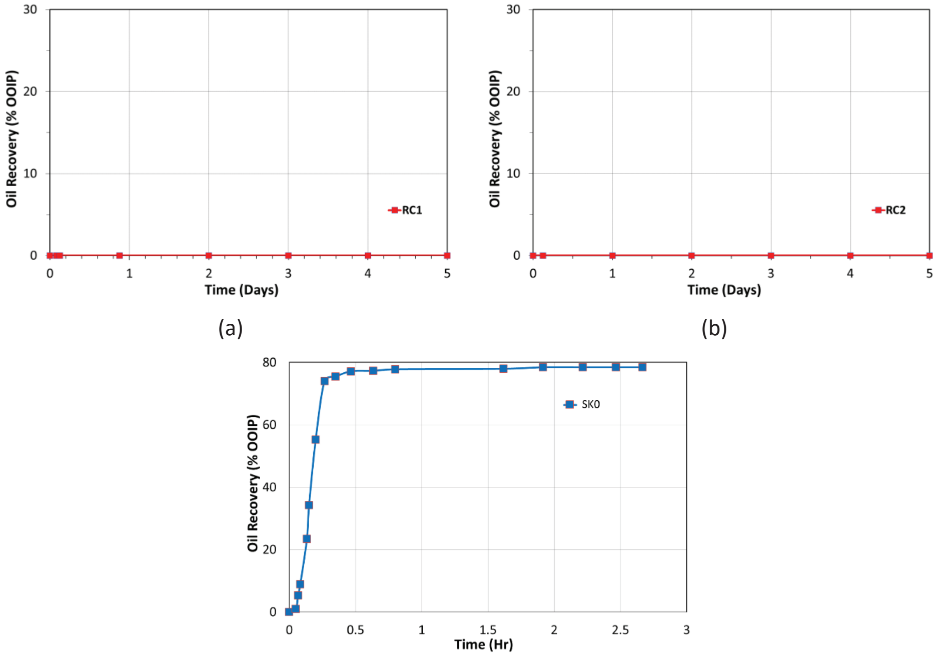
The chromatographic separation areas in RC1 and RC2 were calculated to $A_W = 0.069$ and $A_W = 0.097$, respectively, which suggests that SO_4^{2-} has some affinity to the mineral surfaces present in the reservoir chalk, however much lower than that observed for the strongly water-wet outcrop SK chalk, $A_w = 0.249$, in **Figure 4**. A lower A_w indicates reduced water-wet mineral surfaces in the reservoir chalk, which in turn means that positive capillary forces for mobilizing crude oil by water imbibition in heterogeneous pore systems will be reduced.

The tracer profiles from the tests on outcrop SK and reservoir chalk were compared. The profiles in the reservoir chalk in **Figure 5** possessed a more tilted S-shape compared to that in the strongly water-wet SK chalk core in **Figure 4**. This indicates a decreased water displacement efficiency in the reservoir chalk, which also could affect the oil displacement efficiency during water injection.

Initial wettability of outcrop and reservoir cores

It was observed that outcrop SK and reservoir chalk possessed similar mineral compositions, permeabilities, grain sizes, pore size distributions, and specific surface areas. The porosity of both chalks was high but slightly lower in the reservoir chalk compared to the outcrop SK chalk. The outcrop chalk had previously never seen oil, while the reservoir chalk had been invaded by crude oil containing POC, which could interact with the mineral surfaces, affecting wettability and capillary forces.

The presence of capillary forces in the reservoir and outcrop SK chalk was evaluated by performing SI tests at 23 °C on 100% heptane-saturated cores using DW as the imbibing fluid. The heptane recovery results are presented in **Figure 6**.



(a) (b)

(c)

Figure 6. Recovery of heptane by DW imbibition at 23 °C from the 100 % heptane-saturated mildly cleaned cores (a) RC1, (b) RC2 and (c) outcrop SK0.

In the strongly water-wet SK chalk core, spontaneous imbibition of DW mobilized 75 %OOIP in less than 30 minutes, reaching the ultimate oil recovery plateau of 78 %OOIP after only 2 hours (Hr). The fast and substantial heptane recovery confirms the presence of strong, positive capillary forces, indicative of a strongly water-wet behavior in SK0, in agreement with the results from the surface reactivity test in **Figure 4**. The heptane recovery results by spontaneous imbibition of DW from the mildly cleaned reservoir chalk cores, RC1 and RC2, were, however, completely different. Neither reservoir chalk core was able to imbibe any water, confirming a lack of positive capillary forces, consistent with a neutral to oil-wet behavior, in agreement with the limited water-wet surface area suggested in the surface reactivity test in **Figure 5**. The preserved reservoir cores were mildly cleaned to preserve most of the polar organic components at the mineral surfaces that dictates the core wetting. SI of a 100% saturated mildly cleaned reservoir cores confirms lack of capillary forces and showed that polar organic components from the oil phase was still sticked to the mineral surface. This proves that the original wettability of the core was not changed by mild cleaning. Moreover, the lack of capillary forces in reservoir core might be a result of mud contamination or bad preservation. Mud composition data was not available to analyse. As the drilling campaign was carried out in the 80's, the cores might be wrongly preserved as well.

Oil mobilization from porous rock systems is controlled by capillary forces together with gravity and viscous forces. By assessing reservoir and SK outcrop chalk properties such as mineralogy, pore size distribution, average grain sizes, pore surface area and surface reactivity, it was found that the two chalks were comparable. Thus, the invasion of crude oil into the reservoir chalk has had a dramatic effect on the presence of positive capillary forces and the wetting behavior compared to the outcrop chalk as demonstrated in **Figure 6**.

EOR potential in outcrop chalk

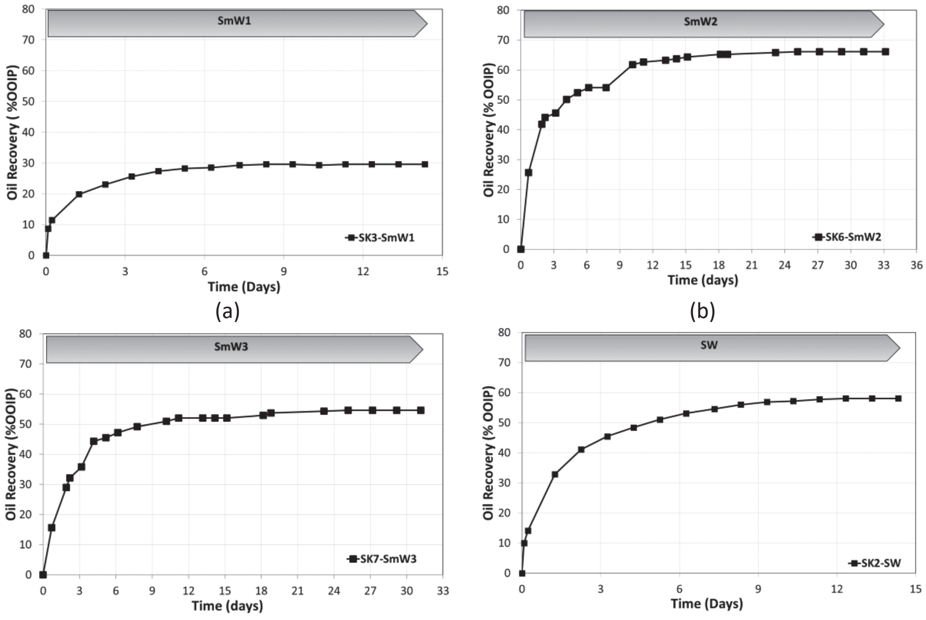
To evaluate the efficiency of the designed brines SmW1, SmW2, and SmW3, **Table 8**, in producing oil by spontaneous imbibition, four SK cores (SK2, 3, 6, 7) were equally restored to mixed-wet conditions. Swi of 10 % was established in all cores before the cores were exposed to the same amount of Oil A in the fluid restoration process followed by core aging.

Spontaneous imbibition in secondary mode

Oil recovery tests by spontaneous imbibition in secondary more were performed at 130 °C. The oil recovered by the three designed brines SmW1, SmW2, and SmW3 were compared against SW performance. The oil recovery results by spontaneous imbibition in secondary mode are presented in **Figure 7**.

The oil recovery after spontaneous imbibition with SmW1, **Figure 7(a)**, showed an ultimate recovery plateau of 30 %OOIP, which was reached within 9 days. For SmW2, **Figure 7(b)**, both the speed of imbibition and ultimate oil recovery significantly increased. After 9 days the oil recovery was 58 %OOIP and further increased to an ultimate recovery of 66 %OOIP after 25 days, confirming that the ion composition of the designed brine had a significant effect on capillary forces generated during spontaneous imbibition and the amount of oil mobilized from heterogeneous pore systems. The SmW1 contained only 10 mM Ca^{2+} and SO_4^{2-} ions, while the SmW2 contained 20 mM Ca^{2+} and SO_4^{2-} in addition to 20 mM Mg^{2+}. A significant increase in positive capillary forces and oil mobilization was observed when Ca^{2+} and SO_4^{2-} were increased by 10 mM in SmW2. By increasing Mg^{2+} ion concentration from 20 to 40mM in SmW3, the ultimate oil recovery decreased to 55 %OOIP, **Figure 7(c),** which is significantly lower than that obtained with SmW2.

SW is known as a wettability alteration fluid in chalk, with a particularly large effect at 130 °C [64]. Here, using SW as a baseline imbibing fluid, **Figure 7(d)**, an ultimate oil recovery of 58 %OOIP was obtained, which is lower compared to SmW2 but slightly higher compared to SmW3. The results confirm that there is a potential for optimizing the SW composition for generating increased positive capillary forces and maximizing the oil mobilization also at high temperatures, 130 °C. The low recovery observed for SmW1 is in line with previous experiences when the amount of Ca^{2+} and SO_4^{2-} is too low [24].



(a) (b)

(c) (d)

Figure 7. Oil recovery by SI at 130°C on equally restored outcrop SK chalk cores with S_{wi} = 0.1 and Oil A. The imbibing brines in secondary mode were (a) SmW1 in core SK3 (b) SmW2 in core SK6, (c) SmW3 in core SK7, and (d) SW in core SK2.

The results from the SI experiments in the outcrop SK chalk (including initial wettability with heptane) and calculated modified Amott water index, I_{W-SI}^{*}, are summarized in **Table 9**.

Table 9. Summary of the SI tests in secondary mode in outcrop SK chalk.

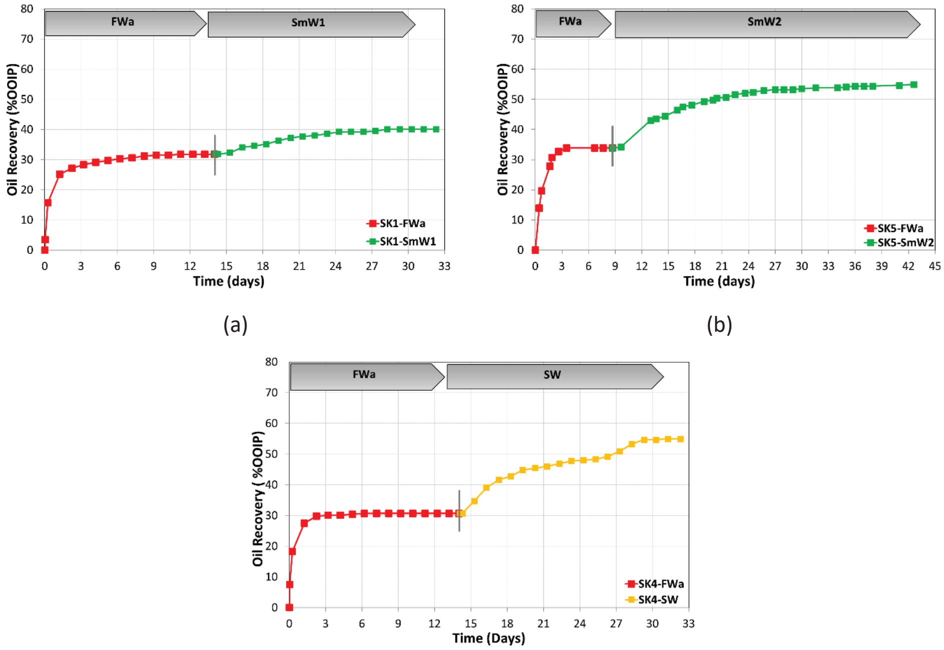
Core	S_{wi} FW %	Oil	Imbibing brine	Temp. °C	Secondary SI, %OOIP	Final I_{W-SI}^{*}
SK0	0	C_7	DW	23	78	1.00
SK2	10	Oil A	SW	130	58	0.74
SK3	10	Oil A	SmW1	130	30	0.38
SK6	10	Oil A	SmW2	130	66	0.85
SK7	10	Oil A	SmW3	130	55	0.71

By using I_{W-SI}^{*}, introduced in **Eq. 1**, the experimental results obtained from the SI experiments could be used to calculate the degree of water wetness in the individual cores after SI of the various brines. The strongly water-wet core SK0 was used as the reference core for a very water-wet system, giving SI_{WWC} = 78

%OOIP. The most water-wet core was obtained using SmW2 as imbibing brine, with an index of $I^*_{W-SI} = 0.85$, followed by SW with $I^*_{W-SI} = 0.74$ and SmW3 with $I^*_{W-SI} = 0.71$. The lowest index of $I^*_{W-SI} = 0.38$ was observed using SmW1.

Spontaneous imbibition in tertiary mode

The effectiveness of SmW1, SmW2, and SW was also tested in tertiary mode after spontaneous imbibition of FW_A. The results are presented in **Figure 8** and summarized in **Table 10**.



(a) (b)

(c)

Figure 8. Oil recovery by SI at 130 °C on equally restored outcrop SK chalk cores with $S_{wi} = 0.1$ FW_A and Oil A. FW_A was used as imbibing brine in secondary mode in all three cores, followed by tertiary imbibition of (a) SmW1 in core SK1, (b) SmW2 in core SK5, and (c) SW in core SK4.

Oil recovery by FW_A imbibition was in the range of 31-34 %OOIP for all three cores, confirming very good experimental reproducibility between the restored cores. This gives the cores an initial modified Amott water index, I^*_{W-SI}, of 0.40–0.44, as summarized in **Table 10**.

Table 10. Summary of the SI tests in tertiary mode in outcrop SK chalk.

Core	S_{wi} FW %	Oil	Temp. °C	Secondary SI			Tertiary SI			$\Delta(I^*_{W-SI})$
				brine	%OOIP	Initial I^*_{W-SI}	brine	%OOIP Ultimate (Extra)	Final I^*_{W-SI}	
SK0	0	C_7	23	DW	78	1.00	-	-	-	-
SK 1	10	Oil A	130	FW_A	32	0.41	SmW1	40 (8)	0.51	0.10
SK 5	10	Oil A	130	FW_A	34	0.44	SmW2	55 (21)	0.71	0.27
SK 4	10	Oil A	130	FW_A	31	0.40	SW	55 (24)	0.71	0.31

After the oil production plateau with FW_A had been reached, the imbibing brines were changed to SmW1, SmW2, or SW. The extra oil mobilized in tertiary mode with SmW1 was 8 %OOIP, whereas SmW2 and SW gave 21 and 24 %OOIP extra oil, respectively. The oil mobilization was significantly lower using SmW1 as imbibing brine, both in secondary and tertiary modes. Thus, due to its reduced content of Ca^{2+} and SO_4^{2-} this brine seemed to be a less efficient wettability modifier, in consistence with previously published experimental work showing that increased concentrations of both Ca^{2+} and SO_4^{2-} improved oil recovery from outcrop SK chalk [5, 8, 22].

Comparing ultimate oil recoveries by spontaneous imbibition of SmW2 and SW in tertiary mode, the results show that both brines reached the same ultimate oil recovery of 55 %OOIP, hence there were no significant differences in oil displacement efficiency between these two brines, despite SmW2 having 7 times lower salinity than SW. However, if spontaneous imbibition of SmW2 and SW were compared in secondary and tertiary mode, increased efficiency was observed for both brines in secondary mode. By imbibing SmW2 in secondary mode the ultimate oil recovery reached 66 %OOIP, while the tertiary ultimate oil recovery was only 55 %OOIP. SW in secondary mode gave an ultimate recovery plateau of 58 %OOIP while ultimate oil recovery in tertiary mode was 55 %OOIP. These results are also in line with previous Smart Water EOR observations for sandstones, where Smart Water was seen to be significantly more efficient in secondary compared to tertiary mode [65]. In tertiary mode with increased water saturation, the contribution from capillary forces will be reduced.

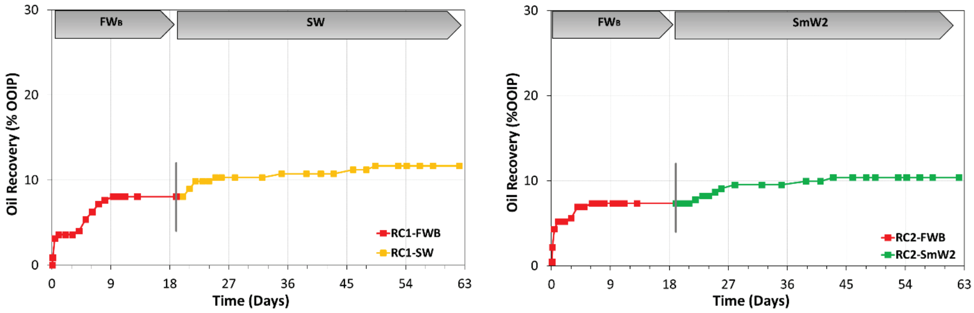
The SI results on outcrop SK chalk clearly indicate that there is room for enhancing waterflooding performance beyond what is possible with SW injection by designing Smart Water brines with modified chemical composition.

EOR potential in reservoir chalk

Smart water EOR potential using SW and ion modified water was evaluated in reservoir chalk. Two reservoir chalk cores, sampled from the reservoir oil leg, were available. Initially, the cores were mildly cleaned with kerosene and heptane for removal of the crude oil without altering the initial wettability of the cores, followed by 5 PV of DW flooding for removal of the initial brine before drying to constant weight.

SI experiments, performed at 23°C on the 100% heptane-saturated cores, **Figure 6**, revealed that no positive capillary forces were available in the mildly cleaned cores, and that initial core wettabilities seemed to be neutral to oil-wet. In the fluid restoration process, S_{wi} of 10 % FW_B was established by desiccator and a 90 % oil saturation was introduced by combining vacuum saturation and injection of Oil B. The core was exposed to less than 1 PV of Oil B to avoid over-exposure of crude oil and an unrepresentative reservoir wettability during the fluid restoration process, in line with the recently published methodology for obtaining reproducible and representative core wettabilities in laboratory studies in both carbonate [46] and sandstone [47] cores.

First, both restored reservoir cores, RC1 and RC2, were spontaneously imbibed at 130 °C with FW_B to quantify the availability of positive capillary forces after fluid restoration. This was followed by SI with SW and SmW2 to evaluate if these brines could increase the capillary forces and mobilize more oil. The results from the SI experiments are presented in **Figure 9**.



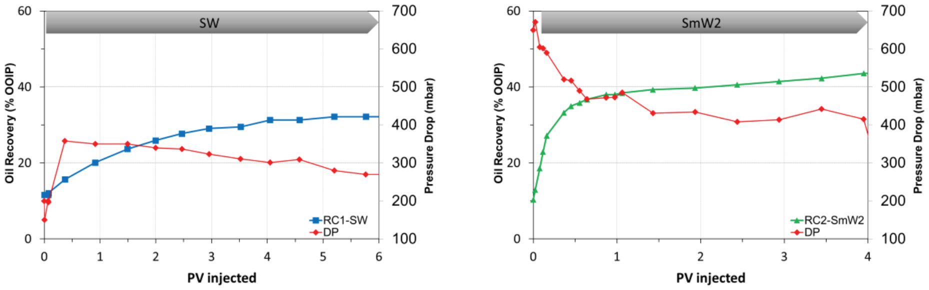
(a) (b)

Figure 9. Oil recovery by SI at 130°C in reservoir cores equally restored with $S_{wi} = 0.1$ and Oil B. FW_B was used as initial and imbibing brine in secondary mode, followed by tertiary imbibition of (a) SW in core RC1, and (b) SmW2 in core RC2.

The first, rapid oil mobilization of ~4-5 %OOIP with FW_B is linked to the thermal expansion of fluids at elevated temperature. The further increase in oil recovery to plateaus of 8 %OOIP after 9 days for core RC1 and 7 %OOIP after 6 days for RC2 can be linked to modest capillary forces. These weak positive capillary forces in the restored reservoir chalk cores were represented by a modified Amott water index of $I^*_{W-SI} < 0.1$, and a neutral wettability behavior. The initial positive capillary forces in the restored outcrop SK chalk cores were significantly stronger, values given in **Table 10**.

At the production plateau, and after 19 days of imbibition, the imbibing brine was changed to SW in RC1 and SmW2 in RC2. A gradual increase in oil mobilization was observed in both cores reaching ultimate oil recovery plateaus of about 11 %OOIP for both cores after 50 and 45 days, respectively. The extra oil mobilized by SW and SmW2 in tertiary mode confirms increased capillary forces due to a wettability alteration process.

After the SI, both cores were mounted into Hassler core holders for VF experiments at reservoir temperature 130 °C. Both cores were flooded at a rate of 0.5 PV/D with the last brine used in the SI test, i.e. RC1 was flooded with SW and RC2 was flooded with SmW2. The oil recovery and pressure drop were logged against time, and the results are shown in **Figure 10**.



(a) (b)

Figure 10. Oil recovery by VF at 130 °C on core (a) RC1 and (b) RC2 already imbibed with FW_B and SW or SmW2, respectively. The injection rate was 0.5 PV/D using (a) SW in RC1, and (b) SmW2 in RC2.

During SW injection in core RC1, the oil recovery gradually increased from 11 %OOIP after SI, reaching an ultimate oil recovery plateau of 32 %OOIP after 5 PV injected, representing an extra oil production of 21 %OOIP, **Figure 10 (a).** For core RC2, **Figure 10 (b)**, the SmW2 injection had a significantly greater impact on the production, increasing from 11 %OOIP after SI, to and ultimate oil recovery of 43 %OOIP after 4 PV injected. This is 11 %OOIP higher than the recovery achieved by SW injection in core RC1.

The recovery profile for core RC1 using SW as injection brine is significantly different from RC2 using SmW2. In **Figure 11**, the oil recovery curves for RC1 and RC2 were compared to explain the difference in recovery performance of the two injection brines.

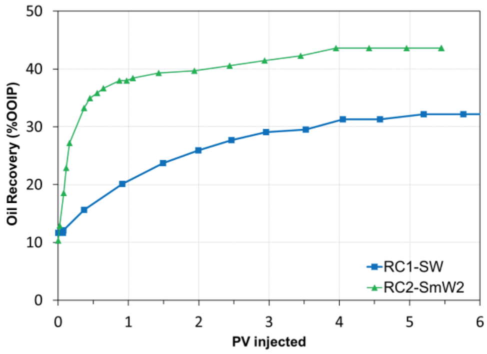


Figure 11. Oil recovery at 130 °C by VF of SW in RC1 and SmW2 in RC2 after SI of FW_B/SW and FW_B/SmW2, respectively. The injection rate was 0.5 PV/day.

During SW injection into RC1, both oil and water was produced from the start as clearly seen in **Figure 11**. Then the O/W ratio gradually declines and reached zero after 5 PV injected with an ultimate recovery of 32%. The SI experiments in front of viscous flooding will create an increased water saturation close to the outer surfaces of the cores. Water will always take the easiest pathway (largest pores/pores with higher water saturations) in heterogeneous systems, which will favor earlier water breakthrough in pore systems without positive capillary forces or in pore systems with positive capillary forces present when injection rate is too high.

During SmW2 flooding in core RC2, only oil production was observed in the start, reaching 27%OOIP before water breakthrough, followed by a gradually reduction in O/W ratio. After 1 PV injected after, the SmW2 recovery had reached 38 %OOIP, compared to only 20 %OOIP for SW.

The core flooding results confirms that the SmW2 brine are significantly more efficient than the SW, reaching a significant higher ultimate recovery of 43 %OOIP in a shorter time, 4 PV injected. The difference in oil mobilization from core RC1 and RC2 must be linked to the ability of the injection brines to create positive capillary forces promoting oil mobilization in heterogeneous systems as observed in the previous performed SI experiments.

The pressure drop profile during SW injection into core RC1 showed a build-up from 200 mbar to 360 mbar after 0.3 PV injected, followed by a steady decline to 270 mbar after 6 PV, **Figure 10 (a)**. The pressure drop profile for core RC2 was completely different. The pressure drop decreased from an initial 670 mbar to 415 mbar after 4 PV, **Figure 10 (b)**. It is difficult to explain this huge difference in pressure drop profiles. Both cores had almost the same water saturation when the VF experiment started. The pore size distribution from MICP measurements confirmed that the cores are heterogeneous pore systems, thus the differences could be linked to pore heterogeneity and fluid distributions. It is important to highlight that pressure drops of more than 270 mbar on cores with a length of 7 cm are significantly higher than what could be expected in the main part of the reservoir between injection and production wells. Hence, the viscous forces applied with an injection rate of 0.5 PV/D are too high to be representative for reservoir systems. A reduction in injection rate to represent the expected viscous forces in the main part of the reservoir will further highlight the importance of positive capillary forces. The difference in pressure drop profiles clearly indicates that the pressure drop does not directly correlate with oil mobilization. Positive capillary forces should also need be taken into account, especially in heterogeneous pore systems [66].

The results from the SI and VF experiments in the reservoir cores (including initial wettability with heptane) are given in **Table 11**.

Table 11. Summary of the SI and VF experiments of reservoir chalk.

Core	Oil recovery, (%OOIP)							
	C7	SI FW_B	SI SW	SI SmW2	SI total	VF SW Secondary	VF SmW2 Secondary	Extra oil by VF compared with SI
RC-1	0	8.1	+2.7	-	10.8	32.0	-	+21.2
RC-2	0	7.3	-	+3.1	10.4	-	43.6	+33.2

Surface reactivity tests performed on the reservoir cores RC1 and RC2 after the SI and VF tests with SW and SmW2, **Figure 5,** showed only a small separation area between the non-adsorbing tracer and adsorbing SO_4^{2-}, suggesting that the cores were still not very water-wet, even after exposure to SW and SmW2.

Improved sweep efficiency by wettability alteration

A plausible explanation for the significantly improved oil displacement efficiency during SmW2 injection in reservoir chalk is that its composition is beneficial for inducing wettability alteration in chalk, resulting in stronger positive capillary forces, increased imbibition rate and mobilized oil, in line with the observations from the SI experiments performed on slightly water-wet outcrop SK chalk, **Figure 7** and **Figure 8**. In the VF experiments performed on heterogeneous reservoir chalk cores at low water wetness, the increased displacement efficiency was not a result of change in mobility ratio and/or relative permeabilities, but rather as an effect of positive capillary forces mobilizing more oil in the displacement front, increasing the mobile oil bank, and delaying the water breakthrough, as illustrated in **Figure 12**. The positive capillary forces created by SmW2 aid the fluid movement into smaller, previously non-swept pores by spontaneous imbibition, thereby increasing the sweep efficiency.

Figure 12 (a) illustrates a slightly water wet porous rock system where the injection brine prefer the higher permeable pore network, but some positive capillary forces mobilizing trapped and bypassed oil from rock matrix/smaller pores due to spontaneous imbibition of the injected brine. **Figure 12 (b)** illustrates the presence of stronger positive capillary forces contributing with increased oil mobilization from trapped/bypassed pores by brine imbibition. The latter situation leads to a more stable waterfront and improved sweep efficiency.

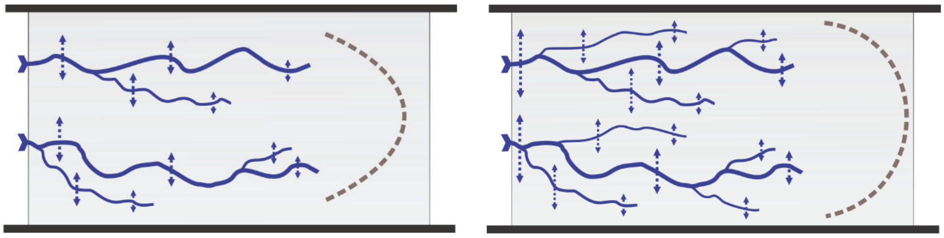

(a) (b)

Figure 12. Oil mobilization and displacement efficiency in heterogenous core systems as an effect of increased positive capillary forces, at (a) slightly water-wet conditions and at (b) water-wet conditions. The stippled arrows represent the positive capillary forces.

SI and VF results indicate that the designed SmW2 is not only the most efficient injection brine for outcrop SK chalk cores possessing significant positive capillary forces, but also seems to be the most efficient injection brine for the reservoir chalk cores possessing significantly weaker positive capillary forces. The ultimate oil recovery from the heterogeneous reservoir chalk cores was significantly lower compared to that from the restored outcrop SK chalk cores. This undoubtedly confirms that the reservoir chalk cores possessed weaker positive capillary forces at arrival to the laboratory compared to the restore outcrop SK chalk. However, whether the restored wettability conditions in the reservoir chalk cores are completely representative of the actual chalk reservoir wettability is hard to say. The reservoir cores seemed inadequately preserved upon arrival, as they were not preserved in wax and had been stored at laboratory conditions for several years. Poor preservation may lead to contact with air and promote evaporation of the lighter fluid components, both possibly impacting the core wettability.

Recently Mokthari et al. [67] published work on reservoir chalk, in which they claimed that the reservoir chalk used behaved completely different from the SK outcrop chalk when it came to the role of SO_4^{2-} in the wettability alteration process. From multiple restorations on the same reservoir chalk core, it was claimed that SO_4^{2-} was not an important ion in the wettability alteration process in reservoir chalk. It is important to highlight that sulphate is not very efficient in the wettability alteration process in chalk at temperatures below 90 °C [61, 62]. Hence, the results from the reservoir cores performed by Mokthari et al. [67] are in line with previous observations on SK outcrop chalk when experiments are performed at 70 ℃. It should be noted that Webb et al. [3] confirmed that SW was an efficient EOR-fluid in reservoir chalk, and that significant experimental work has been performed on mixed-wet reservoir limestone, also consisting of $CaCO_3$, and the benefit of sulphate is unquestionable at temperatures of 90 °C and above [17, 19, 59, 60]. The results of the present study clearly show similarities between outcrop SK chalk and the reservoir chalk used, both SW and SmW2, containing SO_4^{2-}, outperformed FW, not containing SO_4^{2-}, as injection fluid for EOR. More work is needed to draw universal conclusions about all chalk reservoirs, as the composition of the chalk is of importance for the wettability alteration process. Presence of silica or clay in chalk, for example, influences both the initial wettability and crude oil component adsorption, and therefore COBR-interactions during waterflooding [68, 69]. Additionally, presence of $CaSO_4$ in the carbonate or chalk reservoir, will release Ca^{2+} and SO_4^{2-} into the injection brine, and as such even diluted SW or FW, both initially containing low or no SO_4^{2-} , could be efficient EOR-fluids in chalk [59, 60]. Based on this care should be taken before claiming that SO_4^{2-} is not important for wettability alteration in reservoir chalk. Sweep efficiency related to wettability alteration is a complex process involving physical processes and chemical interactions between crude oil, formation brine, injection brine and rock, all being multicomponent phases.

Conclusions

Three Smart Water brines were designed with customized salinity and specific concentrations of surface-active ions (Ca^{2+}, Mg^{2+}, and SO_4^{2-}). Spontaneous imbibition (SI) experiments were conducted on Stevns Klint (SK) outcrop chalk to assess their enhanced oil recovery (EOR) potential as inexpensive alternatives to SW injection. The most promising brine composition identified from the outcrop chalk tests was then applied to two restored reservoir chalk cores at a temperature of 130 °C. The objective was to validate whether the findings from the outcrop chalk could be validated in the reservoir chalk and assess the representativeness of SK outcrop chalk as an analogue for the reservoir chalk.

The conclusions drawn from this study were the following:

- Reservoir chalk and outcrop SK chalk properties such as porosity, permeability, pore size distributions, BET specific surface area, rock composition, and grain sizes were observed to be comparable, suggesting that the SK chalk could be a very good analogue for the reservoir chalk obtained from the NCS.
- The designed SmW2 containing 20 mM Ca^{2+}, Mg^{2+}, and SO_4^{2-} at a salinity of 4630 ppm was the most effective brine in producing oil from slightly water-wet outcrop SK chalk at 130 °C in secondary mode spontaneous imbibition. In tertiary mode, however, it performed on the same level as SW.
- The reservoir chalk cores, poorly preserved, behaved initially neutral to oil-wet, not spontaneously imbibing any water. After core restoration, oil recovery results with spontaneous imbibition of FW in secondary mode showed good reproducibility and similar initial wettability restored in the cores.

- Spontaneous imbibition of SW and SmW2 in tertiary mode after FW imbibition in the reservoir cores showed no significant differences in efficiency.
- Viscous flooding of SW and SmW2 in the reservoir cores after the preceding spontaneous imbibition revealed that SmW2 displaced oil both more rapidly and efficiently than SW.
- Experiments performed on slightly water-wet outcrop SK chalk cores and neutral to oil-wet reservoir chalk confirmed that a Smart Water brine could be designed to be both inexpensive and more efficient than SW at a high temperature of 130 °C. The optimal brine composition was dependent on the total salinity, Ca^{2+}, Mg^{2+}, and SO_4^{2-} ion concentrations.
- The enhanced oil recovery by modified water composition in carbonate rocks is case dependent and the properties of rock, fluid (oil, formation water, and previously injected water), condition (pressure and temperature) should be taken into consideration while designing injection brine in every case.

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V

Reinjection of Produced Water with Polysulphate Additive for Enhanced Oil Recovery.

Md Ashraful Islam Khan, Iván Darío Piñerez Torrijos, Meng Zhang, Skule Strand, Tina Puntervold.

Submitted to Energy and Fuel.

Paper V

Reinjection of Produced Water with Polysulphate Additive for Enhanced Oil Recovery

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Abstract

Processing and disposal of produced water (PW) present increasing economic and environmental challenges, especially in maturing fields. Reinjection of PW can reduce these challenges, but its efficiency as an enhanced oil recovery fluid is limited in carbonates, because of an unfavorable composition for any wettability alteration and improved sweep efficiency to take place. Polysulphate (PS) salt was explored as an additive to produced water for enhanced oil recovery (EOR) from chalk reservoirs.

Oil recovery by spontaneous imbibition tests in mixed-wet outcrop chalk showed that PW with added PS (PW-PS) improved oil recovery in both secondary and tertiary mode at 90 °C and 110 °C. PW-PS was the most effective injection brine compared to seawater and other PS-brines. Chromatographic wettability tests, performed after the oil recovery tests, confirmed that the PW-PS brine had altered the wettability of the mixed-wet chalk to more water-wet, explaining the high oil recovery results.

These findings suggest that PS is a promising additive for improving PW as an injection fluid in carbonate reservoirs when PW reinjection is necessary for reducing the challenges associated with its processing and disposal.

Introduction

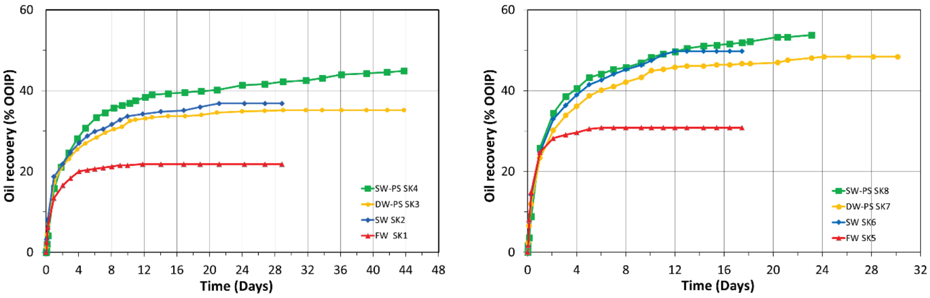
Produced water (PW) is a by-product of oil production that needs to be processed and disposed of in a cost-effective and environmentally friendly manner. PW contains a variety of components that can have negative environmental impacts (Fakhru'l-Razi et al. 2009). In mature oil fields, PW can make up 75% or even higher percentage of total production (Dudek et al. 2020). PW management in offshore environments typically involves either discharging treated water into the ocean or injecting it back into the reservoir. In Norway, more than 75 % of the PW is discharged into the ocean (Dudek et al. 2020), but regulations require that treated PW must meet environmental standards before being discharged (Azizov et al. 2021). As water production increases, processing facilities on offshore platforms may need to be modified to accommodate PW treatment, which increases the cost of disposal. To address environmental concerns, many oil companies consider re-injecting PW into the reservoir as a more sustainable and cost-effective solution (Wood 2019). PW re-injection is increasingly considered a desirable option, particularly for new fields, as regulatory authorities aim for zero discharge. PW re-injection can also support reservoir management, such as pressure support and increase sweep efficiency (Bedrikovetsky et al. 2011).

However, the effectiveness of PW re-injection is limited due to its high total dissolved solids (TDS) and impurities such as oil, grease, and bacteria. As a result, the recovery rate of oil using PW injection is generally low in carbonates (Dudek et al. 2020).

In comparison to PW, Smart Water EOR, which involves the use of specially treated water with controlled ionic composition and chemical properties, has shown improved oil recovery results. The improved performance of Smart Water EOR is attributed to its optimized chemical properties to change the wettability of the carbonate rock surface, which lead to enhanced oil mobilization, reduced scaling, and improved injectivity compared to PW injection (Puntervold and Austad 2008).

Injection of seawater (SW) in chalk reservoirs at high temperatures (T_{res} >100 °C) in the North Sea has been a tremendous success giving significantly higher oil recoveries for mixed-wet, highly fractured reservoirs. The estimated recovery from the Ekofisk chalk reservoir is 50 – 55 %OOIP after SW flooding (NPD 2023). The field observations have been confirmed in laboratory experiments on slightly water-wet outcrop Stevns Klint (SK) chalk cores, giving oil recoveries of 50 – 60 %OOIP both in spontaneous imbibition (SI) and viscous flooding experiments using SW as the injection brine (Puntervold et al. 2007b, Strand et al. 2008). The efficiency of SW over formation water (FW) as injection fluids has also been proven in the laboratory using reservoir cores from the Valhall field, another chalk reservoir in the North Sea (Webb et al. 2005). The main reason for the high oil recovery from these naturally fractured, low-permeable reservoirs is believed to be the ability of SW to induce increased capillary forces by wettability alteration toward more water-wet conditions. The wettability alteration is controlled by a symbiotic interaction between the active ions, calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulphate (SO_4^{2-}). Sulphate is the catalyst and needs to be present for the wettability alteration process to take place, involving the desorption of polar organic oil components (POC) from the chalk mineral surface (Zhang et al. 2007). The efficiency of SW can be improved by removing NaCl from the SW combined with spiking with SO_4^{2-} (Puntervold et al. 2015). At 90 °C, oil recovery using SW depleted in NaCl (SW0Na) increased from 37 to 47 %OOIP compared to ordinary SW and dramatically increased to 62 %OOIP when spiked with 4 times the SO_4^{2-} concentration of ordinary SW (SW0Na4S). Chromatographic wettability tests (CWTs) confirmed that the water-wet fraction of the rock surface increased with the efficiency of the modified SW. The Smart Water EOR observations on North Sea Chalk have also been confirmed using reservoir limestone (Austad et al. 2015). Oil recovery tests on preserved and restored reservoir limestone cores from the Middle East gave an oil recovery plateau of 21 %OOIP after FW injection. By changing the injection brine to Persian/Arabic Gulf SW (McKay et al.), the oil recovery further improved by 6 %OOIP. Finally, the oil recovery increased by an extra 6 %OOIP using GSW depleted in NaCl (GSW0Na), reaching an ultimate oil recovery plateau of 34 %OOIP (Austad et al. 2015). Kilybay et al. (2016) confirmed Smart Water EOR effects from carbonate reservoir cores from Abu Dhabi, in which the ultimate oil recovery was significantly increased compared to SW by increasing the sulphate concentration of SW (SW4S).

A study by Khan et al. (2022) was conducted to evaluate the potential of using polysulphate (PS) salts as an additive to brines for enhanced oil recovery (EOR) in carbonate reservoirs. The main constituents of PS are sulphate, calcium, potassium, and magnesium (ICL 2023), hence containing the ions needed for the wettability alteration of chalk (Zhang et al. 2007). The experiments were carried out using outcrop SK chalk, a rock material commonly used as an analogue to the North Sea chalk reservoirs, and has shown good reproducibility in carbonate wettability studies. Tests showed that 0.5 weight% (wt%) PS salt was >95 % soluble in SW and distilled water (DW). Spontaneous imbibition oil recovery tests on restored chalk cores confirmed that imbibition brines containing PS salt significantly improved oil recovery compared to the FW, **Figure 1**. The PS-containing brines were equally efficient as SW in wettability alteration of chalk.



(a) (b)

Figure 1: Oil recovery by spontaneous imbibition at (a) 90°C and (b)110°C performed on equally restored SK cores. The imbibing brines used were FW, SW, DW-PS, and SW-PS (Khan et al. 2022).

The PW from a reservoir will normally be a mixture of FW, aquifer water, and injection brine (Puntervold and Austad 2008). PW is an increasing problem in the industry due to the increasing PW/crude oil ratio, higher environmental focus, and stricter regulations. In previous experimental work on chalk by Puntervold et al. (2009), it was seen that PW could be made an efficient injection brine by mixing with SW, containing the wettability alteration ions SO_4^{2-}, Ca^{2+}, and Mg^{2+}, in PW:SW ratios of 2:1, 1:1, 1:2, 1:4, and 1:8. In that study it was found that as long as the injection brine contained a fraction of SW, it was more efficient in oil production than pure PW. In this paper, it was investigated if PW can be improved as injection brine by adding PS salt (PW-PS). PS addition is particularly relevant in areas where SW is not available for injection or mixing. Spontaneous imbibition and chromatographic wettability tests were performed to test if PW and PW-PS were able to change the wettability of mixed-wet chalk cores, mobilizing and producing more oil in secondary and tertiary mode at 90 and 110 °C. The efficiencies of both brines were compared against those of FW, SW, and other brines with PS additive.

Experimental work

Materials

Rock samples

Stevns Klint (SK) outcrop chalk, collected from a quarry near Copenhagen, Denmark, was used in these experiments. SK chalk consists of 98 % pure $CaCO_3$ of biogenic origin and is considered a good analogue for North Sea chalk oil reservoirs (Frykman 2001, Khan, Puntervold, et al. 2023). This outcrop has in previous laboratory studies shown similar physical properties and reproducibility in parametric studies (Khan, Strand, et al. 2023, Puntervold et al. 2015, Zhang et al. 2006). Studies using SK chalk have explored EOR strategies employing different injection brines, such as sulphate-rich polysulphate brine (Khan et al. 2022), carbonated water (Khan et al. 2023), brine with ionic liquid (Tafur et al. 2023) and ion-modified injection water (Khan et al. 2023) for chalk that produced rational reproducible results.

The cores were drilled in the same direction from the same block of rock sample, cut, and shaved to a specific dimension of 3.8 cm in diameter and ~7 cm in length. No fractures and heterogeneities were detected by visual inspection. Physical properties such as porosity, permeability, pore size distribution, BET surface area, etc. were measured. Water permeability and porosity were found to be 3-5 mD and 47-50 %, respectively. Small samples collected from the cores were used to measure the BET surface area, which was found to be ~2 m^2/g. Scanning Electron Microscope (SEM) combined with Energy-Dispersive X-ray Spectroscopy (EDS) was used for observing the structure of the porous medium and to determine the composition of the core material given in **Table 1**. Coccolith rings and their fragments, which are the building blocks of this rock material, can be observed in the SEM image shown in **Figure 2**.

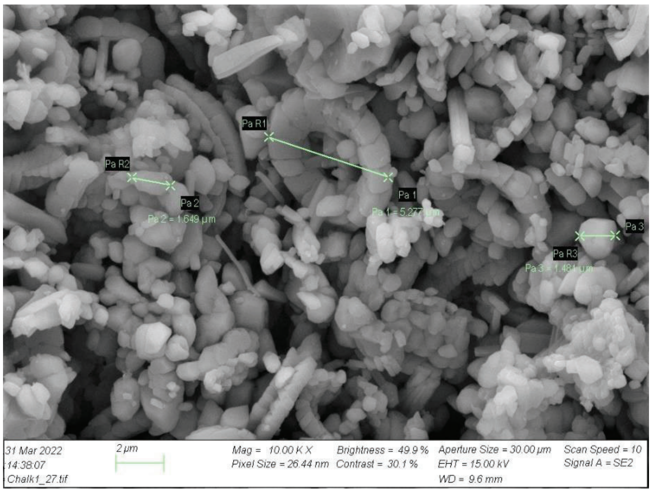


Figure 2: SEM image of virgin Stevns Klint outcrop chalk material at 10 000 times magnification.

Table 1: Elementary composition by atomic wt% of cations in SK outcrop.

Element	Calcium	Silicon	Sulphur	Potassium	Aluminium	Magnesium	Sodium	Total
Atomic (wt%)	98.54	0.57	0.44	0.22	0.13	0.08	0.02	100

The pore size distribution of a representative core sample was measured by mercury injection capillary pressure (MICP) and most of the pore sizes were in the range of 0.1 - 0.6 µm, **Figure 3**.

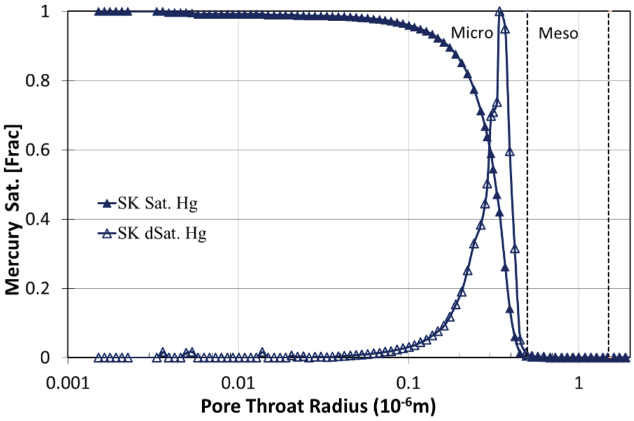


Figure 3: Pore size distribution of SK chalk measured by MICP.

The petrophysical properties of the SK chalk cores used in this work are given in **Table 2**.

Table 2: Petrophysical properties of the SK cores.

Core	SK1	SK2	SK3	SK4	SK5	SK6	SK7	SK8	SK9	SK10	SK11	SK12
Length, cm	7.1	7.1	7.1	7.2	7.0	6.9	7.1	7.0	7.3	7.0	7.0	7.2
Diameter, cm	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Pore volume, ml	38.6	39.1	39.1	40.1	41.3	38.6	37.9	40.0	39.9	39.3	39.0	38.5
Porosity, %	48.6	48.6	48.8	49.2	49.3	49.2	47.4	50.2	48.0	50.1	49.0	48.5
Water Perm., mD	4.1	4.7	3.8	3.8	4.1	4.7	3.8	3.8	3.5	3.4	3.3	3.5
BET specific surface area, m^2/g	2.0											

Crude oil

Stock tank oil (STO) with very low asphaltene content produced from a North Sea oil reservoir was used as a base for the Oil A used in these experiments. The stock tank oil was diluted with 40 wt% n-heptane, centrifuged overnight, and filtered through a 5 µm Millipore filter before storage. No precipitation of asphaltenes was observed. AN and BN were measured by potentiometric titration, using modified versions of ASTM D664 (ASTM International 1989) and ASTM D2896 (ASTM International 1988) developed by Fan and Buckley (2007). The AN and BN of the STO were found to be 2.90 mgKOH/g and 0.95 mgKOH/g, respectively. The respective values for the n-heptane diluted STO were determined to 2.18 mgKOH/g and 0.66 mgKOH/g, respectively, and this oil was named RES40.

Silica gel was used to remove the surface-active polar organic components (POC) from a batch of RES40 oil to prepare another oil, named RES40-0, having AN and BN close to ~0 KOH/g. Afterward, RES40 and RES40-0 were mixed in the proportion of 1:4 to obtain Oil A with lower AN (AN ~0.5 mg KOH/g). The reason behind this procedure is to have an oil that will result in sightly water-wet/mixed wettability after the restoration of SK cores (Standnes and Austad 2000). The final AN and BN of Oil A were measured to be 0.58 mgKOH/g and 0.30 mgKOH/g respectively. The density and viscosity of Oil A were found to be 0.81 g/cm^3 and 2.4 cP. The properties of the three oils are reported in **Table 3**.

Table 3: Oil properties.

Oil	$\rho_{20^\circ C}$ (g/ cm3)	$\mu_{23^\circ C}$ (mPa·s)	AN (mg KOH/g)	BN (mg KOH/g)
Stock tank oil	0.81	-	2.90	0.95
RES40	0.81	2.4	2.18	0.66
RES40-0	0.81	2.1	0.0	0.05
Oil A	0.81	2.4	0.58	0.30

Polysulphate

Polysulphate (PS), also known as polyhalite, is a naturally occurring salt mined from a polyhalite rock layer 1200 m below the surface in the Boulby mine located near the North Yorkshire coast of the United Kingdom. The deposition of polyhalite happened 260 million years ago in the Permian period and is believed to be the only source of PS worldwide (ICL 2023), **Figure 4**.

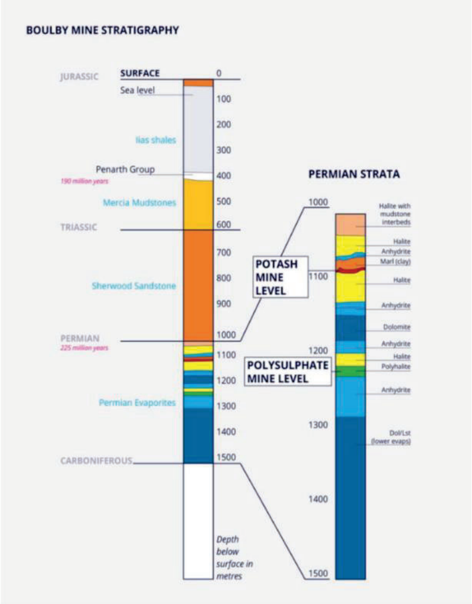
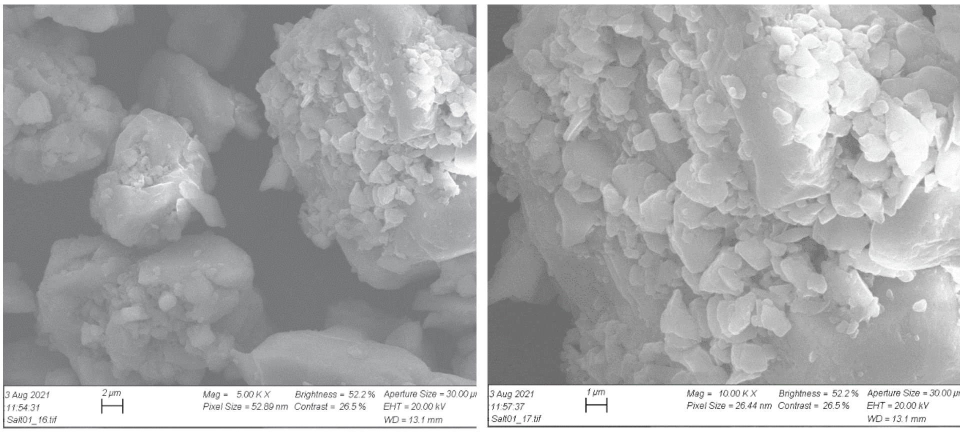


Figure 4: Stratigraphy of the Boulby mine where PS is found in the Permian strata 1200 m below the surface (ICL 2023).

The deposition is estimated to be 1 billion tonnes and mined PS is easily available and mainly used as a fertiliser today (ICL 2023).

The PS salt used in this study was provided by the ICL group. It had a slightly grey colour and was delivered in granulated to powder form. The diameter of the salt particles was predominantly in the range of 5 to 30 µm. High-resolution SEM images of the salt particles are shown in **Figure 5.**



(a) (b)

Figure 5: SEM images of a PS sample at (a) 5000X magnification and (b) 10000X magnification.

EDS analysis was performed to determine the elemental composition of a PS sample, and the atomic wt% of anions and cations present are given in **Table 4**.

Table 4: Elementary composition of PS by atomic weight % of anions and cations.

Anions		Cations	
Element	Atomic wt%	Element	Atomic wt%
Sulfur, S	85.4	Sodium, Na	9.3
Chloride, Cl	14.6	Magnesium, Mg	21.9
		Aluminium, Al	3.2
		Silica, Si	3.3
		Potassium, K	25.5
		Calcium, Ca	36.9

The salt composition was found to be dominated by sulphate anions and calcium, potassium, and magnesium cations. The PS salt was used, as delivered and without further treatment, as an additive to different brines to prepare injection brines containing the important wettability modifying ions (Ca^{2+} and SO_4^{2-}) for carbonate rocks.

Brines

Seawater (SW), formation water (FW), and produced water (PW) used in these experiments were made by dissolving reagent-grade salts in distilled water (DW) and filtering them through a 0.22 µm Millipore filter. The SW composition is based on the composition of North Sea SW. The FW and PW compositions are based on FW and PW from a North Sea chalk reservoir. The PS-containing brines; DW-PS, SW-PS, and PW-PS were made by mixing DW, SW, and PW, respectively, with 5.00 g PS per litre solution. The solutions were mixed for 6 days with a magnetic stirrer before filtration through a 0.22 µm Millipore filter. After filtering, the dried, insoluble particle residue was quantified by weight. It was found that more than 95 % of the PS dissolved in both DW and SW, while 81 % dissolved in PW, due to its higher salinity. Variations in the ion composition of the prepared brines were observed since PS is a naturally occurring salt. To minimize these variations, 20-liter stock solutions of DW-PS, SW-PS, and PW-PS were prepared and used throughout the experimental work. The ion compositions of the filtrated brines were analysed by ion chromatography (IC) and are given in **Table 5**.

SW0T and SW½T brines were used for the chromatographic wettability tests, which was developed by Strand et al. (2006) and is described later, to quantify the water-wet surface area of a carbonate core. SW½T is SW with added tracer ions, Li^+ and SCN^-, while SW0T is SW depleted in SO_4^{2-}. The total dissolved solids (TDS) of SW0T and SW½T were kept similar to that of SW by adjusting the concentration of NaCl. All brine compositions are listed in **Table 5**.

Table 5: Brine composition and properties.

Ions (mM)	SW	FW	PW	DW-PS	SW-PS	PW-PS	SW0T	SW½T
[K^{+}]	10	5.0	5.0	17.4	28.2	20.5	10.0	22.0
[Ca^{2+}]	13	29	31	15.2	29.6	41.0	13.0	13.0
[Mg^{2+}]	45	8.0	8.0	5.8	47.9	15.3	45.0	45.0
[Na^{+}]	450	997	1027	6.3	466.2	1000	460.0	427.0
[Li^{+}]	-	-	-	-	-	-	-	12.0
[Cl^{-}]	525	1066	1096	9.2	528.5	1072	583.0	583.0
[HCO$_3^{-}$]	2.0	9.0	13	-	-	-	2.0	2.0
[SO$_4^{2-}$]	24	-	1.0	31.5	55.9	30.8	-	12.0
[SCN^{-}]	-	-	-	-	-	-	-	12.0
pH	8.0	7.3	7.3	7.5	8.1	6.9	7.7	7.5
TDS (mg/L)	33390	62800	65000	4885	38140	69060	33390	33390
Density (g/cm^3)	1.024	1.040	1.040	1.002	1.025	1.045	1.024	1.024

Core restoration

Prior to the oil recovery experiments, the outcrop SK chalk cores were equally prepared and restored to the same initial fluid saturations and wettability.

Core cleaning

Because the chalk quarry is situated near the seashore, the pore surfaces have been exposed to the ions present in SW. The presence of initial sulphate ions can affect the adsorption of POC onto the chalk mineral surface and influence the wettability of the cores established during core restoration and consequently also the surface response to injection fluids (Austad et al. 2015). Therefore, all cores were initially cleaned by flooding 5 PV of DW at room temperature to remove easily dissolvable salts, particularly sulphate salts (Puntervold et al. 2007a). The cores were then dried at 90°C until a constant weight was reached.

Fluid restoration

Initial Water Saturation (S_{wi}). S_{wi} of 10 % FW was established using a desiccator, according to the procedure described by Springer et al. (2003). The cores were stored in a sealed container for at least 3 days to ensure an even distribution of ions throughout the cores.

Oil Saturation. A core with S_{wi} of 10 % FW was placed in a Hassler core holder, vacuumed and saturated with Oil A from both sides, followed by crude oil flooding, at 50 °C, of 1.5 PV in each direction. Each core was exposed to 4 PV of Oil A in total.

Core Aging. Finally, the core with initial water and oil saturations was wrapped in Teflon tape, to avoid unrepresentative adsorption of POC on its outer surface, placed in a steel aging cell surrounded by Oil A, and aged at 90 °C for 2 weeks to achieve a more homogeneous core wetting.

Oil recovery by spontaneous imbibition

Spontaneous imbibition (SI) experiments were conducted on the restored cores to evaluate the initial core wettability and the effectiveness of different brines as enhanced oil recovery (EOR) fluids.

The experiments were performed in pressurized steel imbibition cells at 90 or 110°C with a supporting brine pressure of 10 bar controlled by $N_{2\,(g)}$, **Figure 6**.

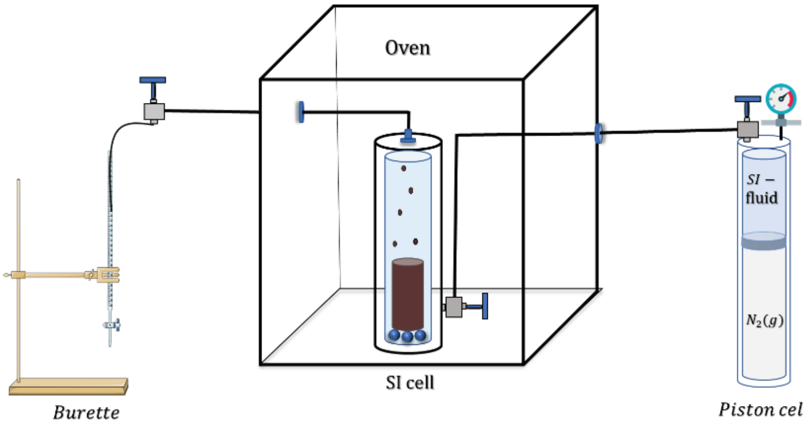


Figure 6: Schematic of spontaneous imbibition setup (Khan et al. 2022).

FW, SW, PW, DW-PS, SW-PS, and PW-PS were used as imbibition brines and the cumulative oil production was measured in the burette and calculated as a percentage of the original oil in place (%OOIP).

Chromatographic wettability test

The chromatographic wettability test (CWT), developed by Strand et al. (2006) was performed on imbibed cores to determine the fraction of water-wet surface area of the chalk core after the ultimate oil recovery had been reached. Sulphate ions have affinity to water-wet mineral surfaces, and a chromatographic separation between a tracer, such as thiocyanate or lithium, will only occur at the water-wet sites. The area between sulphate and thiocyanate or lithium elution curves, A_w, is a relative measure of the water-wet surface area. When a very water-wet core sample is available, the reference area, A_{ww}, could be measured for that rock type and a wettability index, I_{CW}, for the system, calculated (Piñerez Torrijos et al. 2019):

$$I_{CW} = \frac{A_w}{A_{ww}} \qquad \text{(Eq. 1)}$$

Where $I_{CW} = 0$ represents a completely oil-wet system, $I_{CW} = 0.5$ represents a mixed-wet to neutral system, and $I_{CW} = 1$ represents a completely water-wet system. The CWT is performed at room temperature.

After completing the spontaneous imbibition test, the core was mounted in a Hassler core holder and flooded to residual oil saturation (S_{or}) using a brine without sulphate and tracer (SW0T). Then the core was flooded with SW½T brine containing both sulphate and lithium tracer ions. Effluent samples were collected and analysed for the concentration of sulphate and lithium using ion chromatography.

Results and discussion

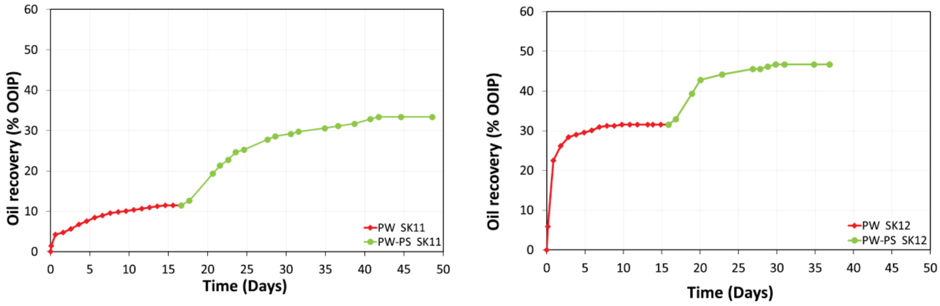
Energy consumption and related greenhouse gas emissions, due to PW handling from mature oil fields are increasing with the water-oil-ratio (WOR). In parts of the world, the PW is reinjected into the reservoir, and in other parts, PW is the only water source available nearby for water injection. In both cases, the oil recovery factor could improve if the PW was modified to behave as an EOR fluid; improving the reservoir sweep efficiency and reducing the S_{or}, prolonging the lifetime of the reservoir.

In this experimental work, it was investigated whether PW could be modified by adding PS salt to become an EOR-fluid with the potential of altering the wettability of chalk and improving the water displacement efficiency, with accelerated oil production as a consequence.

Modifying PW for efficient oil displacement in chalk

A brine with a composition typical of that of PW from a North Sea chalk reservoir (Puntervold and Austad 2008) was tested as a potential injection brine by performing SI tests on two equally restored SK cores at 90 and 110 °C. SI takes into account both the imbibition rate and the ultimate recovery, and provides valuable insights into the presence of positive capillary forces and the wettability of porous systems. Anderson (1986) stated that if water can penetrate an oil-saturated core, the core can be considered to be water-wet to some extent. Puntervold et al. (2021) previously demonstrated this concept by showing that a similarly restored SK chalk core using oil without POCs produced 75%OOIP in less than 120 minutes using FW as the imbibing brine, as a result of strongly water-wet mineral surfaces. In contrast, Puntervold et al. (2022) presented the results from a restored reservoir chalk core where no oil was mobilized by spontaneous imbibition with FW, confirming intermediate to oil-wet conditions.

At 90 °C, core SK11 reached a recovery plateau of 12 %OOIP after 12 days, while only 7 days were needed to reach a recovery plateau of 32 %OOIP for SK12 at 110°C, **Figure 7.**



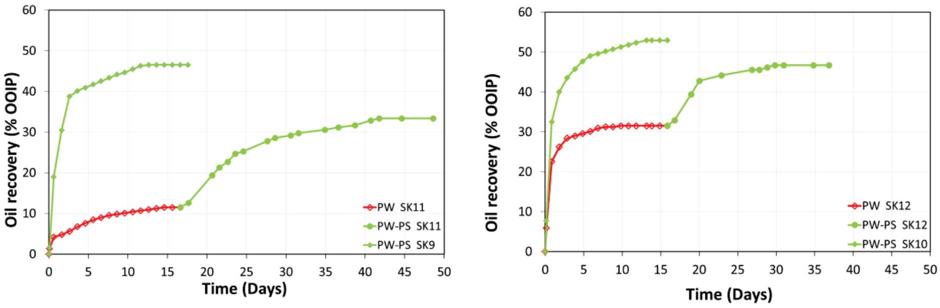
(a) (b)

Figure 7: Spontaneous imbibition oil recovery tests in (a) core SK11 at 90 °C and (b) core SK12 at 110 °C. Both cores were equally restored with S_{wi} = 10 % and exposed to Oil A. PW was used as imbibing brine in secondary mode followed by PW-PS in tertiary mode.

The modest oil recovery obtained shows that both cores exhibited slightly water-wet character. This observation is explained by the fact that PW does not contain the right proportion of necessary ions, Ca^{2+} and SO_4^{2-}, needed for chemical induced wettability alteration of the mixed-wet rock (Zhang et al. 2006), as does SW, which is known to be an EOR-fluid in chalk (Austad et al. 2008, Webb et al. 2005).

After 16 days when no significant change in oil production was observed, the imbibition brines were changed from PW to PW-PS. The oil-brine-rock system responded with a gradual and significant increase in oil mobilization from both cores confirming increased positive capillary forces causing continuing spontaneous water imbibition. At 90 °C a new recovery plateau at 34 %OOIP was reached after imbibition for a total of 42 days, corresponding to an additional recovery of 22 %OOIP by PW-PS imbibition. Only 30 days were needed to reach the new recovery plateau at 47 %OOIP at 110°C, of which an additional 15 %OOIP was produced by PW-PS imbibition. It is important to notice that the speed of imbibition was significantly higher at 110 °C than at 90 °C. The presence of Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions in the PS salt induced increased positive capillary forces by wettability alteration, mobilizing and producing the additional oil observed by PW-PS imbibition. This chemically induced wettability alteration is clearly temperature-dependent, as observed by both speed of imbibition and ultimate oil recovery, and as reported previously (Zhang et al. 2007).

To evaluate the efficiency of PW-PS in secondary mode, two new SK cores were equally restored with S_{wi} = 10% FW and exposure to Oil A. Spontaneous imbibition tests using PW-PS as the imbibing brine in secondary mode were performed on core SK9 at 90 °C and SK10 at 110 °C. The oil recovery results are presented in **Figure 8**, compared against the oil recovery results obtained by SI of PW-PS in tertiary mode.



(a) (b)

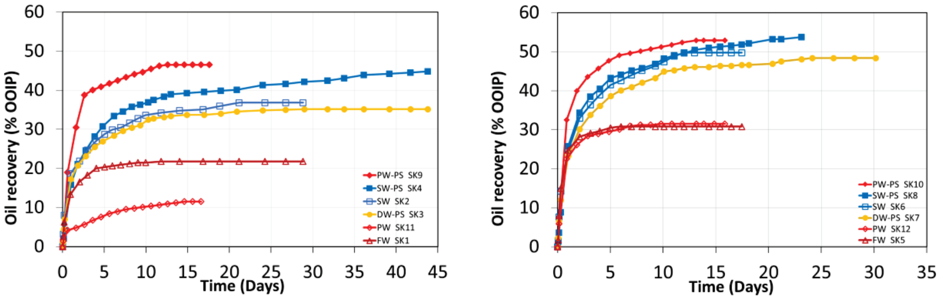
Figure 8: Comparing oil recovery by spontaneous imbibition of PW-PS in secondary and tertiary mode at (a) 90 °C (SK9 and SK11) and (b) 110 °C (SK10 and SK12). All cores were equally restored with S_{wi} = 10 % FW and exposure to Oil A.

Both the rate of imbibition and the ultimate recovery by PW-PS in secondary mode were significantly higher than by using PW in secondary mode. At 90 °C, core SK9 imbibed with PW-PS reached a recovery plateau of 47 %OOIP after 12 days, and 89 % of the oil was expelled after the first 5 days. It should also be noticed that the ultimate recovery by secondary PW-PS was 13 %OOIP larger than that by tertiary PW-PS, corresponding to a 38 % increase in oil recovery. At 110 °C, core SK10 imbibed with PW-PS reached an ultimate recovery of 53 %OOIP after 14 days, and after the first 5 days, 91 % of the oil was expelled. The extra oil recovered by secondary PW-PS imbibition compared to tertiary was 6 %OOIP, corresponding to an oil recovery increase of 13 %.

Examining the temperature effect in more detail it can be derived that the temperature effect is smaller on the oil recovery by PW-PS imbibition in secondary mode, with ultimate oil recoveries of 47 and 53 %OOIP obtained at 90 and 110 °C respectively, 6% higher at 110 °C. While in tertiary mode, PW-PS imbibition resulted in ultimate oil recoveries of 32 and 47 %OOIP at 90 and 110 °C respectively, 15% higher at 110 °C. Nevertheless, these results confirm that PS salt could be used as an additive to PW for it to behave as a Smart Water EOR-fluid at both 90 and 110 °C. A PW brine containing a modified, increased concentration of SO_4^{2-} seemed to be efficient in altering the wettability of the mixed-wet chalk cores at both temperatures. These results agree well with the previously published experimental study by Puntervold et al. (2009), showing that PW mixed with SW (which contains SO_4^{2-}) improved oil recovery noticeably beyond that obtained by pure PW. In areas where SW is scarce, PS as an additive to PW could be considered for EOR purposes in carbonate reservoirs.

Efficiency of PW-PS as imbibition brine

Even though PW initially did not contain a favorable composition to be considered a Smart Water for chalk reservoirs, by adding PS salt the PW-PS proved to be able to alter wettability, improving the oil recovery. But how efficient is PW-PS in comparison to other potential injection brines in chalk? The spontaneous imbibition results using PW-PS as imbibing brine in secondary mode were compared with the previously published results by Khan et al. (Khan et al. 2022) in which FW, SW, SW-PS, and DW-PS were used as imbibition brines at temperatures of 90 °C and 110 °C. The comparison results are shown in **Figure 9**.



(a) (b)

Figure 9: Oil recovery tests by SI on equally restored SK cores. The cores were imbibed at (a) 90 °C and (b) 110 °C using FW, PW, SW, DW-PS, SW-PS, or PW-PS in secondary mode. All cores were equally restored with S_{wi} = 10% FW and exposure to Oil A.

Since all SK cores were sampled from the same chalk block and similarly restored with FW and Oil A, the oil recovery results should be comparable. At 90 °C, **Figure 9(a)**, the SI results with PW and FW as imbibing brines suggest a slightly water-wet behavior because of the modest oil recovery of 12 and 22 %OOIP, respectively. PW and FW do not contain sulphate ions, that are catalysts for the wettability alteration at the chalk surface, hence a very water-wet behavior was not expected by imbibing these brines. It should be emphasized that the PW composition was based on the FW composition from the same North Sea chalk reservoir (Puntervold and Austad 2008), thus the low concentration of sulphate ions in PW, **Table 5**, is expected to have originated from seawater, as the injected brine in the field, or from dissolved rock minerals. However, the concentration is not high enough to cause any wettability alteration. With SW as the imbibing brine at 90 °C in core SK2, a substantial improvement in both the speed of imbibition and the ultimate oil recovery was observed. Now, 37 %OOIP was mobilized after 21 days compared to 12 and 22 %OOIP for PW and FW, respectively, showing that SW induced increased positive capillary forces mobilizing twice the amount of oil. When PS was added to SW in core SK4, the ultimate recovery was even higher, reaching an ultimate oil recovery of 45 %OOIP. By adding PS to DW in core SK3 the ultimate recovery plateau reached 35 %OOIP after 28 days, which is close to the result obtained for SW. However, the highest speed of imbibition and ultimate recovery at 90 °C was achieved using PW-PS in core SK10, resulting in an ultimate oil recovery of 47 %OOIP reached after only 14 days, which at that time was 8 %OOIP higher than the recovery obtained by SW-PS.

At 110 °C, **Figure 9(b)**, the oil recovery results by SI of FW, PW, SW, SW-PS, DW-PS, or PW-PS followed the same trends as those observed at 90 °C. The lowest oil recoveries of 31 %OOIP after 5 days were achieved with FW and PW in cores SK12 and SK5, respectively. The baseline oil production with FW and PW confirmed slightly water-wet conditions, and that the low SO_4^{2-} concentration in PW was insufficient to cause any increased positive capillary forces. When SW was used as imbibition brine in core SK6, the oil recovery increased to 50 %OOIP, confirming a significant increase in capillary forces mobilizing and producing an extra 19 %OOIP of crude oil. By adding PS to DW in core SK7, a brine with Smart Water properties similar to that of SW had been obtained, mobilizing and producing 49 %OOIP after 24 days, which is 18 %OOIP extra oil produced compared to that by FW imbibition. The highest oil recoveries were observed with SW-PS and PW-PS as imbibing brines in cores SK8 and SK10, respectively. With SW-PS as imbibition brine the ultimate oil recovery reached 54 %OOIP after 23 days, which was 4 %OOIP higher than the ultimate recovery obtained by SW imbibition. The most efficient Smart Water brine was PW-PS, reaching the ultimate recovery plateau of 53 %OOIP after only 14 days, a recovery plateau which is 22 %OOIP higher than that obtained by PW imbibition.

The ultimate oil recovery results from **Figure 9** are systemized in **Table 6**.

Table 6: Summary of ultimate oil recoveries obtained by SI at 90 °C and 110 °C

Imbibing fluid	FW	PW	SW	SW-PS	DW-PS	PW-PS
Ultimate oil recovery at 90 °C (%OOIP)	22	12	37	45	35	47
Ultimate oil recovery at 110 °C (%OOIP)	31	33	50	54	48	53
Temperature effect (Δ%OOIP)	9	21	13	9	13	6

Comparing the results from both 90 and 110 °C, PW-PS was observed to be the most efficient imbibition brine, slightly more efficient than SW-PS. By adding 5 g/L of PS salt, the concentration of Ca^{2+}, Mg^{2+}, and SO_4^{2-} significantly increased in DW, SW, and PW brines. In **Table 7**, the chemical compositions of all brines were compared.

Table 7: Comparison of brine compositions

Ions (mM)	SW	FW	PW	DW-PS	SW-PS	PW-PS
[Ca^{2+}]	13	29	31	15.2	29.6	41.0
[Mg^{2+}]	45	8.0	8.0	5.8	47.9	15.3
[SO_4^{2-}]	24	-	1.0	31.5	55.9	30.8
SO_4^{2-}/Ca^{2+} ratio	1.8	0.00	0.032	2.07	1.89	0.751
SO_4^{2-}/Mg^{2+} ratio	0.53	0.00	0.13	5.4	1.17	2.01
pH	8.0	7.3	7.3	7.5	8.1	6.9
TDS (mg/L=ppm)	33390	62800	65000	4885	38140	69060
Density (g/cm^3)	1.024	1.040	1.040	1.002	1.025	1.045

From the imbibition results in **Figure 9,** no direct link between ultimate oil recovery and pH of the imbibition brines could be established as the pH values varied from 6.9 to 8.1 in all brines, and no trend was observed. Additionally, there was no correlation between ultimate oil recovery and salinity, as both the highest and lowest ultimate oil recoveries were obtained at high salinity by imbibition of PW-PS and PW, respectively. The same conclusion can be drawn related to density, as there were no systematic density effects observed.

The EOR-effects are rather Smart Water effects linked to the compositions of the brines and more specifically to the concentrations of divalent ions present in the imbibing brines. The presence of both Ca^{2+} and SO_4^{2-} ions in the brine is crucial for an efficient wettability alteration, as suggested by the Smart Water model proposed by Zhang et al. (2007). FW and PW, which did not contain any sulphate, imbibed the least into the chalk, resulting in the lowest oil recoveries at both temperatures. A SO_4^{2-}/Ca^{2+} ratio close to 2, was observed in SW, DW-PS, and SW-PS. By comparing the compositions of the two most efficient spontaneous imbibition brines, PW-PS and SW-PS it can be observed that PW-PS has a salinity much larger than that of SW-PS, a Ca^{2+}-concentration of 41 mM, which is significantly higher than the 30 mM in SW-PS, a Mg^{2+} concentration three times lower and nearly half the SO_4^{2-} concentration compared to SW-PS. The PW-PS composition had a balanced SO_4^{2-}/Ca^{2+} ratio of 0.75. At the same time, the highest SO_4^{2-}/Mg^{2+} ratio of 2 was observed in PW-PS, suggesting that 2 SO_4^{2-} ions are present for every Mg^{2+} ion. It is well known that Mg^{2+} and SO_4^{2-} form an ion par in aqueous solutions according to the following reaction equation:

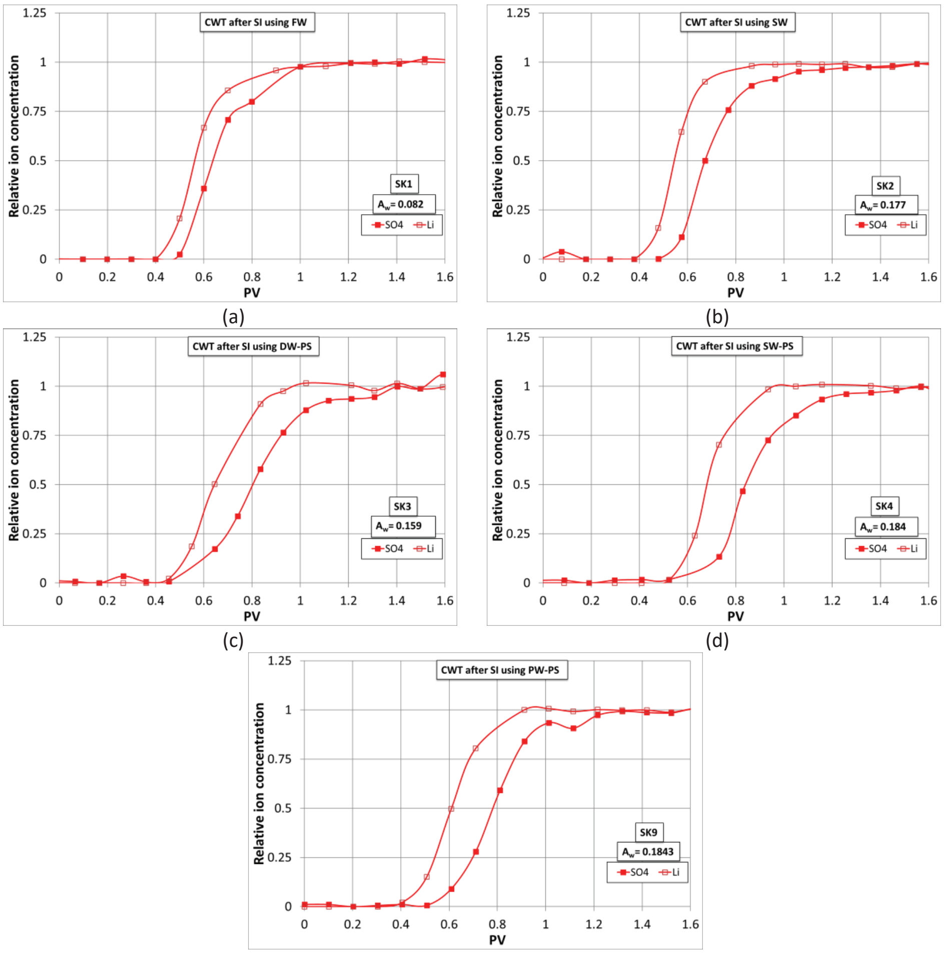
$$Mg^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow MgSO_4\,(aq) \text{ ………………….(Eq. 2)}$$

Thus, a lower SO_4^{2-}/Mg^{2+} ratio could result in less free SO_4^{2-} ions able to participate in the wettability alteration process by imbibition of SW-PS compared to PW-PS. Thus, the SO_4^{2-}/Mg^{2+} ratio could explain the slight difference in imbibition rate between SW-PS and PW-PS observed. A similar effect of decreased SO_4^{2-}/Mg^{2+} ratio on oil recovery by spontaneous imbibition was also observed in a previous study on chalk, in which the Mg^{2+} concentration of a modified injection water was increased to prevent precipitation of $CaSO_4$, but which also ended up with reduced oil recovery efficiency compared to that obtained in a modified brine of lower Mg^{2+} concentration (Khan et al. 2023).

In summary, the results from oil recovery by SI suggest that improved oil recovery by wettability alteration can be obtained by adding PS salts to any make-up brine tested, in the salinity range of ~5000 – 70000 ppm.

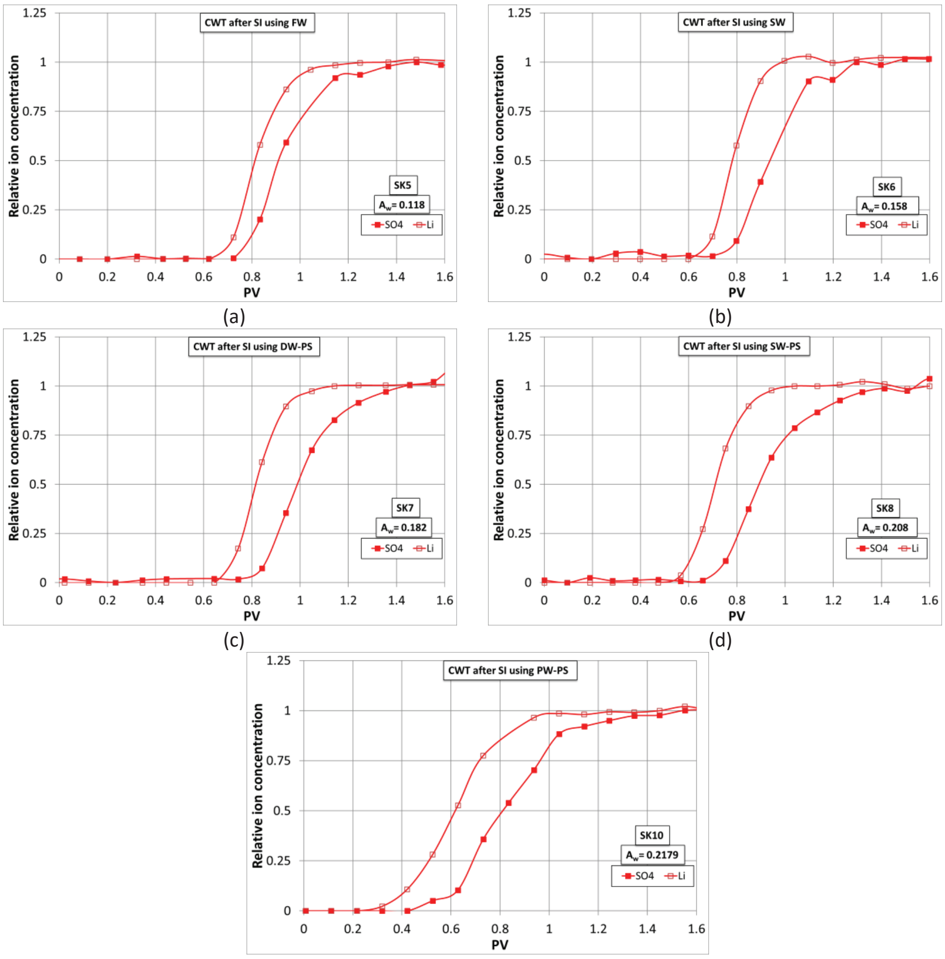
Determining the fraction of water-wet surface area

To confirm that the Smart Water brines used in this study have modified the rock surface wettability in the spontaneous imbibition process, a series of CWTs was performed to determine the fraction of water-wet surface area inside the cores. After the SI tests at 90 °C and 110 °C were completed, the cores were flooded to residual oil saturation at room temperature using the SW0T brine without any tracer or SO_4^{2-} ions, and then flooded with the SW½T, which contained Li^+ tracer and SO_4^{2-}. Effluent samples were collected and analyzed, and the separation between Li^+ and SO_4^{2-} elution curves were plotted for all cores imbibed at 90 °C in **Figure 10**, and for all cores imbibed at 110 °C in **Figure 11**.



(a) (b) (c) (d) (e)

Figure 10: Chromatographic separation after the SI tests at 90 °C using (a) FW, (b) SW, (c) DW-PS, (d) SW-PS and (e) PW-PS as imbibition fluids.



(a) (b) (c) (d) (e)

Figure 11: Chromatographic separation after the SI tests at 110 °C using (a) FW, (b) SW, (c) DW-PS, (d) SW-PS and (e) PW-PS as imbibition fluids.

The results from the CWTs are summarized in **Table 8**. A typical chromatographic separation area for a completely water wet Stevns Klint chalk core at ambient temperature is $A_w = 0.25$ (Khan et al. 2023) Using this number, the chromatographic wettability indices, I_{CW}, have been calculated based on Eq. 1, and are given in **Table 8**.

Table 8: Adsorption area, A_w, and calculated wettability index, I_{cw}, for SK cores at 90 °C and 110 °C

	T = 90 °C			T = 110 °C		
Imbibition brine	Core #	A_w	I_{cw}	Core #	A_w	I_{cw}
FW	SK1	0.082	0.323	SK5	0.118	0.465
SW	SK2	0.177	0.697	SK6	0.158	0.622
DW-PS	SK3	0.159	0.626	SK7	0.182	0.717

SW-PS	SK4	0.184	0.724	SK8	0.208	0.819
PW-PS	SK9	0.184	0.724	SK10	0.218	0.858

Remember that $I_{CW} = 0$ for a completely oil-wet chalk surface, and that $I_{CW} = 1$ for a completely water-wet chalk surface. The lowest I_{cw} values were observed with FW, giving $I_{cw} = 0.323$ at 90 °C and $I_{cw} = 0.465$ at 110 °C. These results confirm a significant reduction in the water-wet surface area after the core restoration, as FW imbibition should not promote any chemical induced wettability alteration because of unfavourable brine composition. For the two cores spontaneously imbibed with SW, SK2, and SK6, a significant increment in water-wet area corresponding to an increased wettability index to $I_{cw} = 0.697$ at 90 °C and to $I_{cw} = 0.622$ at 110 °C was observed, confirming wettability alteration toward more water-wet conditions after SW imbibition. After DW-PS imbibition the wettability indices obtained were $I_{cw} = 0.626$ at 90 °C and $I_{cw} = 0.717$ at 110 °C, which are close to the values observed for SW, confirming that DW-PS has a similar potential to alter the core wettability as does SW. SW-PS brine imbibition gave significantly higher oil recovery than the SW and DW-PS brines and the CWT also resulted in significantly larger wettability indexes of $I_{cw} = 0.724$ at 90 °C and $I_{cw} = 0.819$ at 110 °C. The highest wettability indexes were observed for the PW-PS brine with $I_{cw} = 0.724$ at 90 °C and $I_{cw} = 0.858$ at 110 °C. This brine also induced the most positive capillary forces and gave the highest oil recovery results in SI at both 90 °C and 110°C.

Benefits of implementing PW-PS injection

Water has been injected into oil reservoirs for pressure support and improved displacement for decades. For most oil reservoirs, the injected water source is chosen based on availability, implementation costs, and displacement efficiency. With time, the oil production goes down in maturing reservoirs, while the PW volumes increase. Today, PW is handled by disposal to sea or reinjection into the reservoir. With increased environmental focus and stricter regulations, the cost of PW treatment before disposal is increasing. Further restrictions will probably come in the near future, hence reinjection of PW will then be a reasonable choice. Prior to reinjection, PW needs pretreatment to reach an acceptable water quality to avoid injectivity problems.

The results in this study suggest that PS can be added to PW to behave as a Smart Water in carbonate reservoirs. PS should not significantly increase the PW treatment cost before reinjection but could potentially improve the displacement efficiency of the injection brine. In **Table 9**, the EOR-effects of SW, a standard injection brine, and PW-PS, a potential Smart Water, have been summarized and compared against the results obtained by FW and PW, two other potential injection brines.

Table 9: Summary of secondary ultimate oil recoveries, and the water-wet area obtained at 90 °C and 110 °C

	FW	PW	SW	PW-PS	Δ% by SW	Δ% by PW-PS
Oil recovery by SI at 90 °C (%OOIP)	22	12	37	47	118*	176*
Oil recovery by SI at 110 °C (%OOIP)	31	33	50	53	56*	66*
A_w at 90 °C	0.082	-	0.177	0.184	115**	124**
A_w at 110 °C	0.118	-	0.158	0.218	34**	85**

*   Base line from the average of FW and PW SI recoveries
** Base line from FW CWT

SW and PW-PS both significantly improved positive capillary forces and the oil mobilization compared to FW and PW, resulting in a significant increase in water-wet surfaces of the imbibed cores. Compared to baseline recoveries, the ultimate oil recoveries for SW increased by 118 and 56 % at 90 and 110 °C, respectively, accompanied by an increase in water-wet surfaces of 115 and 34 %. Compared to SW, a significant improvement was observed when PW-PS was used as imbibing brine, increasing the ultimate oil recoveries by 176 and 66 % and water-wet surfaces by 124 and 85 % at 90 and 110 °C, respectively.

The experimental results clearly demonstrated the beneficial effect of PS as a Smart Water additive to the injection brine for mixed-wet chalk. Increased concentrations of the divalent ions Ca^{2+}, Mg^{2+}, and SO_4^{2-} promoted increased positive capillary forces and oil mobilization, which is confirmed by increased water-wet mineral surfaces. Previous studies have also confirmed that SW and modified SW could be used as Smart Water in reservoir limestones (Austad et al. 2015, Kilybay et al. 2016) indicating a potential benefit of using PS minerals as an additive for reinjection of PW also in reservoir limestone.

Conclusions

The petroleum industry is facing increased PW/crude oil ratios and increased environmental focus, which limits PW disposal. In this study, the potential of using PS as an environmentally friendly chemical additive to PW, for it to behave as a Smart Water in chalk reservoirs, was evaluated. A combination of oil recovery tests by SI at 90 °C and 110 °C and wettability studies by CWTs were employed using FW, SW, DW-PS, SW-PS, PW, and PW-PS as imbibing brines. The following conclusions were drawn:

- FW and PW with low sulphate concentrations resulted in less positive capillary forces and low oil mobilization after SI in mixed-wet chalk.
- By adding PS to PW, a significant increase in positive capillary forces was observed in both secondary and tertiary mode.
- Oil recovery by SI of PW-PS in tertiary mode led to an ultimate recovery of 34 %OOIP at 90 °C, which is 22 %OOIP higher compared to the recovery obtained by PW. At 110 °C the ultimate oil recovery was 47 %OOIP, an additional 15 %OOIP produced compared to the production by PW.
- Oil recovery by SI of PW-PS in secondary mode resulted in oil recoveries of 47 %OOIP at 90 °C and 53 %OOIP at 110 °C. Compared to SW, which is considered a Smart Water in chalk, PW-PS increased the ultimate oil recovery with 10 %OOIP at 90 °C and 3 %OOIP at 110 °C.
- When comparing PW-PS with other imbibing brines such as FW, DW-PS, and SW-PS, PW-PS was found to be the most efficient Smart Water brine.
- CWTs confirmed that all PS brines had the ability to change the wettability of chalk toward a more water-wet condition, in line with the SI results.

These findings suggest that PS has significant potential as an additive to PW for EOR in carbonate reservoirs by wettability alteration.

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Carbonated Smart Water Injection for Optimized Oil Recovery in Chalk at High Temperature

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Abstract. Finding cost-efficient ways of increasing oil production with a low carbon footprint is the new challenge for the petroleum industry that wants to meet the net-zero emission goals by 2050. Smart water injection is an EOR process that increases oil production and delays water breakthrough by wettability alteration. Seawater is a smart water in chalk reservoirs, being especially effective at high temperatures. Different studies have shown that the effectiveness of seawater can be further improved by modifying the ion composition before injection.

Carbonated water (CW) has been proposed as a potential EOR fluid. In addition to producing extra oil, the reduction of greenhouse gas (CO_2) in the atmosphere can be achieved by using carbonated smart water as an injection fluid. The main mechanism behind increased oil recovery by injecting carbonated water is believed to be oil viscosity reduction and swelling, as the CO_2 is transferred from the aqueous phase to the oil phase. Wettability alteration has also been proposed as a possible mechanism, and this hypothesis is further investigated in this study along with other proposed mechanisms.

Stevns Klint outcrop chalk was used in this study, this material is recognized as an excellent analogue for North Sea chalk reservoirs. Optimized oil recovery by carbonated water in chalk was investigated at a high temperature (130°C) by flooding carbonated formation water (CFW) and carbonated seawater (CSW), to be compared with high saline formation water (FW) and seawater (SW) flooding. The oil/brine/rock/CO_2 interactions were tracked by measuring the pH of the produced water (PW) and by identifying any mineralogical changes by SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray) analyses. The solubility of CO_2 in different brines was measured and compared with simulation data performed by PHREEQC. The diffusion of CO_2 from the aqueous phase to the oil phase was analysed to check if enough CO_2 can be diffused from the carbonated water into the oil phase.

By flooding CSW in both secondary and tertiary modes, a slight increase in the oil recovery was observed and was found to be the best performing brine. The oil recovery was also slightly increased using CFW in tertiary mode after FW which does not behave like smart water for carbonates.

The solubility of CO_2 was low and increased by increasing pressure and decreasing brine salinity. The acidity of CW did not increase by increasing pressure. No changes in pore surface minerals were observed after CW flooding, confirming limited mineral dissolution. A mass transfer of CO_2 from the brine phase to the oil phase was confirmed in the experimental work, but a significant amount of CO_2 remained in the brine phase.

The main mechanism behind this extra oil observed using CW is most likely not linked to oil swelling and viscosity reduction or mineral dissolution which could affect the porosity and the permeability of the rock system. Wettability alteration is a more likely explanation but needs to be looked further into for confirmation.

1 Introduction

The global energy demand is increasing by more than 1% every year because of the growth of the population and the increase in per capita energy consumption in developing countries. Although energy production from renewable sources is showing strong growth in recent years, oil is still the biggest source of energy production [1]. Therefore, to meet the net zero carbon emission goal by 2050, it is important to find a better way to produce oil in an environmentally friendly manner. Carbon capture, utilization, and storage (CCUS) might be a solution where CO_2 will be captured and used as a product to produce more oil, and therefore, CO_2 will be stored permanently in the reservoir after permanent plug and abandonment.

Previous lab experiments and field trials have shown that injection of CO_2 can increase oil recovery by reducing oil viscosity and increasing sweep efficiency [2]. The injected CO_2 was not fully recovered and thus shows storage possibility. However, direct CO_2 injection shows gravity segregation and viscous fingering effect that causes early CO_2 breakthrough along with technical difficulties in handling CO_2. These problems can be minimized by injecting carbonated water (CW) without sacrificing CO_2 storage potential [3].

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Several mechanisms for CW EOR have been proposed in different literature [4]. The main mechanism behind extra oil recovery is believed to be the mass transfer of CO_2 from the water phase to the oil phase as the solubility of CO_2 is much higher in oil than in water [5-7]. This leads to oil swelling, reduction of interfacial tension (IFT) between oil and rock, and reduction of oil viscosity resulting in reconnection of isolated oil droplets, increases relative permeability of oil, and enhances the oil mobilization, thus increases sweep efficiency [3]. Wettability alteration due to CO_2 mass transfer was also proposed by Sohrabi et al. (2015). CO_2 dissolution into the oil phase destabilises the polar organic components of the oil attached to the rock surface and helps them to move. Decreases in the aqueous phase pH (in CW) also change the surface charges on the water/oil and water/rock interfaces which leads to subsequent changes in the wettability of the system and thus produces more oil [8].

The evolution of solution gas from the heavy oil caused by CO_2 dissolution is also considered one of the mechanisms for oil recovery by injecting CW [9]. The reaction between rock and CW resulting in rock dissolution and increase permeability by creating new a path to mobilize oil might also help to increase oil recovery [10].

Previously, our research has shown seawater (SW) works as smart water at high temperatures by changing the wettability of the reservoir. The effectiveness of SW can be further improved by removing NaCl from SW and spiking it with additional sulphate ions [11]. However, the preparation of this water demands additional energy to treat the water and obtain the desired compositions. Moreover, adding extra chemicals makes the injection less cost efficient. At high temperatures, non-stable sulphate concentration can lead to precipitation, affecting the porosity and permeability of the reservoir. Additionally, both the injection and the production facilities can experience severe scaling problems.

Therefore, there is a need for more environmentally friendly injection water that not only increases the oil recovery but also reduces the risk of precipitation. Injection of carbonated water can be a good alternative for the carbonate reservoir [4]. Many researchers reported extra oil recovery in carbonates by injecting carbonated water along with CO_2 storage possibilities [2].

Initial research done on carbonated water injection (CWI) in the 1940s by the Oil Recovery Corporation reported an extra 15% oil production when CW was injected after conventional water flooding [12]. Lake et al. (1984) have reported additional oil recovery of 26% in the tertiary mode by injecting CW in case of light oil. Recently, extensive research was conducted by Herriot Watt Institute of Petroleum Engineering Centre on CWI for oil recovery by core flooding and micro model which showed extra oil recovery both in the secondary and the tertiary mode [8]. Kilybay et al. (2016) performed a comparative oil recovery experiment by flooding different smart waters and carbonated smart water in carbonate reservoir core plugs and experienced extra oil recovery (~14%) for carbonated smart water injection. This extra oil recovery was attributed to the impact of CO_2 mass transfer from brine to oil inducing a viscosity drop, local flow diversion and trapped oil swelling. Carbonate dissolution and pore enlargement were also proven through NMR porosity and ICP-MS studies [14]. Sand pack flooding experiments conducted by Mosavat (2014) showed it is possible to store CO_2 by injecting CW. Kechut et al. (2011) showed about 47 - 51% of total CO_2 injected can be stored by carbonated water injection through numerical simulations and laboratory experiments.

The objective of this work is to determine if CW can induce EOR effects in chalk and to determine which mechanisms may be behind such effects. Thus, we compared the oil recovery performance of different core floods by injecting different carbonated brines at high temperatures in equally restored chalk cores. The reasons behind the extra oil observed were discussed. The solubility of CO_2 in different brine was studied by experimental work and simulations. The mass transfer of CO_2 from the brine phase to the oil phase was also confirmed through experimental work.

2 Experimental sections

2.1. Core Material

Outcrop Chalk collected from Stevns Klint (SK) quarry, near Copenhagen, Denmark, was used in this experiment. Cores were drilled from the same chalk block in the same direction and cut and shaped to the desired diameter of 3.8 cm and the desired length of 7 cm. All cores were inspected visually, and no visible fractures and distinct heterogeneities were found. These outcrop chalk cores consisted of 98% pure biogenic $CaCO_3$ and are similar to North Sea chalk reservoir cores. SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray) analyses were done to see the changes in the minerals before and after the exposure to different carbonated brines. The specific surface area, (BET), porosity, and permeability of the cores were measured, and the values measured were found to be similar to previously published data [11, 16-21]. The properties of the cores are given in Table 1.

Table 1. Physical properties of the SK cores.

Core #	BET m^2/g	Porosity (%)	Water Permeability k_w (mD)	Pore volume (mL)
SK-3	2.0	48.5	3.7	38.7
SK-4		49.5	3.8	40.9
SK-6		45.4	4.1	36.3
SK-11		47.2	3.8	38.3

2.2 Crude Oil

A low asphaltenic stock tank oil with an acid number (AN) of 2.90 mg KOH/g and a base number (BN) of 0.95 mg KOH/g was used as base oil. This base oil was diluted with 40 weights % of heptane, centrifuged, and filtrated through a 5 µm Millipore filter. The AN of that diluted oil is found to be

~2.1 mg KOH/g and no precipitation of asphaltenic material was observed during storage after filtration. The surface active polar organic components were removed from a batch of the base oil using silica gel that provided an oil of ~0 AN. When the diluted oil and silica-treated oil were mixed, an oil (Oil A) with AN of 0.58 mg KOH/g and BN of 0.30 mg KOH/g was obtained which was used in the experiments. AN and BN of the oil samples were analysed by potentiometric titration. The density and viscosity of the prepared oil were determined to be 0.81 g/cm^3 and 2.4 cP, respectively.

2.3 Brines

Brines used in this experiment were made by mixing deionized water (DI) and reagent-grade salts. All the brines were mixed overnight by magnetic rotation and filtered through a 0.22 µm Millipore filter. SW composition is based on the seawater composition from the North Sea and the FW composition is based on the formation water from a North Sea Chalk reservoir. The properties of the brines are given in table 2.

Table 2. Properties of brines.

Ions(mM)/ Properties	SW	FW
$[Na^+]$	450.1	997.0
$[K^+]$	10.1	5.0
$[Ca^+]$	13.0	29.0
$[Mg^{2+}]$	44.5	8.0
$[Cl^-]$	525.1	1066.0
$[HCO_3^-]$	2.0	9.0
$[SO_4^{2-}]$	24.0	0.0
TDS (g/L)	33.34	62.83
Density (g/cm^3)	1.02	1.04
Bulk-pH	7.8	7.3

Carbonated seawater (CSW) and carbonated formation water (CFW) were prepared by equilibrating access CO_2 (g) with the respective brine in a pressure cylinder at 6-7 bar and 23 °C. The equilibrated carbonated brine was then moved to a separate cylinder at a higher pressure, so no gas cap was formed.

2.4 Core restoration

2.4.1 Establishing initial water saturation (S_{wi})

All cores were initially cleaned by flooding 5 PV of deionized (DI) water at room temperature to remove easily dissolvable salts, especially sulphate salts as described by Puntervold et al. (2007). The cores were then dried at 90°C to a constant weight. The initial formation water saturation (S_{wi}) of 10% was established by using the desiccator technique [22]. After they had reached 10% initial water saturation with formation water, the cores were stored in a sealed container for 3 days to allow an even ion distribution within the cores.

2.4.2 Oil exposure

The cores were then flooded with 4 PV of Oil (1.5 PV in each direction) at 50°C. Finally, the cores were wrapped in Teflon tape to avoid unrepresentative wetting on the outer surface and aged in the same oil for 2 weeks at 90°C to achieve a more homogeneous core wetting.

2.5 Oil Recovery by Spontaneous Imbibition

Spontaneous imbibition (SI) experiment was performed on a restored core to evaluate the degree of water wetness after core restoration. The experiment was performed at 110°C and 10 bar using formation water as the imbibing brine to avoid any chemically induced wettability alteration. The produced oil was collected in a glass burette that has a resolution of 0.1 ml. The volume of oil produced was calculated as % original oil in place (OOIP) versus time. The experimental setup is depicted in the following figure 1.

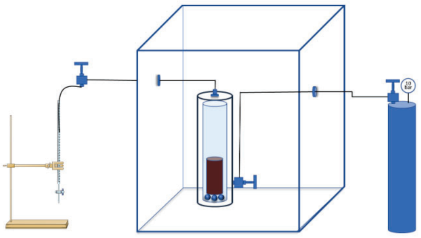


Fig. 1. Schematic of the setup used for spontaneous imbibition experiment.

2.6 Oil Recovery by Viscous Flooding (Forced Imbibition)

All experiments were performed at 130°C. The restored cores were mounted in the Hassler core holder with a confining pressure of 20 bar and a back pressure of 10 bar to prevent boiling. The cores were then successively flooded with different injection brines in secondary and tertiary mode at a constant injection rate of 1 PV/Day. When the recovery plateau was reached, the injection rate of the tertiary injection fluid was increased 4 times (4 PV/Day) to observe any end effects. The pressure drop was recorded during the experiment. Samples of produced water were collected during the experiment, and the pH of produced water were measured to catch any chemical reactions during the brine injections. The oil recovery, pressure drop, and the pH of the produced water was plotted against the PV brine injected. The experimental setup is illustrated in figure 2.

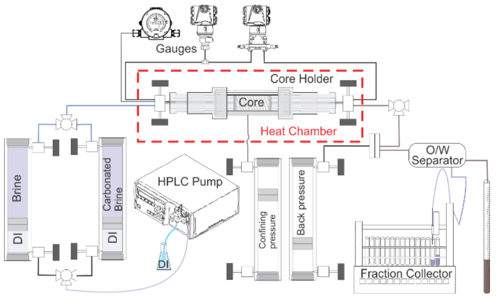


Fig. 2. Schematic of flooding setup.

2.7 Solubility of CO_2 in brines

The solubility of CO_2 in brines at 60°C was measured in the pressure range from 10 to 200 bar. 150 ml of a specific brine (DI, SW, FW) was mixed with 150 ml of CO_2 (g) at 10 bar in a pressured cylinder. The 2-phase system with a CO_2 gas cap above the brine was then temperature equilibrated overnight at 60°C. At each pressure stage the CO_2 – brine systems were mixed and allowed to equilibrate into 2 phases before a single flash of the equilibrated carbonated brine phase was performed. A small volume of the carbonated brine was flashed to standard conditions (SC). The pressure was maintained in the sample cylinder during the flash experiment. The mass of brine collected in the flash apparatus and liberated gas volume at SC was measured by a gasometer. The GOR as mg CO_2 per gram of brine was calculated based on the average of 3 flash experiments at each pressure stage. The pH of the carbonated brine was also measured in freshly taken samples after each flash experiment at ambient conditions.

2.8 Simulation of CO_2 solubility using PHREEQC

PHREEQC (version 3) software was used to simulate the solubility of CO_2 in different brines. The pH of the brines equilibrated with CO_2 was also simulated at specific pressure points at 60°C. The simulated data were then compared with the experimentally obtained data.

3 Results and discussion

3.1. Solubility of CO_2

To understand the potential of carbonated brine in EOR and the storage capacity of CO_2 in aquifers, it is important to understand the solubility of CO_2 in brines at pressure and temperature. Therefore, flash experiments were conducted to measure how much CO_2 is soluble in different brines at 60°C at a wide range of pressures. The amount of dissolved CO_2 in FW, SW, and DI water is presented in figure 3, as an average of the result from 3 flash experiments. The experimental data is also compared with simulated data obtained from PHREEQC.

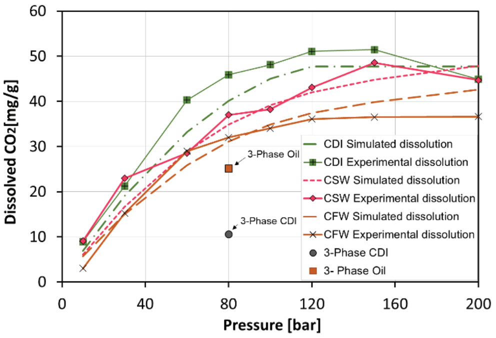


Fig. 3. Solubility of CO_2 in different brines at 60°C was plotted against pressure. Continuous lines are representing experimental data and dotted lines are representing the simulated data. 2 single points are representing the solubility of CO_2 in the water phase and the oil phase when both phases are present.

The experimental results show that the solubility of CO_2 gradually increases with the increase in pressure, but no significant increases are observed at pressures above 100 bar. CO_2 becomes a supercritical fluid when temperature and pressure exceed 31°C and 73 bar, without affecting the solubility of CO_2 in the brine phase. The solubility of CO_2 also depends on the salinity. The highest solubility is observed in DI water, and it decreases with increasing salinity. Thus, the formation water having the highest salinity (62830 ppm) showed the lowest solubility. However, the solubility difference was not more than 40% for FW and DI water at any pressure stages above the critical CO_2 pressure. The solubility of CO_2 in brines is low with maximum values of 50 mg/g in DI water. The solubility is less than 10 mg/g in all the brines at 10 bar which is the injection pressure for all the flooding experiments that will be presented in the next section.

The solubility of CO_2 in DI, SW, and FW has also been simulated using PHREEQC. The results from the simulations are presented in figure 3 and are in line with the experimental data, confirming the low CO_2 solubility at any pressure. This confirms that PHREEQC could be used to estimate CO_2 solubility in other brines or at other process temperatures.

The experimental data is aligned with simulated data and previously published experimental data by Duan et al. (2006) and Spycher and Pruess (2004).

The main mechanism behind extra oil recovery by carbonated water is the mass transfer of CO_2 from the water phase to the oil phase as the solubility of CO_2 is much higher in oil than in water. This phenomenon has been investigated in a 2-phase flash experiment at 80 bar and 60°C. CDI water at 80 bar and 60°C was equilibrated with the same amount of stabilized Oil A. Single flash experiments were performed from both equilibrated phases to SC.

At 80 bar and 60 °C, the CDI is able to dissolve 45 mg CO_2/g DI. After equilibrating with the same amount of crude oil, the amount of CO_2 in DI water was reduced 4 times down to 11 mg/g, while the amount of CO_2 transferred to the Crude oil Phase was 25 mg/g, giving a gas/oil ratio about 2.5 times higher than the gas/water ratio. Thus, this experiment confirms that CO_2 in carbonated water could be transferred to the oil phase as claimed by several researchers [5-7]. This transportation of CO_2 is because of the chemical potential difference between the two phases. But the amount of CO_2 that could be transported from carbonated water is very limited, so it is hard to believe that swelling and viscosity reduction of the oil phase could be the main mechanisms for enhancing oil recovery.

The brine phase collected from the single flash of carbonated water was collected, and the measured pH values for the individual brines at ambient conditions are presented in figure 4.

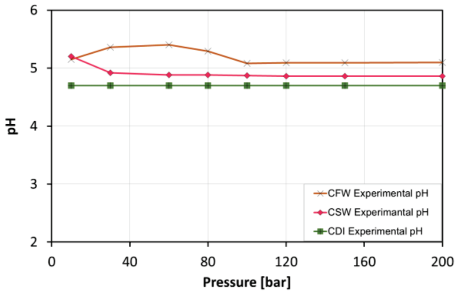


Fig. 4. The pH of different carbonated brines at different pressure and constant temperature (60°C). pH was measured at ambient conditions.

The pH was in the range of 4.7 to 5.2 for all brines and independent on the equilibrating pressure. CFW showed a slightly higher pH (~5) while CDI showed the lowest pH (~4.7).

Carbonic acid (H_2CO_3) is formed by dissolving CO_2 into different brine which is a weak acid (eq. 1). Carbonic acid is then rapidly separated into carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) (eq. 2 and 3) which provide hydrogen ions that give lower pH values (~5).

$$CO_2\ (aq) + H_2O \rightleftharpoons H_2CO_3 \tag{1}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{3}$$

The constant pH values at different pressure points prove that the concentration of protons (H^+) cannot be increased by increasing the amount of CO_2 in the brine phase as we observed by increased pressure. Simulation of the pH of different carbonated brine using PHREEQC confirmed the same trend, figure 5. The simulated pH is lower than the measured because the pH was measured in ambient conditions.

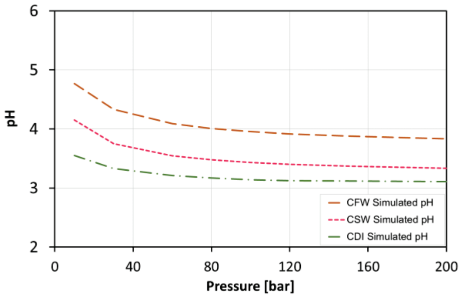


Fig. 5. Simulated pH of different carbonated brines at different pressure and constant temperature (60°C).

As the concentration of protons (H^+) cannot be increased with an increase in pressure, the chemical effect of carbonated water in EOR cannot be increased by increasing pressure.

3.2. Initial wetting of the restored cores

All oil recovery studies performed on equally restored SK chalk cores were taken from the same block to minimize the variation in physical core properties. Spontaneous imbibition (SI) is a practical way to approach and quantify the wettability of oil/brine/rock systems [25]. Both the speed of imbibition and the ultimate recovery gives valuable information to describe the core wettability after the core restoration. SI experiments could easily be performed at reservoir temperature, to reduce uncertainties regarding physical fluid properties and temperature effects. A spontaneous imbibition test was performed on the restored core SK-3 at 10 bar at 110°C. FW was used as the imbibing brine to exclude the effect of chemical induced wettability alteration during the test. The result is presented in figure 6.

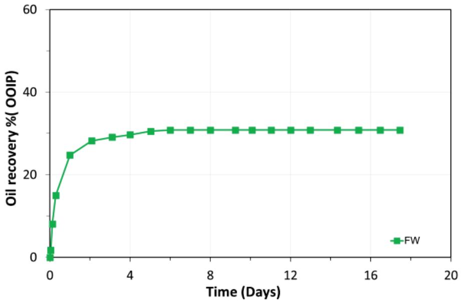


Fig. 6. Spontaneous imbibition into oil (AN=0.58 mgKOH/g) saturated (Swi=10%) chalk core at 110°C using FW as imbibing brine with a constant pressure of 10 bar. Oil recovery (% OOIP) was plotted against time (Days).

The Oil recovery reached its plateau at around 31% of OOIP on the 7th day, confirming positive capillary forces and that the core wettability is clearly on the water wet side.

A simplified wetting index only based on SI experiments can be used to calculate the wettability [26]. The degree of water-wetness can be quantified by a modified Amott water index ($I^{*}_{W\text{-}SI}$) (eq. 4) using a very water-wet core as a reference core.

$$I^{*}_{W-SI} = \frac{SI_C}{SI_{WWC}} \qquad (4)$$

SI_{WWC} is the oil recovery (% OOIP) by spontaneous imbibition from a strongly water-wet SK reference core which have not been exposed to any crude oil. The value of the modified Amott water index is 1 for a strongly water wet core and 0 for a neutral to strongly oil wet core.

To calculate the modified Amott water index for SK cores, we have used a strongly water-wet SK core as the reference core described by Piñerez Torrijos et al. (2019). The reference core was restored with FW, S_{wi}=10%, heptane as oil phase, and FW was used as imbibing fluid at 23°C. A rapid oil production occurred, reaching a recovery of 68% OOIP after 40 minutes and an ultimate recovery of 71% OOIP after 4 hours. Therefore, the value of SI_{WWC} is 71. SI_C for the assessed SK-3 core is 31. $I^{*}_{W\text{-}SI}$ for core SK-3 calculated by eq. 4 is then equal to 0.44 which suggests that the core has intermediate water wetness.

3.3. Flooding experiment

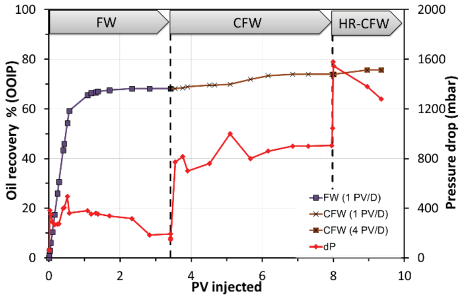
To evaluate the effectiveness of different types of injection brines on oil production, we have used equally restored sister cores of core SK-11, SK-6, and SK-4.

After core restoration, the cores were flooded at 130°C with different injection brines in both secondary and tertiary modes. The experiments were maintained by 20 bar confining pressure and 10 bar back pressure. The injection rate was constant and was 1 PV/D in all experiments performed. In the end, the injection rate was increased four times to evaluate any end effects. 4 different injection brines were used, formation water (FW), seawater (SW), carbonated formation water (CFW), and carbonated seawater (CSW). The carbonated brines were equilibrated with CO_2 gas at 6-7 bar, before the carbonated brine phase was transferred to a separate cylinder. The amount of CO_2 dissolved in the carbonated brines used for injection was then close to 5 mg CO_2/g of liquid. All injection brines were pressurized to 10 bar to match the back pressure of the system before injection.

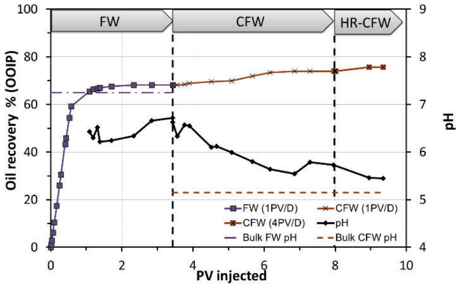
In the first flooding experiment on core SK-11, FW was injected in secondary mode at a rate of 1 PV/D. The pressure difference between the inlet and outlet of the core was monitored. An ultimate oil recovery plateau of 68 %OOIP was reached after 2 PV was injected, figure 7a. The pressure drop (ΔP) gradually increased and reached the maximum value of 450 mbar after 0.5 PV was injected before it declined and stabilized at 150 mbar.

The pH in produced water samples was measured and compared with %OOIP in figure 7b. The first produced water was observed after 0.5 PV was injected (60 %OOIP). The produced water pH was close to 6.5, slightly lower than the bulk FW pH of 7.2.

After 3.5 PV injection, the injection brine was switched to CFW, figure 7. During the next 5 days (5 PV), 5% extra oil was mobilized. The ΔP immediately increased from 150 mbar to 800 mbar which could not be explained by a change in the viscosity of CFW. With 4 times increase in ΔP it is difficult to pinpoint if the extra oil mobilized is a result of the CFW or increased viscous forces.



(a)



(b)

Fig. 7. Oil recovery tests on SK-11 core at 130°C. The flooding sequence was FW-CFW at a flooding rate of 1 PV/D. Oil recovery (%OOIP) was plotted against the PV injected and (a) average ΔP over the core, (b) pH of the produced water samples. At the end the injection rate was increased 4 times to 4 PV/D. Black dotted vertical lines are representing the change of injection fluid or change of injection rate. Coloured dotted horizontal lines represents the bulk pH of the injected fluids.

During CFW injection the pH in produced water samples went down below 6, confirming the presence of CFW which have a bulk pH of 5.2.

Since the chalk cores used in this experiment are mainly composed of calcite minerals, $CaCO_3$ dissolution could happen in presence of water, and $CaCO_3$ breaks into Ca^{2+} and CO_3^{2-} ions. CO_3^{2-} that take up a proton (H^+) from water and becomes HCO_3^- leaving OH^- behind. On the other hand, CO_2 dissolved in water will form a weak Carbonic acid, H_2CO_3 which turns to H^+ and HCO_3^-. Then Ca^{2+} can take two ions of HCO_3^- and becomes soluble $Ca(HCO_3^-)_2$ while OH^- and H^+ combine and become H_2O. Thus, the weak carbonic acid system is buffered in the porous media. This chemical process is illustrated simply in figure 8. The chemical equilibrium depicted in the figure does not change too much regardless of which brine (FW, SW, or DI) is being used.

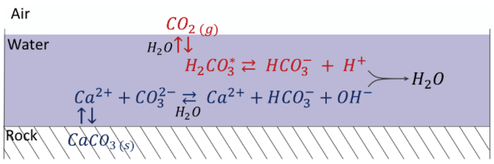


Fig. 8. Simple illustration of chemical processes happening inside the core in presence of both $CaCO_3$ (s) and CO_2.

Therefore, the carbonate is working as a buffer to the injected CFW and increases its pH. Nevertheless, a change in pH can change the reactivity of the polar organic components (POC) towards the positively charged calcite rock surface as seen in the equations below.

$$\mathbf{R-COOH} + H_2O \rightleftharpoons R-COO^- + H_3O^+ \tag{5}$$

$$R_3N\!: + H_2O \rightleftharpoons \mathbf{R_3NH^+} + OH^- \tag{6}$$

Negative charged POC (R-COO$^-$) has the strongest affinity towards the positively charged calcite surface [28]. A reduction in pH could theoretically reduce the amount of R-COO$^-$ species and affect wettability, but the pK$_a$ values for Naphthenic Acids described in Eq. 5 are typically below 4.5 [29] and will not significantly change the amount of non-protonated carboxylic acids.

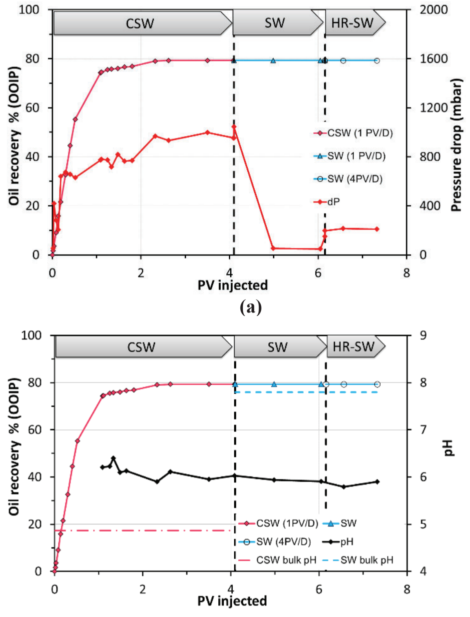
However, the pressure difference during CFW was four times higher than FW. If viscous forces are important in the oil mobilization this could also cause higher oil recovery.

According to Wiebe and Gaddy (1940), the solubility of CO_2 reduces with an increase in temperature. In our experiment, the injection fluid was prepared at room temperature and then injected into the core at high temperature. The significant increase in pressure drop development is most likely linked to gas liberation and a third fluid phase in the pore system.

Many researchers have claimed that when carbonated water (CW) is injected into the carbonate reservoir, the acidic nature increases the dissolution of carbonate minerals which could promote an increase in porosity and permeability [31-34]. These changes in petrophysical properties help to increase oil recovery by creating a new flow path. $CaCO_3$ and $MgCO_3$ are carbonate minerals that can easily react with carbonated water. FW has a high concentration of both Ca^{2+} and Mg^{2+} ions which will limit the dissolution of carbonates even though the pH is somewhat reduced, as illustrated in figure 8. If there was a new flow path created during the oil recovery experiment in figure 7, the pressure drop should have been reduced.

After the oil production reached its plateau during CFW injection, the injection rate was increased from 1 PV/D to 4 PV/D to observe the effect of viscous forces and any end effects. A marginal extra oil mobilization of 1.5 %OOIP. The pH of the produced water was somewhat lower than at 1 PV/day, which could be explained by that the injection fluid has less time to interact with the minerals.

In the second oil recovery experiment on core SK-6, CSW was flooded in secondary mode followed by SW in tertiary mode. Injection of CSW gave an ultimate oil recovery of 79 %OOIP which was reached after 2.5 PV injected, figure 9.



(a)

(b)

Fig. 9. Oil recovery tests on SK-6 core at 130°C with a back pressure of 10 bar. The flooding sequence was CSW-SW-HRSW. The flooding rate was 1 PV/D followed by a higher rate (HR) of 4 PV/D at the end. Oil recovery % (OOIP) was plotted against the PV injected of respective brine and (a) the average ΔP around the inlet and the outlet of the core, (b) the pH of the produced water. Black dotted lines are representing the change of injection fluid or change of injection rate. Colored dotted lines are representing the bulk pH of the injected fluid.

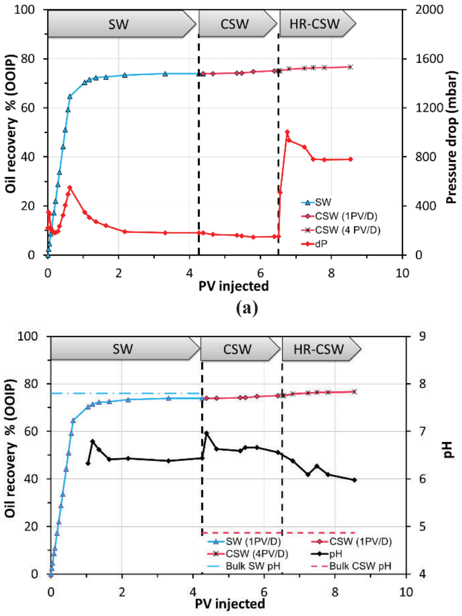
The ΔP was gradually increased during the hole CSW injection of 4 PV, even though water breakthrough took place after 0.5 PV injected. As previously discussed, the solubility of CO_2 reduces in higher temperatures and free CO_2 gas may promote the increase in ΔP.

After switching to SW, no extra oil mobilization was observed, but a significant decline in ΔP developed. This clearly indicates that free CO_2 liberated during CSW injection is taken up by SW and a new 2-phase flow system of Oil A and brine reestablished a more normal ΔP of 80 mbar. The results clearly indicate that CO_2 liberated from the brine phase trapped in the pore system is not easily diffusing into the residual oil but is being taken up in SW when that is passing through.

Increasing the injection rate 4 times did not mobilize any extra oil, but the ΔP increased to 200 mbar confirming typical pressure drop performance for a 2-phase fluid system in a heterogenous core. The pH of produced water is slightly acidic with a pH close to 6 during injection of both CSW and SW injection. This is slightly above the bulk pH of CSW and significantly below the bulk pH of SW.

Comparing the recovery results from FW-CFW injection (figure 7), and CSW- SW injection (figure 9), the CSW is significantly more efficient than FW in secondary mode. We know that SW behaves as a Smart Water and is able to change wettability and improve the sweep by inducing more positive capillary forces [11, 35]. To be able to evaluate if the significant improvement in the oil recovery during CSW injection is a result of wettability alteration by the ions present in the SW, or if the CO_2 present in the aqueous phase also contributes to the extra mobilized oil, a third core flooding experiment was performed on core SK-4 by injecting SW followed by CSW.

SW injection in secondary mode gave an ultimate oil recovery of 74 %OOIP after 2 PV injected. The water breakthrough was observed after 0.5 PV injected when 65 %OOIP was recovered. The experimental result is presented in figure 10.



(a)

(b)

Fig. 10. Oil recovery tests on SK-4 core at 130°C with a back pressure of 10 bar. The flooding sequence was SW-CSW-HR CSW. The flooding rate was 1 PV/D followed by a higher rate (HR) of 4 PV/D at the end. Oil recovery % (OOIP) was plotted against the PV injected of respective brine, and (a) the average pressure drops around the inlet and the outlet of the core, (b) the pH of the produced water. Black dotted lines are representing the change of injection fluid or change of injection rate. Coloured dotted lines are representing the bulk pH of the injected fluid.

The ΔP profile is more normal and follows the same trend as observed during secondary FW injection when no gas phase is present, figure 7. The highest ΔP of 500 mbar was observed after 0.6 PV, gradually declining to 170 mbar when the oil recovery plateau was reached. The PW pH was almost constant and was around 6.5 during the SW injection.

After 4 PV, the injection brine was changed to CSW. During the next 3 PV, a slight increase of 1% OOIP extra oil was observed, indicating a tiny effect of the CO_2 present, supported by a slight decline in the PW pH towards 6. The ΔP during CSW injection indicated no free gas phase developing, and a low and stable ΔP of 150 mbar was observed, peaking at 1000 mbar during high-rate injection, before stabilizing again at 800 mbar. The significant increase in injection rate and ΔP had only a minor effect on oil mobilization, improving the recovery by only 2 %OOIP.

The overall recovery results confirm that by changing the chemistry of the injection brines, significant changes in ultimate oil recoveries could be observed. SW behaves as a Smart Water in mixed wet chalk, and the SW injection improved the ultimate oil recovery of 74% OOIP compared to baseline oil recovery using FW giving 68% OOIP. By adding CO_2 to the brine phase, carbonated brines could be formed. By injecting CSW in secondary mode an ultimate oil recovery of 79% OOIP was reached which is significant above SW recovery. Tertiary injection of CFW after FW and CSW after SW injection indicates smaller EOR effects.

The experimental results clearly demonstrate that the amount of CO_2 that could be dissolved in the brine phase is very limited. A significant amount of the CO_2 will still remain in the brine phase after equilibrium with the crude oil. The classical explanation linked to swelling and viscosity reduction of the oil phase is not likely the main mechanism for the extra oil mobilized during CW injection.

To evaluate the EOR mechanism of carbonated brines, we need to understand what could happen at the mineral surfaces linked to mineral dissolution processes and/or wettability alteration which we know could improve the sweep efficiency in water displacement processes in the presence of CO_2. We clearly observe a pH reduction during CW injection which due to mineral dissolution which was described in figure 8.

3.4. SEM and EDX analysis

Carbonated water will affect the mineral dissolution of calcite as described in figure 8. The effect of carbonate water exposure on mineral composition and pore surface minerals have been investigated by performing SEM and EDX analyses. In table 3, the mineral composition of SK Chalk in atomic weight % retrieved from EDX analyses before carbonated brine exposure is given in Table 3.

Table 3. Atomic weight % of SK cuttings retrieved from EDX before carbonated brine exposure.

Element	Na	Mg	Al	Si	S	K	Ca
Atomic %	0.02	0.13	0.19	0.81	0.54	0.23	98.06

The result confirms that SK chalk is very pure, consisting of more than 98% $CaCO_3$. The rest of the minerals are silicate minerals, Quartz, Clay, and/or Feldspars.

A Scanning Electron Microscopy (SEM) picture of the sample is given in figure 11.

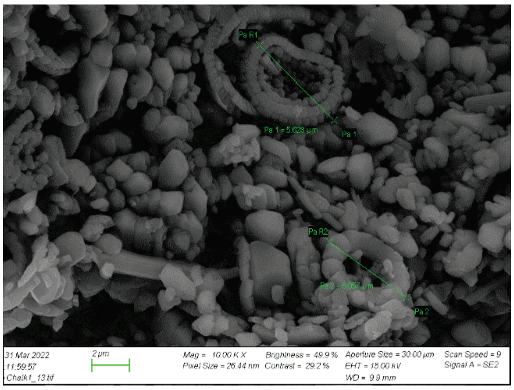


Fig. 11. SEM photo of the core sample before oil recovery test.

The presence of the intact coccolith ring confirms the biogenic origin of the Chalk.

After the core flooding experiments with carbonated brines, rock samples from the flooded cores were taken, dried, and analysed by SEM and EDX to track any mineralogical or visual changes in the mineral surfaces. Figure 12, 13, and 14 is representing the SEM photos from core SK-11, SK-4, and SK-6. Compared with figure 11, no visual changes on the mineral surfaces after carbonated brine exposure were detected. The coccolith rings are still intact and the grain sizes of the rock fragments are similar. No significant changes were found in the elements after the exposure by EDX.

The unchanged cation composition confirms negligible mineral dissolution by carbonated water. A few PV with carbonated brine is not enough to significantly affect the mineral surfaces when we have 2 m^2 of mineral surfaces in one gram of Chalk. At the same time, the calcite dissolution in brines with a high Ca^{2+} concentration as we have in FW and SW should be low due to the common ion effect.

However, Kono et al. (2014) observed significant dissolution of carbonate minerals by SEM. They reported smaller and smoother grains after carbonated water exposure and observed a significant increase of Ca^{2+} in the effluent brine. But in these core experiments, the total pore volume of fluid injected was several hundred, and without reporting injection rates. It is apparent that high injection volumes and rates could cause carbonate dissolution. Riazi (2011) found even sandstone is corroded by carbonated brine due to prolonged exposure to CWI for 2 weeks at the process conditions of 2000 psi and 38°C, which was a static exposure test, not a flooding experiment.

In our experiments, we have flooded SK cores with only about 4 PV which is more realistic to what could happen in the main part of the reservoir. Exposure with several PV with carbonated brines is more realistic to near wellbore effects for injection wells.

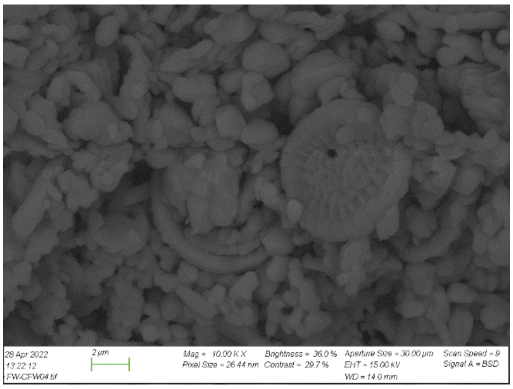


Fig. 12. SEM photo of chalk sample from core SK-11 after the oil recovery test by brine flooding (FW-CFW-HR CFW).

Fig. 13. SEM photo of chalk sample from core SK-4 after the oil recovery test by brine flooding (SW-CSW-HR CSW)

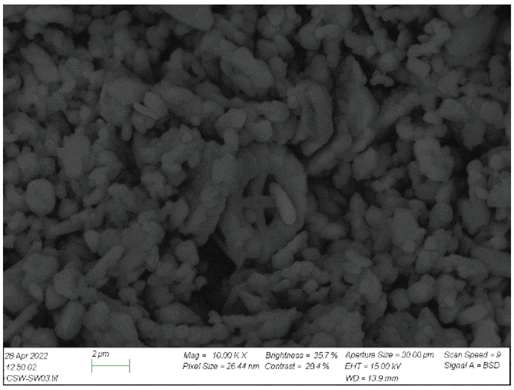


Fig. 14. SEM photo of chalk sample from core SK-6 after the oil recovery test by brine flooding (CSW-SW-HR SW)

4 Conclusions

Stevns Klint chalk was exposed to different carbonated brines at 130 °C to evaluate the effect of carbonated brines as an EOR fluid. The studies were coupled with CO_2 solubility experiments with 2 and 3 phases (CO_2, brines, and oil), as well as PHREEQC simulations. The main findings of this study were:

- The solubility of CO_2 in brine was low and depends on brine salinity. After reaching the super critical conditions of CO_2 the solubility did not increase significantly. The experimental solubility studies validated a relatively good performance of the PHREEQC simulator.
- Oil recoveries were slightly increased in chalk at high temperature both in secondary and tertiary mode. A mechanism linked to swelling and viscosity reduction of the oil phase is not likely be a main mechanism for the extra oil.
- Dissolution of $CaCO_3$ in presence of carbonated brines can also contribute to change in petrophysical properties and thus produce extra oil. However, no changes on pore surface minerals after flooding with carbonated brines were observed by SEM and EDX analyses.
- Wettability alteration might play a vital role in increasing oil recovery but need further investigation.

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VII

Positive Capillary Forces: The Key for Optimized Oil Recovery in Low-Permeable Cores.
Md Ashraful Islam Khan, Skule Strand, Tina Puntervold, Aleksandr Mamonov.
Peer reviewed paper presented in the 36th International Symposium of the Society of Core Analysts, October 2023, Abu Dhabi, UAE.

Paper VII

Positive Capillary Forces: The Key for Optimized Oil Recovery in Low-Permeable Cores

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Abstract. In recent years, Smart Water injection has gained attention as a promising Enhanced Oil Recovery (EOR) technique for both sandstone and carbonate reservoirs. Laboratory studies have shown that Smart Water can significantly improve oil recovery by altering the pore surface wettability in cores towards more water wet conditions. The wettability alteration creates increased positive capillary forces which improves the microscopic sweep efficiency leading to higher ultimate oil recoveries.

The flow of water and oil in reservoirs is controlled by viscous, gravity, and capillary forces. Spontaneous imbibition experiments conducted on restored cores gives a direct measurement of capillary forces. When formation water (FW) as the imbibing brine spontaneously infiltrates the porous system and displaces oil, capillary forces contribute to the oil mobilization. If we observe a gradually and significant increase in oil mobilization when FW is substituted with an injection brine with different ion compositions, this confirms increased positive capillary forces and that the injection brine behaves as a Smart Water.

Numerical models in reservoir simulation primarily focus on viscous forces and often neglect the direct influence of capillary forces on oil mobilization. Despite the availability of capillary pressure (Pc) modelling capabilities which represents capillary forces, the impact or sensitivity of Pc is very low in numerical studies on field scale. To demonstrate the importance of capillary forces in the oil displacement process, a series of oil recovery tests have been performed on low-permeability heterogeneous carbonate chalk cores restored to different initial wetting states. The tests include viscous flooding (VF) and spontaneous imbibition (SI) oil recovery experiments. The results shows that capillary forces play a crucial role in the oil recovery process. Highest ultimate oil recoveries from cores with highest positive capillary forces and oil recovery declines as the capillary forces decreases. Only minor changes in capillary forces have a significant impact on ultimate oil recoveries. The results are in line with Smart Water EOR observations in both Carbonate and Sandstones, where increased positive capillary forces significantly improve the ultimate oil recovery compared to FW.

This study provides valuable insight into the underlying mechanisms of Smart Water EOR and highlights the importance of positive capillary forces in oil recovery processes from heterogeneous systems. It also highlights the importance of core restoration in front of SCAL analyses. It also highlights that capillary forces need to be included when results from laboratory experiments are discussed, and in numerical models to correctly describe the fluid flow in reservoir systems.

1 Introduction

The mobilization of oil from porous rock systems is driven by viscous, gravity, and capillary forces. The ultimate recovery of oil in COBR (Crude oil, Brine, Rock) systems during water injection on a core scale is influenced by various factors such as pore size distribution, oil and water interactions with mineral surfaces, interfacial tensions, fluid viscosities, and applied forces. These factors are crucial in determining the effectiveness of individual drive mechanisms for oil mobilization. The significance of capillary forces and flooding rates in oil recovery has been extensively studied by several authors in since last century, including Hassker et al. (1944), F.M. Perkins (1957), de Haan (1959), Constantinides and Payatakes (2002), Tie and Morrow (2005), Ortiz-Arango and Kantzas (2009), Okoro (2018), Arab et al. (2020), Aslanidis et al. (2021). Their research has shed light on the importance of understanding the role of capillary forces and optimizing flooding rates to enhance oil recovery in carbonate reservoirs.

Reservoir simulation models typically focus on the effects of viscous and gravitational displacement forces and to a large extent neglecting contribution from capillary forces. However, capillary forces can be included in the model through Pc. Numerical simulators commonly incorporate capillary pressure (Pc) in various forms, although the specific modelling approach can vary. However, it is worth noting that many field-scale numerical studies show limited sensitivity or impact of Pc on simulated recoveries.

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In three-dimensional heterogeneous pore networks, the injection brine tends to follow preferential pathways through highly permeable pores with less restrictions. As a result, the displacement of oil from less accessible and low permeable pores heavily relies on the presence of positive capillary forces and spontaneous imbibition (SI).
During water injection in reservoirs with radial flow geometry, low laminar flow rates are expected in the central part, away from the injection and production well. At these low flow rates, time-dependent wettability alteration processes could occur promoting increased capillary forces, endorsing water imbibition into unswept pores, thereby increasing the oil mobilization and overall oil recovery by improved sweep efficiency.

When the differential pressures in the reservoir are high, particularly near the injection and production wells, viscous forces play a significant role in displacing oil efficiently. However, it is hypothesized that at locations with low or negligible viscous forces, capillary forces become dominant in the oil displacement process. In this study, the importance of capillary forces in the oil recovery process from heterogeneous cores have been investigated by comparing oil recoveries through spontaneous imbibition (SI) and low-rate viscous flooding (VF). The experiments were conducted using restored outcrop chalk cores at elevated reservoir temperatures. To minimize variations in the presence of capillary forces, optimized core restauration procedures were implemented. Furthermore, the study aimed to compare the effect of capillary forces on displacement efficiency and ultimate oil recoveries at static conditions with FW, and during dynamic change in capillary forces using seawater (SW) which behaves as a Smart Water.

2 Experimental

2.1 Core Material

The chalk material used in this work was collected from the Stevns Klint (SK) quarry in Denmark. The chalk is very pure and consist of 98% biogenic CaCO3, similar to North Sea chalk reservoirs [10]. All cores were taken from the same block, drilled and shaped to 38 mm in diameter and 70 mm in length. Cores were visually inspected and had no visible fractures or heterogeneities.

Table 1 provides the physical core properties measured, which are consistent with previous published data [10-12].

Table 1. Physical properties of the SK cores.

Core #	Porosity (%)	Water Permeability k_w (mD)	Pore Volume (mL)	BET m^2/g
SK0	48.5	4.3	30.6	2.0
SK1	49.1	4.2	38.2	
SK2	49.2	3.8	38.6	
SK3	48.4	4.1	38.6	
SK4	48.6	4.7	39.1	
SK5	47.3	3.8	38.2	
SK6	49.5	3.9	40.9	
SK7	48.5	4.8	38.6	
SK8	48.6	4.2	39.8	
SK9	47.8	4.1	38.9	
SK10	48.1	4.0	37.8	

Mercury injection capillary pressure (MICP) measurements were performed by Stratum Reservoir, Stavanger, to evaluate the pore throat size distribution of the rock material and is given in **Fig. 1**.

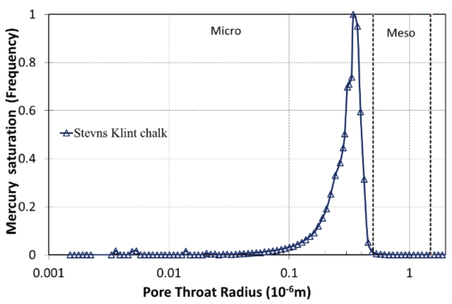

Fig. 1. Pore throat size distribution by MICP for SK outcrop chalk material.

Under the scanning electron microscope (SEM), it is possible to see the grain structure in detail. Cocolithic rings and their fragments as well as the heterogeneity of the chalk surface are clearly visualized in **Fig. 2**.

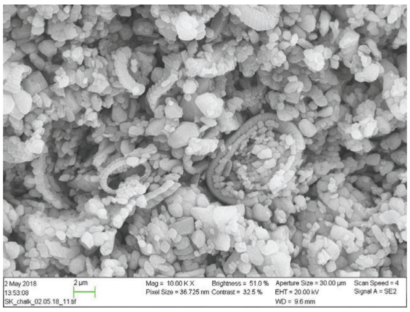

Fig. 2. SEM image of uncleaned SK outcrop chalk at 10000X magnification.

2.2 Crude Oil

A low asphaltenic stock tank oil was used as base oil with an acid number (AN) of 2.90 mg KOH/g and a base number (BN) of 0.95 mg KOH/g. This base oil was diluted with 40% heptane and filtered through a 5 µm Millipore filter to obtain an oil with an AN of ~2.1 mg KOH/g. The surface active polar organic components were removed using silica gel to obtain an oil with ~0 AN. Mixing the diluted oil and silica-treated oil resulted in Oil A with an AN of 0.58 mg KOH/g and BN of 0.30 mg KOH/g. AN and BN of the oil samples were analyzed by potentiometric titration. Measured Oil A density was 0.81 g/cm3 with a viscosity of 2.4 cP at ambient conditions.

2.3 Brines

Reagent-grade salts were mixed with distilled water (DW) to prepare synthetic seawater and formation water brines used in the experiments. All brines were filtered through a 0.22 µm Millipore filter after overnight mixing by magnetic rotation. The composition of seawater (SW) was based on North Sea seawater, and the formation water (FW) was based on a North Sea Chalk reservoir. Table 2 provides the properties of the brines.

Table 2. Properties of brines.

Ions	SW (mM)	FW (mM)
Na^+	450.1	997.0
K^+	10.1	5.0
Ca^{2+}	13.0	29.0
Mg^{2+}	44.5	8.0
Cl^-	525.1	1066.0
HCO_3^-	2.0	9.0
SO_4^{2-}	24.0	0.0
TDS (g/L)	33.34	62.83
Density (g/cm^3)	1.02	1.04
Bulk-pH	7.8	7.3

2.4 Core restoration

To ensure accurate and comparable experimental results, all Stevns Klint (SK) cores were precleaned with DW to remove easily dissolvable salts prior to core restoration that could affect the initial core properties (Puntervold et al., 2007). To minimize number of experimental variables, all restored cores have the same initial water saturation and have been exposed to the same amount of oil.

2.5 Initial water saturation (S_{wi})

The precleaned cores were dried at 90°C to a constant weight. Then 10% initial water saturation (S_{wi}) with formation water (FW) was established using the desiccator technique described by Springer et al. (2003). After reaching the target $S_{wi} = 0.10 \pm 0.01$ by weight, the core was equilibrated in a closed container for at least 3 days to ensure even ion distributions inside the core.

2.6 Oil exposure

The core with established Swi was mounted in a hassler core holder, vacuumed to vapor pressure of water, and saturated and flooded with the oil, 1.5 PV in each direction at 50°C. The core was then wrapped in Teflon tape to avoid unrepresentative wetting on the outer surface before aging in the same oil at 90°C for 2 weeks to establish a more homogeneous core wetting.

2.7 Oil Recovery by Spontaneous Imbibition

Spontaneous imbibition (SI) experiments were carried out on restored cores surrounded by the imbibing brine. Based on the speed and cumulative oil production, this method is a direct measurement of the efficiency of positive capillary forces to mobilize oil from heterogeneous pore systems.

Fig. 3 describes the experimental setup with controlled back pressure, allowing experiments to be performed at higher temperatures to describe presence of capillary forces in cores exposed to oils with and without polar organic components (POC). The SI setup was designed in a manner that the core can be imbibed by the brine from all sides.

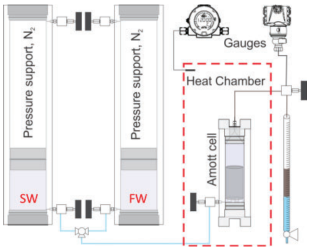

Fig 3. Schematic setup for spontaneous imbibition of a restored core at elevated pressure and temperature using FW and/or SW as Imbibing brines (IB).

Produced oil was calculated as percentage of original oil in place (%OOIP) versus time. The wettability as Amott water index ($I_{w_{SI}}$) can be calculated for a restored core when the reference for a very water wet core of the same kind is known, $(\%OOIP)_{ref}$ [14].

$$I_{w_{SI}} = \frac{(\%OOIP)_{core}}{(\%OOIP)_{ref}} \tag{1}$$

2.8 Oil Recovery by Viscous Flooding (Forced Imbibition)

Viscous flooding experiments, also known as forced imbibition, were conducted to study the oil recovery potential from a restored core with applied viscous forces. The restored core was placed in a Hassler core holder with a confining pressure of 20 bar and a back pressure of 10 bar. Brine injection was performed at a constant rate, controlling the applied viscous forces. The pressure drop and the oil recovery were recorded and presented against the volume of brine injected. The experimental setup is illustrated in **Fig. 4**. Viscous flooding experiments were carried out at 90 and 130 °C using FW or SW brines at an injection rate of 1 PV/day.

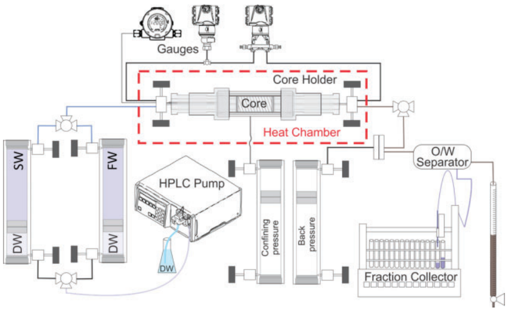

Fig. 4. Schematic viscous flooding setup in hassler core holder at elevated pressure and temperature using FW and/or SW as injection brines.

3 Results and Discussion

The mobility and fluid flow of oil and water in porous rock systems is controlled by viscous, gravity, and capillary forces [15]. Numerical models based on Darcy's law are focusing on the viscous forces to describe fluid flow in reservoirs, without directly considering the contribution of capillary forces in oil recovery experiments.

To demonstrate the importance of capillary forces in the oil mobilization processes, a series of oil recovery experiments were performed on low-permeability heterogeneous Stevns Klint outcrop chalk cores restored to initial state with only limited amount of positive capillary forces. The tests combine spontaneous imbibition (SI) and viscous flooding (VF) experiments to verify presence of capillary forces, and how capillary forces influence oil mobilization during viscous flooding experiments at static and dynamic wettability alteration processes with Smart Water.

The SK chalk is known to be a very good reference to the North Sea chalk reservoirs [10]. It belongs to the same chalk deposition taking place more than 65 million years ago having the high porosity and low permeabilities. The pore size distribution for SK chalk obtained from Mercury injection capillary pressure (MICP) test is presented in **Fig. 1**. A heterogenous pore size distribution was observed with the main parts of pores in the micro–pore region with pore throat radius less than 500 nm.

Heterogeneous sedimentary rocks with small pore sizes are capillary systems. With a wettability on the water wet side, positive capillary forces are present, and water could imbibe and mobilize trapped oil in the pores. This is clearly demonstrated in an Amott test performed on a SK chalk core SK0 with pore space of 30.6 ml restored with an initial brine saturation (S_{wi}) of 10% and 90% heptane (S_o) as oil phase. When SK0 was Spontaneous Imbibed with the brine very active capillary forces were observed, **Fig. 5**.

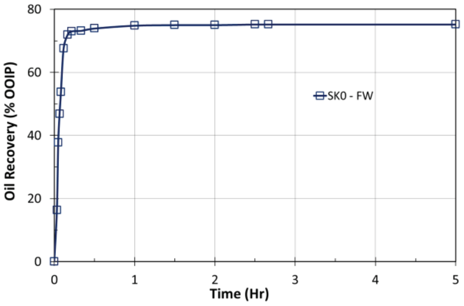

Fig. 5. Spontaneous imbibition (SI) test of SK chalk core SK0. The core was restored with S_{wi}=0.1, and fully saturated with heptane. The same brine was used in to establish initial water saturation and as an imbibing fluid.

72 % of original oil in place (OOIP) was produced in only 10 minutes and the ultimate oil recovery plateau of 75%OOIP was reached after 60 minutes. SK outcrop Chalk behaves strongly water wet, and by only capillary forces the initial oil saturation (S_{oi}) was reduced from 90% to a residual oil saturation (S_{or}) of 15% which is very low for a heterogeneous core system. The Spontaneous Imbibition experiment confirms the importance and efficiency of capillary forces in oil mobilization from heterogeneous pore systems on core scale.

3.1 Oil Recovery by capillary and viscous forces.

To evaluate combined effects of capillary and viscous forces at mixed wet state, a series of oil recovery experiments were performed using initially strongly water wet SK outcrop chalk cores. The cores were restored to initial water saturation of 10 % using FW brine. The core was then exposed to 4 PV of Oil A containing POC before aging.

Core SK7 was initially Spontaneous Imbibed with FW, the same brine representing the initial water saturation of 10 %. After reaching the oil recovery plateau, the core was also flooded with FW at a rate of 1 PV a day until the ultimate recovery plateau was reached. The oil recovery results are presented in **Fig. 6**.

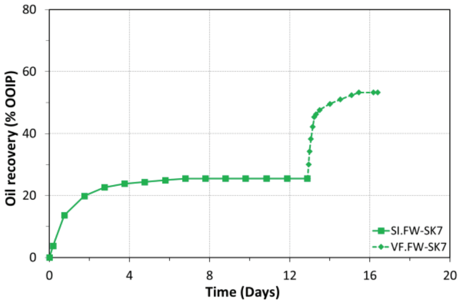

Fig. 6. Oil recovery test on core SK7 at 90°C. The SK chalk core was restored with Swi=0.1 with FW and Oil A (AN of 0.58 mg KOH/g, BN of 0.30 mg KOH/g). The core was Spontaneously Imbibed with FW, followed by viscous flooding with FW at a rate of 1 PV/D.

Spontaneous imbibition with FW will not facilitate any chemically induced wettability alteration during the imbibition process. Core SK7 reached an oil recovery plateau of 25%OOIP after 8 days, confirming presence of positive capillary forces. The restored core wettability could be described as mixed - slightly water wet.

After 13 days, core SK8 was viscous flooded with FW at an injection rate of 1 PV/day. After 3 PV, a new ultimate oil recovery plateau of 53 %OOIP was reached, representing the effect of applied viscous forces which will force FW mainly through larger pores combined with a potential capillary contribution mobilization oil from smaller and less accessible pores in the heterogenous pore network.

To investigate the effect of capillary forces on the oil mobilization during viscous flooding experiments, a parallel experiment was performed on core SK8. Spontaneous imbibition with FW gave an ultimate oil recovery of 23 %OOIP after 9 days, **Fig. 7**, confirming reproducible behavior in the core restoration process.

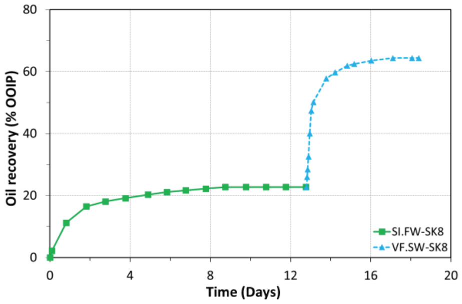

Fig. 7. Oil recovery test on core SK8 at 90°C. The SK chalk core was restored with Swi=0.1 with FW and Oil A (AN of 0.58 mg KOH/g, BN of 0.30 mg KOH/g). The core was spontaneously imbibed with FW, followed by viscous flooding with SW at a rate of 1 PV/D.

By injecting SW instead of FW at the same injection rate of 1 PV/day, the ultimate oil recovery plateau reached 64%OOIP after 5 days, confirming that a significant amount of extra oil was mobilized compared to FW even though the viscous forces applied were the same.

To be able to explain this increased displacement efficiency using SW, a new series of spontaneous imbibition experiments were performed comparing the capillary forces available during spontaneous imbibition with FW and SW. Core SK1 and SK2 went through the same core restoration process as for SK7 and SK8. Both cores were spontaneously imbibed at 90 °C, SK1 with FW and SK2 with SW, **Fig. 8**.

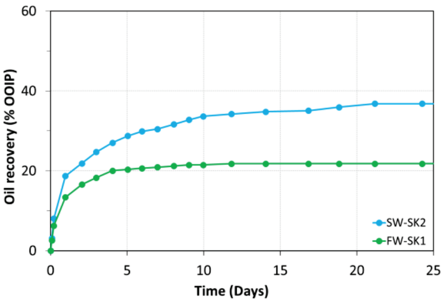

Fig. 8. Oil recovery test on core SK1 and SK2 at 90°C. Both SK chalk core have been restored with S_{wi}=0.1 with FW and Oil A (AN of 0.58 mg KOH/g, BN of 0.30 mg KOH/g). Core SK1 was imbibed with FW and SK2 with SW.

Core SK1 reached an ultimate oil recovery of 22 %OOIP after 11 days, confirming initial restored conditions in line with SK7 and SK8. When SW was used as imbibing brine for core SK2, a significant increase in both speed of imbibition and ultimate oil recovery was observed, reaching 37 %OOIP after 21 days. The extra oil mobilization could only be explained by increased positive capillary forces, facilitated by a chemically induced wettability alteration, in line with the general understanding of Smart Water EOR processes, and specific to SW as a Smart Water in Chalk as observed during viscous flooding of Core SK8 in **Fig. 7**.

Table 3 provides a summary of the experimental results from the mixed wet chalk cores at 90 °C.

Table 3. Experimental results from mixed wet SK cores at 90 °C

	SK01	SK1	SK2	SK7	SK8
S_{wi}, %	10	10	10	10	10
Oil	Heptane	Oil A	Oil A	Oil A	Oil A
SI FW, %OOIP	75	22		25	23
SI SW, %OOIP			37		
VF FW, %OOIP				53	
VF SW, %OOIP					64
$I_{wSI_{FW}}$	1	0.29		0.33	0.31
$I_{wSI_{SW}}$			0.49		

Spontaneous Imbibition test results confirm a dramatic reduction in capillary forces and oil mobilization when the cores were exposed to Oil A instead of heptane. The restored core wettability could be expressed by an Amott water index (I_{wSI}) calculated for all SI experiments performed by using 75 %OOIP as the reference for a very water wet core, **Fig. 5**.

$$I_{wSI} = \frac{(\%OOIP)_{core}}{(\%OOIP)_{ref}} \qquad (1)$$

The Amott Water index gives an average initial $I_{wSI_{FW}} = 0.31$ for the restored SK cores using Oil A. By introducing SW as an imbibing brine, the final Amott Water index for core SK2 increased to $I_{wSI_{SW}} = 0.49$. This relatively small change in water index towards more water wet conditions has a significant effect on capillary forces. During SW injection into core SK8 the increased positive capillary forces mobilized 11 %OOIP or actually 21 % extra oil compared to the FW flooding of core SK7.

All the experiments presented have been performed at 90 °C. To evaluate how temperature affect capillary forces during core restoration and recovery potentials, a new series of experiments have been performed. All cores were prepared following the same core restoration procedure as described previously.

Cores SK3 and SK4 were spontaneously imbibed at 110 °C, where FW was used as the imbibing brine for core SK3 and SW for core SK4. The results are given in **Fig. 9**.

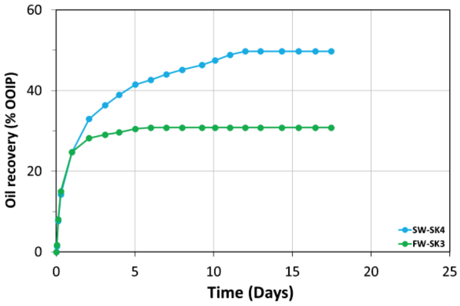

Fig. 9. Oil recovery test on core SK3 and SK4 at 110°C. Both SK chalk cores have been restored with S_{wi}=0.1 (FW) and Oil A. Core SK3 was imbibed with FW and SK4 with SW.

In **Fig. 10**, the spontaneous imbibition is performed at 130 °C, where core SK9 is exposed to FW and SW for core SK10.

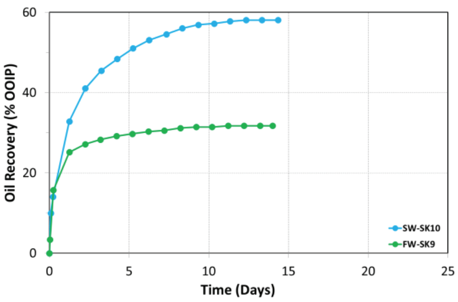

Fig. 10. Oil recovery test on core SK9 and SK10 at 130°C. Both SK chalk cores have been restored with S_{wi}=0.1 (FW) and Oil A. Core SK9 was imbibed with FW and SK10 with SW.

It was observed that as the temperature increases, the oil recovery and capillary forces increases during FW imbibition. At 90 °C, the recovery was 22 %OOIP, while increasing to 31 %OOIP for SK3 at 110°C, and further to 32 %OOIP for SK9 at 130°C.

By using SW as an imbibing brine, increased speed of imbibition and ultimate oil recoveries were observed as the temperature increased. The ultimate oil recovery reached 37 %OOIP at 90 °C, 50 %OOIP at 110°C, and 58 %OOIP at 130 °C. This represents a significant increase in capillary forces compared to FW and demonstrates the reported Smart Water EOR effects for SW with increasing temperature (refs).

To verify if increased capillary forces present will also influence the ultimate oil recovery during viscous flooding experiments, two core flooding experiments were performed at 130 °C to assess the oil recovery potential of FW and SW brine in the secondary mode. By employing a rather low injection rate, the capillary forces were permitted to contribute to the oil mobilization process, **Fig. 11**.

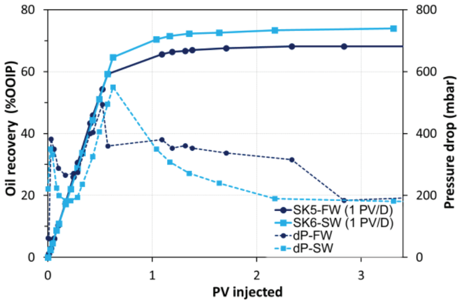

Fig. 11. Oil recovery test on SK chalk core SK5 and SK6 at 130°C, restored with S_{wi}=0.1 (FW) and Oil A. Both cores were viscous flooded with an injection rate of 1 PV/day, core SK5 with FW and core SK6 with SW. Oil recovery (%OOIP) and pressure drop (mbar) were plotted against PV injected.

A piston-like fluid displacement was observed on both cores. The first produced water for core SK5 exposed to FW was observed after 60%OOIP and 0.57 PV injected. The recovery %OOIP and the PV injected at the time of water breakthrough might be different due to uncertainties in dead volume calculation and produced fluid volume reading. For core SK6 exposed to SW, the numbers are 64 %OOIP and 0.62 PV. Increased positive capillary forces during SW injection significantly improved the displacement efficiency, giving an ultimate oil recovery plateau of 74 %OOIP after 2 PV injected, compared to 68 %OOIP for FW.

The pressure drop observations showed similar trends for both FW and SW injection, confirming that that the additional oil recovery with SW should be attributed to stronger positive capillary forces. It is important to highlight that an injection rate of 1 PV/day into a core with a length of 70 mm represents 0.2 ft/day which is quite low for core experiments. Still, pressure drop of more than 500 mbar after 0.6 PV injected was observed, stabilizing at 200 mbar at residual oil saturation (S_{or}).

A core typically represents the properties of a matrix block in a reservoir. If the pressure drop at S_{or} is scaled up using a linear tube flow model, a matrix block with a length of 1 m will see a pressure drop of 2.8 bar. On the reservoir scale with well distances of 300 meter from injector to producer, the pressure drop will then be above 850 bar (12 000psi) which is unrealistic in nature. This excludes matrix flow in low permeable reservoirs, and the pathways for viscous water through the oil-bearing zones are fractures, high permeable zones and/or the largest matrix pores. The reservoir matrixes normally hold more than 90% of the reserves and mobilization of the matrix oil is then completely dependent on the presence of positive capillary forces and the access to water from the pathways. In Smart Water EOR the aim is to improve the capillary forces and mobilize even more oil. The same water pathways will also control the main flux of oil from the matrix to the producers.

The same phenomena have also been reported from low permeable reservoir sandstone cores. Aghaeifar et al. (2019) highlighted the importance of capillary forces in oil mobilization processes by Smart Water injection. Low Salinity (LS) brine improved the positive capillary forces compared to FW, SW, and modified SW brines, and improved the displacement efficiency giving significantly higher ultimate oil recoveries in low-rate core flooding experiments. The findings highlighted the importance of including capillary forces in fluid flow models for porous systems. The contribution from capillary forces have also to be accounted for in reservoir simulators to give reliable estimates of oil production on reservoir scale, and to improve reservoir management decisions [17].

Conclusions

The results highlight the importance of understanding the effect of capillary forces on fluid flow in porous media. Selected core restoration procedures in the laboratory will influence the capillary forces present in restored cores, and replication reservoir properties are important before performing expensive and time–consuming laboratory core experiments.

The main findings of this results are-

- Cores represent reservoir matrix blocks and are heterogeneous pore systems. Presence of positive capillary forces in the cores is very important for oil mobilization.
- Only small improvements in capillary forces have a significant effect on oil mobilization and ultimate oil recoveries during brine injection, both in cores at constant capillary forces, and in cores with dynamic increase of positive capillary forces facilitated by Smart Water.
- Very high pressure drop is observed during 2 phase flow in low permeable cores even at very low injection rates, excluding the importance of viscous forces in matrix flow.
- Improved core restoration procedures are needed to replicate the capillary forces in reservoir matrix blocks. SCAL analyses should be performed at conditions present in the main part of the reservoir.

The effect of capillary forces needs to be accounted for when oil recovery processes from core experiments should be explained and mathematically modeled. Capillary forces need also to be included during upscaling of laboratory results to reservoir scale, to estimate oil production in reservoir simulators, and to improve reservoir management decisions.

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