

Final report

1.1 Project details

Project title	Smart Water - Advanced Waterflooding of Danish Oil and Gas Reservoirs
Project identification (program abbrev. and file)	Smart Water Journalnr.: 64011-0009
Name of the programme which has funded the project	EUDP—10-II
Project managing company/institution (name and address)	Center for Energiressourcer (CERE) DTU, Adresse: DTU Kemi, Kemitorvet, bygning 206, 2800 Kgs Lyngby
Project partners	DTU, DONG Energy, Mærsk Oil
CVR (central business register)	30 06 09 46
Date for submission	April 3rd 2016

1.2 Short description of project objective and results

Objective

Oil recovery of Danish oil resources may increase by intelligent modification of the injected water. The goals of the project were thus:

- 1) Can we find the mechanisms behind the action of smart water?
 - a) What is the effect of difference in reservoir lithology? How does the effect on sandstone and chalk differ?
 - b) What is the effect of difference in composition of reservoir hydrocarbons?
- 2) Can we point to new and cheaper smart water? Could we use existing shallow aquifers in the North Sea as injection water?

Results

- 1) It is now clear that several mechanisms can interplay: 1) fines formation, 2) wettability alteration and 3) poroelastic response.
 - a) Fines formation and poroelastic response can probably be significant in chalk, whereas wettability alteration could be relevant in greensand reservoirs.
 - b) Objective 1b was not met.
- 2) From interpretation of available logs no shallow fresh water was found under the Danish North Sea.

Formål

Gennem styring af injektionsvandets sammensætning, er der mulighed for at olieindvindingen fra danske felter kan øges. Projektets mål var derfor:

- 1) Kan vi afdække mekanismerne bag effekten af smart water?
 - a) Hvad indflydelse har forskellen i litologi? Hvad er effekten på grønsand og på kridt?
 - b) Hvad er effekten af forskellig kulbrintesammensætning?
- 2) Kan vi hente injektionsvand fra tænkelige grundvandsforekomster under Nordsøen?

Resultater

- 1) Vores forskningsresultater tyder på at flere mekanismer kan have virkning: 1) udfældning af partikler i porevandet, 2) ændring i fugtpræference og 3) poreelastisk respons.
 - a) Partikeludfældning og poreelastisk respons kan have betydning i kridtet, mens fugtpræferenceændringer kunne have indvirkning i grønsand.
 - b) Dette formål blev ikke opfyldt.
- 2) Ud fra tolkning af eksisterende borehulslogs lykkedes det ikke at udpege egnede ferskvandslag under dansk Nordsø.

1.3 Executive summary

WP1:

Smart Water flooding experiments were completed at 130°C and 60°C for chalk reservoirs. The individual effect of different sodium and magnesium salts were analyzed. A novel Smart Water Enhanced Oil Recovery (SmW-EOR) method was developed for sandstone reservoirs at low temperature (60°C). An emulsification study with fines has been completed including both soluble and insoluble salts. Fines formation in core plugs was correlated to oil recovery for over 128 core flooding experiments. Consistent correlation between fines formation and oil recovery for both injection and effluent brines was observed. Based on these studies a fines based emulsification mechanism of SmW-EOR was proposed.

1. Core flooding experiments:

A series of core flooding experiments have been conducted. The following conclusions have been drawn from these experiments.

- **Chalk Reservoir at high temperature:** SmW-EOR can be obtained without direct use of Ca^{2+} , Mg^{2+} , PO_4^{3-} and BO_3^{3-} ions. Variation in composition of sodium salts in the injection brine can have a significant effect on EOR. It also clearly proves that through a smart flow scheme, NaCl brines can also be used for enhanced oil recovery.
- **Chalk Reservoir at low temperature:** SmW-EOR is possible even for low temperature reservoirs, but the composition and sequence of brine injection needs to be significantly different from the general recommendations for high temperature reservoirs. The study suggests that SmW-EOR can be considered in significantly many more oil fields than previous estimations have indicated.
- **Sandstone Reservoir at low temperature:** Low salinity brine injection has shown a possible increase in oil recovery for both carbonate and sandstone reservoirs. The effect of high salinity EOR has only been proved for carbonate reservoirs. The conducted water flooding experiments have proved that it is possible to get a noticeable increase in oil recovery by injecting high concentration of MgSO_4 into sandstone reservoirs.

2. Geochemical Modelling:

- **Fines and emulsification:** Conducted emulsification experiments and Extended UNIQUAC simulations prove that formation of fines provides a direct link between the observed emulsion formation and SmW-EOR. Moreover, the research work has shown that fines can not only alter the sweep efficiency of the flooded water but also enhance the mobility of trapped oil through emulsion formation.
- **Injected brine analysis:** Geochemical modelling has shown that the observed EOR during Smart Water injection correlates to the amount of fines formed in the core plug. The Extended UNIQUAC model can be used as a rigorous mathematical tool for understanding the SmW-EOR in chalk. It also quantitatively explains a series of previous experiments reported in the literature and shows the importance of fines formation in SmW-EOR for more than 128 core flooding experiments.
- **Effluent brine analysis:** Calculations have shown that brine speciation at reservoir condition is significantly different from that at surface conditions. During EOR core flooding, significant amounts of fines are produced which are closely correlated with the increments in oil recovery. These produced fines have previously been unaccounted for. The Extended UNIQUAC model can be used to accurately calculate the amounts of these fines.
- **Multiple brine injection:** The optimum fines formation potential at reservoir scale can be significantly different in Dan Block A and Dan Block B from the Halfdan field and the West Flank of the Dan field. Based on the injection/production well network and studies in literature, the composition leading to optimum fines formation in two cases has been studied. A core slab flooding equipment has also been proposed to optimize the possibility of fines formation through brine mixing aimed at developing a brine injection strategy for Dan Block A and Dan Block B.

3. WP-2 Petrophysics and petrography

WP-2 had the objective to identify and quantify the physical processes on a pore scale that are responsible for changes in petrophysical and mechanical properties of rocks caused by smart water flooding.

The work package includes petrophysical and rock physical modeling prior, during and after flow through experiments. Initial petrophysical characterization of the dry selected rocks includes porosity, permeability measurements, and measurements of the elastic waves in dry conditions. The elastic waves and electrical resistivity are also measured at full water saturation. Low field Nuclear Magnetic Resonance (NMR) spectrometry was used to detect changes in wettability and pore-fluid distribution caused by the flow through experiments. NMR measurements are performed at full water, water and oil at irreducible water saturation and after flooding. Ultrasonic velocities and electrical resistivity of the samples are measured continuously during aging and waterflooding and the data are interpreted to detect changes with respect to strength and pore geometry. While investigating the petrophysical properties of reservoir rocks, information concerning the mineralogy is an important factor for the establishment of a rock physical model. Therefore, additional experiments are performed; X-ray diffraction (XRD), backscatter electron microscopy images (BSEM), mercury injection capillary pressure (MICP) curves and specific surface analysis (BET) illustrate the mineralogy and texture of the rock samples before the injection.

We thus link the two observations: that variation of the injected water salinity and of its ion balance may result in large additional oil recovery, and that variation in pore water salinity can result in changing rock stiffness. This points to an EOR squeezing sponge effect.

Due to the late completion of flooding experiments, samples are still being cleaned for hydrocarbons and the last petrophysical experiments and after-testing petrography are not yet completed, but under way.

Parallel studies. In parallel to the planned sample characterization for the flow through experiments, experimental work was done to study mechanisms: 1. Geomechanical tests on chalk saturated with pore water of different composition revealed a significant pore water effect on pore elasticity (Katika et al. 2015). 2. Low field NMR studies on chalk samples saturated with different pore waters showed that fines formation in the pore space can be detected by NMR (Katika et al. 2014). 3. Low field NMR was used to develop a method for quantifying sample affinity to water as compared to oil for a series of samples. It was found that the Gorm field chalk prefers water, whereas Solsort-field greensand has mixed affinity in the sense that quartz grains prefer water, and chlorite prefers oil (Katika et al. 2016).

WP-2 also had the objective to investigate North Sea logging data for indications of fresh water bearing shallow aquifers. This work was completed in collaboration with DONG Energy, but no fresh water bearing aquifers was found (master thesis of Jacob Fabricius Riis co-supervised by Hans Øbro and Ida Fabricius).

4. WP-3 Flow and transport modelling

The goal of WP3 was mathematical flow and transport modelling. According to the initial project description, in this workpackage the thermodynamic (equilibrium) model was supposed to be combined with a transport model taking into account possible chemical reactions and porosity/permeability modification on the basis of the theory of geochemical flows. This theory should have been extended onto two-phase flows and was supposed to take into account complex phase equilibria conditions. The combined model was supposed to be adjusted on the basis of the experimental data obtained. Different extensions of the model were supposed to be implemented depending on the necessity for modeling of the experimental data. If, for example, erosion/scaling would be found to be important factors, motion of the reservoir fines was also be investigated. Similarly, if emulsification would be found to be of importance, the model for smart water injection would involve formation and motion of emulsions in porous media. Such models were developed within the workpackage (see the description below).

The goals of WorkPackage 3 were achieved to a full extent. A **one-dimensional model for flows of oil and water with dissolution and precipitation has been built and implemented into a numerical difference scheme**. A new effect of non-additivity of a volume in dissolution and precipitation has been studied.

Detailed comparison with the experimental data on both flow-through and oil displacement experiments has been carried out. A special attention was paid to the data where the concentrations of ions in the effluent were reported. Comparison shows a clear correlation between the concentration of the sulfate ions in the injected brine and the amounts of additional oil produced. Other ions play less role. The two mechanisms of adsorption of the ions: fast reversible and slow irreversible adsorption, have been analyzed with regard to recovery.

Another important advance, **a model for motion of the separate oil ganglia**, was not foreseen in the initial description of the project. This model is important for explanation of the slow additional production of oil on the late stages of waterflooding, after many porous volumes injected. This innovative model needs further development if working on the smart water flooding of petroleum reservoirs will be continued within other projects.

The work in WP3 has resulted in creation of a number of innovative models for displacement of oil by smart water. Comparison with experimental data has demonstrated that these models are capable of reproducing some essential features of waterflooding. Further implementation of these models into a 3D reservoir-scale simulator would be desirable.

1.4 Project objectives

The issues we addressed:

- 1) Can we find the mechanisms behind the action of smart water? What is the effect of difference in reservoir lithology? How does the effect on sandstone and chalk differ?
- 2) Can we point to new and cheaper smart water? Could we use existing shallow aquifers in the North Sea as injection water?

The issues we had planned to but did not address.

- 3) What is the effect of difference in composition of reservoir hydrocarbons?
We had to limit our number of tested samples to 10 in total, so we found that this issue should be left for future research.
- 4) Formulation of proposal for pilot water flooding in Danish North Sea oil and gas reservoirs.
Due to the general delay of the project this issue was also left for future research.

The research involved flow through experiments followed by modelling as well as wireline log analysis aimed at assessing potential North Sea water-sources.

The work was organized in three working groups.

Coordination among groups was done via weekly administrative (every second week) or scientific (every second week) meetings.

WP1-DTU Chemical Engineering. Lead: Kaj Thomsen: Solid-pore water chemical interaction, dissolution and precipitation of minerals, Co-lead Philip Fosbøl: Core flooding experiments.
Participants: Ioannis Xiarchos, Krishna Hara Chakravarty, Karin Petersen, Tran Thuong Dang.

W2-DTU Civil Engineering. Petrophysical effects, including changes in wettability, pore compressibility, and effective permeability. Petrophysical log analysis (Lead: Ida Fabricius, participants M. Monzurul Alam, Konstantina Katika).

WP3-DTU Chemical Engineering. Mathematical modeling of fluid transport (Lead: Alexander Shapiro, participant Artem Alexeev).

The core laboratory at GEO provided technical assistance in relation to development of the flooding cells at DTU Chemical Engineering.

The core laboratory at GEUS saturated the core samples with water and hydrocarbons to irreducible water saturation.

Failure to meet milestones –unexpected problems

One major unexpected problem in the project was the development of flooding cells to high temperature and geophysical monitoring and development of flooding procedure. It proved much worse than we had anticipated: We had planned this part of the project including calibration to last 9 months. In reality it lasted more than 2½ years and not only caused delay, but also limited the number of completed tests and let us to leave out addressing issue 3) and 4) of the objectives. A part of the WP-2 after-testing petrophysics and petrography is for the same reason still under way, but will be completed in 2016.

1.5 Project results and dissemination of results

Main activities and technical results

WP-1

Smart Water Coreflooding Experiments (WP1)

Core flooding equipment:

Automated core plug aging equipment was developed to continuously monitor the core plug wettability variation at reservoir conditions. Figure 1 shows the lay out description of the core flooding equipment. It can be broadly divided into 3 major sections including: a. the injection brine section (at room temperature, shown in red box); b. Core holder section (used for both aging and flooding at reservoir conditions) and c. the data acquisition unit (shown in green box).

Injection brine section

The injection unit consists of an ISCO pump (Awolayo et al. 2014) which is connected to the six cylindrical tanks which can contain the injection fluids. The ISCO pump used in the equipment is a dual piston ISCO pump (Behenna 1995) and has a combined maximum capacity of 206 ml. It can operate up to a pumping pressure of 670 bar. The maximum achievable flow rate is 50 ml/min. As pressure is increased from the pump the cylindrical tanks embody pistons that displace their content. The cylindrical containers have a fluid capacity of 600 ml, thus ensuring a flow of 30 PV (Pore Volumes) of brine through standard Stevns Klint chalks (Standnes and Austad 2000). These injection brine holders are capable of sustaining temperature and pressure up to 150°C and 700 bar respectively. The injection unit is fully automated and can be completely controlled and altered by the software connected to the data acquisition system (Baldygin et al. 2014). The injection brine section is connected to the core holder through a purge valve thus ensuring continued flow during brine alteration for EOR core flooding studies.

Core holder section:

In the core holder section, four major injection connections are being introduced to the Hassler type steel core holder. It includes the axial and radial ISCO pumps, the brine injection line, heating connection, and the electric wires. At reservoir conditions, the axial and radial pressures on the mineral grains are differ-

ent (Hermann et al. 1974), as radial or confining pressure simulates the overburden pressure on the core and axial pressure ensures good contact between the end plates and the core. In previous water flooding experiments, this distinction has not been applied to the core flooding experiments (Zahid et al. 2010). Thus, to mimic the reservoir conditions, individual axial and radial pressures are applied on the core plugs during its aging and flooding process. A back pressure regulator (BPR) connected to the core outlet sets the outlet pressure for the experiment (Zhang et al. 2000). This can be used to simulate the pore pressure within the core plug. As previously recommended (Baldygin et al. 2014), the injection brine unit is connected to the Hassler core holder through the purge valve connection. Thermocouples are connected at the inlet and outlet of the core holder to maintain the experimental temperature. It has been shown that temperature has a major effect on petrophysical properties and oil productions (RezaeiDoust et al. 2009). Thus the temperature variation in the core plug was tested and it was observed that the dual heating connection ensures less than 1°C gradient in the core plug when elevated to 130°C. Thus the temperature in the core plug remains consistent and no unexpected gradient influence in petrophysical properties or oil production may arise. Electric wires are also introduced through both the injection and the effluent sides of the core holder. It is connected to the labview™8.6 software monitored and controlled oscilloscope. This electric wire is used to send spike signals generated from the oscilloscope into the electric and seismic sensor fitted in the heads of the core holder from either side. A detailed description and engineering drawing of the moveable head assembly and the pressure sleeves from the effluent side and the brine injection side are shown in Figures 2 and 3 respectively. These injection and effluent units can be maintained and operated at pressures up to 700 bar and temperatures up to 150°C. Core plugs with a dimension of 75 mm length and 37.5 mm diameter can be fitted into the core holder. The core placement procedure is illustrated in Figure 4. After placing the core plug in the core holder, it is placed horizontally and connected with the following components: To study the flow across different directions, pressure transducers are installed to measure the inlet, outlet, axial, radial and back pressures.

Data acquisition unit

An in-house data acquisition system (SmartWater v0.99.1) has been developed and used to continuously monitor the aging and flooding of the core plug and all its pressure profiles. The different injection connections from the Hassler core holder are connected to a single acquisition center, which is controlled by the software smartwater v0.99.1. It is used to record liquid injection rate, pressures, temperature, electrical resistance, and sound velocity measurements. The system is based on National Instruments' labview™8.6 (Wang and Zhou 2012) and has the capability to control the injection pump along with the injection fluid tanks via the pneumatic valves used. The selected flooding sequence and associated pore volumes of injection fluids can be programmed and executed automatically using smartwater v0.99.1. The live monitored data is produced, plotted and recorded for further analysis. Sound Wave Acquisition 1.0.6.6 software is selectively used to connect the oscilloscope signals passed through the core plug to produce its sound velocity and resistance (voltage drop) electrical resistivity during aging. As shown in Figure 5, section 3, a plastic insulating strip ensures no flow of electric signal from the body of the core holder. Thus it enables the resistivity across the core plug can be obtainable through the core plug during high temperature conditions as well. The installed transducers are used to collect the pressure readings by customized software that is built in National Instruments' labview™8.6. Thus through this software it is also possible to control the injection parameters.

Experiment

Core Plugs

Two core plugs originating from the Dan field, 4 chalk core plugs from Gorm field and 4 green sand core-plugs from Solsort was used for water flooding studies. The detailed properties of the core plug used in this study are given in Table 1 and 2, while the CT-scan of the coreplugs is reported in Figure 6-15.

Crude oil

The origin of the oil has been shown to considerably influence the oil/brine interactions (Zahid et al. 2011) and the final oil recovery (Zahid et al. 2010) during smart water studies. In order to mimic reservoir conditions of the North Sea, crude oil originating from the same Dan field of North Sea was used for the water flooding experiments. SARA analysis of the crude oil was conducted; and the crude oil had a viscosity of 8.83 cp and it contained 0.3% of asphaltene. Acid and base numbers were measured by Metrohm 702 SM Titrino using the method developed by Fan and Buckley (modified version of ASTM D2896 for the base number titration and ASTM D664 for the acid numbers titration). The oil properties are reported in Table 3. Since heavy oil fractions behave differently in water floods (Liu et al. 2006), the fractional carbon content in the oil was analyzed using GC-MS and both the mass fraction and mole fraction corresponding to each carbon number is reported in Figure 16. The GC-MS analysis showed it was a light oil with very small of heavy oil fraction (C40-C57: 4.46 mole%; C57+: 2.19 mole %). To accurately determine the quantity of the oil from effluent samples, the crude oil was marked by $[^{14}\text{C}]$ radio tracer. Radio tracer was provided by Perkin Elmer in the chemical form of stearic acid ($\text{CH}_3(\text{CH}_2)_{16}^{14}\text{COOH}$) (Sugiharto et al. 2009). Each one liter of North Sea crude oil was marked by 1.25 ml of solution, containing ^{14}C stearic acid in toluene (7.4 MBq/ml). The doped crude oil was used to saturate the core plugs.

Smart waterflood

Two sets of brines have been used in the core flooding experiments (Table 5). The produced fluid was collected in the effluent tubes. The amount of produced oil in each tube was measured by image analysis and by using the liquid scintillation method.

The first brine set is tagged as sodium campaign which includes: *Na/Lq1*, *Na/Lq2*, *Na/Lq3* and *Na/Lq4*. *Na-Lq1* contained 0.6 m NaCl, which represents North Sea water composition, which is currently being injected in Dan field. Cl^- was substituted by SO_4^{2-} in *Na-Lq2*, while the Na^+ concentration was kept constant. Keeping the Na^+ concentration constant, *Na-Lq3* contained 0.3 m NaCl and 0.15 m Na_2SO_4 . *Na-Lq4* was prepared by using high concentration of Na_2SO_4 (0.75 m) and NaCl (0.6 m) to represent the high saline North Sea brine enriched by SO_4^{2-} .

The second brine set is tagged as magnesium campaign which includes: *Mg/Lq1*, *Mg/Lq2*, *Mg/Lq3*, *Mg/Lq4*, and *Mg/Lq5*. *Mg-Lq1* contained 0.3 m MgCl_2 which replicates the impact of Mg^{2+} enriched brine in the absence of SO_4^{2-} . Cl^- was replaced by SO_4^{2-} in *Mg-Lq2*, while the Mg^{2+} concentration was kept constant. *Mg-Lq3* contained MgCl_2 (0.3 m) and MgSO_4 (0.15 m). Finally, *Mg-Lq4* consisted of MgCl_2 (0.3 m) and MgSO_4 (0.75 m) which replicates the impact of high concentration of SO_4^{2-} and Mg^{2+} . *Mg-Lq5* (0.06 m) represents the diluted sea water. Deionized water (DIW) was also injected in both sodium and magnesium campaigns. The density of the discussed brines was measured at room temperature and is shown in Table 6.

The total ion concentration and anion composition of the magnesium campaign was exactly the same as in the sodium campaign. As reported in Table 5, the replacement of sodium by magnesium was the only alteration between the two sets of injection brines.

Injection sequence

High Temperature Chalk

In the two core flooding experiments the same brines were injected in different sequences. In the first core (M1X12H) flooding *Na-Lq1* was used initially, as it mimics the presently sea water flooded state of the Dan field reservoir. At regular intervals, the flooding was paused thrice for different time intervals and injection of *Na-Lq1* was resumed each time. This ensured ample time for kinetics of any possible reaction to take place. 25 PV of *Na-Lq1* were injected in total. Subsequently, 15 PV of *Na-Lq2* were in-

jected. The flooding with Na-Lq2 was paused once and then resumed. The oil production did not increase after 40 PV of brine injection. Following the same series of injections in the second core plug (M1X10H), first Na-Lq2 was injected. Subsequently Na-Lq3, Na-Lq4 and Na-Lq1 were injected into M1X10H. During each of the brine injections, the water flooding was paused regularly to ensure ample time for kinetics of any possible reaction. Otherwise, the flow rate was kept constant at 0.2 ml/min throughout the water-flood. In both core plugs finally deionized water was injected into the core plug. This is to ensure ejection of any mobile oil that may otherwise remain in the core plug or in the equipment. The flooding test was conducted continuously at 130 °C with an axial pressure of 400 bar and a radial pressure of 390 bar. A back pressure of 350 bar was used to avoid the formation of a pressure drop across the core plug.

Low Temperature Chalk

Four chalk coreplugs were divided into two groups. Each group was water flooded with same brine set, but with different injection sequences (Table 7). N3X4H and N3X11H were water flooded in the sodium campaign. N3X4H was initially water flooded with *Na-Lq1* for 23.06 (PV) to simulate the reservoir conditions. In low salinity water flooding, pause and resumption of injection of the same brine has been shown to increase oil production considerably (Alvarado et al. 2014); so multiple pauses in brine injection were made to study the effect of pauses extensively. Pause intervals ranging from 1 hr to 380 hours were applied at different PVI. Pause and reinjection was continued until no additional oil was recovered with reinjection of *Na-Lq1* brine. Water flooding was followed with *Na-L2*, *Na-Lq3*, and *Na-Lq4* for 13.9, 9.36, and 13.41 PV, respectively. Several pauses in water flooding were introduced during each of the three brine injections, to study brine selective effect of pause/reinjection in water floods. In N3X11H the injection was initiated with *Na-Lq2* for 12.23 PV, with three major pauses in the flooding. The injection was continued with *Na-Lq3* and *Na-Lq4*, and *Na-Lq1* for 14.01, 12.21, 2.87 PV, respectively. Pauses were introduced at regular intervals during the brine injections to study the effect of individual brines on pause in water floods.

N3X17 and N3X9H were water flooded in the magnesium campaign. N3X9H was initially water flooded with *Mg-Lq1* for 20.3 PV with 3 major pauses in the waterflood. Thereafter it was water flooded with *Mg-Lq2*, and *Mg-Lq3* for 19.57, and 8.28 PV, respectively. Flooding was stopped thereafter because of a significant increase in injection and differential pressure (the flow was blocked due to corrosion of the purge valve in the injection line). In N3X17V the injection sequence was altered and flooding was initiated with *Mg-Lq2* for 24.37 PV, thereafter *Mg-Lq3*, *Mg-Lq4*, and *Mg-Lq1* were injected for 8.28, 15.15 and 13.68 PV. Finally deionized water was flooded to for 11.33 PV to produced ions that may have formed electric double layer on the mineral surface.

Low Temperature Greensands

The first brine set is tagged as the sodium campaign which includes: *Na-Lq1*, *Na-Lq2*, *Na-Lq3*, *Na-Lq4*, and *Na-Lq5*. *Na-Lq1* contained 0.6 m NaCl, which represents North Sea water composition, which is currently being injected in the Dan field. Cl⁻ was substituted by SO₄²⁻ in *Na-Lq2*, while the Na⁺ concentration was kept constant. Keeping the Na⁺ concentration constant, *Na-Lq3* contained 0.3 m NaCl and 0.15 m Na₂SO₄. *Na-Lq4* was prepared by using high concentrations of Na₂SO₄ (0.75 m) and NaCl (0.6 m) to represent the high saline North Sea brine enriched by SO₄²⁻. *Na-Lq5* (0.06 m) is made by 10 times diluting *Na-Lq1* to study the influence of injection of low salinity brine into core plugs.

The second brine set is tagged as the magnesium campaign which includes: *Mg-Lq1*, *Mg-Lq2*, *Mg-Lq3*, *Mg-Lq4*, and *Mg-Lq5*. *Mg-Lq1* contained 0.3 m MgCl₂ which replicates the impact of Mg²⁺ enriched brine in the absence of SO₄²⁻. Cl⁻ was replaced by SO₄²⁻ in *Mg-Lq2*, while the Mg²⁺ concentration was kept constant. *Mg-Lq3* contained MgCl₂ (0.3 m) and MgSO₄ (0.15 m). Finally, *Mg-Lq4* consisted of MgCl₂ (0.3 m) and MgSO₄ (0.75 m) which replicates the impact of high concentration of SO₄²⁻ and Mg²⁺. *Mg-Lq5* (0.06 m) represents the diluted sea water. Deionized water (DIW) was also injected in both sodium and mag-

nesium campaigns. The density of the discussed brines was measured at room temperature and is shown in Table 7.

Throughout the experiments, the flooding was paused at regular intervals to provide sufficient time for crude oil – brine – rock interactions. All the experiments were conducted at 60°C with a radial pressure of 390 bar, an axial pressure of 400 bar, and a back pressure of 300 bar to simulate the reservoir condition. Core plugs weight and CT-scan images were recorded after flooding to distinguish any possible modification in core properties (Detailed data are presented in Figure 7-15 and Table 4).

Chemical Analysis

Collected effluents were analyzed with 2100 dv ICP-OES acquired from Perkin. Nitric acid was used to dilute the samples for 10, 100, and 1000 times to figure out the concentration limit of the equipment. The brines were analyzed for 5 times to ensure the consistency of the experiments. Above 95% consistency was yielded in the obtained brine composition. Composition of various relevant ions including Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , CO_3^{3-} were determined at constant interval in PVI. The effluent brine compositions are reported in Figure 17-26.

Results

High Temperature Chalk

In Core plug M1X12H *Na-Lq1* was first injected for 10.31 PV at a rate of 0.2 ml/min. 62.37% of the OOIP was produced due to the injection of *Na-Lq1*. 25% of OOIP was produced before the initial water break through (Figure 27). The axial and radial pressures remained consistent around 400 bar and 390 bar (see supplementary Figure 1). Following the initial water break through, the pressure difference across the core plug gradually decreased from 20 bar to 4 bar. Thereafter, the injection of brine was stopped at 10.31 PV for 36.83 hours to ensure adequate period for adsorption or dissolution/attrition of potential ions and salts. The injection of *Na-Lq1* was resumed at the same rate of 0.2 ml/min and an additional 2.89% of OOIP was produced within 0.4 PV of brine injection (Figure 27). On further injection, no additional increase in oil recovery was observed. As observable from ICP-OES analysis in Figure 17, Ca^{2+} and CO_3^{2-} concentrations in the effluent samples also significantly increased. This indicated that the pause in waterflooding allowed dissolution/attrition of calcite from the core plug. As observable from Figure 27, injection of *Na-Lq1* was continued for 2.1 PV and no major oil recovery was observed. The brine injection was thereafter stopped at 12.41 PV, for a relatively short period of 16.41 hours. Resumption of *Lq1-Na* injection led to an additional production of 0.63% of the OOIP within the first 0.5 PV of brine injection. During the same PV the concentration of Ca^{2+} and CO_3^{2-} in the effluent brine also increased (Figure 17). Further continuing injection of 8 PV did not result in any major oil production. A small fraction of oil was continuously produced in the effluent though. An additional 1% of OOIP was produced during this 8 PV of brine injection (Figure 27). Small amounts of Ca^{2+} and CO_3^{2-} ions were released during these 8 PV, but no significant increase in Ca^{2+} or CO_3^{2-} concentration was observed in the effluent brine (Figure 17). Subsequently the flooding was again stopped for 58.23 mins, to further facilitate dissolution/attrition from the mineral surface. Resumption of *Na-Lq1* injection at the same steady rate of 0.2 ml/min showed a significant increase in oil production by 1.46% of the OOIP within the first 0.35 PV of brine injection. Calculating the effluent brine concentration during the same period showed a sudden rise in both Ca^{2+} and CO_3^{2-} ions, further indicating dissolution/attrition of calcite mineral. Injection with the same brine was continued for 4.35 PV (i.e. from 20.96 PV to 25.31 PV); no major oil production or calcite dissolution/attrition was observed during this injection. A minor fraction of oil (0.68% of OOIP) was continuously produced. The injection was thereafter stopped for 62.23 hours and new brine, *Na-Lq2* was subsequently injected at the same rate of 0.2 ml/min for 8.62 PV (from 25.52 to 34.21 PVI). The axial and radial pressures remained consistent around 400 bar and 390 bar, and the pressure difference across the core plug also remained consistent around 4 bar. Injection of *Na-Lq2* showed a similar trend and an additional

0.76% of OOIP was produced in the first 3.02 PV (i.e. 25.52 to 28.54 PV) with observable dissolution/attrition of calcite. Further continuing injection of *Na-Lq2* did not lead to any major oil production and only 0.14% of OOIP was additionally produced. Both the amount and rate of oil production for *Na-Lq2* was significantly less than that observed during resumption of *Na-Lq1* injection. No Ca^{2+} or CO_3^{2-} was produced in the effluent. The brine injection was thereafter stopped for 72 hours. Subsequently, injection of *Lq2-Na* was resumed for 0.52 PV which led to a quick increase in oil production by 0.5% of OOIP within 0.22 PV (Figure 27). After a total injection of 34.8 PV, the injection was stopped twice at short intervals for 72 hours. Thereafter, continuing injection with the same brine for 4.84 PV produced an additional recovery of 1.01% of OOIP. Further injection did not produce any additional oil recovery. Finally *Na-Lq3* was injected into the same core plug for 10 PV at the same rate of 0.2 ml/min but no additional oil recovery was observed. It is possible that most of the displaceable oil had been produced from the core plug. To further analyze the effect of sodium salts in oil production, a similar flooding was continued in a similar reservoir core plug M1X10H.

In Core plug M1X10H first *Lq2-Na* was injected for 5 PV at a rate of 0.2 ml/min. 41.46 % of the OOIP was produced due to injection of *Na-Lq2* brine. 25% of OOIP was produced before initial water break through (Figure 28). The axial and radial pressures remained consistent around 400 bars and 390 bars. Following the initial water break through the pressure difference across the core plug gradually decreased from 20 bars to 6 bar (see supplementary Figure 2). The injection of *Na-Lq2* was stopped for 15 hours after 3.99 PVI of brine injection. Resumption of *Lq2-Na* injection did not show any major change in oil recovery rate. During injection of *Lq2*, a nominal fraction of Ca^{2+} was observable in the effluent and no possible dissolution/attrition of calcite is observable from the effluent composition in Figure 18. Thereafter *Na-Lq3* was injected in the core plug at the same rate of 0.2 ml/min for 5.35 PV (i.e. from 5.00 to 10.35 PV). The axial and radial pressures remained consistent around 400 bar and 390 bar, and the pressure difference across the core plug also remained consistent around 5.8 bar. During injection of *Na-Lq2* a consistent increase in oil recovery was observed and an additional amount of 1.7 % of OOIP was produced (Figure 28). While injecting *Lq3*, no major increase in Ca^{2+} or CO_3^{2-} was observed in the effluent. Pausing the water flooding also did not lead to any considerable dissolution/attrition of calcite. The injection of *Na-Lq3* was stopped for 16 hours after 8.42 PVI. Reinjection of brine *Lq3-Na* did not show any major change in oil recovery rate. Moreover with *Lq2* also no considerable dissolution/attrition of calcite was observed. Subsequently *Na-Lq4* was injected in the core plug at the same rate of 0.2 ml/min for 5.21 PV (i.e. from 10.35 to 15.56 PV). The axial and radial pressures remained consistent around 400 bar and 390 bar, and the pressure difference across the core plug also remained consistent around 6 bar (see supplementary Figure 2). During initial injection of brine *Na-Lq4*, no observable major increase in oil recovery is observed. In line with previous brines, the injection of *Na-Lq4* was stopped for 16 hours after 13.58 PVI. But unlike previous brines, resumption of the injection of brine *Na-Lq4* showed an observable increase in the rate of oil production. 0.54% of OOIP was additionally produced during reinjection of brine *Na-Lq4*. Along with the increase in oil production (Figure 28) the Ca^{2+} concentration in the effluent also correspondingly increased. Finally, *Na-Lq1* was injected into the core plug. The axial and radial pressures did not remain consistent and a noticeable decrease by 3-5 bars was observed on both radial and axial pressures. The pressure difference across the core plug also showed major fluctuations and increased up to 25 bar, which otherwise remained consistent around 6 bar (see supplementary Figure 2). During injection of *Na-Lq1* a consistent increase in oil recovery was observed and an additional amount of 1.33 % of OOIP was produced. After a total injection of 17.82 PV, further injection was stopped twice at short intervals for 17.75 hours. Thereafter continuing injection with the same brine for 3.08 PV (i.e. from 17.82 to 20.9 PV) produced an additional recovery of 0.57% of OOIP. *Na-Lq1* injection into the core plug led to a significantly release of both Ca^{2+} and CO_3^{2-} ions in the effluent (Figure 18). The CT-scan of the core plug after flooding (Figure 6) shows a major fracture in M1X10H. The observed pressure variation (Supplementary Figure 2) and the exceptional release of Ca^{2+} and CO_3^{2-} ions in the effluent (Figure 18) indicate that the fracture may have taken place during *Na-Lq1* injection at 18 PVI. Finally deionized water was injected which did not lead to any additional oil recovery. 44.31% of the OOIP was ultimately recovered.

Low Temperature Chalk

Core plug N3X4H was flooded in the sodium campaign. The oil recovery profile is plotted in Figure 29 and a detailed pressure profile is reported in supplementary Figure 3. Initially it was water flooded with *Na-Lq1* to mimic the water flooding condition after injection of sea water for 23.6 PVI. Herein after production of 40.78% of OOIP in 1.25 PVI, the production rate decreased considerable for the following 0.6 PVI of brine injection and no observable oil was produced. The water flood was correspondingly paused for 43 hours and *Na-Lq1* was reinjected. Reinjection (after pause) considerably increased the production rate by 24% of OOIP, observed over 2.6 PVI (from 1.7 to 4.3 PVI) of *Na-Lq1* was injection. Because of the subsequent decrease in the rate of oil production consistent for 0.8 PVI (from 4.3 to 5.1 PVI), flooding was paused for 18 hours and *Na-Lq1* was reinjected. Reinjection led to a quick increase in brine production by 1.6 % of OOIP in 0.5 PVI (from 5.1 to 5.6 PVI), and the production rate dropped subsequently for the following 1.4 PVI of brine injection. On observing the trend, the subsequent pause interval was increased to 73 hrs. Reinjection led to an additional oil production of 6.61% of OOIP over 1.6 PVI. Thereafter the rate of oil production declined and subsequently an 18 hours pause (at 9.1 PVI) was applied on the water flood. Subsequent brine injection led to oil production of 3.69% of OOIP in 2.38 PVI. Further continued flooding did not produce any noticeable additional oil recovery. Several pauses of varied intervals including; 79 hours (at 14.02 PVI); 3.1 hours (at 16.27); 10 hours (at 18.83 PVI); 382 hours (at 21.11 PVI) and 90 hours (at 23.25 PVI) was introduced to further increase the oil production. But varied pause intervals from 3.5 hours to 382 hours and continued reinjection of *Na-Lq1* did not produce any additional oil recovery. Thus pause/reinjection led to production of 77.58% of OOIP in 11.63 PVI and 7 pauses of varied intervals. 5 pauses/reinjections of varied intervals over following 12 (11.6 to 23.6 PVI) did not produce any additional oil recovery. Subsequently the experiment was continued with injection of *Na-Lq2* where the sodium concentration remains the same as first injection brine while sodium sulfate replaced sodium chloride. 7 pauses of different intervals (17 hr to 376 hrs) were introduced to explore the effect of pause between brine injections. No additional oil was observed after 13.9 PV (from 23.6 to 38.5 PVI) of injection. Third injection sequence (*Na-Lq3*) was started. It contained sodium sulfate and sodium chloride while sodium concentration remains similar to the previous injection sequences. 2 pauses (19.3 hours at 40.3 PVI and 12 hours at 43.3 PVI) and reinjection of *Na-Lq3* was introduced while flooding was continued 9.3 PV (from 38.5 to 47.8 PVI) but no additional oil production was observed over brine variation of pause in brine injection. Finally, *Na-Lq4* with high concentration of sodium sulfate and sodium chloride was injected for 13.41 PV. No additional oil was observed in this step.

Core plug N3X11H was flooded in the sodium campaign but with a different injection sequence compared to core plug N3X4H. The oil recovery profile is plotted in Figure 30 and a detailed pressure profile is reported in supplementary Figure 4. It was initially flooded with *Na-Lq2* to investigate the initial oil recovery with sodium sulfate. It was injected for 12.23 PV and oil recovery was stabilized after 3.4 PVI at 55.68% of OOIP. Since several pauses in the injection led to no oil production for further brine injection in N3X4H, only 3 pauses/reinjections were made at regular intervals when oil production rate had considerably decreased and no visible noticeable oil was produced for over 2 PVI of brine injections. The first pause of 24 hours at 6.5 PVI led to an additional oil production of 0.5% of OOIP in the subsequent 0.6 PVI of brine injection. Because significant amount of oil was not produced after 24 hours of pause in waterflooding, the interval for the second pause was increased to 95 hrs. Reinjection of *Na-Lq3* led to an increment in OOIP by 2.13% over 1 PVI (10 PVI to 11 PVI). The third pause of 111 hours was introduced at 12.23 PV and thereafter *Na-Lq3* was injected, which led to an increment in oil production 1.91 % OOIP over 1.2 PVI (from 12.2 PVI to 13.4 PVI). Subsequently with *Na-Lq3* a 1 hr pause was introduced at 19.28 PVI which led to minor oil production of 0.5% of OOIP. Thereafter *Na-Lq3* was replaced by *Na-Lq4* following a pause of 3.1 hours at 26.42 PVI. Waterflood over 2 PV (after the pause) led to additional oil production of 0.3% of OOIP. Finally *Na-Lq4* for 2.87 PVI and no additional oil production was observed without implementing pauses in the waterflood.

These core floods showed that various alterations in composition of Na salts can cause an increase in oil production and increment in oil production after pause is not selective to any particular brine composition

- although the increment in oil recovery observed with pause in *Na-Lq1* injection was considerably greater (24% of OOIP after 43 hours pause, N3X4H core plug) than observed with other brine combinations. Subsequently it was observed that pause in water flooding decreases the differential pressure across the core plug as observable in supplementary Figure 4, and subsequent reinjection further establishes the differential pressure across the core plugs ensuring consistent flow through pore space. Thus pause in water flooding causes alteration in core plugs differential pressure (as observable in supplementary Figure 4). Therefore, to distinguish the effect of pause in waterflooding from variation in differential pressure, the inlet pressure was selectively reduced thrice (at 32.17, 35.27 and 38.47 PVI). Herein the obtained differential pressure profile mimics the observed pattern during various pauses. But these variation in inlet pressure profile for both *Na-Lq4* (at 32.17 and 35.27 PVI) and *Na-Lq1* (at 38.47 PVI) did not produce any additional oil recovery. This further indicated that the increase in oil recovery observed should be correlated to the pauses intervals and not just to the associated pressure variations.

Core plug N3X9H was flooded in the magnesium campaign. The oil recovery profile is plotted in Figure 31 and detailed pressure profile is reported in supplementary Figure 5. First injection step was injection of *Mg-Lq1*, which contained magnesium chloride. It was injected for 20.1 PVI and oil recovery was stabilized at 53.75% after 2.8 PVI. Subsequently, 3 pauses were made during injection to the core plug. At 9.46 PVI a 122hours pause was introduced and reinjection led to an increment in oil production by 2.6% of OOIP in the following 1.5 PVI. Second pause of 627 hours took place at 17.25 PVI, which increased oil production by 1.81% in the succeeding 0.75 PVI. The third pause was of 16 hours at 20.08 PVI, but on reinjection it did not produce any additional oil recovery. Afterwards, *Mg-Lq2* was injected for 20.01 PVI (from 20.08 to 40.09 PVI) with three pauses during flooding. A small pause of 5 hours led to a minute increment in oil production by 0.1% of OOIP in the following 0.3 PVI. Thereafter, a second pause of 14.7 hours was made, which led to a noticeable increment in oil production by 1.68% of OOIP during the next 2.5 PVI (from 29.4 to 31.9). Finally, a pause of 58 hours in brine injection was introduced at 35.21 PV, which led to an increment in oil production of 0.9% of OOIP in the next 1.5 PVI. Finally *Mg-Lq3* was injected after a pause of 16 hours but no additional oil production was observed. Thereafter, due to corrosion on the purge valve in the injection line at 42.51 PVI increased the inlet pressure and differential pressure considerably. Therefore, flooding was subsequently stopped at 48.43 PVI. No additional oil production was observed during this period.

The core plug N3X17V was water flooded in the magnesium campaign starting with injection of *Mg-Lq2* for 23.06 PV for 24.37 PVI. The oil recovery profile is plotted in Figure 32 and a detailed pressure profile is reported in supplementary Figure 6. After initial water breakthrough and 54.1% (of OOIP) oil production rate, oil production started decreasing. Subsequently, brine injection was paused for 13 hours to allow further attrition of CaCO_3 and $\text{Mg}^{2+}/\text{Ca}^{2+}$ ion substitution to take place on the mineral surface. Reinjection of *Mg-Lq2* led to an additional 2.5% of OOIP in 1.3 PV and again a decline in production rate was observed. No major oil production was observed for the subsequent 8 PV of brine injection. Consequently, the second pause of 125 hours was introduced at 15.4 PV; reinjection of *Mg-Lq2* led to significant increase in oil recovery by 3.8% of OOIP within 1.4 PVI. The third pause of 49hr was introduced at 21.6 PVI and following reinjection for 2.9 PVI produced 4.35 % OOIP. Injection was continued after 645 hours pause, by injecting *Mg-Lq3* for 8.28 PV, which initially produced 1.6% OOIP within 1.8 PVI. Production thereafter declined and no major increment in oil recovery was observed for continuous flooding. 3 pauses of 304 hours (at 26.15 PVI), 73 hours (at 29.8 PVI) and 45 hours (at 70.44 PVI) were made to further enhance the oil production, but no major increment in oil production was observed. Thereafter *Mg-Lq4* was injected for 15.01 PV. Initially, the brine alteration did not produce any additional oil recovery, but following a pause of 2.3hours (at 39.02 PVI) an increment in oil production by 1.2% of OOIP took place with 0.8 PVI of brine injection. Thereafter *Mg-Lq1* and Deionized water was injected for 13.68 and 11.33 PVI after 3.1 hours of pause, but no additional oil production was observed.

Greensand Low Temperature:

Core plug D3H was flooded in the sodium campaign and the oil recovery profile is plotted in Figure 33 and a detailed pressure profile is reported in supplementary Figure 7. Initially the core was water flooded with *Na-Lq1* to mimic the water flooding condition after injection of sea water. The brine was injected for 14.38 pore volume (PV) and the oil recovery was stabilized at 47% after 5 PV of injection. Thereafter, water flooding was paused for 5.6 hours, which resulted in a 0.05% increase in oil recovery. The flooding was continued for another 4 PV but no additional oil recovery was observed. The experiment was continued with injection of *Na-Lq2*. No additional oil was observed after 10.86 PV of injection. Third injection sequence (*Na-Lq3*) was started after a 7.2 hours of pause in the experiment. Oil recovery gradually increased after 4 PV of injection but remained unchanged for the other 4 PV of injection. Finally, *Na-Lq4* with high concentration of sodium sulfate and sodium chloride was injected for 14.12 PV. No additional oil was observed in this step.

Core plug D7H was flooded in the sodium campaign but with a different injection sequence compared to core plug D3H. The oil recovery profile is plotted in Figure 34 and a detailed pressure profile is reported in supplementary Figure 8. It was initially flooded with *Na-Lq2* to investigate the initial oil recovery with sodium sulfate brine. It was injected for 10.8 PV and oil recovery was stabilized after 5 PV at 13.68% of OOIP. Injection was continued after 13.3 hours of pause, by injecting *Na-Lq3*. It was injected for 11.28 PV and no additional oil was recovered. The injection was paused for 104.6 hours and *Na-Lq4* was injected. The oil recovery increased for more than 1% in the beginning of the injection sequence. The injection was continued for 11.32 PV and no additional oil recovery was observed even after 15.58 hours pause during injection sequence. Thereafter *Na-Lq1*, *Na-Lq5*, and DIW were injected for 11.81, 9.92, and 9.82 PV. They mimic the injection of sodium chloride, diluted brine and deionized water after injection of high salinity brines. No additional oil was observed in this injection sequence. There were several pauses in the injection sequence varying from 2 hours to 20 hours.

Core plug D4H was flooded with magnesium campaign and the oil recovery profile is plotted in Figure 35 and detailed pressure profile is reported in supplementary Figure 9. First injection step was injection of *Mg-Lq1*. It was injected for 16.3 PV and oil recovery was stabilized at 45% after 4.5 PV of injection. Afterwards, the oil recovery remained unchanged until the end of *Mg-Lq1* injection. Injection was paused for 3.8 hours and 0.25 hours during this step. Afterwards, *Mg-Lq2* was injected after 20.3 hours of pause. It reflects the effect of substituting magnesium chloride with magnesium sulfate at constant magnesium concentration. Oil recovery was increased for more than 1% after the injection was started. However, no additional oil recovery was observed after 12.04 PV of injection with a pause of 76.6 hours during injection. Injection was continued by injecting *Mg-Lq3*, *Mg-Lq4*, *Mg-Lq5*, and DIW for 10.36, 10.36, 11.63, and 7.97 PV, respectively. There were pauses varying from 1.6 hours to 132.6 hours during this injection, while no additional oil was recovered. It reflects the effect of injecting low and high concentration of sulfate and chloride after injection of magnesium chloride and magnesium sulfate.

Core plug D17H was flooded in the magnesium campaign but with a different injection sequence compared to D4H. The oil recovery profile is plotted in Figure 36 and a detailed pressure profile is reported in supplementary Figure 10. It was initially water flooded by *Mg-Lq2*, which contained magnesium sulfate. It was injected for 16.21 PV and oil recovery was stabilized at 36% after 3.5 PV. There were two pauses for 18.3 and 86.1 hours during this injection step. Each of the pauses was followed by an increase in oil recovery for more than 1%. Injection was continued after 13.8 hours pause, by injecting *Mg-Lq3* for 11.04 PV. The only increase in oil recovery is right after 12.9 hours of pause, while it remained unchanged in other time intervals. Thereafter *Mg-Lq4* was injected after 90.1 hours of pause for 11.07 PV. Contrary to previous core plugs, oil recovery increased gradually for 3% over 9 PV of injection. A pause for 131.4 hours during this injection did not seem to have an effect on the rate of increase in oil recovery. Finally *Mg-Lq1* was injected after 14.9 hours of pause and was continued for 9.68 PV. There was a pause for 69.61 hours but the oil recovery remained unchanged.

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WP-1

Chemical modelling report

Introduction:

Water flooding has been consistently termed the most effective method for recovering oil from various reservoirs. Various benefits of using water floods are: (1) Light to medium gravity oil can be displaced by injection of water; (2) In oil bearing porous networks water can be relatively easily injected; (3) high availability and low cost of water is also a major benefit; and (4) Low initial capital and operating cost makes injection of water provides favorable economics over other EOR methods (Yousef et al. 2012). But consistent water flooding in most carbonate reservoirs often leads to oil production of less than 40% of the original oil in place (OOIP) (Akbar et al. 2001). Thus innovative variation to traditional water flooding is required so that it can increase the recovery fraction from the matured fields. SmW-EOR is a newly developing low cost non-toxic EOR method (Webb et al. 2005; Karoussi et al. 2007; Fjelde et al. 2009; Strand et al. 2006). Through various reports in literature consensus has been achieved that altering brine composition and salinity can increase the recovery fractions both in sandstone and carbonate reservoirs (Yildiz et al. 1999; Fogden 2011; Lebedeva and Fogden 2011; Gupta et al. 2011; Delshad et al. 2013; Parracello et al. 2013; Robertson, 2007; McGuire et al. 2005; Alagic et al. 2011; Webb et al. 2005; Karoussi et al. 2007; Zhang et al. 2007). Various research groups have recommended different mechanisms to explain the observed increase in oil production for brine variations, but no clear mechanism for this technology has been universally accepted and several extensive investigation programs have been established to understand the scientific basis (Austad et al. 2008; Zahid et al. 2010; Gupta et al. 2011; Alvarado et al. 2014).

A series of meticulous experiments to fundamentally understand this phenomenon has been conducted by Austad and his co-workers (Strand et al. 2006; Zhang et al. 2007; Austad et al. 2008; Zhang et al. 2006; Puntervold et al. 2009). Based on these studies it has been recommended that increased water wetness is achieved by using high concentration of potential ions (including SO_4^{2-} , Ca^{2+} and Mg^{2+}) in the brine solution. SO_4^{2-} ions along with Ca^{2+} and/or Mg^{2+} ions can cause desorption of adsorbed carboxyl groups from the mineral surface, which can in turn increase the residue oil mobility by making the system more water wet. Use of Na salts are believed to have no direct influence on oil production and are termed as non-active ions (Zhang et al. 2007). Reducing their concentration enhances the effectiveness of the potential ions. Moreover, precipitation must be avoided during SmW-EOR as it can choke the core plug and adversely affect the oil production. Collectively in most studies, the importance of soluble Ca^{2+} , Mg^{2+} and SO_4^{2-} ions has been substantiated. A vast fraction of these studies have been conducted with Stevns Klint outcrop cores from Denmark (Austad et al. 2005; Zhang et al. 2006; Puntervold et al. 2009); but similar pattern of oil production has also been observed for the Middle East carbonates as well (Strand et al. 2006; Yi and Sarma 2012).

Other experimental studies show fundamental difference to the proposed wettability alteration mechanism (Zahid et al. 2011; Zahid et al. 2012a; Zahid et al. 2012b; Gupta et al. 2014; Alvarado et al. 2014). Observed successful SmW-EOR with SO_4^{2-} enriched brines for completely water wet cores (Zahid et al. 2010) is contrary to the proposed wettability alteration mechanism (Austad et al. 2005). Emulsification of oil and dissolution of rock were suggested to be the possible reasons for the observed EOR in completely water wet systems, but no detailed mechanism was provided. High SO_4^{2-} brines have shown prominent increase in oil recovery for Stevns Klint outcrops chalks but similar experiment with Dan field reservoir core plug have shown no additional oil production (Zahid et al. 2011). Spontaneous imbibition experiments using SO_4^{2-} enriched brine have shown no increase in oil recovery for Rørdal Chalk (Denmark) and Niobrara Chalk(USA) formations, while SO_4^{2-} effect for Stevns Klint chalks have shown to be significantly dependent on initial mineral wettability (Fernø et al. 2011). Herein, for Niobrara chalk imbibition of SO_4^{2-} enriched brine led to increased water wetness but no corresponding increase in oil recovery was observed. This observation remain fundamentally contradictory to wettability based (Austad et al. 2008) EOR. It has been observed that an increased oil recovery can be obtained in the absence of SO_4^{2-} ions. This also proves that the desorption of carboxyl ions following SO_4^{2-} adsorption is not necessarily the fundamental mechanism (Gupta et al. 2011). Further studies have shown that oil emulsions can be formed by a buildup of a viscoelastic interface (Moradi et al. 2011; Moradi et al. 2013; Wang and Alvarado, 2012; Alvarado et al. 2014a). Collectively wettability alteration (Strand et al. 2006; Zhang et al. 2007; Austad et al. 2005) mineral dissolution (Pu et al. 2010; Yousef et al. 2011) and emulsification (Moradi et al. 2011; Moradi et al. 2013; Wang and Alvarado, 2012; Alvarado et al. 2014b) are different mechanisms that have been proposed to explain this phenomenon of SmW-EOR for carbonates.

In all of the above cited results; experiments with higher sulfate concentration in the injected brine has led to a higher oil recovery. In all of the cited experiments, it has been attempted to correlate the composition of the injected brines with the observed oil recovery. But in the proposed mechanism it is suggested that Mg^{2+} replaces Ca^{2+} from the mineral surfaces. Thus the Mg^{2+} concentration is decreased in the brine solution and the Ca^{2+} concentration is increased equivalently in the pore space. Thereby, the possibility of precipitation is significantly enhanced, particularly at higher temperatures. Ion substitution followed by electrolyte speciation thus leads to the formation of a new brine composition in the pore space. This new brine interacts with the crude oil in the pore space and alters its displacement efficiency. Therefore, it is important to calculate the actual concentration of the brine in the pore space. The properties of this brine composition should be correlated with the reported oil recovery. In this study the calculation of the brine composition in the pore space, using the Extended UNIQUAC model (Thomsen and Rasmussen 1999) was conducted to calculate the amount of fine formation taking place in reservoir condition and further fine based emulsification experiment and DFT based mineral surface calculations was also conducted to understand the behavior of these fines (which has been reported in the Appendix Paper 1-X- **see section 1.5 for full reference**).

In this report, the correlation between the experimental results and Extended UNIQUAC calculations (Appendix Paper I-X) and other reported studies in literature has been discussed. A possible correlation between fines formation, emulsification and oil recovery has also included. The obtained results are compared to studies reported in the literature (Austad et al. 2009; Gupta et al. 2011; Pu et al. 2012; Zahid et al. 2012), to explore the possible mechanism behind SmW-EOR.

Results & Discussion:

Types of Cation Substitution

The DFT calculations in this study (Paper I) and another similar previous study (Sánchez et al. 2014) shows that substitution of Ca^{2+} by Mg^{2+} on the calcite surface is possible in two different ways:

1. The adsorbed Ca^{2+} ion on the mineral surface can be replaced by the injected Mg^{2+} ions. Herein there is no associated formation of magnesite or dolomite (Karimi et al. 2015). This substitution only requires the ions to have enough entropy to pass the energy barrier for adsorption or desorption on the mineral surface. Herein total amount of additional Ca^{2+} released must not increase above a monolayer of Ca^{2+} of the mineral surface. For North Sea chalks such substitution can readily take place at a flooding rate of 0.2 ml/min (Strand et al. 2008). The total amount of additional Mg^{2+} adsorbed by this process remain limited by the total amount adsorbed Ca^{2+} available on the mineral surface.

Example (Strand et al. 2008): In figure 1a it is observable that injecting Mg^{2+} into the core plug increases the release of Ca^{2+} ions from the core plug. Initially, there is no production of Mg^{2+} in the effluent brine. After 2 PV of effluent brine production, the concentration of Ca^{2+} decreases and no additional Ca^{2+} is observed in the effluent. The effluent Mg^{2+} concentration also becomes equal to the injected brine concentration. This indicates that after the initial substitution on the mineral surface further substitution gets constrained. Lack of further availability of adsorbed surface Ca^{2+} is likely to be the associated reason.

2. The other process of possible mineral substitution is the substitution on the calcite surface. As explained by Austad (Austad et al. 2009) and DFT calculations (Sánchez et al. 2014) herein the Ca^{2+} from the grain is removed from its crystal lattice permanently and is released in the pore space. And in place of the Ca^{2+} ion in the lattice, the Mg^{2+} ion from the brine gets introduced. During continuous flooding the mineral changes from calcite to dolomite and eventually to magnesite (Austad et al. 2009). In comparison to the amount of Mg^{2+} present in sea water, the amount of Ca^{2+} available in the chalk minerals is significantly greater, thus this mineral surface substitution is not limited by Ca^{2+} and can be observed for several PVI (Strand et al. 2008) .

Example (Strand et al. 2008): Figure 1b shows effluent resulting from sea water injection to a reservoir core plug at 1 PV/day. Slow injection into a high specific surface core plug was conducted. The effluent brine concentration observed in this experiment is shown in figure 1b. Herein it is observable that the injection of Mg^{2+} was continued for 5.5 PV and throughout this injection the

produced brine contained significantly less Mg^{2+} and an elevated amount of Ca^{2+} . Unlike the previous example, the substitution did not stop after 2 PV of brine injection in this case and thus replacement of ions from the mineral lattice must have taken place. The total Ca^{2+} released from the mineral surface is equivalent to 5 Ca^{2+} ion monolayers on the mineral surface. This also indicates that along with adsorbed Ca^{2+} ions, ions in the mineral crystal must have participated in the substitution.

It must be noted that surface Mg^{2+} adsorption does not necessarily always lead to release or desorption of Ca^{2+} ions. Mg^{2+} adsorption can take place on a free calcite surface. But this phenomenon can only be observed for 1-2 PV since it is limited by the amount of available free surface. Substitution from the mineral lattice is always associated with a decrease in Mg^{2+} and corresponding increase in Ca^{2+} concentration. Observed decrease in concentration of Mg^{2+} for 1 PV at 70°C during water flooding, with no associated increase in Ca^{2+} indicate free site adsorption of Mg^{2+} on calcite (Zahid et al. 2012). These two types of ion substitution in the core plug are schematically represented in Figure 2.

Extent of Ion Substitution

The ion substitutions of Ca^{2+} by Mg^{2+} are well established in literature (Elstnerova et al. 2010; Austad et al. 2009; Veizer 1983; Boggs 2009; Gupta et al. 2011; Vo et al. 2012). Because the common cations in the carbonate mineral have the same charges and similar ionic radii, substitution of cations is common. Substitution of Mg^{2+} (ionic radius 0.072 nm) for Ca^{2+} (ionic radius 0.100 nm) is readily obtained. On the other hand the larger Ca^{2+} ion does not substitute for Mg^{2+} in the mineral surface (Boggs 2009). In the calcite structure, disordered cation substitution of Mg^{2+} for Ca^{2+} can occur, up to several mole percentages. Calcite containing more than 4-5 mol % magnesite can be easily obtained with various calcite minerals (Boggs 2009). Some calcite has shown to produce up to 30% mol $MgCO_3$ (Veizer, 1983; Boggs 2009). The extents of ion substitution that takes place with reservoir and outcrops have also been proved to be significantly different; as explained in the following experiments from literature.

- In Stevns Klint chalk up to 100% of the lattice surface Ca^{2+} has been shown to be substituted consistently by Mg^{2+} injection (Austad et al. 2009). Herein both surface adsorbed ions and mineral lattice ions have shown to be substituted easily. Through XRD analysis it has also been shown that dolomite can be formed on the mineral surface (Megawati et al. 2015).
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- Similar studies with reservoirs rocks from the North Sea have not shown similar ion substitution for the same rate of brine injection (Zahid et al. 2012). Herein both Dan field core plugs and Stevns Klint chalk were flooded with a similar scheme at 2 PV/day. In case of Dan field chalks, both the injected brine composition and the effluent Mg^{2+} was 1093.73 ppm, while similar injection of brine with 1093.73 ppm of Mg^{2+} into Stevns klint chalk showed production of only 900-920 ppm of Mg^{2+} in the effluent brine (at 70°C). This indicates that Mg^{2+} must have been adsorbed during the water-flood. This ion substitution for Stevns Klint chalk was associated with increase in oil production by 10.2% of OOIP, while Dan field outcrop neither showed a decrease in effluent concentration during the flooding nor was an increase in oil production observed. It was concluded that core plug behavior of outcrops are different from that of reservoir core plugs (Zahid et al. 2012).
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- Advanced ion management of limestone core plugs from the Middle East was studied using various brine compositions (Gupta et al. 2011; Vo et al. 2012). The rate of brine injection was 5-10 PV/day (1-2 ft/day displacement). The amount of additional Ca^{2+} ion produced in the effluent was plotted against the amount of missing Magnesium ion in the effluent. In figure 3, a one-to-one correlation between increase in Ca^{2+} ion concentration and decrease in Mg^{2+} ion concentration can be observed. It can be attributed to ion substitution. The amount of ion substitution that took place was typically around 0.003-0.005 mol/liter with a maximum of 0.009 mol. The injected Mg^{2+} concentration was 0.053 mol. Therefore, with an injection rate of 5-10 PV/day into Middle East core plugs typically 7.54% (with a maximum of 16.98%) of Mg^{2+} gets substituted on the mineral surface. Other studies with Middle East core plugs have consistently shown 50% Mg^{2+} for 12 PV when the brine injection rate was controlled at 1 PV/day (Shariatpanahi et al. 2010; Vo et al. 2012).
- Furthermore, a spontaneous imbibition experiment was conducted with highly porous (30 to 45 %) and moderately permeable (3-8 mD) outcrops originating from various sites including Stevns Klint chalk (Denmark), Rørdal chalk (Denmark) and Niobara chalk (United States) respectively (Fernø et al. 2011). Same flooding and aging conditions was maintained for all the core plugs. No additional increase in oil recovery was observed for increased SO_4^{2-} concentration at 130°C for Niobara and

Rørdal chalks. A consistent increase in oil recovery was observed for aged Stevns Klint chalk. Ion substitution is an essential step for increased oil production according to wettability alteration (Austad et al. 2009), calcite dissolution (Pu et al. 2010) and fines formation (Chakravarty et al. 2015) mechanism. No additional oil production was observed for Niobara and Rørdal core plugs (when flooded at identical condition) (Fernø et al. 2011) also imply that the extent of ion substitution for Stevns Klint chalk must have been significantly different from that of Niobara and Rørdal chalks.

It is well accepted and proven that ion substitution on calcite surfaces can take place when Mg^{2+} brines are injected in Chalk and limestone core plugs. The effect of pressure and temperature on Mg^{2+}/Ca^{2+} ion substitution has been extensively studied in literature. It has been studied meticulously for both chalks and limestone core plugs over a temperature range from 70°C to 130°C (Punternvold et al. 2008). This certainly provides information about the effect of individual ions in smart water flooding, and thus helps in understanding the underlying fundamental mechanism (Austad et al. 2009). But the reservoir temperature does not undergo any major change during injection of different smart water floods. Therefore, these properties are constant for the reservoir and cannot be altered to attain more favorable flooding conditions. If the reservoir temperature is intentionally altered (alike to laboratory variations (RezaeiDoust et al. 2009)) by additional processes during smart water flooding then considering its effect on ion substitution is very important. Other than the temperature and pressure condition of the water flood, the extent of substitution depends on two major parameters:

1. Origin of the core plug: Outcrops like Stevns Klint chalk readily substitute on mineral surface (Strand et al. 2008), while North Sea reservoir chalk does not show the same extent of ion substitution (Zahid et al. 2011). Also not all outcrops show similar ion exchange, as Rørdal chalk (from Denmark) and Niobara chalk (from United States) show no major ion substitution (Fernø et al. 2011), while even reservoir core plugs from Middle East show consistent ion substitution (Shariatpanahi et al. 2010).
2. Rate of brine injection: Quick injection at 5 PV/day or more shows release of only adsorbed ions from the mineral surface from Stevns Klint chalk (Strand et al. 2008). A pause of 10 hours or more can cause ion substitution from tight North Sea reservoir core plugs as well (core flooding report; Figure 27-32). Furthermore, when brine was injected at 2 PV/day, no ion substitution was observed for the same reservoir core plugs from North Sea (Zahid et al. 2011). The measured composition of injected and effluent brines were identical. Therefore it was suggested that substitution does not take place for core plugs from North Sea reservoirs. But experiments in this study show that ion substitution on the mineral lattice can be observed (core flooding report; Figure 20) on reinjection of brine after following a pause (in water injection) of 8 hours or more. Pause time and degree of ion substitution showed a linear correlation. This correlation was studied up to 78 hours of pause time. This indicates that ion substitution does take place for North Sea reservoir chalks, but its substitution kinetics is much slower than Stevns Klint outcrop chalk.

In the literature, recommendations for reservoirs chalks have been made (Punternvold et al. 2014) based on ion substitution experiments on Stevns Klint outcrop chalks. But ion substitution experiments with Stevns Klint chalk have shown to be different from North Sea reservoir core plugs (Zahid et al. 2011). In the above discussion and in previous studies (Zahid et al. 2011; Fernø et al. 2011) it has been shown that the origin of core plugs has a major effect on the extent of ion substitution that take place during water floods. Before recommending a suitable Smart Water for any oil fields, a detailed ion substitution variation at reservoir condition for variation in injection rate must therefore be studied. It must be noted that the release of additional Ca^{2+} during effluent analysis is fundamental to all proposed mechanisms including wettability alteration (Austad et al. 2009), mineral dissolution (Pu et al. 2010) and fines formation (Chakravarty et al. 2015). Therefore, experiments on degree of ion substitution as a function of injection rate at reservoir conditions must be conducted for every oil field to understand the behavior of the proposed brine when injected in the reservoir.

Smart water flooding is mostly being considered for oil fields that are presently being flooded with sea water. Therefore, the effluent brine composition data during initial water flooding and after a pause in production/reinjection can be used to study the extent of ion substitution that takes place for the given reservoir (Yousef et al. 2012). Also, the oil industry can use the data from previously conducted water flooding experiments to study the degree on Mg^{2+}/Ca^{2+} ion substitution for each reservoir.

This study therefore emphasizes that the degree of Mg^{2+}/Ca^{2+} ion substitution against rate of brine injection must be studied individually for each reservoir. Unlike temperature, the rate of injection can be easi-

ly altered in oil fields to attain optimum ion substitution and EOR irrespective of the associated mechanism. Based on FTIR and TGA analysis it has been shown that the ion substitution on mineral surfaces cannot be the sole cause of an increase in oil production (Karimi et al. 2015). Therefore, change in brine composition, speciation and possibility of insoluble fines formation because of ion substitution should be considered.

Implication of Ion substitution:

Irrespective of the type of substitution that take place, an additional amount of Ca^{2+} is produced in the core plug (Shariatpanahi et al. 2010). This release of Ca^{2+} from the core plug and associated absence of Mg^{2+} changes the brine speciation significantly. Since $\text{CaSO}_4(\text{s})$ has very low solubility (Marshall et al. 1964), particularly at high temperatures, the additional Ca^{2+} cause a significant increase in the amount of anhydrite precipitation in the core plug (Paper V, Figure 1). This anhydrite formation thus can cause a decrease in sulphate concentration in the effluent as previously observed (Strand et al. 2008). Normally, in most calcite water flooding experiments, a decrease in sulphate concentration in the effluent is associated with adsorption of SO_4^{2-} ions on the mineral surface (Strand et al. 2006). But due to release of additional Ca^{2+} ions from the mineral surface, precipitation of $\text{CaSO}_4(\text{s})$ could also be the reason. Therefore, during water flooding (where ion substitution is observable), all SO_4^{2-} that remains inside the core plug cannot be associated to adsorption on the core plug. A fraction of the SO_4^{2-} has likely precipitated as CaSO_4 .

In a smart water study (Fathi et al. 2011), a flow through experiment was conducted and it was observed that a fraction of Ca^{2+} , Mg^{2+} and SO_4^{2-} ions remained inside the core plug. It was interpreted as adsorption of ions due to their adhesion to the calcite surface. But, as a parallel interpretation, the decrease in Mg^{2+} concentration in the effluent can be explained by ion substitution on the mineral surface (as proposed Austad et al. 2009); while anhydrite precipitation in the core plug (following the ion substitution) may have led to an associated decrease in Ca^{2+} and SO_4^{2-} concentration in the effluent. Thus all SO_4^{2-} ions that remain inside the core plug may not necessarily be associated to SO_4^{2-} adsorption on the calcite surface.

This understanding can therefore be summarized in two points:

1. Core plug dependent ion substitution can alter the brine speciation and lead to salt precipitation
2. Decrease in effluent SO_4^{2-} concentration can be caused by SO_4^{2-} adsorption and by anhydrite precipitation.

Fines interaction with Crude oil:

The possible change in brine speciation following ion substitution has not been considered when interpreting water flooding experiments. A decrease in SO_4^{2-} concentration in the effluent has been assumed directly associated to its adsorption on the mineral surface (Fathi et al. 2011). All of the injected brine has generally been considered to remain soluble. Correspondingly, properties such as interfacial tension (IFT) and contact angle analysis are used to analyze the interaction of different brines with oil and water. But, formation of insoluble salts in the core plug has not been previously realized so the interaction of insoluble salts with crude oil had not attained much attention. Therefore an analysis of fines-crude oil interaction in the presence of different brines was conducted. As discussed in the SPE-173855-MS (Paper II) and SPE-174335-MS (Paper III) and SPE-179765 (Paper IV) it was observed that the fines grains of insoluble salts can produce water soluble oil emulsions. The availability of polar compounds in the oil and insoluble salts in the brine solution were observed to be prerequisites for the formation of these emulsions. But the amount of emulsion formation did not show any direct correlation to the amount of acid/base present in the oil. This was consistently observed for more than 70 different samples (including both crude and designed oil). It was observed that stearic acid doped crude oil readily emulsified in presence of fines, but heptanoic acid only showed partial emulsification. This indicates that two different crude oils with the same acid number but with different acid composition can lead to significantly different amounts of emulsification.

Furthermore, crude oils from different sources (oil fields) have different acid compositions. Therefore, for oil originating from different sources, a linear relation between acid number and amount of oil emulsification can't be expected. This phenomenon shows a direct correlation to observed oil production from different waterfloods (Zahid et al. 2010; Standnes and Austad 2000; Zhang and Austad 2005) as discussed below.

- Zahid et al. 2010 observed that dissimilarity of oil type had significant effect on oil recovery, but no correlation was established between Total Acid Number and EOR. Herein water flooding experiments were conducted where oil originating from 3 different sources was used including Latin America, North Sea and Middle East. The experimental setup and flooding scheme was completely identical for the three crude oils. The three oil samples had the following acid number trend: *Latin America > Middle East > North Sea*. It is expected that reservoirs with oil with higher acid number shall produce less oil because of the strong adhesion between oil and mineral surface (Standnes and Austad 2000) so the expected oil recovery trend was: *Latin America < Middle East < North Sea*. But when smart water was injected the observed oil recovery trend was: *North Sea < Latin America < Middle East*. Least oil production for North Sea Oil, and highest oil production for Middle East oil was consistently observed over nine different core flooding experiments. Latin American oil had significantly higher acid number and should have produced significantly less amounts of oil (as proposed by Standnes and Austad 2000), but that wasn't observed. This showed that for oil originating from different sources, the acid number shows no direct correlation to oil production (Zahid et al. 2010). And oils with similar acid number may not necessarily have similar recovery fractions.
- This observed pattern in oil recovery, (wherein availability of acid affects the oil production, but shows no correlation precisely) is very similar to the pattern of emulsification observed in the conducted experiments (wherein availability of acid affects the oil emulsification, but shows no correlation precisely). This shows a correlation between fines based emulsification and oil production.
- Standnes and Austad 2000 observed a very consistent decrease in oil production for an increase in acid number. Both rate of oil production and ultimate oil recovery decreased with increasing acid number (from AN=0 to 1.73 (mg KOH/g)). A spontaneous imbibition experiment achieving 10% production of OOIP took more than 1000 hours for AN=0.52; while the same was attained in less than 10 hours with lower acids numbers. In a similar study (Zhang and Austad 2005) the wettability index was shown to have an inverse correlation to acid number in the temperature range from 40°C to 120°C. At 40°C, the wettability index dropped from 0.88 to 0.57 with a gradual increase in acid number. These studies show that the acid number has a direct correlation to oil production and mineral wettability. But unlike the previous example (Zahid et al. 2010), oil originating from different sources was not used for obtaining variation in acid number. In both the experiments (Standnes and Austad 2000; Zhang and Austad 2005) a specific oil originating from the North Sea was used. It was diluted with hexane to decrease the acid number. Therefore, the various oil samples used in this experiment did not have any variation in type of acid, only its amount varied with samples. So, for increase in composition of a specific acid, a consistent correlation between acid number and oil production was observed.
- Paper II: figure 3; increase in concentration of heptanoic acid shows a linear increase in amount of acid participation in emulsification. This indicates increased adhesion between the grains and crude oil. For a given acid type, an increase in Acid Number shows direct correlation to both fines based oil emulsification and oil production. Correlation between acid number and oil recovery (Zahid et al. 2010) or acid number and fines based emulsification (Paper I) is lost if the samples have dissimilar acid types.

To summarize; oil originating from the same source when diluted with alkane show direct correlation between acid number, fines based emulsification and oil production. Oils originating from different sources show no direct correlation between acid number, fines based emulsification and oil production. Therefore, more detailed compositional analysis is required. Nevertheless, the pattern of fines based emulsification and oil production remains consistent over variation in oil types and composition. Thus, fines based emulsification of oil as observed in this study could be a possible reason for the observed EOR for completely water wet systems.

Furthermore, contact angle measurements with both aged and unaged chalks have shown similar results (Jabbar et al. 2013). Contact angle measurements have shown that oil soluble heavy fatty acids (like stearic acid) play a significant role in wettability alteration on calcite and carbonate surfaces. Moreover, the chain length (or heavier acids) showed higher contact angles indicating more oil wetness. It further shows that oil with similar acid numbers, when containing heptanoic acid have significantly less contact angle as compared to stearic acids (Jabbar et al. 2013). In Paper II, the same phenomenon was observed during fines based emulsification, stearic acid showed more active participation in emulsification than

heptanoic acid. Contact angle studies further reestablishes the point that if oil samples contain different acidic compounds, then direct correlation between acid number and oil production cannot be obtained, and further analysis of the oil is required.

The behavior of Kaolinite (clay mineral) during fines based emulsification was also reported in Paper II and Paper III. No consistency between acid number and emulsification is observed here neither, and the acid type present in the oil is shown to play a prominent role. Spontaneous imbibition experiments with kaolinite containing Berea sandstone have also shown that for crude oil originating from different sources, no correlation is observed between variation in acid number and oil production (Suijkerbuijk et al. 2012).

In the proposed wettability alteration mechanism (Austad et al. 2009), the increase in oil recovery is primarily caused by the desorption of carboxyl acids from the mineral surface. Therefore, the acid number should show a direct correlation to oil production (Standnes and Austad 2000). But we observe that it is only observed for a specific type of variation in acid number. As discussed above, there is suitable evidence (Zahid et al. 2010; Jabbar et al. 2013; Moradi et al. 2013) that the acid number shows no direct correlation to oil production. Therefore, a more detailed analysis of oil composition is required, when oils originating from different sources are compared.

Through Scanning electron Microscope, micro-CT scans and X-ray analysis, emulsification of oil has been observed due to interactions with clay fines particles in sandstone core plugs (Fogden et al. 2011). The images show that loosely bound, partially oil-fines lining sandstone grains are stripped by the adhering oil during its recovery and redeposited on grains further downstream (Figure 4). Low salinity brine injection increases the fraction of fines thus mobilized by weakening their bonds to grains and strengthening their bonds to oil. It was thereafter suggested that these more oil-wet fines stabilize the water-in-oil curved menisci. The fines therefore aid in maintaining the connectivity of the oil phase and thus increase its production. Overall it was concluded that mobilization of fine particles is a major candidate in the mechanism for low salinity enhanced oil recovery. More importantly, the images from this study (as shown below in figure 5) clearly show that oil-in-water emulsions do form in core plugs at elevated temperature and availability of fine particles in water increases the stability of the oil droplets significantly (Fogden et al. 2011). Experiments without fine particles yielded no oil droplets in water for any variation in brine composition. The reported results within core plugs (Fogden et al. 2011) are consistent with the observed pattern of emulsification using Gas Chromatographic analysis. It further supports the importance of mobile fines interaction with residual oil in its displacement and increased production.

Fines based emulsification at reservoir condition:

The conducted experiments reported in Paper II, III and IV were not conducted at reservoir temperature. So, the possible formation of water soluble emulsions due to interaction between polar fractions of oil and insoluble salt fines in reservoir condition has remained unexplored.

Fine particle based oil droplets formations in water have been previously observed through CT-scan studies (Fogden et al. 2011). These observations were made for clay particles which were completely insoluble fine grains already available in the core plugs. Changing high salinity to low salinity brine allows the mobilization of these clay particles, which in turn increase the displacement of oil (as shown in figure 4 and 5).

But unlike sandstones, in case of chalk reservoirs there are no insoluble, potentially mobile fine particles (like clay) already present in the core plug. The presented work (Paper V) shows that brines with a high fraction of potential ions (Ca^{2+} , Mg^{2+} and SO_4^{2-}), when undergoing ion substitution in the core plug, leads to formation of insoluble anhydrite salt. The produced insoluble anhydrite fine particles can emulsify the residue oil. Therefore, experimental evidence of emulsification of crude oil on interaction with insoluble salts formed from Smart Waters (like SW-4SO₄: sea water with four times sulphate) should be observable at reservoir condition as well.

Previously, emulsification of oil at reservoir conditions has been observed with different high salinity smart waters. In crude oil from the middle east, different brine solutions were added, including DW (de-ionized water), SW0S (sea water without sulphate), SW $\frac{1}{2}$ S (sea water with $\frac{1}{2}$ sulphate concentration), SW (normal sea water with no alteration to sulphate concentration), SW1 $\frac{1}{2}$ S (sea water with 1 $\frac{1}{2}$ times sulphate concentration), SW2S (sea water with twice sulphate concentration), SW2 $\frac{1}{2}$ S (sea water with 2 $\frac{1}{2}$ times sulphate concentration) and SW3S (sea water with 3 times sulphate concentration).

Emulsification experiments has been conducted at 37°C and 110°C (as shown in figure 6, Zahid et al. 2011). It was observed that at 110°C the brine containing enriched sulphate concentration resulted in a new micro emulsion phase. It was reported that emulsification of crude oil takes place with increase in sulphate concentration at high pressure/temperature condition in the DBR JEFRI PVT cell (Zahid et al. 2011).

Speciation calculation for the reported brine compositions were conducted at various pressure/temperature conditions using Extended UNIQUAC model. The amount of fines formation taking place because of changes in brine composition and pressure, temperature variation is plotted in figure 7. It was observed that with increase in pressure and temperature the stated brines gradually became super saturated which resulted in the formation of insoluble fine particles. As shown in figure 7, brines enriched with SO_4^{2-} (sea water with 1½ times sulphate concentration or more) gradually started fines formation from 70°C and beyond. At 110°C the amount of fines formation that took place was directly proportional to the available SO_4^{2-} concentration. Micro-emulsion formation was observed for SW1½S to SW3S at 110°C (Zahid et al. 2011) and at the same conditions it is observed that the brines become supersaturated and leads to formation of fines. As shown in figure 6a, low sulphate brines including SW, SW½S and SW0S showed no micro-emulsion formation (Zahid et al. 2011) even at 110°C.

The Extended UNIQUAC brine speciation calculation also show that all low sulphate brines including SW, SW½S and SW0S remained soluble at 110°C. Moreover at 37°C no micro-emulsion formation was observed in the reported experiment for all brine variations including low sulphate and high sulphate brines. As shown in figure 7 at 37°C none of the brines were supersaturated. This shows a one-to-one correlation between fines formation and oil emulsification at reservoir conditions for high salinity smart water floods as well. This further reestablishes the idea that formation of insoluble mobile salts can increase the adhesion between the residue oil and flooded water through formation of emulsions. Thus it can increase the displacement of oil and lead to an increased oil production.

The established one-to-one correlation between fines formation and oil emulsification is valid for the experiment conducted at reservoir temperature for oil brine combination. But a similar correlation between oil emulsification and fines formation during core flooding has not been established. Nevertheless in a subsequent study, exactly the same oil (Middle East oil) and same brine composition (SW0S and SW3S) was used in water flooding experiments of completely water wet core plugs, and a significant increase in oil recovery was observed (Zahid et al. 2010). In Paper V (Figure 8, 9 and 10) a direct correlation between fines formation and oil recovery for this particular set of experiments (Zahid et al. 2010) has been established for 15 core plug waterfloods. Figure 7 establishes a direct correlation between the amount of fines formation and emulsification, while Paper V establishes a one-to one correlation between fines formation and oil production. Therefore, collectively it establishes a step by step correlation between fines formation, oil emulsification and oil recovery even for a completely water wet core plug; thus proving a more detailed correlation between fines formation and SW-EOR.

Extended UNIQUAC calculation and fines-SmWEOR correlation:

Emulsification indicates an increased adhesion between the oil water interfaces due to the presence of insoluble mobile salts. These emulsifications can be caused by the interaction of insoluble fines with crude oil. Previous studies for Berea sandstone indicated that mobile fines available in flooded water can release trapped oil from the mineral surface and increase its mobility by making the surface more water wet (Tang and Morrow 1999). It is possible that the insoluble fines may have a similar behavior in chalk as well, but strong correlation between the amount of fines and the observed oil recovery needs to be established to prove this. This called for a reanalysis of all smart water core flooding experiments reported in the literature, by taking the above two points in consideration.

Traditional waterflooding interpretation:

In spite of the observed correlation between fines based oil emulsification and oil recovery, the wettability alteration mechanism has been proposed in the literature (Austad et al. 2009). In this proposed mechanism it has been consistently suggested that SO_4^{2-} must remain soluble in the core plug (Austad et al. 2009). After ion substitution on the calcite surface, the soluble sulphate gets adsorbed and leads to a release of adsorbed carboxyl compounds. This changes the mineral wettability to a more water wet state

and enhances oil displacement. It is represented as a flow chart in figure 8. In the supporting data to this mechanism it has been shown that when the injection brine contained high concentrations of SO_4^{2-} ions a corresponding increase in oil production was observed (Fathi et al. 2011). Increasing Mg^{2+} and Ca^{2+} concentration in the injection brine has also shown an increase in oil recovery (Fathi et al. 2010). Decreasing NaCl concentration also leads to higher oil recovery (Zhang et al. 2006). It has been re-established over several studies that a high concentration of soluble sulphate (in presence of calcium or magnesium ions) has the most prominent influence on increasing oil recovery. It is the soluble SO_4^{2-} ion that replaces the adsorbed carboxyl ions from the calcite surface (Zhang et al. 2006; Austad et al. 2005; Austad et al. 2009; Fathi et al. 2011; Fathi et al. 2010).

According to the mechanism, the ionic composition of the interacting brine (at reservoir condition, after ion substitution) should correlate to oil recovery, as following adsorption of soluble SO_4^{2-} ions on the mineral surface release of adsorbed carboxyl compound takes place. As shown in Figure 8, three major correlation analyses are conducted for the interpretation:

1. The variation in composition of injection brine is correlated to the observed oil recovery. Herein the composition and speciation of the injection brine at room temperature is used during correlation to the oil recovery. Based on this correlation, the efficiency of different ions in oil production is measured.
2. Secondly the composition of the injection brine (at room temperature) is correlated to the composition of effluent brine obtained in effluent tubes at room temperature. Based on this correlation ion substitution, surface adsorption and salt precipitation are quantified.
3. The obtained adsorption, substitution or precipitation from the correlation study between the two brine compositions in injection and effluent tubes at room temperature is correlated to oil production from the high temperature core plug.

Brine speciation in core plug:

Based on the above stated three analysis steps, interpretations are made on the individual effects of each ion during smart water flooding in chalk and limestone reservoirs. But it has been neglected previously that ion substitution modifies the brine composition leading to dissolution and precipitation of various salts. Various salts including CaSO_4 , CaCO_3 , BaSO_4 and MgCO_3 (Marshall et al. 1964) have very low solubilities. Thus, their precipitation cannot be ignored. As shown in the flow chart (Figure 9), in this thesis work it is attempted to correlate the reported oil recovery with the amount of soluble SO_4^{2-} present in the modified brine and the corresponding fines formation taking place using Extended UNIQUAC model (Thomsen and Rasmussen 1999).

The Extended UNIQUAC model is a thermodynamic model for aqueous solutions of electrolytes and non-electrolytes (Thomsen and Rasmussen 1999). The optimized parameters of this model are based on a large amount of experimental data (Garcia et al. 2005; Thomsen and Rasmussen 1999; Christensen and Thomsen 2003; Garcia et al. 2006). The experimental basis of this model enables it to describe the phase behavior and the thermal properties of solutions containing electrolytes with great accuracy.

As explained in Paper V, 62 coreflooding experiments were analyzed. A direct correlation between the amount of fines formation and the reported oil recovery was observed. These calculations clearly show that the properties of the brine present in the pore space – after substitution – should be correlated with the reported oil recovery. Substitution of Ca^{2+} by Mg^{2+} can change the brine properties significantly and fines formation through possible precipitation of CaSO_4 is significantly enhanced. The amount of fines formation consistently correlates with the observed oil recovery for several core flooding experiments. This correlation between fines formation and oil recovery has been observed during variation of all major core plug properties, including Acid Number (Paper V: figure 2 and 3); temperature (Paper V: figure 2-5,7-11); rock type (Paper V: figure 5 and 6); wettability (Paper V: figure 9-11); aging temperature (Paper V: figure 4); formation brine (Paper V: figure 8), origin of oil (Paper V: figure 10) and brine composition (Paper V and VI). And the amount of soluble SO_4^{2-} ions present in the brine solutions is only partially correlated with the observed oil recovery. This proves that Extended UNIQUAC model can be used as a very useful tool to exactly calculate the amount of fines formation for different brine combinations for a diverse range of pressure and temperature conditions. The calculated amount of fines formed can then be used for determining the expected amount of oil recovery.

Further, Extended UNIQUAC brine speciation calculation of various water floods of chalk and limestone core plugs from reports in literature show that brine speciation gets altered due to the interaction between two brines. When formation water is replaced by injection of new smart waters, or when one smart water flood is replaced by another (with different brine compositions) then the interaction between the two brines leads to a new brine speciation and new fines formation in certain cases. Herein the combined effect of ion substitution and brine mixing can also be observed (core flooding report, Figure 20 and 22). Therefore correlation was studied between fines formation and oil recovery for multiple brine injection water floods. As shown in Paper VI, further correlation between oil production and fines formation has been observed for 42 additional coreflooding experiments, involving multiple temperature variations and multiple brine injections. As indicated in Figure 10, the observed correlation in Paper VI clearly shows that the efficiency of the injected brine clearly depends on the composition of the brine previously injected in the core plug. The amount of fines formation due to the interaction of the existing brine with the new injection brine show a one-to-one correlation to the oil recovery. The soluble salts thereafter available in the core plug only show partial correlation to the oil recovery. This correlation between fines formation (due to mixing of brines) and oil recovery has been observed for, completely water-wet, mixed wet and oil wet core plugs. Therefore, even when wettability alteration (to greater water wetness) is not possible, a correlation between fines formation and oil recovery is observed.

Thus, brine properties/speciation in core plugs at reservoir conditions is significantly different from brine properties/speciation at ambient conditions. And the amount of fines formation taking place in the core plug show good correlation to oil recovery.

Produced brine Vs Effluent brine:

When brine is produced from the core plug, it is stored into the effluent tubes at room temperature. Samples of these effluent brines are thereafter taken for accurate brine compositional analysis using ICP-MS (or similar other tools) (Gupta et al. 2012). The obtained brine composition (at room temperature is thereafter correlated to injection brine composition and increased oil production.

Speciation properties of the brine when produced from the core plug at reservoir condition can be significantly different from that at room temperature. As shown in Paper V, Figure 1, at elevated pressures, the solubility of $\text{CaSO}_4(\text{s})$ significantly increases when moving from reservoir condition (110°C - 130°C) to lower temperature (50°C or less). The speciation of the produced brine after cooling no longer reflects the speciation of the brine which was produced along with the increased oil productions, at elevated pressure and temperature conditions. The brine speciation at the flooding conditions was calculated by Extended UNIQUAC model using the composition of the reported effluent brines at room temperature. This gives the exact composition of the soluble ions and insoluble salts produced from the core plug at the flooding conditions (Elevated pressure and temperature). In Paper VII (and represented in the flow chart figure 11) this distinction between effluent brine and produced brine was established. The amount of mobile, insoluble fines particles that actually passed through the small pore throats of the porous core plugs showed a direct correlation to the observed oil recovery.

In this study it is observed that, following ion substitution, the amount of mobile fines produced from the core plug is comparable to the soluble salt fraction in the produced brine. Therefore this prominent existence of mobile fines cannot be ignored during water flood interpretations. Moreover oil recovery has also been shown to increase with increase in temperature, with a direct correlation to the corresponding increase in fines formation (Paper VII, figure 2-4). On the other hand, the decrease in soluble sulphate concentration of the produced brine (Shariatpanahi et al. 2010) show an inverse correlation to oil production for high temperature water flooding (Paper VII, figure 2-4). Decreased solubility of anhydrite fines is the primary associated reason. Furthermore, mobile fines are also produced exactly when brine alteration takes place (Paper VII, figure 5-7). This indicates that fines formation takes place because of mixing of existing and injected brine as previously predicted in the core plug brine calculations (in Paper V and VI). This fines production is exactly observed for the specific PVI (Paper VII, figure 5-6) when an associated increase in oil production was observed (Gupta et al. 2012). Emulsification experiments also showed strong adhesion between fines and crude oil. This further reestablishes the point that trapped oil from the mineral surface can be released and made transportable along the water flood by adhesive interaction with small mobile fine particles as previously recommended (Tang and Morrow 1999).

The amount of static fines observed in a water flood experiment can be directly calculated from the mass difference between the injection and the effluent brine. These static fines account for adsorbed ions and

insoluble salts particles that may have been initially mobile, but with increase in grain size became stuck in the pore throat, and thus was not produced in the effluent. These static fines, when stuck in the pore throats, can alter the flow of the flooded water, and therefore its optimal utilization is essential as it can also block the inject neck and choke the core plug. The observed variation in oil recovery between permeable outcrop chalks and low permeable reservoir chalks (Zahid et al. 2012; Strand et al. 2005, Faith et al. 2011) could be associated to variations in fines mobility, and static fines formation in different porous networks. Flow through simulation of porous media need to be conducted to further quantify this phenomenon. It must be also noticed that the ratio of static fines to mobile fines observed in small core plugs will not remain the same when implemented at reservoir scale. As with further mobilization of fines the grain size of the mobile fines may continuously increase because of their interaction with the supersaturated brine and thus they can eventually get stuck in the pore throats (Muecke 1979). This gradual conversion of mobile fines into static fines with increase in grain size is an important kinetics phenomenon which needs to be well studied before consideration of implementation of these supersaturated brines in typically low permeability chalk reservoirs like Dan field in North Sea (Røgen et al. 2005).

Scaling challenges is another important issue that may arise during implementation of smart water EOR in high temperature reservoirs (Moghadasi et al. 2003a; Moghadasi et al. 2003b; Haarberg et al. 1992). As shown previously, the produced brine contains significant amounts of mobile fines in core plug water flooding experiments. But in these experiments the produced brines quickly move to the effluent tubes at room temperature, (where solids like anhydrite are completely soluble Paper VII: figure 2-5). Therefore there is no risk of precipitation of brine in the experimental production pipes. But unlike core plug water-flooding experiments conducted in laboratory (Zahid et al. 2011; Strand et al. 2005; Gupta et al. 2012), at reservoir scale these supersaturated brines have ample time in the production pipe, where it remains at elevated pressure/temperature condition (Moghadasi et al. 2003b). Thus there is a significant possibility of precipitation of salts in the production pipes (Moghadasi et al. 2003a). It must be noted that in core flooding equipment the production brine undergoes an almost instant change from reservoir temperatures of 110°C-130°C to ambient conditions of 24°C. But in reservoir productions pipes, as the brine moves towards the surface, no such instant change in surrounding temperature take place (Moghadasi et al. 2003b). These supersaturated brines are therefore susceptible to precipitation and thus can cause hindrance in oil production. To mimic the reservoir scenario and study the possibility of scaling, the effluent pipe in the core flooding equipment can be elongated and kept in a high temperature/pressure bath, so as to ensure ample time is provided for studying the kinetics of anhydrite precipitation during oil recovery from production pipes.

In this study, the observed correlation between insoluble mobile fines and oil production is consistent over various studies. But through high resolution imaging (including use of micro-CT scan) the exact interaction between the two should be further studied. Herein the study provides no information on whether the supersaturated brine fraction is in the form of nucleated grains or remains non-nucleated throughout its flow through the porous network in the core plug. Because of the continuous mobility of the supersaturated brine and significant availability of nucleation mineral surfaces it is not expected that the supersaturated brine may have remained completely non-nucleated (Bird et al. 1986). But nevertheless, the grain size still remains unknown. And interaction of these adhesive fines with the crude oil also requires further investigations of SEM/micro-CT scan (and Nano-CT scan if possible) of chalk core plugs while smart water flooding. Study of SEM/micro-CT scan of chalk core plugs during water flooding can be done similarly to previously conducted SEM/micro-CT scan studies for clay bearing sandstone core plugs (Fogden et al. 2011).

Injection brine Vs Injected brine:

Just like the produced brine and the effluent brine do not have same speciation, it is possible that the injection brine (i.e. composition of brine at room temperature) and the injected brine (i.e. the same brine at reservoir condition) may have different speciation (Paper IX).

Injection of various brines including SW0NaCl (Sea Water with no NaCl); SW0NaCl-2SO₄ (Sea Water with no NaCl, twice SO₄²⁻); SW0NaCl-3SO₄ (Sea Water with no NaCl, thrice SO₄²⁻), SW0NaCl-4SO₄ (Sea Water with no NaCl, four times SO₄²⁻) have been recommended for North Sea Chalk reservoirs at 130°C (Punternold et al. 2014). Extended UNIQUAC brine speciation calculations have been conducted for the brines that have been recommended in literature for injection in North Sea Chalk reservoirs at 130°C. Significant differences in soluble ion composition between injection brine and injected brine are observed due to change in pressure/temperature conditions (Paper IX). Correspondingly, a considerable amount of anhydrite precipitation is observed for all recommended brines including SW0NaCl-nSO₄ ∇ n= 2,3,4. Most

spontaneous imbibition experiments are conducted at 10 bars to 50 bars (Punternvold et al. 2014; Faithi et al. 2011; Strand et al. 2006), while reservoir pressure can easily go up to 400 bars (Yousef et al. 2012). Extended UNIQUAC calculations of brine speciation of injection brines was conducted over pressure variations from 10 bars to 600 bars. Precipitation of anhydrite fines in the reservoir is observed at both experimental and at reservoir conditions (as shown in Paper IX, figure 2-5). According to this observation the flow chart of core plug smart water studies was further modified as shown in Figure 11.

This initial precipitation does not depend on the mechanism of smart water EOR. Neither does it depend on whether ion substitution takes place on the mineral surface or not. It is a phenomenon of the recommended brines at reservoir conditions, and is independent of the associated smart water EOR mechanism. But it certainly has three important implications for smart water floodings.

- According to the wettability alteration mechanism, the use of high potential ion fraction (either by removing NaCl: SW0NaCl or by enhancing potential ions: SW-4SO₄) is recommended for North Sea chalk fields at 130°C (Austad et al. 2009; Punternvold et al. 2014). And it has been suggested that while using these brines, precipitation in the core plug must be avoided (Austad et al. 2009). But as shown in Paper IX the recommended brine will cause precipitation at North Sea chalk fields at reservoir conditions 120-140°C irrespective of interaction with oil or mineral surface. Therefore, the use of recommended high potential ion fraction brines (SW0NaCl-nSO₄ √ n= 2,3,4) and avoiding precipitation are two contradictory requirements for all core plugs at 130°C.
- As shown in Paper IX, the previously observed high oil recovery for high potential ion fraction brines (SW0NaCl-nSO₄ √ n= 2,3,4) (Punternvold et al. 2014), can be explained using fines formation mechanism. Herein subtracting the initial precipitation from the total precipitation taking place in the core plug after ion substitution shows a consistent correlation to oil recovery even for brines containing very high potential ion fraction (like SW0NaCl, SW4Ca). It must be noted that the amount of supersaturation caused in the core plug following the ion substitution must be dominant over the precipitation taking place during injection before ion substitution.
- Most oil producing chalk reservoirs including chalks from North Sea reservoirs are known for their extremely low permeability (Røgen et al. 2005). Therefore irrespective of the associated mechanism, if these (SW0NaCl-nSO₄ √ n= 2,3,4) recommended brines (Punternvold et al. 2014) are considered for injection into reservoirs, it must be injected with full awareness that these brines are supersaturated at reservoir conditions and its implication in these low permeability chalks needs to be pre-considered. Furthermore particularly for low permeability core plugs (like Dan field from North Sea, Røgen et al. 2005) it must be noted that additional precipitation after ion substitution will also take place. Unlike precipitation on injection (which is a brine property), this precipitation depends on the extent of ion substitution taking place in the pore space, thus in effected by core plug properties and injection rate.

To summarize: Precipitation shall take place when these previously mentioned recommended brines (Punternvold et al. 2014) are injected into low permeability reservoirs. The amount of fines formation taking place after substitution shows good correlation to the observed oil recovery. Based on the above stated Extended UNIQUAC Speciation calculation, and water flood interpretation, a summarized flow chart has been developed as shown in Figure 12.

Fines formation with soluble CO₂

Water alternate Gas (WAG) injection, and carbonated water injection for increasing oil recovery has been implemented in various oil fields (Dang et al. 2014). The injection of soluble CO₂ coupled with smart water can alter the brine speciation significantly (Dang et al. 2014). Availability of CO₂ leads to dissolution of calcite in the pore space (Mackay et al. 2014). This not only changes the permeability of the core but the additional Ca²⁺ in the pore space can lead to anhydrite fines formation. Initial study in Paper VII show good correlation between anhydrite fines formation and additional oil recovery due to brine alterations in the presence of soluble CO₂ with WAG- CO₂ and carbonated water injection. This further opens the possibility of smart water flooding implementation into oil fields in which CO₂ is already being injected.

What is the mechanism for SW-EOR?

In the founding work for enhanced oil recovery through salinity variation, by Tang and Morrow 1999; it was reported that fines were essential for observing any increase in oil recovery. Based on a series of studies the following conclusion was made:

“Repeated waterfloods on a single reservoir sandstone core indicated that potentially mobile fine particles play a key role in the sensitivity of oil recovery to salinity. This conclusion was tested using Berea sandstone after fines had been stabilized by firing at 800°C and metal oxides removed by acidizing. Recovery of crude oil from this fired and acidized sandstone was essentially independent of salinity.” -(Tang and Morrow 1999)

In sandstone core plugs the fine particles in form of kaolinite clay are already present in the core plug. Decreasing the salinity leads to the removal of Na^+/Cl^- electric double layer (Nasralla et al. 2014) and allows the clay fines to mobilize in the pore space. In this study we observe a similar behavior for chalk core plugs. Although fines are not present in the chalk core plug but from the various reported (high potential ion) (Faithi et al. 2010; Faithi et al. 2011; Zahid et al. 2010; Strand et al. 2005; Zhang et al. 2006) smart water floods and based on Extended UNIQUAC calculation it is observed that fines formation was consistently taking place (Paper V & VIII). Four major reasons have been identified why fines formation can take place in the core plug.

1. Ion Substitution: $\text{Mg}^{2+}/\text{Ca}^{2+}$ substitution on the mineral surface can change the brine speciation by release of additional Ca^{2+} in the pore space, thus causing fines formation (Paper V)
2. Mixing of two different brines can also cause supersaturation in the pore space and cause fines formation. Herein it must be noted that fines formation can take place during (Paper VI):
 - a. interaction of injected brine with formation water
 - b. during alteration of injection brine, thus interaction between two injected brines
3. Available soluble gas in the brine like CO_2 can cause significant change in the speciation. Insoluble, yet readily available salts like CaCO_3 ; MgCO_3 and $\text{CaMg}(\text{CO}_3)_2$ can easily get dissolved in presence of water dissolved CO_2 . Thus altering both permeability of core plug and brine speciation (Paper VIII).
4. In several experiments the pressure and temperature conditions of the core plug have been consistently varied to study the effect of injection brine at different conditions. This variation in pressure and temperature condition can also alter the brine speciation and lead to fines formation (Paper V& VI).

Fines have been shown to have an affinity for oil, as it can emulsify the crude oil in water both at room temperature and at reservoir conditions (Paper II-IV). The fines formed in the core plug (as a result of the variations in brine injection) also interacts with the trapped oil. And if the affinity between the residue oil and the fines is greater than the oils affinity to the mineral surface then it can release the trapped oil from the mineral surface (Fogden et al. 2011). These mixed wet fines which have consistent interaction to both the oil phase and the smart water, ensures flow of residue oil along with the flooded water. Herein adhesion of these mixed wet mobile fines with residue oil causes release of trapped oil from the mineral surface (Fogden et al. 2011; Tang and Morrow; Nasralla et al. 2014) which leads to increased water wetness on the mineral surface (Strand et al. 2006).

It must be noted that the fines must remain mobile in the core plug and should interact with the flooded water and the residue oil for increasing the displacement efficient of the oil (Tang and Morrow; Nasralla et al. 2014; Paper VII). In previous experiments there was also no EOR effect for cores that were initially 100% saturated with crude oil when fines were initially immersed in the oil phase (Tang and Morrow 1999). These fines did not interact with any flooded water and could therefore not form any adhesive complex between the two fluid phases. Development of mixed-wet fine particles, and change in colloidal forces with brine composition does not occur when the fines remain completely associated with a single fluid phase i.e. crude oil or brine. It was therefore suggested that adsorption from crude oil, the presence of mobile fines, and initial water saturation are all necessary prerequisite conditions for increase in oil recovery for salinity variations. As shown in Figure 13, this observed recovery behavior in sandstone was ascribed to partial stripping of mixed-wet fines from pore walls during the course of waterflooding (Tang and Morrow 1999).

Adsorption onto surfaces in sandstone includes the outer surfaces of fine particles that coat the pore walls as illustrated in Fig. 8a (Tang and Morrow 1999). Electron microscopy has shown the distribution of the predominant kaolinite on sandstone grains (Fogden et al. 2011). While chalk core plugs also have adsorbed $\text{Ca}^{2+} / \text{Mg}^{2+}$ ions adsorbed on the calcite surface (Kerisit et al. 2004). Supersaturation of brine

following ion substitution takes place when Mg^{2+} rich brine substitutes on this mineral surface (Paper V & VI). Due to supersaturation, insoluble fine particles are likely to nucleate on the available mineral surface. Therefore, the core will contain crude oil which adheres to fine particles, which during water flooding has two possibilities:

- Crude oil can remain as drops which adhere to fines at pore walls as part of the trapped oil fraction. From cryo-microscopic analysis (Robin et al. 1991), it has been reported that residual crude oil consistently associate with patches of fines in the core plug. An observed decrease in oil production rate for high precipitation in core plug (static fines) also supports this.
- The mixed-wet fine particles are stripped away from the pore walls by the flowing oil and tend to locate at the oil-water interface (Fig. 8b). Previous studies have also shown stable formation of mixed-wet particles at the oil/water interface (Muecke 1979).

Israelachvili has shown that the forces which determine stripping of mixed-wet fines from pore walls depend on a balance between mechanical and colloidal (DLVO) forces (Israelachvili, 1991). Mechanical forces include capillary forces, resulting from adhesion of crude oil to the fines, and viscous forces from the flooding water, which tend to promote stripping. Any mechanical barrier to dislodgment will oppose stripping. Colloidal forces between fine particles will depend on the balance between van der Waals attractive forces and ion selective electrostatic repulsion. Consequently, the forces that govern the stability of colloids also come into play in the displacement of oil. The ion substitution and fines formation alters the forces on the mineral surface when brine 1 (mostly sea water) is injected. But, after continuous flooding a preferential flow path is developed in most fractured low permeability oil fields (Brown 1987). Thus Ca^{2+} ions on the pore walls of the preferential flow path gradually undergoes ion substitution by the Mg^{2+} ions of the injected brine as shown in Figure 14 (a)

A majority of the water flows through these preferential flow paths (Brown 1987). The injected (Mg^{2+} ions) brine therefore does not have the same extent of interaction with the remaining calcite pore walls.

When brines typically containing higher concentrations of potential ions (compared to sea water) are injected into the core plug, formation of new insoluble salts take place on injection or after substitution (Paper V). These additional, newly formed fines are initially small grains which can flow through the porous network (Zhang et al. 2000). The mobile fines present in the flooded water form mixed-wet surfaces because of its natural adhesion of fines to oil (Muecke 1979). These fines therefore can enhance the adhesion on the oil water interface, thus leading to release of trapped oil from the mineral surface, and eventually making the surface water wet. The observed increase in wettability is caused by the increased adhesion between residue oil and mobile fines from imbibing fluid or flooded water (Tang and Morrow 1999). In case ion substitution doesn't take place (for the specific injection rate), then no fines formation take places and neither any increase in oil recovery is observed (Zahid et al. 2011) nor any variation in wettability is expected. For Rørdal outcrop chalks, spontaneous imbibition of SW_4SO_4 neither led to any variation in mineral wettability nor was production of any additional oil observed (Fernø et al. 2011). These observations support the notion that the rate of ion substitution play a major role in fines formation and displacement of oil.

Thus, the injection of additional fines forming smart water brines enhances the displacement efficiency of the residue oil. Furthermore, with continued flow and interaction of these mobile fines with the supersaturated brine solution, a gradual increase in grain size takes place (Wellman et al. 2003). After sufficient increase in size, fines eventually get stopped at the pore throats (As shown in figure 14b). This leads to the formation of static fines in the pore space (Zhang et al. 2000). Formation of static fines blocks the pore throats and thus forces the water to divert its flow from its initial preferential flow path (Nasralla et al. 2014). Therefore the sweep efficiency is altered and new surfaces for further ion substitution are made available (as shown in figure 14c). When large amounts of water are flooded through these new surfaces, the interaction between Mg^{2+} ions and pore walls also increase (as recommended by Austad et al. 2009). Ca^{2+} in these new surfaces can undergo ion substitution because of the injected Mg^{2+} ions thus leading to new brine speciation and fines formation on the newly swept pore walls. These newly formed fines can also increase the adhesion between the flooded water and residue oil (Tang and Morrow 1999). When the forces at the oil-water interface (due to interaction with mobile fines) are greater than the corresponding adhesion on the mineral surface, the release of residue oil from these newly flooded regions takes place. Thus, the mobility of oil is increased and eventually leads to enhanced oil recovery. After ion substitution in the pore walls is completed, further flooding of brine will produce no additional fines and thus this channel will also behave similar to the preferential flow paths. Static fines formation can still take place due to the gradual increase in grain size from the newly formed fines (Zhang et al. 2000).

Formation of static fines can thereafter further alter the flow pattern of injected brine and produce new surfaces for ion substitutions and thus causing further water wetness and increased displacement efficiency of residue oil. Kinetics of fines formation and its rate of growth in the supersaturated brine solution in the pore space therefore plays a major role in altering the sweep efficiency of the flooded water. Influence on reservoir permeability will be observed when static fines formation takes place in the reservoir. Expected precipitation because of existence of super saturated brines/mobile fines causes no alteration in the reservoir permeability.

For low salinity brine injection in sandstone, both (1) sweep alteration based on fines migration (Nasralla et al. 2014) and (2) mixed-wet fines based wettability alteration of mineral surface (Tang and Morrow 1999) have been recommended as possible mechanisms. Increasing oil recovery with a decrease in salinity gives possibility of supersaturation; only mobilization of already present fines (clay) particles can take place in either case (Nasralla et al. 2014; Tang and Morrow 1999). Injection of high salinity brines in chalks consistently results in supersaturated solutions in the core plug. Depending on the kinetics of growth in grain size these will eventually lead to enhanced oil recovery. As previously stated (Tang and Morrow 1999) these fines can form mixed-wet particles when they are small and mobile. This results in an increase of the adhesion at the oil/water interface. The increase in grain size results in static fines which can alter the flow pattern and the sweep efficiency of the injected brine as previously proposed for sandstones (Nasralla et al. 2014).

The existence of supersaturated brine results in the continued growth of fines and allow fines to behave both as facilitator and obstructor of fluid flow depending upon their size in porous chalk reservoirs during smart water flooding.

Precipitation on injection and after substitution:

Formation of small fines particles of insoluble salts can take place when the brine solution is supersaturated. The kinetics depends on the availability of a surface for nucleation and on the flow rate of the supersaturated brine (Zhang et al. 2000). Recommended brines for injection into North sea chalk reservoirs (SWONaCl-nSO₄ √ n= 2, 3 and 4) (Puntervold et al. 2014), are shown to supersaturate at reservoir condition (Paper IX). Therefore injection brines (like SWONaCl-nSO₄ √ n= 2,3,4) will form insoluble salt grains near the point of injection. These insoluble salts can either form in the injection pipes or near the injection point in the reservoir. All injected water will pass through the particular injection well and the same pipe line and injection region. Grain formed due to supersaturation will be continuously interacting with major fractions of the injected supersaturated water. This allows a quick growth of the insoluble salt grains. All of the injection brine become supersaturated at the same temperature (thus same region) in the pipe line, and follows a similar kinetics when injected into the core plug (Pruess and Müller 2009). Therefore the growth of these insoluble salt nuclei and their precipitation will always take place near the injection point. The kinetics of this process therefore needs further attention. Unlike precipitation on injection, a supersaturated solution produced as a result of ion substitution has a very different kinetics as described below.

- The brine injected in a reservoir gets diverted in different directions in the porous network. Therefore, the amount of brine flowing through a specific pore space in the reservoir is much less than the amount passing through the injection pipe or the injection region. Thus, the fines formed in the reservoir are in contact with smaller volumes of supersaturated brines. Therefore, the grains of insoluble salts likely have a relatively low growth rate.
-
- Once ion substitution has completely taken place at a specific pore wall, the pore wall becomes inert to further flow of brines and thus promotes no growth of the insoluble salts. Precipitation of salts on injection is a property of the brine and is independent of ion substitution. Continued flow of brine through the injection point consistently creates supersaturated solution (because of increase in temperature) thus continuous formation of insoluble precipitated grains will take place specifically near the injection point.
-
- After continued injection, the precipitation of additional insoluble salt (or fines formation) only takes place when a new surface is accessed (either through wettability alteration or by alteration of the sweep efficiency). Thus, fines formation following ion substitution takes place throughout the flooded pore space in the reservoir, and no specific region can be selected.
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- Fines formation can also take place because of mixing of injection brine with formation brine, or mixing of two injected brines. Dissolved sour gases like CO₂ in carbonated water also affect the solubility and cause fines formation. In core plug experiments, the temperature and pressure of the core plug are often altered. Each of these phenomena can cause supersaturation of brine in the entire flooded region of the reservoir, and not at any specific location. Therefore small insoluble fine particles start forming throughout the reservoir with continued flooding. Thus forming mobile fines and enhancing oil displacement.
-
- The mobile fines formed from smart water flooding are likely to gradually interact with each other and with the supersaturated brine. As a result, the fines will increase in size and eventually form static fines. Since these fines are formed throughout the reservoir, static fines will remain spread in the flooded regions of the reservoirs. North Sea reservoir chinks are known for their Medium-high porosity and yet low permeability porous network, constituting very small pore throats of 10 nm to 100nm (D'Heur 1984). Therefore fines are likely to get blocked at pore throats after their initial growth (10 nm to 100nm). Thus small grains of static fines are likely to be observable throughout the reservoir. This ensures that even the static fine grains forming in the reservoir are likely to remain separated and no specific region can be selected where static fines are likely to get accumulated.

Precipitation on injection is region specific and associated with quick growth. A large amount of precipitation on injection can also choke core plugs and thereby have a negative influence on oil recovery. Consequently, if precipitation on injection is greater than that after ion substitution, then the expected increase in oil recovery for injection of high potential ions is no longer observed. Thus only the amount of fine formation taking place after ion substitution shows a one-to-one correlation to the oil recovery for high potential ion containing brine as well.

It must be noted that precipitation on injection takes place near the injection area; fines formation takes place throughout the reservoir. Both have an associated kinetics of growth of its grain size. In coreflooding studies, the injection point and the rest of the core plug are not at distances corresponding to reservoir conditions. So a greater overlap of the two kinetic patterns is more likely to take place in a core plug study. In reservoir flooding, the precipitation on injection would take place near the injection point and only the soluble salts will move into the reservoir. And following ion substitution (Austad et al. 2009), these soluble salts will get supersaturated; form fines (Paper V), and follow their own growth kinetics (Zhang et al. 2000).

At reservoir scale, precipitation on injection takes place near the injection point, while fine formation takes place throughout the reservoir whenever a new surface is available. In reservoirs, the injection point and reservoir pore space are separated over hundreds of meter. Also the fine forming brine may have been injected several months or years ago. Thus the injection precipitation shall have taken place considerably prior to the fine formation. Therefore the influence of precipitation on injection over precipitation after ion substitution is limited as they are separated over large distances and time. In core plugs the injection point and a new pore space in the core plug are few millimeters away so the precipitation on injection can have a major influence on fine formation kinetics. Typically 1 PV/day to 5 PV/day is injected in a core plug. The fine forming brine is only supersaturated for a few hours. Because of close proximity in both time and distance in core flooding experiments, the kinetics of precipitation on injection can have a considerable effect on fine formation following ion substitution.

Therefore the influence of precipitation on injection will have relative much less influence on fines formation taking place in the entire flooded region (because of separation over distance) at reservoir scale than at core plug scale as the injection point and the flooded region remain in close proximity of each other at core plug scale.

Besides fines formation, there are other parameters influencing the final oil recovery. It has been shown through DFT calculation (Paper I) that adsorption of Mg²⁺ on calcite surfaces releases energy which can desorb corresponding carboxyl from the mineral surfaces. Ion substitution causes a change in mineral properties (from CaCO₃ to CaMg(CO₃)₂), which also decreases the adhesion between crude oil and mineral surface. Therefore, injection of Mg²⁺ (in absence of SO₄²⁻ or fines formation) can also cause a minor increase in oil recovery. Imbibition of brines with soluble salts like SW0SO₄+Mg²⁺ (i.e. sea water without SO₄²⁻ but with added Mg²⁺), have shown to alter oil recovery (Zhang et al. 2006). But compared to fines forming brines like SW4S+Mg (which produced 62 % of OOIP at 130°C), brines with soluble salt SW0SO₄+Mg (produced 27% of OOIP at 130°C) had significantly smaller effect on the displacement effi-

ciency of oil. Furthermore, instead of injecting pure NaCl brine (dominant in sea water), injection of a brine with dissolved CaCl_2 has been shown to alter the oil production (Ligthelm et al. 2014). Soluble salts can also alter the forces at the oil water interface. In the presence of fines, the effect of soluble salts has therefore been studied in Paper III. Injection of large amounts of MgCl_2 dissolved in sea water after completely removing all NaCl will be significantly more expensive than injecting brines with high concentration of potential ions (Yousef and Ayirala 2014).

When water flooding is conducted at higher temperature, the increase in temperature causes adsorbed carboxyl groups to be more readily desorbed following adsorption of Mg^{2+} ions on calcite surfaces (Paper 1, figure 9), This desorption of carboxyl groups also promotes the mobility of oil and effects final oil production as previously observed (for SWOS-Mg RezaeiDoust et al. 2009).

Instead of water flooding at higher temperature core plugs can be aged at a higher temperature in Ca^{2+} rich brine. Aging under these conditions also leads to higher adsorption of oil (Paper 1; Zhang et al. 2005). Thus aging core plugs at high temperature creates strong mineral adhesion between surface polar fractions of oil. If imbibition experiments are subsequently performed at lower temperature it will show that oil production is adversely effected due to the high adhesion between mineral surface and polar oil fractions (Zhang et al. 2005). But these parameters, including aging temperature and aging time can only be altered in laboratory scale core plug experiments. In field scale implementations, these parameters remain specific to the reservoir and cannot be changed as the reservoir oil has already aged over millions of years at specific temperatures.

For mimicking specific oil fields, recovery parameters such as aging temperature and crude oil properties should be the same as the reservoir conditions so that realistic water flooding can be conducted (Zhang et a. 2006). Optimum aging through resistivity monitoring should also be conducted (Paper X), to ensure that reservoir wettability is attained. During field specific implementation properties such as injection rate and brine speciation can be easily altered. Before reservoir scale implementation such properties should be further studied in laboratory experiments. Parameters such as core plug lithology, pressure, temperature (both flooding and aging), formation brine, and aging time shall anyways remain constant for a given reservoir. The variation of some of these parameters in laboratory investigations before field specific implementation may not be equally important.

Based on these studies the optimum amount fine formation has been calculated at different temperature/pressure conditions for both precipitating and non-precipitating brines (on injection) (Paper X: Figure 2-6). For optimum use of both ion substitutions based fine formation and mixing based fine formation are core slab flooding equipment has also been proposed (Paper X: Figure 10-12); which can be used for analysis of core flooding experiments for Dan field block A in particular.

Conclusion:

In most previous core flooding studies, properties of the injected brines have been correlated with the observed oil recovery. But ion substitution on the mineral surface can change the composition and properties of the injected brine significantly. This study suggests that properties of the brine present in the pore space – after substitution - should be correlated with the reported oil recovery. Substitution of Ca^{2+} by Mg^{2+} can change the brine properties significantly and fines formation through possible precipitation of CaSO_4 is significantly enhanced. The amount of fines formation consistently correlates with the observed oil recovery for the studied 128 core flooding experiments. The amount of soluble SO_4^{2-} ions present in brine solutions is only partially correlated with the observed oil recovery. The study also indicates that the observed wettability alteration towards a more water wet state could be an effect and not the primary cause of SW-EOR. The Extended UNIQUAC model can be used as a very useful tool to exactly calculate the amount of fines formation for different brine combination for a diverse range of pressure and temperature conditions.

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WP-2

Introduction

It has been documented, that the composition of injected water can affect the crude oil/water/rock interactions in a favorable way so as to improve oil recovery in reservoir rocks as sandstones (Seccombe et al. 2008; Vledder et al., 2010) and limestones (Morrow et al., 1998; Strand et al., 2006; Austad et al., 2008), but the mechanisms are not clear. Several observations have been reported indicating that the injection of water may result in changes in the solid-fluid interface and the rock stiffness. Precipitation, fines formation or migration and dissolution reactions, as well as adsorption reactions and changes in wettability that might influence the solid/fluid interface have been advocated (Fathi et al., 2010; Madland et al., 2011; Ali et al., 2011). Furthermore, the strength of the rock is related to the fluid used for saturation and the injection of water may result in weakening of the rock (Risnes et al., 2003, Andreassen et al., 2010, Megawati et al., 2012). The research of this work package focuses on the impact of water injection on the mechanical and physical properties of the rock.

Authors have illustrated that the mechanical properties of chalk are coupled to the fluid present in the pore space of chalk (e.g. Andreassen et al., 2010). The mechanical properties of chalk are related to the porosity, the stiffness properties of the grains and how well the grains contact each other. Changes in these properties may be induced due to injection. The water injection has also been associated with compaction; an important drive mechanism for oil recovery from porous chalk reservoirs (Austad et al., 2008). Simulation studies for the high porosity chalk reservoirs at the Valhall field have indicated that half of the oil production is due to the rock compaction recovery mechanism (Cook and Jewell, 1996). However, rock compaction causes severe environmental problems such as surface subsidence, and sea-floor deformation, leading to sinking of offshore platforms, buckled seabed pipelines, and operational problems (Settari, 2002). It is therefore necessary to understand the mechanisms behind the compacting reservoirs, in order to take advantage of the oil recovery mechanisms while minimizing the problems it creates. According to Risnes et al. (2005), strong interaction between the highly polar water molecules and the chalk surface may develop repulsive forces when two surfaces are in close contact and therefore weaken the chalk. Delage et al., (1996) proposed that capillary changes occur between water and oil within the chalk.

A suggested theory regarding water weakening of chalk is the substitution process taking place inside the chalk when seawater-like brines are injected at high temperatures (Korsnes et al., 2006). According to the proposed mechanism, Mg^{2+} in the aqueous phase substitutes Ca^{2+} at intergranular contacts, in the presence of SO_4^{2-} . On the other hand, experiments on Stevns and Leige chalk by Madland et al., (2011), demonstrated that sulphate is not needed to have a significant amount of deformation. Water analysis of the produced fluids was performed and the magnesium ions were found less in the produced than the injected pore water. Two mechanisms were proposed; substitution of calcium and magnesium without the presence of sulfates in the porewater and the precipitation of magnesium as part of a new mineral phase (Madland et al., 2011; Andersen et al., 2012).

Nermoen et al. (2015), observed the effect of various brines and oil on the elastic properties of Liege chalk from Belgium, as derived from mechanical testing. The proposed mechanism is that chalk saturated with brines, which cause high electrostatic potential on the surface of chalk, are the weakest. Nermoen et al. (2015), introduced the repulsive electrostatic stresses as a mechanism that separates the grains of chalk and therefore weakening the saturated sample. The authors introduced the electrostatic stress in the effective stress relationship, as a mechanism that decreases the effective stresses in chalk under the presence of certain fluids and ions.

Rock materials and brines

Reservoir chalk

Chalk is a sedimentary rock of high homogeneity on the scale where physical properties are measured, and its properties fall in wide ranges. Porosity and specific surface are main determining factors for other properties. Chalk has been studied widely (e.g. Fabricius, 2003) and the relation between porosity, permeability, capillary entry pressure, and elastic moduli has been investigated. The selected reservoir chalks of Tor Formation are from the Dan (M-1X) and Gorm (N-3X) field in the North Sea (Bæk, 2014). Horizontal and vertical plugs, 75 mm length and 37 mm diameter, were used for aging and flooding experiments and side and end trims were selected for the petrophysical investigation.

Reservoir greensand from Solsort field

The aged and flooded greensand is a mixture of quartz grains and chlorite grains from the Solsort field (Bæk, 2014) in the North Sea. The mineral responsible for the microporosity of greensand is chlorite which is known for a high paramagnetic index (Hurlimann et al., 2004) and high stiffness ($K_0 = 164.3$ GPa) (Wang et al., 2001). Horizontal core plugs, 50 mm length and 37 mm diameter, were used for aging and flooding experiments and side and end trims were selected for the petrophysical investigation.

Brines and oil

The formation water for each field is given in Table 1. The cores were saturated with dead oil from the Dan field (Bæk, 2014) in North Sea.

Methods

An overview of the experimental procedure can be found in Figure 1. Chalk samples from the Dan and Gorm field and greensand from the Solsort field, all in the North Sea, were characterized for their petrophysical properties at dry and saturated conditions and thereafter aged and flooded. In dry conditions the grain density, porosity and Klinkenberg corrected permeability were determined. The core plugs were CT-scanned to ensure their homogeneity. Side trims from the same cores were used for the determination of their specific surface by BET and mineralogy by X-ray diffraction (XRD). Scanning electron microscopy (SEM) photos were acquired from polished thin sections. Mercury intrusion capillary pressure (MICP) was used for the determination of their pore size distribution and their mineralogy was determined and examined by BET and XRD. Finally, the V_p and V_s were acquired at 2 MPa unconfined stress to define their elasticity at dry conditions. Later, all core plugs were fully saturated with water and low field NMR spectrometry, V_p , V_s and electrical resistivity measurements were performed in wet conditions. Using a predetermined method (flushing for greensand and evaporation for chalk), the core plugs reached their irreducible water saturated state and the rest of the pore space was occupied with dead oil from the North Sea. Thereafter the core plugs were examined by NMR and CT-scan. Chalk from the Dan field (M-1X) was aged and flooded at 130°C and chalk from the Gorm field (N-3X) and greensand from the Solsort field were aged and flooded at 60°C.

Mineralogical composition

Carbonate content of chalk samples

The carbonate content of chalk was quantified by dissolving approximately 100 mg of crushed rock in hydrochloric acid (HCl) and subsequent titration with NaOH. The above-mentioned procedure was performed on the side trims of each chalk plug.

Insoluble residue of chalk samples

The insoluble residue (IR) in chalk, representing all the non-carbonate minerals, was determined from the selected side trims of each plug after the removal of the carbonate content by gradual dissolution in acetic acid.

BSEM images

Backscatter electron micrographs (BSEM) of all lithologies were recorded with a Quanta 200 (FEI) scanning electron microscope on polished thin sections of the end trims of selected core plugs.

X-ray diffraction

Both powdered original side trims and IR samples were analyzed by X-ray diffraction (XRD) by using Cu K- α radiation with a Philips PW 1830 diffractometer.

Soxhlet extraction cleaning

The plugs were cleaned for salt and hydrocarbons by Soxhlet extraction. The samples were refluxed by methanol to remove salts and toluene to remove the hydrocarbons. Clean plugs were dried in an oven at 55°C for two days.

Porosity-Permeability

Helium porosity and Klinkenberg corrected permeability were measured on cleaned and dried plugs. Both measurements were conducted on a PoroPerm Production 2 gas porosimeter from Vinci Technologies. The bulk volume of the samples was determined utilizing mercury immersion and Archimedes' principle. The dimensions were also determined using a calliper (accuracy ± 0.1 mm).

Specific surface area

The specific surface area (S_{BET}) of the side trims of all plugs with respect to weight (m^2/g) was obtained with the nitrogen adsorption method. Brunauer, Emmet and Teller (BET) inversion (Brunauer et al., 1938) was used to calculate the S_{BET} (multi-point). The BET measurements were performed, using the Autosorb iQ gas sorption system from Quantachrome Instruments.

Capillary pressure curves

The mercury capillary pressure test provided information concerning the throat size distribution of the dry rocks. The experiments were performed on side trims from the selected material utilizing a Poremaster[®] PM 33-GT-12, mercury porosimetry analyzer. Conversion of pressure data to throat size distribution was performed with the Poremaster software from Quantachrome[™] Instruments. Mercury was injected with pressure up to 60000 psi in small chips of the rock (10 g).

Ultrasonic data and electrical resistivity measurements dry and water saturated

Elastic wave velocities were measured on the dry and fully water saturated rocks at ambient temperature by placing the plugs between two pistons of a loading frame under uniaxial unconfined compressive conditions at 2 MPa. After water saturation the velocities and electrical saturation were measured under the same conditions. The compressional and shear wave velocity were measured by recording the travel time of a transmitted ultrasonic wave at 200 kHz through the sample. The electrical resistance of the saturated cores was measured at ambient temperature simultaneously with velocity, from a variable resistor connected in series with the sample in a 1 kHz AC circuit of 1 volt power supply (Figure 2). The electrical resistivity was determined from the known length and diameter of the plug.

Water and oil saturation.

Chalk-Evaporation method

The water film thickness was selected according to Larsen and Fabricius (2004), for each type of chalk. Water saturation was averaged over the internal surface of the formation by applying Kozeny's equation, resulting in a pseudo water-film thickness (h_w) which determined the final irreducible water saturation for all chalk samples (S_{wir}). After the determination of the irreducible water saturation (S_{wir} , %), the chalk samples were fully water saturated with a percentage of the salinity of the formation water, equal to S_{wir} . They were later left in ambient conditions for the water to evaporate through the pores, till the final weight indicated that the weight of the water in the pores, as determined from the porosity and grain and fluid density, was equal to the S_{wir} percent of the initial fluid volume. The cores were sealed in a core holder where dead oil was injected in a constant low flow rate till the rest of pore space was filled with oil. All samples spent 12 hours in a pressure vessel at 1600 psi fully covered with oil in order to ensure full saturation. Complete saturation was verified by using the dry and saturated weight, grain volume by helium expansion, water and oil density.

Greensand- Flushing technique

For the case of irreducible water saturation, greensand was firstly fully saturated with the formation water. The water of greensand was removed while oil was flushed into the pore space till no more water is expelled from the rock. This point was considered the irreducible water saturation level of greensand. All samples spent 12 hours in a pressure vessel at 1600 psi fully covered with oil in order to ensure full saturation. Complete saturation was verified by using the dry and saturated weight, grain volume by helium expansion, water and oil density. Aging and waterflooding

A high temperature-high pressure core flooding apparatus was utilized for the flow through experiments. The core flooding system consists of a Hassler type core holder to hold 1.5 inches diameter core plugs, two pumps controlling the axial and radial stress applied on the core and a heat jacket to maintain the high temperatures (max 150°C). A back pressure regulator maintains the pore pressure and records it during flooding, a pneumatic valve control regulates the flow from the four cylinders injecting the smart water in the core plug and an additional pump is connected to the cylinders to assist the fluid injection. An oscilloscope and a resistance reader are connected to the pistons in touch with the core plug, in order to determine the arrival of the elastic waves and electrical resistance respectively throughout the flow through experiments. The sensors recording the elastic waves and resistivity are in contact with the core plug. A pneumatic pressure booster is used to channel the effluents (fluids exiting the core during flooding) in the fraction collector. The core flooding setup is shown in Figure 3.

Ultrasonic data and electrical resistivity measurements during aging and flooding

After the saturation with water and oil at irreducible water saturation, the core plugs were sealed in the coreholder (Figure 3) for aging and later flooding. During aging and waterflooding, ultrasonic waves and electrical resistance data were recorded every 15 minutes to detect changes with respect to strength and pore geometry of the rock due to aging and injection. Travel time was calculated from the first break for compressional, P-wave and from the zero crossing for the shear, S-wave (Figure 4). Overall accuracy of the measurement is ± 50 m/s for P-waves and ± 100 m/s for S-waves. The velocities were measured using the length of the core. The system delay was determined prior to each experiment (using metal plugs of known length) and it was removed from the travel time.

Low-field NMR measurements

NMR measurements were made using a GeoSpec2 NMR Core Analyzer at frequency of 2.25 MHz, temperature of 35°C and atmospheric pressure. T_2 relaxations were measured using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences. The T_2 relaxation spectra were generated using the WinDXP (Oxford In-

struments, UK) software. All measurements were conducted at high Signal to Noise Ratio (SNR>200) for bigger reliability of our results. The recycle delay (repetition time) was selected at 40 s, number of echoes at 16000, and the CPMG inter echo spacing (τ) at 50 μ s. The $\pi/2$ and π pulses were 9.75 μ s and 19.5 μ s, respectively.

Results

Before flooding- Petrophysical investigation

All samples subjected to waterflooding are shown in Tables 2-4, including the name of the wells and their depth.

Chalk from Dan field

Chalk from the Dan Field has a uniform grain size distribution, and the pore space is homogeneous. The BSEM images of chalk from the Dan field are shown in Figure 5. The petrophysical properties of the core plugs; including BET specific surface area, carbonate content, porosity, grain density, and permeability are shown in Table 5. The elastic waves at dry and fully water conditions and electrical resistivity at 2 MPa are shown in Table 6 and Table 7 respectively.

Chalk from Gorm field

Chalk from the Gorm Field has a bimodal grain size distribution, but the pore space is homogeneous. The BSEM images of a chalk from the Gorm field are shown in Figure 6. The results from the XRD analysis are shown in Table 8. The petrophysical properties of the core plugs; including BET specific surface area, carbonate content, porosity, grain density, and permeability are shown in Table 9. The elastic waves at dry and fully water conditions and electrical resistivity at 2 MPa are shown in Table 10 and Table 11 respectively.

Greensand from Solsort field

Greensand from the Solsort field (Bæk, 2014) in the North Sea is a mixture of quartz grains and chlorite grains. The BSEM images of a greensand sample from the Solsort field are shown in Figure 7. The results from the XRD analysis are shown in Table 8. The petrophysical properties of the core plugs; including BET specific surface area, porosity, grain density, and permeability are shown in Table 12. The elastic waves at dry and fully water conditions and electrical resistivity at 2 MPa are shown in Table 13 and Table 14 respectively.

Saturation -- Low field NMR measurements

Table 15 and 16 summarize the final levels of saturation for the chalk from the Dan and Gorm field, respectively, before they were aged and flooded. Table 17 gives information about the saturation of the greensand samples.

Low field NMR measurements were performed on the saturated rocks at three different stages: first measurement at full water saturation, second measurement at full water and oil saturation at irreducible water saturation and final measurement after the waterflooding (residual oil saturation).

Chalk from Dan field

Figures 8 to 10 show the T_2 distributions of the chalk samples from the Dan field in fully water saturated conditions, oil and water at irreducible water saturated conditions and after flooding.

Chalk from Gorm field

Figures 11 to 13 show the T_2 distributions of the chalk samples from the Gorm field in fully water saturated conditions, oil and water at irreducible water saturated conditions and after flooding.

Greensand from Solsort field

Figures 14 to 16 show the T_2 distributions of the greensand samples from the Solsort field in fully water saturated conditions, oil and water at irreducible water saturated conditions and after flooding.

Aging and waterflooding

Chalk from Dan field

M-1X-6H

Core plug M-1X-6H was aged from the 9/6/2014 till the 26/05/2014 and flooded from the 11/07/2014 till the 14/08/2014. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the core holder for the aging. Figures 17 to 20 show the changes in the axial and radial stresses, compressional and shear wave velocities of the M-1X-6H chalk sample from the Dan field during aging and flooding at 130°C.

M-1X-10H

Core plug M-1X-10H was aged from the 31/01/2014 till the 03/03/2014 and flooded from the 03/03/2014 till the 03/04/2014. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the coreholder for the aging. Figures 21 to 24 show the changes in the axial and radial stresses, compressional and shear wave velocities of the M-1X-10H chalk sample from the Dan field during aging and flooding at 130°C.

Chalk from Gorm field

N-3X-17V

Core plug N-3X-17V was aged from the 13/10/2014 till the 25/11/2014 and flooded from the 26/11/2014 till the 01/02/2015. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the coreholder for the aging. Figures 25 to 28 show the changes in the axial and radial stresses, compressional and shear wave velocities of the N-3X-17V chalk sample from the Gorm field during aging and flooding at 60°C.

N-3X-11H

Core plug N-3X-11H was aged from the 26/06/2014 till the 20/09/2014 and flooded from the 25/09/2014 till the 21/10/2014. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the coreholder for the aging. Figures 29 to 32 show the changes in the axial and radial stresses, compressional and shear wave velocities of the N-3X-11H chalk sample from the Gorm field during aging and flooding at 60°C.

N-3X-9H

Core plug N-3X-9H was aged from the 25/09/2014 till the 10/11/2014 and flooded from the 04/12/2014 till the 24/01/2015. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the coreholder for the aging. Figures 33 to 36 show the changes in the axial and radial stresses, compressional and shear wave velocities of the N-3X-9H chalk sample from the Gorm field during aging and flooding at 60°C.

N-3X-4H

Core plug N-3X-4H was aged from the 26/05/2014 till the 05/08/2014 and flooded from the 14/08/2014 till the 11/11/2014. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the core holder for the aging. Figures 37 to 40 show the changes in the axial and radial stresses, compressional and shear wave velocities of the N-3X-4H chalk sample from the Gorm field during aging and flooding at 60°C.

Greensand from Solsort field

D3H

Core plug D3H was aged from the 02/04/2015 till the 22/04/2015 and flooded from the 24/04/2015 till the 02/05/2015. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the core holder for the aging. Figures 41 to 43 show the changes in the axial and radial stresses, compressional and shear wave velocities of the D3H greensand sample from the Solsort field during aging and flooding at 60°C.

D4H

Core plug D4H was aged from the 04/05/2015 till the 19/05/2015 and flooded from the 21/05/2015 till the 08/06/2015. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the core holder for the aging. Figures 44 to 46 show the changes in the axial and radial stresses, compressional and shear wave velocities of the D4H greensand sample from the Solsort field during aging and flooding at 60°C.

D7H

Core plug D7H was aged from the 02/04/2015 till the 22/04/2015 and flooded from the 27/04/2015 till the 12/05/2015. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the coreholder for the aging. Figures 47 to 49 show the changes in the axial and radial stresses, compressional and shear wave velocities of the D7H greensand sample from the Solsort field during aging and flooding at 60°C.

D17H

Core plug D17H was aged from the 24/04/2015 till the 19/05/2015 and flooded from the 22/05/2015 till the 30/06/2015. Time zero ($t = 0$ d) in all graphs is considered the moment the core plug was sealed inside the coreholder for the aging. Figures 50 to 52 show the changes in the axial and radial stresses, compressional and shear wave velocities of the D17H greensand sample from the Solsort field during aging and flooding at 60°C.

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WP-3

The role of WP3 within the project was modelling of transport of fluids in porous media, as relevant to the SmartWater process. A model was supposed to be built and adjusted to the experimental data obtained within other workpackages. If necessary it should have incorporated new effects, found to be important for the SmartWater process. The results and the references are thoroughly discussed in the two papers of A. Alexeev et al., as well as in the Ph.D. Thesis of A. Alexeev, where further details may be found.

The questions that have remained unanswered during previous studies were (among others):

What are the specific interactions between the ions dissolved in brine and the rock surface that cause additional oil production? Do the rock dissolution and the solid precipitation play any role? What is the effect of fluid compressibility? Does mobilization of the separate oil ganglia make any contribution to the total production? And, most importantly, what is the relative weight of all these and other effects with regard to interpretation of the available experimental results.

In order to advance in answering these questions, the modeling has been carried out. Physical models have been constructed for the two-phase flows in porous media involving dissolution and precipitation of solid, as well as motion of the disconnected oil ganglia. Advanced numerical methods have been applied to study the models. Their outcome has been interpreted in terms of the new physical effects. Comparison to experimental data has been carried out.

The WP3 was supposed to be carried out by a PhD student. Such a student (Artem Alexeev) was employed at the early stage of the project, after an extensive round of tests and interviews.

We have set up a model for the reactive transport in porous media to investigate how different mechanisms influence the oil recovery, pressure distribution and composition of the brine during displacement of oil by smart water. We considered several relevant physical and chemical phenomena, such as mineral dissolution, adsorption of potential determining ions on carbonate rocks, and mechanisms that influence mobilization of the trapped oil and its transport.

Dissolution of minerals occurs due to the different compositions of the injected brine and the formation water that is initially in equilibrium with the reservoir rock. We modeled displacement of oil by brine of a different salinity. Dissolution and precipitation could affect both the porosity/permeability of the rock and the density of the brine. Extending previous studies, we accounted for the different individual volumes of mineral in solid and in solution, which were found to affect the velocity of the oil displacement front.

The rate of dissolution was found to significantly influence evolution of the rock properties. At low reaction rates, dissolution occurs across the entire region between the injection and production sites. As a result, the porosities and permeabilities of the rock vary almost everywhere, although with the different rates. Fast dissolution resembles *formation of wormholes* with a significant change in porosity and permeability close to the injection site.

Smart waterflooding is usually applied at late stages of reservoir production, in order to produce additional oil trapped in the swept zones after conventional flooding. Such oil is usually present in a form of disconnected oil drops, or *oil ganglia*. Accounting for the flow of such ganglia required development of a new model, different from the classical Buckley-Leverett approach to the two-phase flows.

On the micro-level, both water and oil can be present in each single pore and interact during the flow. We found that presence of the water on the surface of the rock and in the corner filaments of pore bodies results in a larger velocity of the viscous flow of the oil phase due to the increased area of the moving oil-water interface. Moreover, the flow of oil may be induced solely by the action of viscous forces at the oil-water interface, which appears to be *a new mechanism for the transport of disconnected oil ganglia* in

porous media. We derived correlations that allow calculating the flow velocities of oil velocities in single pore bodies based on the pore fluid saturations.

Based on the microscale considerations, we develop a laboratory and reservoir scale model accounting for the effects associated with oil ganglia. Oil ganglia could be mobilized and carried by the slow flow of wetting films of brine on the pore walls. As a result of numerical modeling of the tertiary recovery process, it was found that *production of oil ganglia may continue for a long time* of injection of around 10 to 20 PVI.

Unlike the conventional models of chemical flooding, where mobilized oil bank travels ahead of the concentration front, the oil ganglia model predicts that *the mobilized oil may be produced much later than the water front comes*. Such delays were observed in some experiments, where mobilized oil was produced during a long time, after several pore volumes of injection.

One of the possible chemical mechanisms through which the mobilization of the residual oil may occur in carbonates is alteration of the electrostatic potential of the surface. Reduction of the surface charge due to adsorption of the potential determining ions results in the decrease in oil affinity towards the surface of the rock. We established *a mathematical model that takes into account adsorption of the potential determining ions*: calcium, magnesium, and sulfate, on the chalk surface. We investigated how the composition of the injected brine affects the equilibrium surface composition and how the adsorption process affects the composition of the produced brine. We compared the developed model with several sets of the experimental data available in the literature. The computations suggested that *there is no evidence of usually assumed stronger adsorption of magnesium ion compared to calcium* at high temperatures. The two types of adsorption: *fast reversible adsorption and long irreversible (or slightly reversible)* needed to be introduced, in order to explain the observed effects.

In order to investigate the effect of surface composition on the flooding efficiency, we combined the adsorption model with the traditional Buckley-Leverett model for the oil-water flows in porous media. On this basis we performed simulations of the experiments concerning flooding in the water-wet outcrop chalk. Computations of the equilibrium surface composition demonstrated *a correlation between the concentration of the adsorbed sulfate and the ultimate recovery* observed in the experiments. A more negatively charged surface of chalk could be a factor that affects the recovery efficiency without wettability modification.

Realization of objectives

We suffered extreme delay in the experimental core flooding setup, but progressed along the track in accordance with the research plan and met half of our objectives.

Increased turnover, exports, employment N/A

Dissemination of results

Peer reviewed papers:

Katika, K., Addassi, M. Alam, M.M. & Fabricius, I.L. 2014: " Changes in Specific Surface as observed by NMR, caused by saturation of Chalk with porewater bearing divalent Ions" *Diffusion-fundamentals* 22,1-14.

Alexeev, A. Shapiro, A. & Thomsen, K. 2015 "Modeling of dissolution effects on waterflooding" *Transport in Porous Media* 106, 545-562.

Katika, K. Addassi, M., Alam, M.M. & Fabricius, I.L. 2015 : "The effect of divalent ions on the elasticity and pore collapse of chalk evaluated from compressional wave velocity and low-field nuclear magnetic resonance (NMR)" *Journal of Petroleum Science and Engineering* 136, 88-99.

Alexeev, A. Shapiro, A. and Thomsen, K. (in press)."Mathematical Model for Tertiary Recovery by Mobilization of Oil Ganglia" *Transport in Porous Media*

Katika, K., Ahkami, M., Fabricius, I.L., Fosbøl, P.L., Halim, A.Y., Shapiro, A., Thomsen, K., & Xiarchos, I. (under revision after review) Comparative analysis of experimental methods for quantification of small amounts of oil in water.

Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. (in review) Interactions of Fines with Oil and its Implication in Smart Water Flooding, SPE Reservoir Evaluation & Engineering-Formation Evaluation (**Paper II**)

Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. (in review) Importance of Fines in Smart Water Enhanced Oil Recovery (SmW-EOR) for Chalk Outcrops, SPE Reservoir Evaluation & Engineering-Formation Evaluation (**Paper V**)

Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. (in review) Effect of Soluble Salts in Emulsification of Crude Oil during Smart Water Enhanced Oil Recovery, Journal of Petroleum Science and Engineering (**Paper XI**)

Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. (in review) Effect of insoluble fines in emulsification of Crude Oil during Smart Water Enhanced Oil Recovery (SW-EOR), Journal of Petroleum Science and Engineering (**Paper XII**)

Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. (to be submitted) Modeling of salt solubility and dissolutions in smart water flooding of carbonate reservoir using 1 Extended UNIQUAC model (**Paper IX**)

Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. (to be submitted) Parallel injection of multiple brines through various injection wells for optimum fines formation during smart water flooding. (**Paper X**)

Katika, K., Saidian, M., Prasad, M., & Fabricius, I.L. (to be submitted) Low field NMR spectrometry of chalk and argillaceous sandstones: rock - fluid affinity assessed from T1/T2 ratio.

Conference contributions:

Alam, M.M., Katika, K. & Fabricius, I.L. 2013: "Wettability of quartz surface as observed by NMR transverse relaxation time (T2)." Paper presented at 75th EAGE Conference & Exhibition incorporating SPE EUROPEC 2013, London, United Kingdom.

Alam, M.M., Katika, K. & Fabricius, I.L. 2013: "Effect of dissolved ions on bound water on water wet mineral surfaces as indicated by NMR transverse relaxation time (T 2)" *SEG* September 2013. SEG Technical Program Expanded Abstracts 2013: 2732-2736.

- Katika, K., Alam, M.M. & Fabricius, I.L. 2013: "Nuclear Magnetic Resonance and Elastic Wave Velocity of Chalk Saturated with Brines Containing Divalent Ions." Paper presented at 75th EAGE Conference & Exhibition incorporating SPE EUROPEC 2013, London, United Kingdom.
- Katika, K., Alam, M.M. & Fabricius, I.L. 2013: "Nuclear magnetic resonance and sound velocity measurements of chalk saturated with magnesium rich brine." *Poromechanics V: Proceedings of the Fifth Biot Conference on Poromechanics*. American Society of Civil Engineers, 2013, 678-684.
- Alam, M.M., Katika, K., & Fabricius, I.L. 2014: "Effect of salinity and specific ions on amount of bound water on quartz, calcite and kaolinite, as observed by NMR transverse relaxation time (T_2)." 76th EAGE Conference & Exhibition 2014. Amsterdam RAI, The Netherlands, 16-19 June 2014.
- Katika, K.; Adassi, M.; Alam, M.M. & Fabricius, I.L. 2014. "Differences in the Texture of Chalk as observed by NMR." Poster session presented at 12th International Bologna Conference on Magnetic Resonance in Porous Media, Wellington, New Zealand.
- Xiarchos, I., Fosbøl, P.L., Alam, M.M., Sigalas, L., Bilal-Shaukat, C., Fabricius, I.L., Shapiro, A. & Thomsen, K. 2014: "Smart Water Flooding Experiments with Automated Equipment for Inline Resistivity and Sound Velocity Measurements." 21st World Petroleum Congress, Moscow, June 14-19, 2014.
- Alexeev, A. 2015 Low Salinity Waterflooding and Mineral Dissolution, Presented at the 6th International Conference on Porous Media (interpore 6); Milwaukee, Wisconsin, USA, May 27-30 2015.
- Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. 2015 Behavior of Ca²⁺ and Mg²⁺ ions during Smart Water Flooding On Chalk Reservoirs, SPE-174261-MS (**Paper I**)
- Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. 2015 Interactions of Fines with Base Fractions of Oil and its Implication in Smart Water Flooding, SPE-174335-MS (**Paper III**)
- Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. 2015 Brine Crude Oil Interactions at the Oil-Water Interface. SPE-174685-MS (**Paper IV**)
- Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. 2015 Fine Formation during brine-crude oil-calcite interaction in Smart Water Enhanced Oil Recovery for Caspian Carbonates, SPE-177379-MS (**Paper VI**)
- Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. 2015 Significance of fines and their correlation to reported oil recovery, SPE-177711-MS (**Paper VII**)
- Chakravarty, K.H., Fosbøl, P.L. & Thomsen, K. 2015 Formation of anhydrite due to interaction between water soluble CO₂(aq) and calcite mineral during enhanced oil recovery, SPE-178129-MS (**Paper VIII**)
- Katika, K. & Fabricius, I.L. 2015: "Electrical tortuosity, Kozeny's factor and cementation factor modelled for chalk. Third International Workshop on Rock Physics, Perth, Australia; 04/2015.
- Katika, K.; Halim, A.Y.; Shapiro, A & Fabricius, I.L. 2015: "Quantification of the recovered oil and water fractions during water flooding laboratory experiments." Proceedings of the 77th EAGE Conference & Exhibition 2015.
- Katika, K. Saidian, M. & Fabricius, I.L. 2016: "Wettability of chalk and argillaceous sandstones assessed from T1/T2 ratio " 78th EAGE Conference & Exhibition 2016 Vienna, Austria, 30 May - 2 June 2016

1.6 Utilization of project results

The results from our research are not yet ready to be put into practical use, but has given scientific results as for example the production-promoting role of oil-solid water emulsions, the combined use of NMR and ultrasonic data in petrophysical interpretation, and the slow production of oil ganglia during flooding. These results give optimism with respect to follow up experimental work and modelling.

Research education:

A Ph.D. thesis of K. Katika entitled Rock Physics of Reservoir Rocks with Varying Pore Water Saturation and Pore Water Salinity (DTU Civil Engineering) was successfully defended 25 of February 2016.

A Ph.D. thesis of A. Alexeev entitled Modeling of Salinity Effects on Waterflooding of Petroleum Reservoirs (DTU Chemical Engineering) was successfully defended 11 of March 2016.

A Ph.D. thesis of Krishna Hara Chakravarty entitled Modelling of Salt Solubilities for smart Water flooding in Carbonate Reservoirs using Extended UNIQUAC Model (DTU Chemical Engineering) will defended in 2016.

The following M.Sc theses associated with the Smart Water project was completed:

Jacob Fabricius Riis 2012	Shallow fresh water in central North Sea
Leonardo Meireles 2014	NMR Log response and interpretation
Daniel Jonas 2015	Combined Interpretation of NMR Core and Logging Data
Martin Einarsve 2014	Numerical Modelling of Oil Production by Smart Waterflooding
Mehrdad Ahkami 2015	Smart Waterflooding of Petroleum Reservoirs: Verifying the Models with Experimental Data

Jacob Fabricius Riis presently works for Schlumberger
Leonardo Meireles is presently a PhD student at DTU-Civil Engineering investigating poroelastic and fracturing effects of pore fluid
Danial Jonas presently works for DONG Energy.

1.7 Project conclusion and perspective

Smart Water flooding experiments were completed at 130°C and 60°C for chalk reservoirs. The individual effect of different sodium and magnesium salts were analyzed. A novel Smart Water Enhanced Oil Recovery (SmW-EOR) method was developed for sandstone reservoirs at low temperature (60°C). An emulsification study with fines has been completed including both soluble and insoluble salts. Fines formation in core plugs was correlated to oil recovery for over 128 core flooding experiments. Consistent correlation between fine formation and oil recovery for both injection and effluent brines was observed. Based on these studies a fines based emulsification mechanism of SmW-EOR was proposed.

Petrophysical and petrographic evaluation of samples tested by flooding are still awaiting the last data, but a series of associated experiments have given promising results:

1. Low field NMR can reveal the formation of fines within the pore space of a saturated sample. NMR can also reveal growth of existing crystals in rock frame.
2. Rock mechanical testing of chalk monitored by velocity of elastic waves indicates that elasticity as calculated from ultrasonic data was can reveal the poroelastic effect of smart water. Chalk saturated with low-salinity brine was stiffer than chalk saturated with high-salinity brine, especially potential determining ions.
3. A new method for interpretation of low field NMR indicates that reservoir chalk has preferred affinity for water whereas the studied reservoir greensand is mixed wet: quartz having largest affinity for water whereas chlorite has larger affinity for reservoir oil.

The mathematical modelling has resulted in creation of a number of innovative models for displacement of oil by smart water. Comparison with experimental data has demonstrated that these models are capable of reproducing some essential features of waterflooding. Further implementation of these models into a 3D reservoir-scale simulator would be desirable.

The effects that still need further advance in modelling are formation of the reservoir fines and their role in formation of the emulsions that have been observed in the course of the experimental work within present project and the BioRec project running in parallel. These effects may play an important role. Partly they were covered by the scaling and ganglia models considered within the present project. However, the experimental data are still insufficient in order to make quantitative predictions. Advance in experimental studies followed by innovative modelling may be required in order to account for these effects.

Annex

Relevant links